ABSTRACT

Title of Thesis: Quantitative Evaluation of Substituent Effects on Stabilization Energies of Strained and Unsaturated Molecules

Tyler A. Stevenson, Master of Science, 1984

Thesis directed by: Professor Arthur Greenberg

Thermodynamic stabilization energies are presented for a series of monosubstituted vinyl, cyclopropyl, ethynyl, and phenyl compounds. The energies are calculated using ab initio molecular orbital calculations at the 4-31G level, and also with published experimental heat of formation data. Correlation analyses are then attempted with the dual substituent parameter approach with the stabilization energies. The analyses are also attempted with a triple-parameter approach using Topsom's theoretically calculated X, F, and R^o constants. Among the findings are the facts that π-donating substituents correlate well, while π-accepting substituents do not. Indications of the relative sensitivities of hydrocarbon frameworks to substituent electrostatic and resonance effects are analyzed. Photoelectron spectroscopy and carbon-13 chemical shift data of the substituted olefinic compounds are also examined to provide further insights.

QUANTITATIVE EVALUATION OF SUBSTITUENT EFFECTS ON STABILIZATION ENERGIES OF STRAINED AND UNSATURATED MOLECULES

by
Tyler Arthur Stevenson

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APPROVAL SHEET

Title of Thesis: Quantitative Evaluation of Substituent Effects on Stabilization Energies of Strained and Unsaturated Molecules

Name of Candidate: Tyler A. Stevenson
Master of Science, 1984

Thesis and Abstract Approved:

4/25/84
Arthur Greenberg Date
Associate Professor
Department of Chemical
Engineering and Chemistry

5/2/84
Joel F. Liebman Date
Professor of Chemistry
Department of Chemistry
University of Maryland
Baltimore County

5/7/84
Carol Venanzi Date
Assistant Professor
Department of Chemical
Engineering and Chemistry

VITA

Name: Tyler Arthur Stevenson

Permanent address:

Degree and date to be conferred: Master of Science, 1984

Date of birth:

Place of birth:

Secondary Education: Jefferson Twp. H. S., 1976

Collegiate institutions attended	Dates	Degree	Date of Degree
New Jersey Institute of Technology	1982-1984	M.S.	1984
Montclair State College	1981-1982	----	----
University of Delaware	1976-1980	B.A.	1980

Major: Chemistry

Publications: J.F. Liebman, L. Laydon, A. Greenberg, and T. Stevenson, "Entropy Changes of Isodesmic Equations", submitted to *Tetrahedron Letters*.

A. Greenberg, T. Stevenson, M. Charton, "Bilinear Relationships Between Thermodynamic Parameters-The Uniqueness of Alkynes", to be submitted to *J. Org. Chem*.

A. Greenberg and T. Stevenson, "Linear Free Energy Relationships Indicating Stabilization Mechanisms in Substituted Strained and Unsaturated Molecules", to be submitted to *J. Org. Chem*.

Positions held: Polymer Chemist, Benjamin Moore & Co., 1984- Newark, NJ.

Research Assistant, N.J.I.T., Summer 1983.

Tutor, Educational Opportunity Program, N.J.I.T., Summer 1983.

Teaching Assistant, N.J.I.T., 1982-1983.

Formulations Chemist, Benjamin Moore & Co., 1980-1982.

DEDICATED TO MY FAMILY

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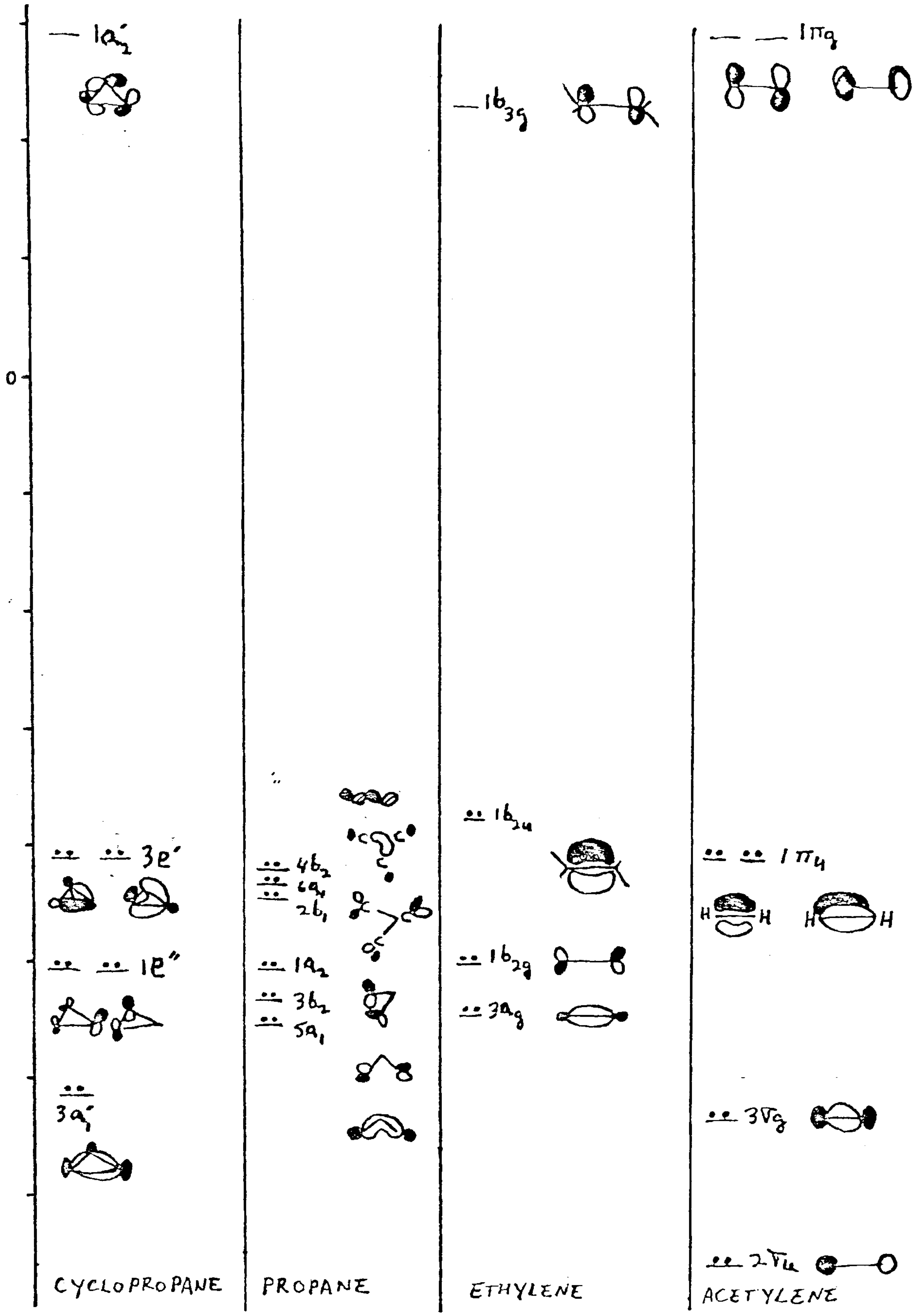
CHAPTER I

EXPLANATION OF SUBSTITUENT ELECTRONIC EFFECTS

The mechanisms by which a strained ring is affected through substituent electronic effects have been outlined by Dill, Greenberg, and Liebman.[1] These researchers pointed out two major effects: 1) An inductive effect which operates through the localized exocyclic ring-substituent bond, i.e., the le" molecular orbital of cyclopropane[2], and 2) a resonance effect which operates through the delocalized molecular orbitals of a ring, i.e., the 3a', 3e', and la$_2$' orbitals of cyclopropane[2] (see Fig. I.1, any MO pictured herein is from reference 2).

The first component of the substituent electronic effect is the one presumably described by Taft's inductive substituent constant (as compiled by Charton) and Topsom's electronegativity and/or field effect parameters (see Chapt. V). It should be pointed out here that a substituent's stabilizing effect on a strained ring is measured relative to its effect on an acyclic species (e.g., isopropyl). This is described in detail in Chapt. III. The substituent inductive effect on strained ring systems as compared to unstrained acyclic systems has been proposed by Dill, et al.[1] These workers point out that if a substituent is σ electron donating, it will form a bonding pair with the ring that is largely localized on the ring, i.e., the le" MO of cyclopropane. The same will occur for bonding with the acyclic species, but since the exocyclic

FIG. I.1


$1a_2'$
$1b_{3g}$
$1\pi_g$
0
$3e'$
$4b_2$
$6a_1$
$2b_1$
$1b_{2u}$
$1\pi_u$
H
H
H
H
$1e''$
$1a_2$
$3b_2$
$5a_1$
$1b_{2g}$
$3a_g$
$3a_1'$
$3\sigma_g$
$2\sigma_u$
CYCLOPROPANE
PROPANE
ETHYLENE
ACETYLENE

ring orbital is lower in energy than the counterpart of the unstrained molecule, net stabilization of the ring molecule occurs relative to the unstrained molecule (see Fig. I.2).

For the case of a σ electron withdrawing substituent, the opposite occurs. The bonding electron pair is now largely localized on the substituent. Since the exocyclic ring orbital is lower in energy than the corresponding orbital of the unstrained molecule, the energy gain is greater for the acyclic model, and hence destabilization occurs in the strained ring (see Fig. I.3).

Recent studies by Topsom and coworkers, to be discussed later, bear out the conclusion that there are actually two "non-resonance" substituent effects of import when considering a reaction site of close proximity to the substituent (see Chapt. V). These are the inductive or electronegative (through-bond), and field (dipole) effects. Admittedly then, the above proposal for a substituent's inductive (the correct term is electrostatic, covering all non-resonance effects) effect is an over- simplification. Hopefully, the correlation analyses will tell us much more about the substituent electrostatic effect on a strained ring.

The second component of the substituent electronic effect, the resonance effect, operates through the delocalized ring orbitals, and it should be described by Taft's σ_R and /or Topsom's σ_{R}o constants (see Chapt. V). For cyclopropane, the MO's involved in the resonance effect are the σ-character orbitals of overall π symmetry, 3e' and $1a_2'$ (see Fig. I.1).

Fig. I.2   X = electropositive

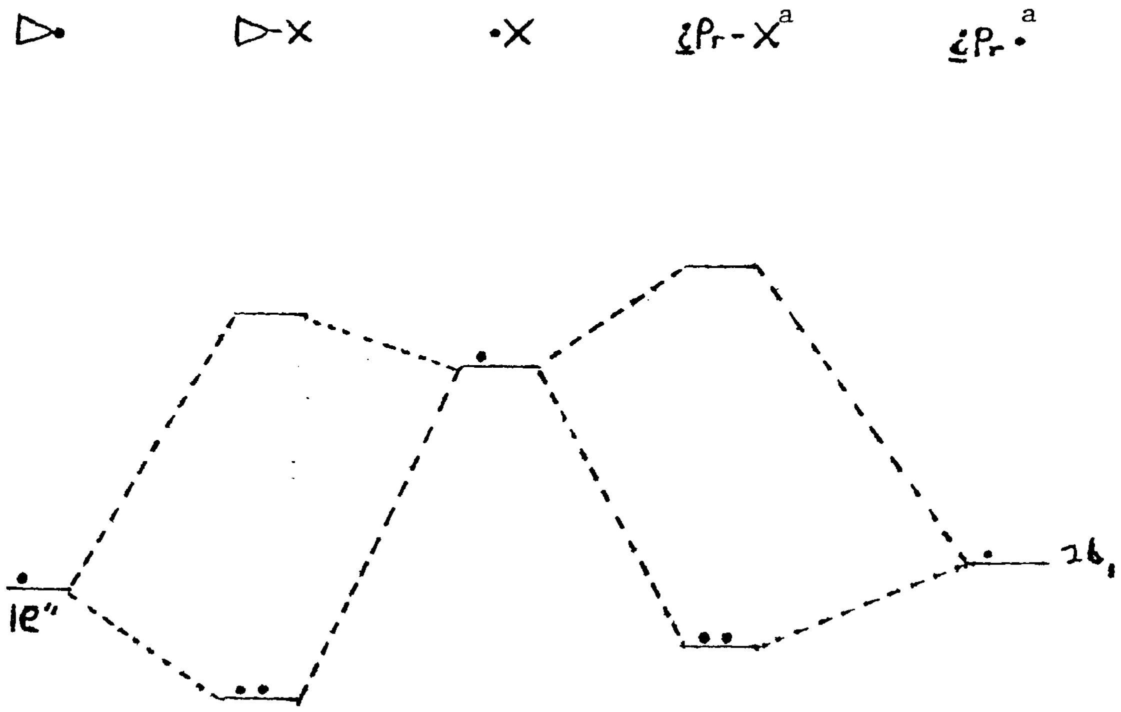
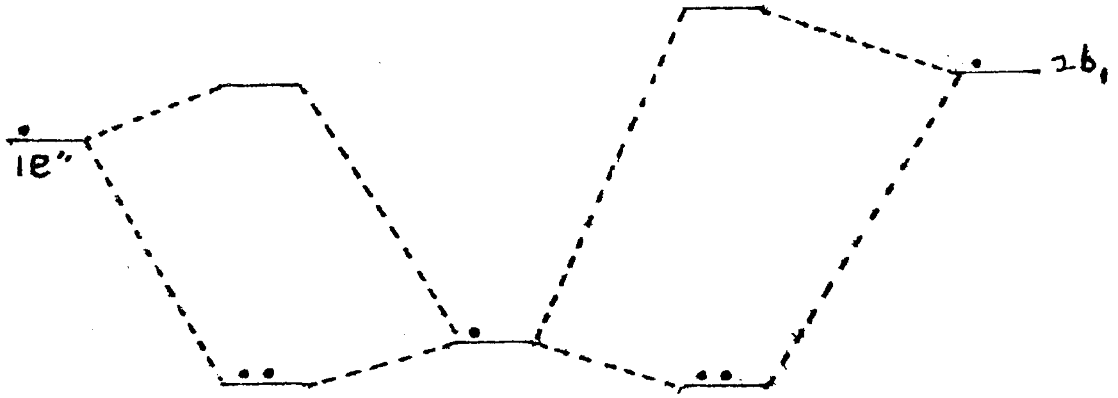


Fig. I.3   X = electronegative



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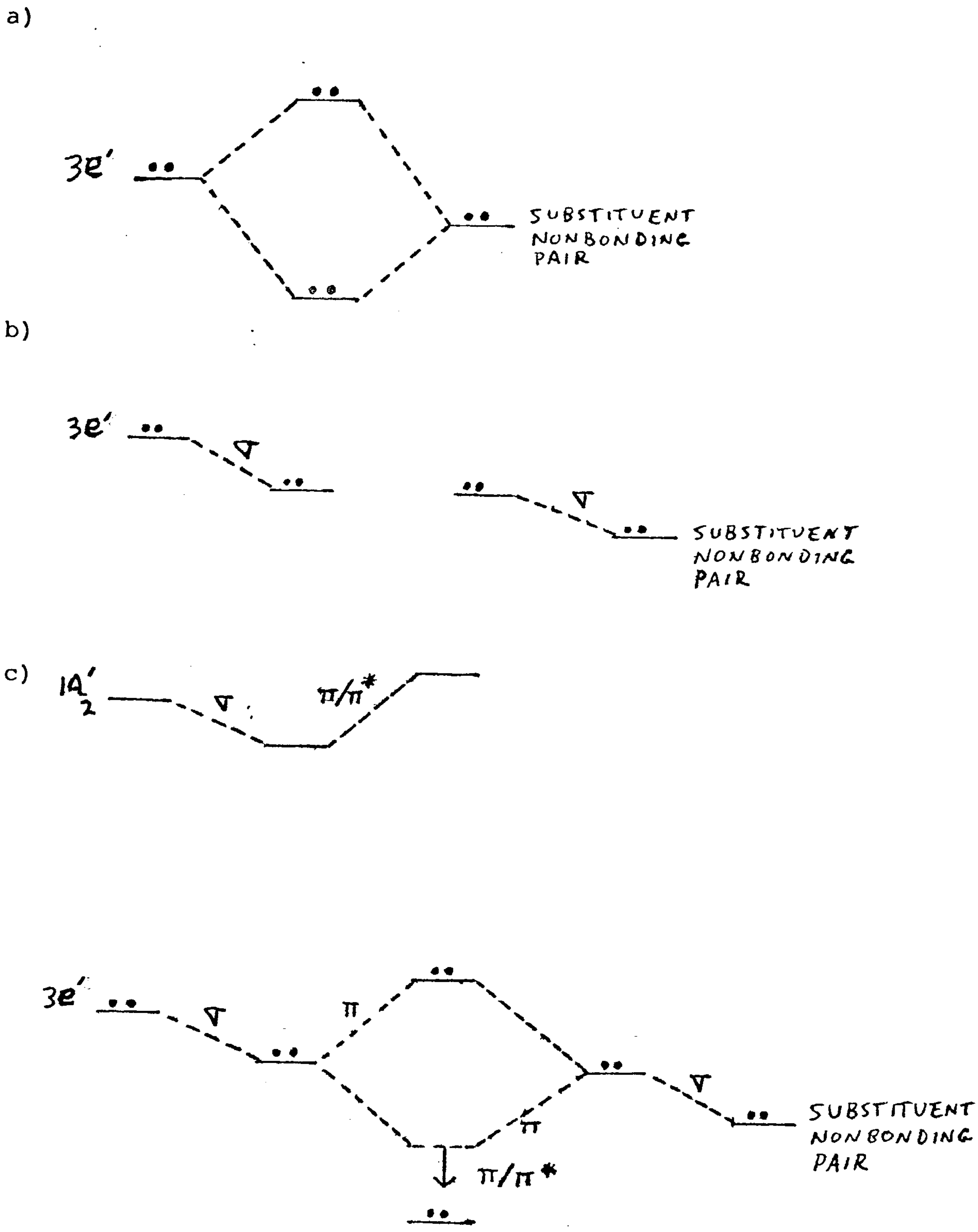
a) Note that here and throughout this work, iPr is isopropyl.

The effects of a π-electron donating substituent on a π system have been discussed by Dill, et al.[1] in the context of strain reduction, and Rabalais[3] in the context of photoelectron spectra. In this study the π-donors (e.g., OH, OMe, NH_2, F) normally had lone pairs of electrons in proper orientations to interact with the π-systems studied. Figure I.4 shows the interaction between cyclopropane and a halogen. In Fig. I.4, a), the halogen nonbonding pair and cyclopropane's π-type pair interact to form a bonding and an antibonding orbital. For this case the bonding pair is largely localized on the substituent, thereby stabilizing these electrons, while the antibonding pair is largely made up of the ring π-type electrons, thereby destabilizing this orbital. This would have the effect of increasing ring strain. Superimposed on this would be the substituent's electronegativity effect which if electron withdrawing, would work against the resonance effect (Fig. I.4, b)). It depends on the individual substituent if the resonance effect is outweighed by the electronegativity effect. Furthermore, there is the most important interaction, that of the substituent π electrons and the framework LUMO, or low-lying π^* type molecular orbital. Fig I.4, c) is an example of the final ordering of orbitals for the case of a typical π-donating substituent. The main source of stabilization in this system is the lowering in energy of the substituent nonbonding pair, which could not occur in bonding to an acyclic species. It is this π/π^* interaction that builds up exocyclic bonding. Notice that in this case the ring

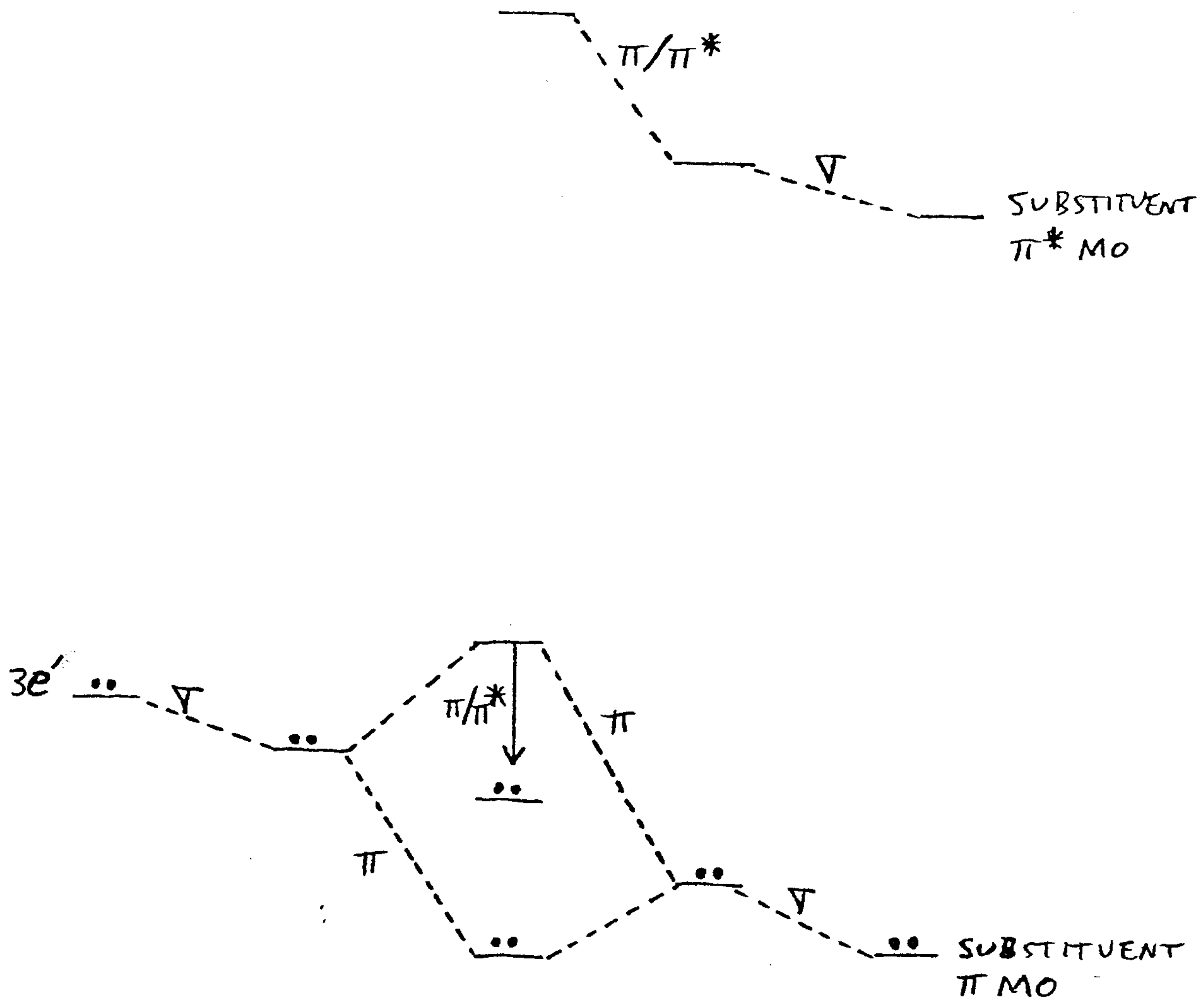
Fig. I.4


a)
3e'
SUBSTITUENT NONBONDING PAIR
b)
3e'
∇
∇
SUBSTITUENT NONBONDING PAIR
c)
1A'2
∇
π/π*
3e'
∇
π
π
∇
π/π*
SUBSTITUENT NONBONDING PAIR

and π^* orbitals are slightly lowered in energy due to the substituent's electronegativity, but the resonance interaction causes an overall destabilization of the π orbital. Remember that a substituent's stabilizing or destabilizing effects cannot be determined from the overall MO diagram of Fig. I.4, c), because one must compare this to the substituent effect on an acyclic model, and also because the field effect is not included. What it does tell us is the overall MO ordering in a substituted ring due to electronegativity and resonance effects. In conclusion, π electron donation has a stabilizing effect due to the favorable interaction between the electrons of the substituent and the LUMO of the strained ring.

π electron accepting substituents also have a stabilizing mechanism (see Fig I.5). Like π-donors, π-acceptors have similar elecronegative effects, and similar resonance effects between the two filled π-type MO's. Also like π-donors, the most important stabilizing interaction here is between a HOMO and LUMO, in this case between the ring π-type orbital and the π^* type orbital of the substituent. Figure I.5 shows an example of a complete MO diagram for cyclopropane and a π-accepting substituent. The stabilization for this example comes from the lowering of the substituent's and the substrate's π electrons. Note however that the MO diagram will depend on the individual substituent. For this case, the ring strain will generally be reduced, unless the interaction between the two filled MO's is strong enough to destabilize the ring π-type electrons. Both cases of the above molecular

FIG. I.5



orbital diagrams will be discussed further in the section on photoelectron spectroscopy.

In conclusion, the strained ring-substituent system is stabilized relative to the unstrained acyclic-substituent system if the substituent is a donor or acceptor, ignoring the overall electrostatic effect. It is somewhat harder to predict the stabilization or destabilization that would occur from a substituent's electrostatic effect(s). It is not known at this point if the proposal by Dill, et al. is sufficient for this purpose.

It is the purpose of this thesis to attempt correlations of stabilization energies of small strained and unsaturated molecules with substituent constants. Through successful correlations one might predict the relative importance of electrostatic (electronegative and field) versus resonance effects for stabilization. One might further predict the relative importance of electronegative and field effects, and thereby either substantiate or disqualify the proposal of Dill, et al. Furthermore, data from the various correlations will be compared to each other, hopefully offering insight on the similarity or dissimilarity of the various strained systems, and to other measurable physical data (IP's, EA's, photoelectron spectra, and ^{13}C chemical shifts.

CHAPTER II

THEORETICAL ENERGIES, EXPERIMENTAL HEATS OF FORMATION, AND GEOMETRIES

Total molecular energies needed herein have been calculated by the ab initio molecular orbital method using the Gaussian 70 series of programs.[4] The levels employed are Pople's minimal STO-3G[5] and extended 4-31G[6,7] basis sets.

The majority of the energies have been obtained through an exhaustive literature search, but many were calculated in this work to complete the series. It was discovered through correlation analyses of the stabilization energies that the data obtained by use of the 4-31G energies is far superior to that of the STO-3G energies, since better agreement with experimental data were found for the former. This is in agreement with work done by George,[8] in which heats of isodesmic and homodesmotic equations at various levels of calculation were compared involving some of the species investigated here. This in itself is proof of the validity of the correlation analyses. For these reasons we will therefore concentrate on the energies calculated at the 4-31G level.

Total molecular energies are available at various levels of optimization: The standard geometry of Pople and Gordon,[9] partial optimization, full optimization at a lower calculational level (e.g., 4-31G//STO-3G), full optimization (4-31G//4-31G), or experimental geometry (4-31G//EXP). The above notation is that used by Pople and coworkers. It is not necessarily the order of increasing "best" energies. For example, energies calculated at partial basis set optimization are quite often lower than energies calculated using experimental geometries, and energies at full basis set geometry optimization are lower by definition.

For calculations of stabilization energies the best available total energies have been employed. Many of the calculations performed herein have been done not only because an energy value was not available in the literature, but also because it was felt for some cases substantial improvements could be made.

Fig. II.1

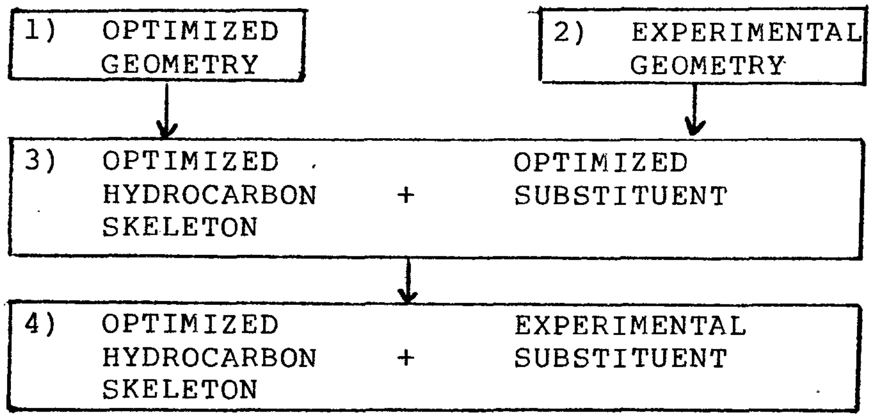


Fig. II.1 is a flow chart of the decreasing order of desired geometries employed for calculation of energies at one particular basis set in this work. When published optimized geometries were presented in the literature without a total energy, the latter was calculated using the specified structure. Model 3) was the one most commonly employed here. It was discovered that piecing a geometry together from optimized parts provides a good model. For example, if the

4-31G optimized methyl group and sp^3-sp^3 carbon bond length are taken from the structure of ethane of ref. 10, and used to construct the geometry of propane by substituting the methyl group for a hydrogen on ethane, the resulting geometry is very close to the 4-31G optimized geometry of propane in ref. 11. Obviously, this will break down where nonbonded interactions are important, but this problem is not significant in our current work. In certain cases some bond lengths were manually optimized (using energy reduction as the criterion) following the geometry resulting from model 3). Lastly, where no optimized information could be found on the substituent, its experimental geometry was placed on the optimized carbon skeleton. It should be noted that the experimental geometry where available was also normally employed (hence, its position in the flow chart), but rarely did the resulting energy surpass the model of choice. This is due in part to inadequacies of the theoretical calculations, the fact that the calculation is really for a molecule in a hypothetical vibrationless state, as well as due to the differences in the same parameter (i.e., bond length determined by microwave spectroscopy or electron diffraction, etc.). The construction of an appropriate geometric model often became more complex than described above; each case is discussed in turn in the following table of individual energy accounts (Table II.1).

In the case of model 3), the building of a structure can be made more diffucult for the molecules with π systems because the skeleton structure itself changes on substitution, and the skeleton-substituent bond may be difficult to find at the proper degree of hybridization. As will be mentioned later, Allen has presented data showing that the exocyclic ring-substituent bond in cyclopropane is $sp^{2.2}$ hybridized.[12]

Various papers by Allen,[12,13] in which he analyzed computer compiled data of X-ray crystallographic structures of substituted ethylenes and cyclopropanes, provided much data concerning these bond lengths. Allen's data supports Hoffmann's[14] predictions concerning cyclopropane ring bond length changes when bonded to π-acceptor substituents: That is that the distal bond is shortened and the vicinal bonds lengthened. There has also been much work on substituted cyclopropanes by Skancke, Penn, Boggs, and Flood (see refs. 15, 16, 17, 18, 19). Durmaz and Kollmar's investigation of cyclopropane's bond length changes when bonded to π-electron donor substituents also provides much needed geometrical data.[20] It should be noted that much of the theoretical work on cyclopropane geometries was done at the double zeta and 4-21G levels of calculation, which being close to the 4-31G level, were employed with confidence for model 1).

In the following table of energies and experimental heats of formation, it should be noted that whenever models 3) or 4) are used, the STO-3G and 4-31G optimized structures of ethane, acetylene, and ethylene are from ref. 10, the STO-3G optimized structure of propane is from ref. 21, the 4-31G geometry of propane is from ref. 11, the STO-3G geometry of cyclopropane is from ref. 21, and the 4-31G cyclopropane structure is from ref. 22. No phenyl compounds were calculated here. All energies are in hartrees, all bond lengths are in angstroms and all angles are in degrees. We employ 627.5 kcal per hartree.

Most of the tabulated experimental heat of formation data was taken from the computer-analyzed work of Pedley and Rylance.[23] All heats are in the units of kcal/mole and refer to the gas phase at 298K. Some heats of formation have been estimated here and are explained under the appropriate substituents. If the heat of formation has been estimated in different fashions for a particular molecule with various results, the one employed in the correlations has been listed in the table, and the other mentioned in the footnotes.

Note also that in the following tables, if at a certain calculational level the geometry is listed as being calculated at that particular level (either STO-3G or 4-31G), this may mean full geometry optimization, or it may mean that the geometry used was pieced together from various structures that have been optimized. Consultation of the reference is necessary to find which is the case. However, if the total energy was not calculated in this work, it is most likely that the energy was fully optimized for the above case. Also, abbreviations used in the following tables under the geometry headings are as follows: EXP = experimental, DZ = double zeta, STD = standard geometry of Pople and Gordon[9], part = partially optimized.

TABLE II.1

THEORETICAL TOTAL ENERGIES AND EXPERIMENTAL HEATS OF FORMATION FOR SUBSTITUTED SATURATED AND UNSATURATED SPECIES

X = H

	STO-3G	GEOMETRY	4-31G	GEOMETRY	ΔH_f^o
Me-X	-39.72686	STO-3G[a]	-40.13977	4-31G[b]	-17.8[c]
Et-X	-78.30618	STO-3G[a]	-79.11593	4-31G[b]	-20.1[c]
<u>i</u>Pr-X	-116.88642	STO-3G[a]	-118.09381	4-31G[b]	-25.0[c]
HCC-X	-75.85625	STO-3G[a]	-76.71141	4-31G[d]	54.5[c]
Vi-X	-77.07396	STO-3G[e]	-77.92216	4-31G[d]	12.5[c]
<u>c</u>Pr-X	-115.66616	STO-3G[a]	-116.88385	4-31G[f]	12.7[c]
Ph-X	-227.89136	STO-3G[g]	-230.37591	STD[h]	19.8[c]

a) Ref. 21 b) Ref. 11 c) Ref. 23 d) Ref. 10 e) Ref 24
f) Ref. 22 g) Ref. 25 h) Ref. 26

X = Cl

	STO-3G	GEOMETRY	4-31G	GEOMETRY	$\Delta H_f{}^o$
Me-X	-439.72311	STO-3G[a]	-498.52260	EXP[b]	-19.6[g]
Et-X	-532.30610	STO-3G[c]			-26.8[g]
iPr-X	-570.88777	STD[a]			-34.7[g]
HCC-X	-529.8495	STO-3G[d]	-535.0979	STO-3G[d]	
Vi-X	-531.07818	part STO-3G[f]	-536.32548	STO-3G[e]	5.0[h]
cPr-X					
Ph-X					12.3[g]

a) Ref. 27 b) Ref. 28 c) This work; C-C = 1.544, C-Cl = 1.813, ∠CCCl = 110.6 from partially STO-3G optimized geometry of Et-Cl from ref. 27; C-H = 1.086, ∠HCH = 108.2 from STO-3G optimized geometry of ethane (ref. 10). d) Ref. 29 e) Ref. 30; note typographical error in energy in reference, see ref. 31. f) Ref. 31 g) Ref. 23 h) Experimental value from ref. 23 is 8.9 kcal/mol. Above value derived from group contribution theory (see ref. 32); used on recommendation of J.F. Liebman (see also Kolesov, Patina, Russian Chem. Rev. 1983, 52, 405.

X = F

	STO-3G	GEOMETRY	4-31G	GEOMETRY	ΔH_f^o
Me-X	-137.16906	STO-3G[a]	-138.85861	4-31G[b]	-56.8[k]
Et-X	-175.75356	STO-3G[c]	-177.84496	4-31G[d]	-62.5[l]
_i_Pr-X	-214.33694	STO-3G[e]	-216.82730	STO-3G[e]	-70.1[m]
HCC-X	-173.3071	STO-3G[f]	-175.4099	STO-3G[f]	
Vi-X	-174.53295	STO-3G[c]	-176.65117	4-31G[g,n]	-33.2[m]
_c_Pr-X	-213.11698	EXP,STD[h]	-215.60992	DZ[i]	
Ph-X	-325.35102	part STO-3G[j]	-329.10477	STD[g]	-27.7[m]

a) Ref. 33 b) Ref. 11 c) Ref. 25 d) Ref. 34 e) Ref. 35 f) Ref. 29 g) Ref. 26 h) Ref. 1; total energy calculated here = -213.11667 using DZ geometry of ref. 20. i) This work; DZ geometry of ref. 19 employed. Total energy = -215.58445 using DZ geometry of Durmaz (ref. 20) with C-H = 1.071 from 4-31G study of cyclopropane (ref. 27). j) Ref. 36 k) Average of two estimated values: -57.8 kcal/mol (ref. 37), -55.9 kcal/mol (ref. 38). l) Average of three estimated values: -62.2 kcal/mol (ref. 37), -62.5 kcal/mol (ref. 38), -62.9 kcal/mol (ref. 39). m) Ref. 23 n) Since compilation of this table, a slightly better energy has been calculated: -176.65147, ref. 40.

$X = CH_3$

	STO-3G	GEOMETRY	4-31G	GEOMETRY	ΔH_f^o
Me-X	-78.30618	STO-3G[a]	-79.11593	4-31G[b]	-20.1[i]
Et-X	-116.88642	STO-3G[c]	-118.09381	4-31G[b]	-25.0[i]
*i*Pr-X	-155.46684	STO-3G[d]	-157.07118	STO-3G[e]	-32.1[i]
HCC-X	-114.44898	STO-3G[c]	-115.70133	4-31G[b]	44.6[i]
Vi-X	-115.66038	STO-3G[f]	-116.90510	4-31G[b]	4.8[i]
*c*Pr-X	-154.24850	part STO-3G[e]	-155.86313	part STO-3G[e]	6.2[j]
Ph-X	-266.47491	part STO-3G[g]	-269.35568	STD[h]	12.0[i]

a) Ref. 33 b) Ref. 11 c) Ref. 21 d) Ref. 25 e) Ref. 41
f) Ref. 42 g) Ref. 36 h) Ref. 26 i) Ref. 23 j)
Calculated in ref. 1;; employed $\Delta H_f^o{}_{(l)}$ and Trouton's Rule.

X = OMe

	STO-3G	GEOMETRY	4-31G	GEOMETRY	ΔH_f^o
Me-X	-152.13387	STO-3G[a]	-153.83622	EXP[b]	-44.0[k]
Et-X	-190.71511	STO-3G[c]	-192.82002	EXP[d]	-51.7[k]
iPr-X	-229.29180	STD[e]			-60.2[k]
HCC-X	-188.2710	STO-3G[f]	-190.40837	EXP,4-31G[g]	
Vi-X	-189.49628	STO-3G[h]	-191.63602	4-31G[h]	-26.0[l]
cPr-X	-228.07522	EXP,STD[e]	-230.58874	4-31G,DZ,EXP[i]	
Ph-X	-340.30921	part STO-3G[j]	-344.08385	part STO-3G[j]	-16.2[k]

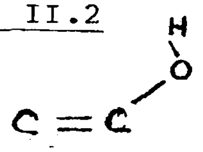
a) Ref. 25 b) Ref. 43 c) This work; model 3) employed with STO-3G values for ∠COC and the sp^3 C-O bond from ref. 44 of trans methyl vinyl ether. Conformation taken from ref. 45 (heavy atom planarity). d) This work; experimental geometry from ref. 45 employed. e) Ref. 1 f) Ref. 29 g) This work; mostly experimental geometry: C≡C = 1.186, CC-H = 1.050 from ref. 46 of HCC-OH, CC-O = 1.31, O-CH_3 = 1.43, ∠COC = 113.4 from ref. 47 of HCC-OMe. Geometry around methyl assumed 1/2 of 4-31G ethane structure of ref. 10. h) Ref. 48 i) This work; used same ring structure and conformation as cyclopropyl alcohol of ref. 20, OMe geometry experimental result of Et-OMe from ref. 45. Manually optimized ring-substituent bond and found to be 1.416. j) Ref. 49 k) Ref. 23 l) Estimated in ref. 1.

X = OH

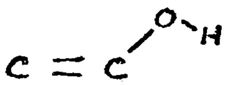
	STO-3G	GEOMETRY	4-31G	GEOMETRY	ΔH_f^o
Me-X	-113.54919	STO-3G[a]	-114.87152	4-31G[b]	-48.2[n]
Et-X	-152.13306	STD[c]	-153.85411	STD[d]	-56.1[n]
iPr-X	-190.71486	STD[e]	-192.83683	STD[f]	-65.1[n]
HCC-X	-149.6928	STO-3G[g]	-151.44421	4-31G[h]	
Vi-X	-150.91668	STO-3G[c,p]	-152.67074	4-31G[i,p]	-29.8[o]
	-150.91311	STO-3G[c,q]	-152.66732	4-31G[i,q]	
cPr-X	-189.49629	DZ[j]	-191.62354	DZ[k]	
Ph-X	-301.73038	part STO-3G[l]	-305.12115	STD[m]	-23.0[n]

a) Ref. 33 b) Ref. 11 c) Ref. 25 d) Ref. 24; E_t from this work using experimental geometry from ref. 45 = -153.85295; E_t also calculated in this work using model 3) with 4-31G structure of ethane from ref. 10, C-O = 1.429, O-H = 0.951, ∠COH = 113.2 from 4-31G study of Me-OH (ref. 11), and found to be -153.85398. e) Ref. 1 f) Ref. 50 g) Ref. 29 h) Ref. 51 i) Ref. 52, see Fig. II.2. j) This work; double zeta geometry of ref. 20 employed with C-H = 1.081 from STO-3G study of ref. 21. O-H = 0.990, ∠COH = 105.2 from STO-3G study of vi-OH (ref. 52). ∠HCOH = 60° as suggested in ref. 20, see Fig. II.3).. k) This work; same as above except C-H = 1.071 from 4-31G study of ref. 22 and O-H = 0.952, ∠COH = 115.0 from 4-31G study of vi-OH from ref. 52. l) Ref. 36 m) Ref. 26 n) Ref. 23 o) Ref. 53 p) Cis, Fig. II.2. q) Trans, Fig. II.2.

Fig. II.2

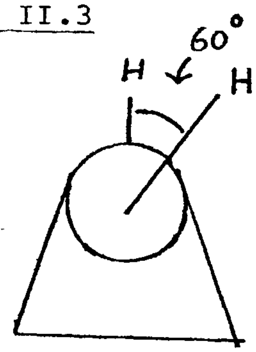


cis



trans

Fig. II.3



$X = NH_2$

	STO-3G	GEOMETRY	4-31G	GEOMETRY	ΔH_f^o
Me-X	-94.03286	STO-3G^{a}	-95.07166	4-31G^{b}	-5.5^{n}
Et-X	-132.61586	STO-3G^{c,o}	-134.05115	4-31G^{d,o}	-11.4^{n}
	-132.59704	STD^{c,p}	-134.04795	STD^{c,p}	
iPr-X	-171.19553	part STO-3G^{e,o}	-173.03065	STD^{g,o}	-20.0^{n}
	-171.17822	STD^{f,p}	-173.02879	part 4-31G^{h,p}	
HCC-X	-130.17681	STO-3G^{a,o}	-131.6616	4-31G^{r,o}	
	-130.15781	STD^{f,p}			
Vi-X	-131.39614	STO-3G^{s,o}	-132.87158	part 4-31G^{i,o}	
	-131.38871	STO-3G^{a,p}	-132.87521	4-31G^{j,p}	
	-131.36912	STD^{f,q}	-132.85890	STD^{c,q}	
cPr-X	-169.97773	STD,EXP^{f,o}	-171.82541	DZ,4-31G^{k,o}	18.4^{n}
Ph-X	-282.20892	part STO-3G^{l,o}	-285.31795	STD^{j,o}	20.8^{n}
	-282.20519	part STO-3G^{m,p}	-285.32500	STD^{j,p}	

a) Ref. 25 b) Ref. 11 c) Ref. 24 d) This work; model 3) employed, 4-31G NH_2 structure from ref. 11 of Me-NH_2 (C-N = 1.450), conformation taken from ref. 54, see Fig. II.4.
e) Ref. 55 f) Ref. 1 g) Ref. 50 h) This work; model 3) used with C-N = 1.47, N-H = 1.01, ∠HNH = 120, standard values from ref. 9, see Fig. II.5 for conformation. i) This work; model 3) used, 4-31G pyramidal NH_2 group from ref. 11 of Me-NH_2. C-N = 1.39 from ref. 56. j) Ref. 26 k) This work; double zeta result of ref. 16 used with NH_2 geometry from 4-31G study of Me-NH_2 of ref. 11. C-H = 1.071 from 4-31G study of cyclopropane of ref. 22. l) Ref. 20 m) Ref. 36 n) Ref. 23 o) Pyramidal NH_2. p) Planar NH_2, conjugated with π system if bonded to unsaturated species. q) Planar and perpendicular NH_2, unconjugated with π system. r) Ref. 46, note fully optimized, close to planar. s) Ref. 56

Fig. II.4

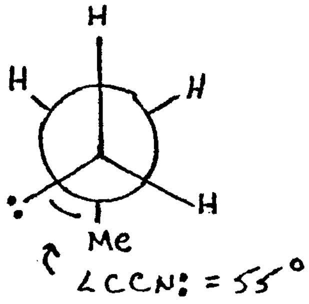
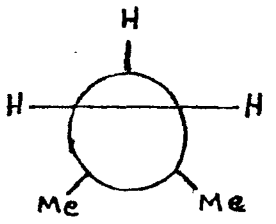


Fig. II.5



$X = CH_2^-$

	STO-3G	GEOMETRY	4-31G	GEOMETRY	ΔH_f^o
Me-X	-77.40459	STD^{a,g}	-78.38126	4-31G^{b,g}	
	-77.38421	STD^{a,h}	-78.36268	part 4-31G^{c,h}	
Et-X	-115.96992	STD^{d,h}	-117.36467	4-31G^{b,g}	
			-117.34778	part 4-31G^{c,h}	
*i*Pr-X	-154.56616	STD^{a,g}			
	-154.54520	STD^{a,h}			
HCC-X	-113.61013	STD^{a}	-115.03353	4-31G^{b}	
Vi-X	-114.82318	STD^{a,g}	-116.22676	4-31G^{b,h}	29.0^{e}
	-114.83832	STO-3G^{e,h}	-116.18251	4-31G^{f,i}	
	-114.75510	STD^{a,i}			
*c*Pr-X	-153.35314	STD^{a,j}			
	-154.37247	STD^{a,g}			
Ph-X	-265.67483	part STO-3G^{b}	-268.68709	part STO-3G^{b}	

a) Ref. 1 b) Ref. 11 c) Ref. 58 d) Ref. 59 e) Ref. 60 f) Ref. 61 g) Pyramidal CH_2^-. h) Planar CH_2^-, conjugated. i) Planar CH_2^-, unconjugated (perpendicular). j) Planar CH_2^-, bis.

$X = O^-$

	STO-3G	GEOMETRY	4-31G	GEOMETRY	$\Delta H_f^o(g)$
Me-X	-112.69311	STD[a]	-114.21840	4-31G[b]	-38.5[i]
Et-X	-151.27926	part STO-3G[c]	-153.19990	part STO-3G[c]	-48.5[i]
iPr-X	-189.86608	part STO-3G[c]	-192.18789	part STO-3G[c]	-58.8[i]
HCC-X	-148.92418	STD[a]	-150.8778	4-31G[d]	
Vi-X	-150.13481	STO-3G[e]	-152.0624	4-31G[f]	-38.3[a]
cPr-X	-188.66822	EXP,STD[a]	-190.98167	DZ[g]	
Ph-X	-300.97376	STD[h]			

a) Ref. 1 b) Ref. 11 c) Ref. 55 d) Ref. 46 e) Ref. 62 f) Ref. 63 g) This work; double zeta geometry of ref. 20 used with C-H = 1.071, ∠HCH = 114 from 4-31G study of cyclopropane from ref. 22. h) Ref. 57 i) Ref. 64

$X = NH_3^+$

	STO-3G	GEOMETRY	4-31G	GEOMETRY	$\Delta H_f^\circ(g)$
Me-X	-94.45956	part STO-3G[a]	-95.43739	part STO-3G[a]	147.6[f]
Et-X	-133.04715	part STO-3G[a]	-134.42205	part STO-3G[a]	138.8[f]
*i*Pr-X	-171.63360	part STO-3G[a]	-173.40627	part STO-3G[a]	127.8[f]
HCC-X	-130.56022	STD[b]			
Vi-X	-131.81514	STO-3G[c]	-133.22214	STO-3G[c]	173[g]
*c*Pr-X	-170.40219	EXP,STD[b]	-172.19149	DZ[d]	170.6[f]
Ph-X	-282.63403	STD[e]			176.5[f]

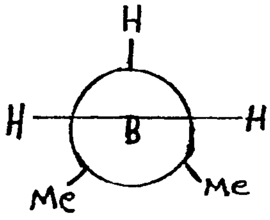
a) Ref. 55 b) Ref. 1 c) Ref. 65 d) This work; double zeta geometry from ref. 20 employed with C-H = 1.071, ∠HCH = 114 from 4-31G study of cyclopropane of ref. 22. N-H = 0.994 from ref. 11, 4-31G study of $Me\text{-}NH_2$ (assumed tetrahedral). e) Ref. 57 f) Ref. 66 g) Ref. 67 gives experimental $\Delta H_f^\circ(g)$ for $(CH_3CHNH_2)^+$ = 157 kcal/mole (i.e. vinylamine is protonated on the beta carbon, not nitrogen). Ref. 68 predicts difference of 16.2 kcal/mole between $CH_3CHNH_2^+$ and $CH_2{=}CHNH_3^+$ at 4-31G level.

X = BH_2

	STO-3G	GEOMETRY	4-31G	GEOMETRY	$\Delta H_f^o(g)$
Me-X	-64.66769	STO-3G[a]	-65.34844	4-31G[b]	
Et-X	-103.24302	STD[c]	-104.31919	STD[d]	
iPr-X	-141.81980	STD[e]	-143.29581	4-31G[f]	
HCC-X	-100.82309	STO-3G[g]			
Vi-X	-102.02522	STD[h,k]	-103.14016	STD[h,k]	
	-102.01463	STD[e,l]	-103.12736	STD[h,l]	
cPr-X	-140.61436	STO-3G[i,m]			
	-140.60513	STO-3G[j,n]			
Ph-X					

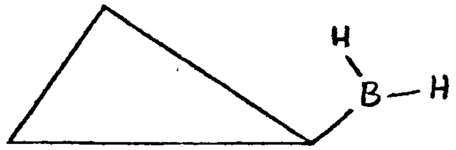
a) Ref. 69 b) Ref. 11 c) Ref. 24 d) Ref. 70 e) Ref. 1 f) This work; model 3) employed with BH_2 group from ref. 11. BH_2 group taken from Me-BH_2 with C-B = 1.568. See Fig. 2.6) for conformation. g) Ref. 71 h) Ref. 24 i) This work; model 3) employed with BH_2 structure from ref. 69 of Me-BH_2. C-B = 1.570 as starting point, with this geometry E_t = -140.61382. C-B then varied by 0.05 and minimum found at 1.55. Ring was also partially distorted: Vicinal bond was lengthened to 1.512, note however that ring optimization is incomplete. j) This work; model 3) employed with starting point geometry of i). k) Planar BH_2. l) Perpendicular BH_2. m) Bis, see Fig. II.7). n) Symmetrical, see Fig. II.7).

Fig. II.6

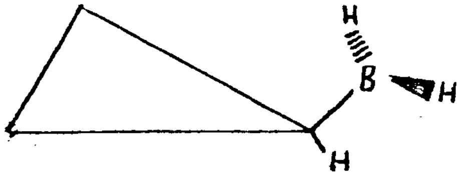


PERPENDICULAR

Fig. II.7



BISECTED

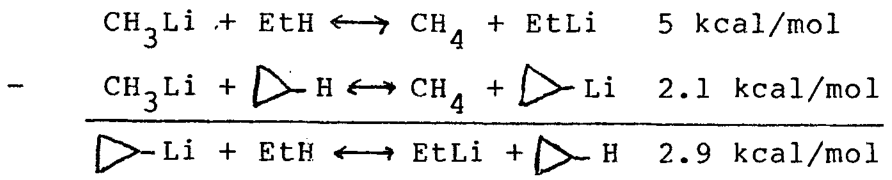


SYMMETRICAL

$X = Li$

	STO-3G	GEOMETRY	5-21G[i]	GEOMETRY	$\Delta H_f^o(g)$
Me-X	-46.42159	STO-3G[a]	-46.96000	4-31G[b]	
Et-X	-84.99605	STO-3G[c]			-15.2[h]
iPr-X	-123.56856	STD[d]			
HCC-X	-82.60886	STD[d]			
vi-X	-83.79930	STO-3G[e]			
cPr-X	-122.36459	STO-3G[f]			
Ph-X	-234.60099	STD[g]			

a) Ref. 33 b) Ref. 11 c) Ref. 72 d) Ref. 1 e) Ref. 25 f) Ref. 73 g) Ref. 57 h) Ref. 23 i) No energies given unless fully optimized. This is because stabilization energies for the unsaturated species (except substituted phenyl) are available at the 5-21G//4-31G level from ref. 74 by appropriate subtraction of the energy of one isodesmic equation from another. For example, for ethyl stabilization (see Chapt. III) of cyclopropyllithium, a value of 2.9 kcal/mol is obtained (see Table III.3):



$X = CH_2^+$

	STO-3G	GEOMETRY	4-31G	GEOMETRY	$\Delta H_f°(g)$
Me-X	-77.40806	STO-3G[a]	-78.19496	STO-3G[b]	219[f]
Et-X	-115.99632	STO-3G[a]			208[f]
*i*Pr-X	-154.57389	STD[c]			199[f]
HCC-X	-113.56391	STO-3G[d]	-114.78923	STO-3G[d]	281[g]
Vi-X	-114.80953 -114.75464	STO-3G[e,h] STO-3G[e,i]	-116.02511 -115.96939	STO-3G[e,h] STO-3G[e,i]	226[g]
*c*Pr-X	-153.39490 -153.35301	STO-3G[d,j] STO-3G[d,k]	-154.99277 -154.94407	STO-3G[d,j] STO-3G[d,k]	
Ph-X	-265.65231	STO-3G[d]	-268.50168	STO-3G[d]	

a) Ref. 25 b) Ref. 75 c) Ref. 1 d) Ref. 76 e) Ref. 77 f) Ref. 78 g) Ref. 79 h) Planar CH_2^+. i) Perpendicular CH_2^+. j) Bis. k) Symmetrical.

X = NC

	STO-3G	GEOMETRY	4-31G	GEOMETRY	$\Delta H_f o(g)$
Me-X	-130.23319	STO-3G[a]	-131.69360	EXP[b]	41.3[j]
Et-X	-168.81638	STO-3G[c]	-170.67496	part 4-31G[d]	33.8[k]
iPr-X					
HCC-X	-166.36674	Dunning[e]	-168.26375	Dunning[e]	
Vi-X	-167.59314	STO-3G[f]	-169.48569	6-31G[g]	
cPr-X	-206.17892	STO-3G[h]	-208.44363	4-31G,6-31G[i]	
Ph-X					

a) Ref. 80 b) This work; experimental geometry of ref. 81 employed. c) This work; model 1) employed with STO-3G optimized geometry of ref. 82 employed, except hydrogen geometry around carbon from STO-3G geometry of ethane (ref. 10). d) This work; model 3) employed with N$\equiv$C = 1.167 from 6-31G study of vi-NC (ref. 83). C-N = 1.415, interpolated from STO-3G studies of Et-CN and Et-NC from ref. 82 and 4-31G study of Me-CN from ref. 11. e) This work; model 1) employed with geometry from Dunning basis set study of ref. 84. f) 83 g) This work; model 1) employed with 6-31G geometry from ref. 83. h) This work; model 3) used, N$\equiv$C = 1.175 from STO-3G study of vi-NC (ref. 83); ring-NC bond = 1.42, interpolated from ring-CN bond of ref. 17, 6-31G vi-CN bond of ref. 83 and STO-3G result of vi-NC bond from ref. 83. i) This work; model 3) employed, N$\equiv$C = 1.167 from 6-31G study of vi-NC of ref. 83; ring-NC bond = 1.39, interpolated as in h) using 6-31G study of vi-NC from ref. 83. j) Ref. 85 k) Calculated here using ΔH_i=-21.5 kcal/mole of ref. 85 and $\Delta H_f o$ of Et-CN = 12.3 kcal/mole of ref. 23.

$X = CO_2Me$

	STO-3G	GEOMETRY	4-31G	GEOMETRY	$\Delta H_f°(g)$
Me-X	-263.3907	STO-3G[a]	-266.4298	STO-3G[a]	-98.0[k]
Et-X	-301.97056	STO-3G[b]	-305.41253	4-31G,EXP[c]	-102.5[l]
iPr-X					-109.1[o]
HCC-X	-299.52650	STO-3G,EXP[d]	-303.00509	4-31G,4-21G[e]	
Vi-X	-300.74673	STO-3G[f,m]	-304.22496	4-31G,EXP[h,m]	-79.6[k]
	-300.74579	STO-3G[g,n]	i,n		
cPr-X	-339.33413	STO-3G,EXP[j,m]	i,m		-73.6[o]
	-339.33367	STO-3G,EXP[j,n]	i,n		
Ph-X					-68.8[k]

a) Ref. 63 b) This work, see Fig. II.8); model 3) used with CO_2Me STO-3G geometry from ref. 63 of methyl acetate with hydrogen geometry around C_4 taken as 1/2 of STO-3G structure of ethane (ref. 10). Note heavy-atom planarity assumed. c) This work, see Fig. II.8); model 4) used with experimental geometry of CO_2Me group from ref. 45 of HCO_2Me. C_2-C_3 = 1.514 from ref. 12. d) This work; model 3) employed with CO_2Me STO-3G geometry from ref. 63, with hydrogen geometry around methyl taken as 1/2 of STO-3G geometry of ethane (ref. 10). Acetylene-substituent bond taken as 1.473, see e). e) This work; model 3) employed with 4-21G geometry of CO_2Me group from ref. 86. Acetylene-substituent bond taken as 1.473, interpolated from experimental geometry of propynal from ref. 87 and STO-3G results of vi-substituent bond for vi-CO_2Me and vi-CHO (see appropriate molecules within). Actual interpolated value = 1.463, but did not converge for this value, therefore lengthened to 1.473. f) This work, see Fig. II.9); model 3) used with CO_2Me STO-3G structure same as in b). Used standard value of C_2-C_3 = 1.46 from ref. 9 for starting point, then manually optimized C_1-C_2 and C_2-C_3 by .01 Å and found C_1-C_2 = 1.316 and C_2-C_3 = 1.52 for the energy minimum. g) This work; used resulting geometry of f). h) This work; model 4) employed with experimental CO_2Me group from ref. 45 of HCO_2Me. For C_2-C_3 used 1.470 from Allen (ref. 12). i) Attempted this work, did not converge. j) This work; model 3) used with CO_2Me group used in b), ring-substituent bond = 1.484 from ref. 12. k) Ref. 23 l) Estimated here from the following equation:

$CH_3CH_2CO_2Me = CH_3CO_2Me - CH_3CO_2Et + CH_3CH_2CO_2Et$; all $\Delta H_f°(g)$ values from ref. 23. m) Cis, see Fig. II.9). n) Trans, see Fig. II.9). o) R. Fuchs, unpublished data, personal communication.

Fig. II.8

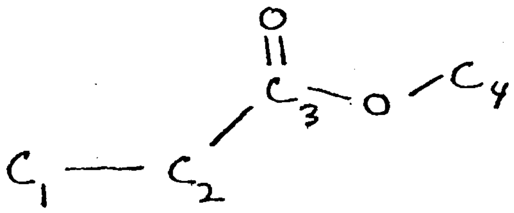
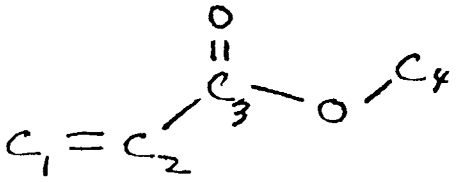
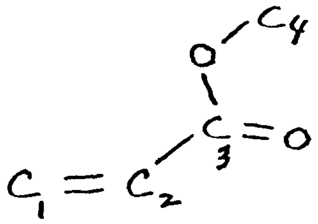


Fig. II.9



CIS



TRANS

X = CF_3

	STO-3G	GEOMETRY	4-31G	GEOMETRY	ΔH_fo(g)
Me-X	-370.68983	EXP[a]	-375.33319	4-31G[b]	-178.8[k]
Et-X	-409.26338	part STO-3G[c]	-414.31301	4-31G[d]	
iPr-X					
HCC-X	-406.8226	STO-3G[e]	-411.89036	EXP[f]	
vi-X	-408.04156	STO-3G[g]	-413.11525	4-31G,EXP[h]	-146.8[k]
*c*Pr-X	-446.62879	STD[a]	i		
Ph-X	-558.85759	part STO-3G[j]			-143.2[k]

a) Ref. 1 b) Ref. 11 c) This work; model 3) employed with STO-3G geometry of ethane from ref. 10 and CF_3 geometry from Greenberg (personal communication), C-CF_3 = 1.51, C-F = 1.37, all angles = 109.47. d) This work; model 3) employed with 4-31G CF_3 group from ref. 11 of Me-CF_3. Note C-CF_3 was mistakenly taken as 1.495 rather than 1.492, but it is felt that this error makes little difference in E_t. e) 29 f) This work; experimental geometry of ref. 88 employed. g) This work; model 3) employed with CF_3 group same as in c). C-CF_3 bond was varied by 0.01 A, and E_t given is for 1.55, but a minimum was not reached; it is felt that a minimum would be achieved for a slightly longer bond length. h) This work; experimental geometry of ref. 89 used except C-F = 1.361 from 4-31G study of Me-CF3 from ref. 11 and HCH and C-H values used from 4-31G study of ethylene (ref. 10). i) Attempted here; exceeds capabilities of program (too many orbitals). j) Ref. 36 k) Ref. 23

$X = NO_2$

	STO-3G	GEOMETRY	4-31G	GEOMETRY	$\Delta H_f o(g)$
Me-X	-240.42465	STO-3G[a]	-243.27451	4-31G[b]	-17.9°
Et-X	-279.00844	STO-3G[c]	-282.25646	4-31G[d]	-24.4°
*i*Pr-X					-33.2°
HCC-X	-276.53945	STO-3G[e]	-279.81649	STD[f]	
Vi-X	-277.78097 -277.77366	STO-3G[g,q] STO-3G[h,r]	-281.06442	4-31G[i,q]	9.0[p]
*c*Pr-X	-316.36521 -316.36075	4-21G[j,s] 4-21G[j,t]	-320.02569 -320.01871	EXP,4-21G[k,s] 4-21G[l,t]	
Ph-X	-428.59301	part STO-3G[m]	-433.51617	STD[n]	16.2°

a) Ref. 90 b) Ref. 11 c) This work; model 3) employed with NO_2 STO-3G structure from ref. 90 of Me-NO_2. Attempted C-N bond at various bond lengths and found minimum at 1.53 in agreement with ref. 90. Ref. 45 points out that this molecule has heavy atom planarity, but found minimum when the NO_2 group was rotated 90 degrees from this position (see Fig. II.10)). d) This work; model 3) employed with conformation found from STO-3G study. 4-31G structure of NO_2 and C-NO_2 from ref. 11 of Me-NO_2. e) This work; model 3) employed with STO-3G geometry of NO_2 from ref. 90 of Me-NO_2. C-N = 1.39; interpolated from sp^3C-NO_2 bond = 1.53 of ref. 90 and 1.47 of Pople's standard values, and spC-NO_2 = 1.33 of Pople's standard values (ref. 9). f) Ref. 26 g) This work; model 3) employed with STO-3G structure of NO_2 group from ref. 90 of Me-NO_2. First tried C-N = 1.47 from microwave result of Loos and Günthard (ref. 91), and then manually optimized by increments of 0.01, finding a minimum for C-N = 1.50. The C=C bond was also varied by 0.01, and did not change from original length of 1.306. E_t using experimental values of Loos and Günthard = -277.76239. h) This work; geometry found above was employed. E_t using experimental geometry of ref. 91 = -277.75483. i) Ref. 26, conformation not given, but due to full geometry optimization, assumed minimum energy conformer. j) This work; model 1) employed with 4-21G geometry of ref. 15. Using experimental geometry of ref. 92, Malangone (ref. 93) found total energies of -316.35512 and -316.34955 for the bisected and symmetrical geometries respectively. k) This work; using 4-21G geometry of ref. 15, the calculation would not converge, therefore used experimental ring of *c*Pr-NO_2 of ref. 92 and 4-21G NO_2 of ref. 15. Note also that C-N = 1.475, the 4-21G value for the symmetrical conformation, because convergence could not be achieved using the shorter bisected result. l) This work; model 1) employed with 4-21G geometry from ref. 15.

m) Ref. 36 n) Ref. 26 o) Ref. 23 p) Estimated here from the following equation: Ph-NO$_2$ (16.2 kcal/mole) + vi-CH$_3$ (4.8 kcal/mole) = Ph=CH$_3$ (12.0 kcal/mole) + vi-NO$_2$. All values of $\Delta H_f o(g)$ from ref. 23. Note $\Delta H_f o(g)$ estimated by Shaw (ref. 94) is 13.4 kcal/mole. q) Planar NO$_2$, see Fig. II.11). r) Perpendicular NO$_2$, see Fig. II.11). s) Bis conformation, see Fig. II.12). t) Symmetrical conformation, see Fig. II.12).

Fig. II.10

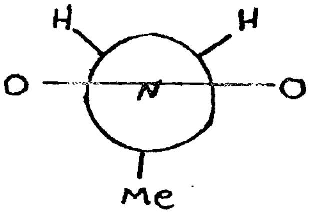
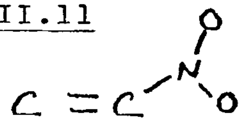
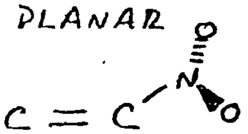


Fig. II.11

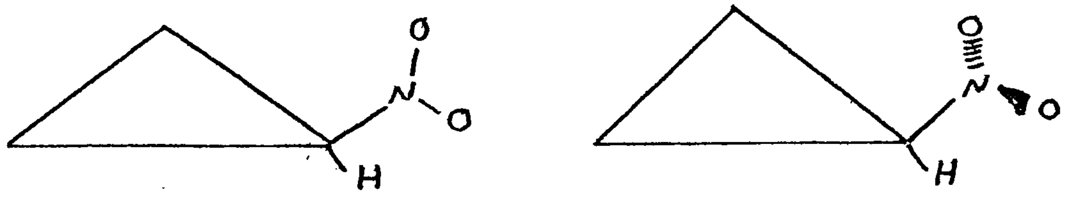


PLANAR



PERPENDICULAR

Fig. II.12



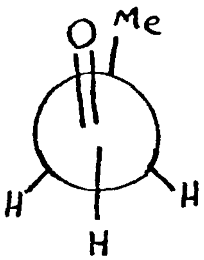
BISECTED SYMMETRICAL

X = CHO

	STO-3G	GEOMETRY	4-31G	GEOMETRY	ΔH_fo(g)
Me-X	-150.94599	STO-3G[a]	-152.68653	4-31G[b]	-39.6[o]
Et-X	-189.52293	part STO-3G[c]	-191.66552	4-31G[d]	-44.8[o]
iPr-X	-228.10411	STO-3G[e]			-51.5[o]
HCC-X	-187.0855	STO-3G[f]	-189.26094	STD[g]	
Vi-X	-188.30276	STO-3G[h,q]	-190.47804	4-31G[i,q]	-16.2[p]
	-188.30273	STO-3G[h,r]	-190.47909	4-31G[j,r]	
cPr-X	-226.88794	STO-3G[k,q]	l,q		
	-226.88884	STO-3G[k,r]	l,r		
Ph-X	-339.11863	part STO-3G[m]	-342.93279	STD[n]	-8.8[o]

a) Ref. 25 b) Ref. 11 c) Ref. 95 d) This work; model 3) employed with and 4-31G CHO group from ref. 52 of Me-CHO, C-CHO = 1.494. Conformation from ref. 45 (see Fig. II.13)). e) This work; STO-3G CHO group geometry from ref. 52 of Me-CHO, Pr-CHO bond = 1.537. See Fig. II.14). f) Ref. 29; Et = -187.08020 using experimental geometry of ref. 87. g) Ref. 26 h) This work; model 1) employed with STO-3G optimized geometry from ref. 25. E_t used however was -188.30353 from ref. 25 of unknown conformation. i) This work; model 1) used with 4-31G structure from ref. 96. j) Ref. 26 k) This work, see Fig. II.15); model 3) used with CHO geometry from STO-3G result of acrolein from ref. 25. Ring-C bond used was 1.464; interpolated from this work's result for vi-COMe = 1.52, vi-CHO = 1.51 from ref. 25, and Allen's bond length for cPr-COMe = 1.474 (ref. 12). l) Not converging using model 3). m) Ref. 36 n) Ref. 26 o) Ref. 23 p) Ref. 97. ΔH_fo=-20.6, estimated in ref. 98. q) Cis conformation. r) Trans conformation.

Fig. II.13



CARBONYL ECLIPSES METHYL

Fig. II.14

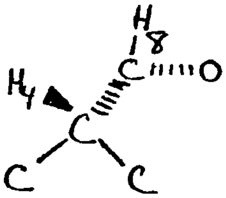
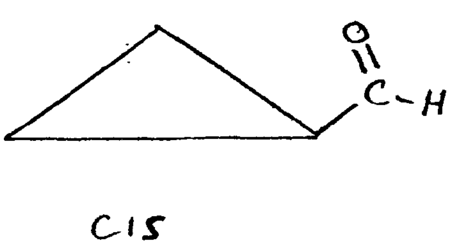
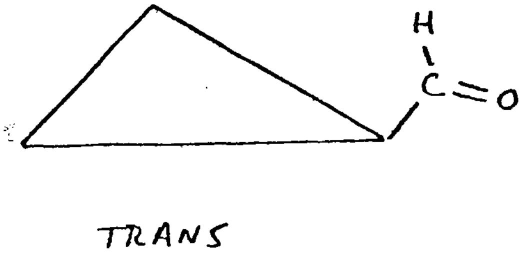


Fig. II.15



CIS



TRANS

X = COMe

	STO-3G	GEOMETRY	4-31G	GEOMETRY	$\Delta H_f°(g)$
Me-X	-189.53603	STO-3G^{a}	-191.67699	EXP^{b}	-51.9^{m}
Et-X	-228.11378	STO-3G^{c}	-230.65561	4-31G^{d}	-57.6^{m}
iPr-X	-266.69364	STO-3G^{e}			-62.7^{m}
HCC-X	-225.6743	STO-3G^{f}	-228.25181	STD^{g}	
Vi-X	-226.89211	STO-3G^{h,o}	-229.46562	STD^{i,o}	-32.1^{n}
	-226.89006	STO-3G^{h,p}	-229.45784	STD^{i,p}	
cPr-X	-265.47820	STO-3G^{j,o}	-268.43155	4-31G^{k,o}	-28.4^{q}
	-265.47036	STO-3G^{j,p}	^{l,p}		
Ph-X					-20.7^{m}

a) Ref. 25 b) Ref. 28 c) This work, see Fig. II.17); model 3) employed with all heavy atoms lying in a plane. STO-3G geometry of MeCO group from ref. 52 of acetaldehyde: C_2-C_3 taken as equal to C_3-C_4 (1.537) and $\angle C_2C_3O$ taken as equal to $\angle OC_3C_4$ (122.85). d) This work, see Fig. II.17); model 3) employed, 4-31G structure of MeCO group from acetaldehyde of ref. 52. C_2-C_3 taken as equal to C_3-C_4 (1.494), $\angle C_2C_3O$ = 124.2, $\angle C_2C_3C_4$ = 116. e) This work, see Fig. II.18); model 3) employed with STO-3G structure of MeCO group from ref. 52. Hydrogen geometry around C_5 taken as same as STO-3G result for ethane (ref. 10). C_1-C_4 taken as equal to C_4-C_5 (1.537), and $\angle C_1C_4O$ taken as equal to $\angle C_5H_4O$ (122.85). f) Ref. 29 g) Ref. 26 h) This work, see Fig. II.16); model 3) employed with STO-3G values for C=O and C_3-C_4 from ref. 52 of Me-CHO (1.217,1.537), 4-31G values for angles around carbonyl carbon from ref. 96 of trans acrolein ($\angle C_2C_3O$ = 123.7, $\angle C_2C_3C_4$ = 115.9), and standard value from ref. 9) of C_2C_3 used as a starting point. C_1-C_2 and C_2-C_3 were then manually optimized by increments of 0.01 A for cis configuration and found to be 1.316 and 1.52 respectively. This same geometry was then used to find the energy of the trans isomer. i) Ref. 26 j) This work; model 3) employed, STO-3G structure of COMe group from ref. 52 of acetaldehyde except angles around carbonyl carbon from ref. 96 of trans acrolein. Exocyclic ring-carbon bond taken as 1.474 from ref. 12. k) This work; model 3) employed, 4-31G structure of MeCO group from ref. 52 of acetaldehyde, 4-31G angles around carbonyl carbon from ref. 96 of trans acrolein. Exocyclic ring-carbon bond = 1.474 from ref. 12. For this geometry E_t = -268.43151. The distal bond was manually optimized (shortened by 0.013 A) to arrive at above energy. The starting point was a distal bond shortening of 0.026 A to 1.475 as recommended by Allen (ref. 13) l) Not converging. m) Ref. 23 n) Ref. 98, estimated value. o) Cis conformation. p) Trans conformation. q) R. Fuchs, unpublished data, personal communication.

Fig. II.16

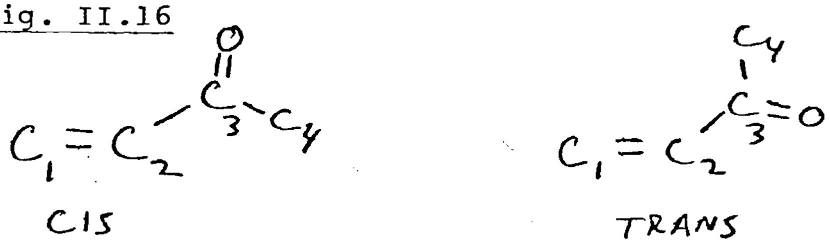


Fig. II.17

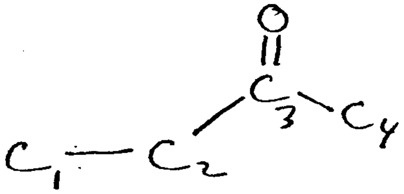
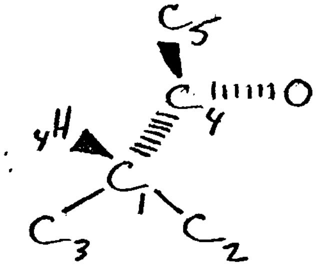


Fig. II.18



X = CN

	STO-3G	GEOMETRY	4-31G	GEOMETRY	ΔH_fo(g)
Me-X	-130.27155	STO-3G[a]	-131.72827	4-31G[b]	15.4[l,o]
Et-X	-168.85092	STD[c]	-170.70592	4-31G[d]	12.3[l]
iPr-X	-207.42583	STD[c]			5.9[l]
HCC-X	-166.41104	STO-3G[e]	-168.3033	STO-3G[f]	
vi-X	-167.62729	STO-3G[g]	-169.51575	4-31G,6-31G[h,n]	43.2[l]
cPr-X	-206.21484	EXP,STD[c]	-208.47677	4-21G[i]	43.2[l,m]
Ph-X	-318.44420	part STO-3G[j]	-321.96792	STD[k]	51.6[l]

a) Ref. 80 b) Ref. 11 c) Ref. 1 d) This work; model 3) employed, C-CN = 1.455, C N = 1.142 from 4-31G study of Me-CN of ref. 11. e) Ref. 99 f) Ref. 29 g) Ref. 83 h) This work; model 3) employed: C-CN = 1.432, C N = 1.148 from 6-31G study of vi-CN from ref. 83. i) This work; complete geometry from 4-21G study of ref. 17. Total energy calculated here using experimental geometry of ref. 100 found to be -208.47583. j) Ref. 36 k) Ref. 26 l) Ref. 23 m) An experimental value of H_fo(g) = 45.2 kcal/mole was also found (ref. 101), but above value was employed for its better agreement with theoretical results. n) Since final draft, a slightly better energy has been calculated: -169.51592, ref. 40. o) Note since final draft a different value has been found (17.7 kcal/mol), see An, Xu-Wu; Mansson, M., J. Chem. Thermo. 1983, 15, 287-293.

X = vi

	STO-3G	GEOMETRY	4-31G	GEOMETRY	$\Delta H_f^o(g)$
Me-X	-115.66038	STO-3G[a]	-116.90510	4-31G[b]	4.8[e]
Et-X	-154.23771	STD[c]	-155.88080	STD[c]	-0.1[e]
iPr-X					-6.5[e]
HCC-X			-153.48883	STD[d]	69[f]
Vi-X	-153.02036	STO-3G[c]	-154.69906	STO-3G[c]	26.3[e]
cPr-X					
Ph-X			-307.14078	STD[d]	35.3[e]

a) Ref. 42 b) Ref. 11 c) Ref. 41 d) Ref. 26 e) Ref. 23
f) Ref. 38

$X = CCH$

	STO-3G	GEOMETRY	4-31G	GEOMETRY	$\Delta H_f^o(g)$
Me-X	-114.44898	STO-3G[a]	-115.70133	4-31G[b]	44.6[e]
Et-X	-153.02533	STD[c]	-154.67829	STD[c]	39.5[e]
*i*Pr-X					32.6[g]
HCC-X	-150.59577	STO-3G[c]	-152.28374	STO-3G[c]	113.0[g]
Vi-X			-153.48883	STD[d]	69[f]
*c*Pr-X					
Ph-X			-305.94397	STD[d]	78.2[g]

a) Ref. 21 b) Ref. 11 c) Ref. 41 d) Ref. 26 e) Ref. 23
f) Ref. 102 g) Ref. 38

CHAPTER III

STABILIZATION ENERGIES

The calculation of stabilization energies follows from the calculation of strain energy, thus we will first discuss the concept of ring strain.

Rings smaller than cyclohexane have inherent angle strain, and are therefore less stable thermodynamically than cyclohexane, although still quite stable.[103] It is also widely recognized that the reason for this strain is the fact that the C-C-C bond angles are forced to be less than the preferred (idealized) tetrahedral angles of 109.47° for sp^3 hybridized carbon. For the smallest ring, cyclopropane, the intra-ring bond angles are 60°[104] thereby introducing considerable strain.

The concept of strain can be examined from another point of view: That is, from the types of molecular orbitals occupied relative to those occupied by unstrained species (Fig. I.1). By observing the computer-generated molecular orbital pictures of cyclopropane,[2] one can see that two degenerate "π-type" molecular orbitals are occupied, as compared to the more strongly bonding σ type orbitals of propane.[1] The small angles then, are in fact the reason for the ring strain because they cause the high-energy π type MO's to form.

Ethylene and acetylene may be thought of as cyclic systems having strain (cycloethane and bicyclo[0,0,0]ethane) because high energy orbitals are occupied in place of low energy σ orbitals.[1,103]

Cyclopropane has about equal strain per carbon as ethylene (Table III.1), while acetylene has more than twice the strain per carbon of these species. This is because there are two weak bonds instead of one in acetylene.

TABLE III.1
STRAIN E, kcal/mole*

	4-31G	EXPERIMENTAL
ethylene	21.1	22.3
cyclopropane	31.2	27.4
acetylene	52.1	58.4

*Method for determination of strain energy discussed shortly, best possible model employed (homodesmotic equation).

A method of calculating strain energies was developed by George, et al.,[105] and a version of it applied by Dill, et al.[1] This involves what is termed a homodesmotic reaction, or what Dill, et al., call a "group separation reaction." This type of reaction is a special case of the isodesmic reaction, as defined by Hehre, et al.[106] An isodesmic reaction is one in which there is a retention of a number of bonds of a given formal type while changing their relation to one another. Hehre calls the resulting energy the "bond separation energy." The following is Hehre and coworkers' isodesmic equation for the bond separation of cyclopropane:

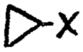
1)  $+ 3CH_4 = 3CH_3CH_3$

The resulting bond separation energy could be taken as the strain energy of cyclopropane. George argues however, that a homodesmotic equation, that is, one in which there are equal numbers of each type of C-C bond, and the C-H bonds are in as similar an environment as possible, would approximate the "true" strain energy much more closely. The following would be the homodesmotic equation for the strain energy of cyclopropane:

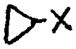
2)  $+ 3CH_3CH_3 = 3CH_3CH_2CH_3$

Notice that there are three $C(H)_2(C)_2$ groups and six $C(H)_3(C)$ groups on either side of the equation. It can readily be seen that reaction 2) should be more relevant than reaction 1) in determining the strain energy of cyclopropane since the chemical environments of each atom are more closely approximated in reaction 2). George offers proof of this by comparing isodesmic and homodesmotic strain energies for various species to their conventional strain energies.

Various workers, including Klein[107] and Allen[12], have shown that the cyclopropyl carbon is hybridized between sp^2 and sp^3: Klein by observation of the exocyclic C-C bond of methylcyclopropane, and Allen by observation of the X-ray determined ring-substituent bond lengths for a series of suubstituted cyclopropanes. Allen claims that the ring-substituent hybrid bond is approximately $sp^{2.2}$. As was mentioned, this is the reason for the ring strain. The exothermicity of eq. 2) measures the change of energy from bonds of π character to those of σ character. If a substituent is introduced to the strained ring, it can be characterized by two unsubstituted and one substituted secondary carbon (for cyclopropane). It follows then, that the strain energy of substituted cyclopropane is given by the energy difference of the following equation:

3)  + $3CH_3CH_3 = 2CH_3CH_2CH_3 + CH_3CH(X)CH_3$; $-\Delta E = \Delta E_{strain}$

Notice that once again the chemical environments are conserved. Now to find the overall stabilization energy (substituted cyclopropane versus parent compound), reaction 2) is subtracted from reaction 3) to give:

4)  + $CH_3CH_2CH_3 =$  + $CH_3CH(X)CH_3$; $\Delta E = \Delta E_{stab}$

Equation 4) involves nothing more than switching the substituent from the cyclic to the acyclic species. The endothermicity of this equation gives the stabilization energy of the substituted ring relative to the substituted isopropyl group.

The isopropyl model could also be used for the substituted ethylene series, where if thought of as "cycloethane," the homodesmotic equation of strain energy would be the same as for cyclopropane, the difference being two instead of three isopropyl groups needed to balance.

Substituted acetylene would require a somewhat different model, each carbon actually being a tertiary member of a "ring" as opposed to being a secondary member of a ring. For this case isobutane (i.e., tert-butyl model) is required. The following would simulate the strain and stabilization energies of acetylene:

5) $HCCH + 3CH_3CH_3 = 2CH(CH_3)_3; \quad -\Delta E = \Delta E_{strain}$

6) $HCC\text{-}X + CH(CH_3)_3 = HCCH + X\text{-}C(CH_3)_3; \quad \Delta E = \Delta E_{stab}$

Unfortunately, literature values for both the calculated energies and experimental heats of formation of substituted isopropyl and t-butyl groups are not numerous, and for the extended basis sets rarer still, as well as expensive to calculate. For these reasons we have employed ethane as our strain-free species for all comparisons (eq. 7) in addition to isopropane:

7) $\text{ring-}X + CH_3CH_3 = CH_3CH_2\text{-}X + \text{ring-}H$

Admittedly, the stabilization energy given by this isodesmic reaction as opposed to the proper homodesmotic reaction may not be as meaningful, but it should provide useful results for our purposes since we essentially aim to compare effects of various substituents to each other. The biggest problems may arise for the acetylene series, where a tertiary carbon should be used for comparison, and we are using a primary carbon; or for highly polarizing substituents such as NH_3^+.

The work was also done with methane as the model, primarily because available experimental heats of formation are more plentiful for substituted methanes than ethanes, and also because available theoretically calculated energies are probably more accurate (i.e., more thoroughly and consistently optimized).

In the following table, ΔE_{stab} refers to the stabilization energy calculated at the 4-31G level with always the best available energy used. For example, this means that for vinyl alcohol, the cis conformation is the one employed. ΔH_{stab} refers to the stabilization energy calculated with experimental heats of formation. It is noteworthy that substituents which are stabilized relative to the methyl model and perhaps even the ethyl model are often destabilized relative to the isopropyl model. An example of this is cyclopropylammonium ion which has a strongly polarizing substituent (see Table III.3). Only where two three-carbon moieties are compared (cyclopropyl versus isopropyl) does the best understanding emerge for this substituent.

TABLE III.2

VINYL-X[a]

STABILIZATION ENERGY MODEL:	METHYL		ETHYL		ISOPROPYL	
X	ΔE_{stab}[b]	ΔH_{stab}[c]	ΔE_{stab}[b]	ΔH_{stab}[c]	ΔE_{stab}[b]	ΔH_{stab}[c]
H	0.0	0.0	0.0	0.0	0.0	0.0
Cl	12.8	5.7		0.8		-2.2
F	6.4	6.7	0.0	3.3	-2.8	0.6
CH_3	4.3	5.4	3.2	2.8	3.5	0.6
OMe	10.9	12.3	6.1	6.9		3.3
OH	10.6	11.9	6.6	6.3	3.5	2.2
NH_2	13.3		11.2		10.2	
OAc		7.6[d]		1.8[d]		-2.3[d]
CH_2^-	39.6		35.0			
O^-	38.6	30.1	35.3	22.4	28.9	17.0
NH_3^+	1.5	4.9	-3.9	-1.6	-7.8	-7.7
CN	3.2	2.5[i]	2.3	1.7		0.2
NC	6.1		2.8			
CHO	6.4	6.9[e]	4.6	4.0[e]		2.2[e]
COMe	3.9	10.5	2.4	7.2		6.9
CO_2Me	8.0	11.9	3.9	9.5		
NO_2	4.7	3.4[f]	1.1	-0.8[f]		-4.7[f]
CF_3	-0.2	-1.7	-2.5			
Li	4.8		9.8		13.1	
BH_2	5.9		9.2		10.0	
CH_2^+	30.0	23.3		14.6		10.5
vi	7.3	8.8	7.5	6.2		4.7
HCC-	3.2[g]	5.9	2.7[h]	3.1		1.1

a) All energies in kcal/mole. b) 4-31G calculated energies used. c) Experimental heats of formation used. d) All $\Delta H_f o(g)$ values from ref. 23. e) If $\Delta H_f o(g)$ of vi-CHO estimated by Hegedus (ref. 98) is used, stabilization energy would be overestimated as compared to value listed. f) Used $\Delta H_f o(g)$ for vi-NO_2 that was estimated here, not Shaw's value (see Chapt. II). g) Note if vi-CCH was better optimized, this value would be greater. h) Note that both 1-butyne and vi-CCH desire improved geometry optimization, this good value is probably due to a cancellation of errors (see Chapt. IV). i) Note that this value would be 0.2 if An's value for $\Delta H_f o(g)$ of Me-CN is used (see Table II.1).

TABLE III.3

CYCLOPROPYL-X[a]

STABILIZATION ENERGY MODEL:	METHYL		ETHYL		ISOPROPYL	
X	ΔE_{stab}[b]	ΔH_{stab}[c]	ΔE_{stab}[b]	ΔH_{stab}[c]	ΔE_{stab}[b]	ΔH_{stab}[c]
H	0.0	0.0	0.0	0.0	0.0	0.0
Cl						
F	4.5		-1.9		-4.7	
CH_3	2.0	4.2	0.9	1.6	1.2	-0.6
OMe	5.3		0.5			
OH	5.0		0.9		-2.1	
NH_2	6.1	6.6	4.0	3.0	3.0	-0.7
OAc						
CH_2^-						
O^-	12.0		8.7		2.3	
NH_3^+	6.3	7.5	1.0	1.0	-3.0	-5.1
CN	2.8	2.7[f]	1.8	1.9		0.4
NC	3.7		0.5			
CHO						
COMe	6.6	7.0[e]	5.0	3.6[e]		3.4
CO_2Me		6.1		3.9		2.2
NO_2	4.5		0.8			
CF_3						
Li	-2.1		2.9		6.2	
BH_2						
CH_2^+	33.7					

a) All energies in kcal/mole. b) 4-31G calculated energies used. c) Experimental heats of formation used. d) Note that Hopkinson, et al. (ref. 108), found the strain energies of cyclopropane, cPr-F, cPr-CN, and cPr-NC at the 3-21G//3-21G level using the isopropyl model. The corresponding stabilization energies by this model are 0, -5.1, 1.0, and -2.2 kcal/mole. Note that the stabilization for cPr-F in this work is in good agreement, and that the same order of stabilization appears for this work using the ethyl model. e) Points not included in any correlations, aquired after completion of this work. f) Note that if $\Delta H_f o(g)$ for Me-CN from An is used, this value would be 0.4 (see Table II.1).

TABLE III.4

ETHYNYL-X[a]

STABILIZATION ENERGY MODEL:	METHYL		ETHYL		ISOPROPYL	
X	ΔE_{stab}[b]	ΔH_{stab}[c]	ΔE_{stab}[b]	ΔH_{stab}[c]	ΔE_{stab}[b]	ΔH_{stab}[c]
H	0.0	0.0	0.0	0.0	0.0	0.0
Cl	2.3					
F	-12.8		-19.2		-21.9	
CH_3	8.6	7.6	7.6	5.0	7.9	2.8
OMe	0.3		-4.5			
OH	0.7		-3.4		-6.4	
NH_2	11.5		9.4		8.4	
OAc						
CH_2^-	50.6		46.0			
O^-	55.0		51.7		45.3	
NH_3^+						
CN	2.1		1.2			
NC	-0.9		-4.2			
CHO	1.7		0.0			
COMe	2.0		0.5			
CO_2Me	2.3		-1.8			
NO_2	-18.6		-22.2			
CF_3	-9.1		-11.4			
Li	31.2		36.2		39.5	
BH_2						
CH_2^+	14.2	10.3		1.6		-2.5
vi	7.6[d]	8.1	7.9[d]	5.5		4.0
HCC-	6.8	3.9	6.3[f]	1.1		-0.9

a) All energies in kcal/mole. b) 4-31G calculated energies used. c) Experimental heats of formation used. d) Note that if vi-CCH were better optimized, this value would be greater. f) Note that if 1-butyne were to be better optimized, the value of ΔE_{stab} would be lower.

TABLE III.5

PHENYL-X[a]

STABILIZATION ENERGY MODEL:	METHYL		ETHYL		ISOPROPYL	
X	ΔE_{stab}[b]	ΔH_{stab}[c]	ΔE_{stab}[b]	ΔH_{stab}[c]	ΔE_{stab}[b]	ΔH_{stab}[c]
H	0.0	0.0	0.0	0.0	0.0	0.0
Cl		5.7		0.8		-2.2
F	6.3	8.5	-0.1	5.1	-2.9	2.4
CH_3	2.3	5.5	1.2	2.9	1.5	0.7
OMe	7.2	9.8	2.4	4.4		0.8
OH	8.5	12.4	4.4	6.8	1.4	2.7
NH_2	10.8	11.3	8.7	7.7	7.7	4.0
OAc						
CH_2^-	43.7		39.2			
O^-						
NH_3^+		8.7		2.2		-3.9
CN	2.2	1.4[f]	1.3	0.6		-0.9
NC						
CHO	6.3	6.8	4.6	3.9		2.1
COMe		6.4		3.0		2.8
CO_2Me		8.4		6.0		4.5
NO_2	3.5	3.5	-0.2	-0.7		-4.6
CF_3		2.0				
Li						
BH_2						
CH_2^+	44.3					
vi	-0.3[d]	7.1	0.0[d]	4.5		3.0
HCC-	4.1	4.0	3.6[e]	1.2		-0.8

a) All energies in kcal/mole. b) 4-31G calculated energies used. c) Experimental heats of formation used. d) Note that if the energy of styrene were to be better optimized, the stabilization energy would be greater). e) Note that if the geometry of 1-butyne were to be better optimized, this value would be lower. f) Note that if $\Delta H_f^o(g)$ for Me-CN from An is used, this value would be -0.9 (see Table II.1).

CHAPTER IV

COMPARISON OF THEORETICAL TO EXPERIMENTAL STABILIZATION ENERGIES

A comparison of the theoretical and experimental stabilization energies is necessary to support the validity of this work. There are really only enough experimental heat of formation data for meaningful comparisons with the vinyl and phenyl series using the methyl and ethyl models of stabilization energy. The issue of which is the best model is irrelevant here since all we are doing is comparing theoretical and experimental data for given equations. It is also worthwhile realizing that the calculations are for molecules hypothetically vibrationless "i.e., not even 0 K", while the experimental data is for 298 K. Table IV.1 lists the correlations along with the substituents employed.

Correlations 1)-7) are with the stabilization energies calculated using the methyl model (CH_3-X; i.e., methyl stabilization energies) in the isodesmic equation. For correlations 1), 2), and 3), with substituted vinyl, Cl was left out because the stabilization energy grossly disagrees with experiment, possibly because this is the only third-row element considered. Note also that there is uncertainty in the experimental $\Delta H_f o(g)$ value for $H_2C=CH-Cl$ (see Chapt. II). The COMe substituent was also left out because the experimental stabilization energy is believed to be too large. Note that $\Delta H_f o(g)$ of methyl vinyl ketone was estimated by Hegedus,[98] and is believed to be too large in the negative direction since the experimental stabilization energy is so large. Hegedus also estimated $\Delta H_f o(g)$ for acrolein by the same method, and found it to be -20.6 kcal/mole as compared to -16.2 kcal/mole found by Schiess.[97] If Hegedus' value is used, the experimental methyl stabilization energy of acrolein would be overestimated (11.3 vs. 6.9 kcal/mole). Satisfactory correlations are now found for equations 1)-3) for a considerable number of points. The difference between correlations 1) and 2) is that the ion substituents (CH_2^+, NH_3^+, and O^-) were left out of eq. 2). The slope appears to be strongly biased due to the large stabilizations afforded by the carbonium and oxyanion substituents. Eq. 3) is a significant improvement over eq. 2) because the HCC- substituent was left out. The theoretical stabilization energy of vi-CCH would be larger if this molecule were better optimized (see Table III.2).

For the benzene series using the methyl model, corr. 4), a fair result is found. Note that the slopes of correlations 3) and 4) are almost equal, which shows that the 4-31G calculated stabilization energy has a definite relationship with the experimentally found energy. Note that in corr. 4) the vi substituent was omitted because it is believed that the 4-31G energy of styrene desires improvement (see Table III.5).

Equation 5) gives the correlation of theoretical versus experimental methyl stabilization energy for substituted cyclopropane. While conclusions must be moderated because there are only five points, it is still noteworthy that the slope is similar to those of the vinyl and phenyl series, the intercept is close to zero, and there is a small standard error. Correlation 6) is with substituted ethynyl. Here also, the slope is biased due to the large stabilization imparted by CH_2^+.

The first attempt at correlating theoretical ethyl stabilization energies versus experimental ones for the vinyl series was not completely successful (eq. 8)). However, upon closer inspection, the outlying substituents were found to be COMe, CO_2Me, F, O^-, and NH_3^+. In the calculation of the experimental stabilization energy for the first three of these substituents, an estimated heat of formation value was employed. The COMe substituent has the same problem as mentioned above in the description of the methyl stabilization energies. The $\Delta H_f o(g)$ of Et-CO_2Me was estimated in this work, and appears to be too large in the negative direction since the experimental stabilization energy is so large, while $\Delta H_f o(g)$ of ethyl fluoride was the average of three estimated values,[61,62,11] and also appears to deviate in the negative direction. There will obviously be difficulty in the determination of $\Delta H_f o(g)$ for molecules with O^- and NH_3^+ as substituents. Without these substituents a satisfactory correlation is obtained in equation 9). Note that it was previously pointed out that the 4-31G energy of vi-CCH is poor, but that the theoretical ethyl stabilization energy for this compound is very close to the experimental value. This is because the 4-31G energy of 1-butyne is also poor, and a cancellation of errors occurs in the isodesmic equation (see Table III.2).

For correlations of ethyl stabilization energies in the phenyl series (eq. 10) and 11)), a fair correlation is obtained when eliminating the fluoride substituent as above. Notice that once again the slopes are similar for the vinyl and phenyl series (0.89 vs. 0.86). Note that in correlations 10) and 11) that the vi- and HCC- substituents were not included. This is because it is believed that the 4-31G energies of styrene and 1-butyne desire improvement (see Table III.5).

Correlations involving isopropyl stabilization energies are essentially meaningless due to the fact that there is a limited amount of data, and that this data is generally not too accurate because of the lack of geometry optimization in the calculation of total energies. Nevertheless, three correlations involving this model were performed (see correlations 14), 15) and 16).

It should also be mentioned that there were estimated heat of formation values employed that did not seem to damage these correlations. These were for methyl fluoride, methyl vinyl ether, nitroethylene, and methyl cyclopropane (see Chapt. II)

Correlations 7), 13), and 16) include all possible points, and are concerned with each particular stabilization model over all four of the strained species.

TABLE IV.1[a]

corr.	framework	n^p	R^{2p}	R^p	Std. Error	m^p	b^p
	A) METHYL STABILIZATION						
1)	vinyl	15	0.94	0.97	2.73	1.26	-2.10[b]
2)	vinyl	12	0.89	0.94	1.27	0.82	0.15[c]
3)	vinyl	11	0.94	0.97	0.93	0.74	1.00[d]
4)	phenyl	10	0.87	0.93	1.26	0.73	0.48[e]
5)	cyclopropyl	5	0.90	0.95	0.98	0.85	-0.15[f]
6)	ethynyl	5	0.88	0.94	2.02	1.17	0.43[g]
7)	all four[o]	38	0.84	0.92	3.10	1.15	-1.40
	B) ETHYL STABILIZATION						
8)	vinyl	14	0.85	0.92	3.66	1.43	-2.11[h]
9)	vinyl	9	0.91	0.96	0.81	0.89	0.81[i]
10)	phenyl	9	0.57	0.76	2.06	0.75	-0.09[j]
11)	phenyl	8	0.80	0.90	1.43	0.86	0.04[k]
12)	cyclopropyl	5	0.88	0.94	0.61	1.28	-0.38[l]
13)	all four[o]	34	0.76	0.87	3.10	1.27	-0.99
	C) ISOPROPYL STABILIZATION						
14)	vinyl	6	0.95	0.98	3.12	1.55	0.94[m]
15)	cyclopropyl	4	0.65	0.81	1.82	0.87	1.69[n]
16)	all four[o]	17	0.85	0.92	3.10	1.45	0.86

a) All theoretical stabilization energies calculated at the 4-31G level.

b) Substituents: H, F, Me, OMe, OH, CN, CHO, CO_2Me, NO_2, CF_3, CH_2^+, O^-, NH_3^+, vi, HCC−

c) Substituents: H, F, Me, OMe, OH, CN, CHO, CO_2Me, NO_2, CF_3, vi, HCC−

d) Substituents: H, F, Me, OMe, OH, CN, CHO, CO_2Me, NO_2, CF_3, vi

e) Substituents: H, F, Me, OMe, OH, NH_2, CN, CHO, NO_2, HCC−

f) Substituents: H, Me, NH_2, CN, NH_3^+

g) Substituents: H, Me, CH_2^+, vi, HCC−

h) Substituents: H, F, Me, OMe, OH, CN, CHO, COMe, CO_2Me, NO_2, O^-, NH_3^+, vi, HCC−

i) Substituents: H, Me, OMe, OH, CN, CHO, NO_2, vi, HCC−

j) Substituents: H, F, Me, OMe, OH, NH_2, CN, CHO, NO_2

k) Substituents: H, Me, OMe, OH, NH_2, CN, CHO, NO_2

l) Substituents: H, Me, NH_2, CN, NH_3^+

m) Substituents: H, F, Me, OH, O^-, NH_3^+

n) Substituents: H, Me, NH_2, NH_3^+

o) All possible pts. used with all four frameworks (vinyl, cyclopropyl, ethynyl, and phenyl). Substituents cautioned against in the text were also employed.

p) m = slope and b = y-intercept in the following equation:

$$\Delta E_{stab}(\text{theor}) = m\,\Delta H_{stab}(\text{exp.}) + b$$

n = number of pts., R = correlation coefficient

CHAPTER V

SUBSTITUENT CONSTANTS FOR CORRELATION ANALYSES

During the course of this project two sets of parameters have been employed for correlation analyses: Taft's σ_I and σ_R as compiled by Charton,[109] and Topsom's σ_X, σ_F, and σ_R^o.[26,110,111,112] The terminology used will be that outlined by Topsom.[110] A substituent's electronic effect is made up of field, F (through space or dipole), electronegative, X (through-bond polarization or inductive), and resonance effects. The term "inductive effect" is often used to cover both the field and through-bond effects, as it is by Charton and Shorter.[109,113] Topsom uses the term "electrostatic" to cover both effects and equates the term "inductive" with "electronegative."

It should be noted here that the Hammett equation is normally used to correlate free-energy changes and not enthalpy changes as it is in this work,[113,p.22] and that correlations involving enthalpies of reaction have generally not been successful. It is assumed that the entropy change for the isodesmic equations employed in the calculation of stabilization energies is negligible, thereby allowing the correlation of enthalpy changes. To show that the entropy change is negligible, a search was performed on the entropies of substituted vinyl, phenyl, and methyl compounds from the compendium of Stull, Sinke, and Westrum (ref. 38). Table V.1 lists the resulting entropy change using the methyl model of stabilization energy for the two unsaturated species.

TABLE V.1

ENTROPY CHANGE FOR THE ISODESMIC EQUATION

$$B\text{-}X = BH + CH_3\text{-}X - CH_4$$

X	B = phenyl[a]	B = vinyl[a]
Me	-0.59[b]	0.36[b]
OH	1.68	----
CO_2H	-0.85	0.16
NH_2	1.52	----
CN	1.28	0.65
F	0.74	----
Cl	0.94	0.89
Br	1.04	0.85
I	0.69	----
$HC{=}CH_2$	1.14	5.11
$C{\equiv}CH$	2.24	0.46

a) All units in e.u., all values from ref. 38. b) Symmetry correction factor of Rln2 employed.

It can be seen that for a typical isodesmic equation employed, there is very little variance in the resulting entropy from substituent to substituent. Therefore the following assumption will be made: $\Delta H \sim \Delta G$. Furthermore, because we are considering only gases in the isodesmic equation, we can state $\Delta E \sim \Delta H \sim \Delta G$. Note that there is an abnormal increase in entropy for the case of vinyl substituted with vinyl. This is understandably due to the strong π interaction in 1,3 butadiene, which favors the all-planar transoid conformer.

Charton's tabulation of Taft constants are based on the ionization of benzoic acid,[109,113] and for these correlations the dual-substituent parameter (DSP) approach of Ehrenson, Brownlee, and Taft has been employed:[114]

$$1)\quad \log k/k_o = \rho_I \sigma_I + \rho_R \sigma_R + \delta$$

where ρ_I and ρ_R are the sensitivity parameters for the inductive and resonance effects respectively, as compared to unity for the ionization of benzoic acid. See Table V.2 for the σ_I and σ_R constants employed. Note that in this work σ_I and σ_R are correlated versus ΔE and not log k/ko (remember it is assumed $\Delta E \sim \Delta H \sim \Delta G$). This correlation will yield the following equation:

$$2)\quad \Delta E = m_I \sigma_I + m_R \sigma_R + \delta'$$

Since:

$$3)\quad \Delta E \sim \Delta H \sim \Delta G = -2.303RT(\log k/k_o),$$

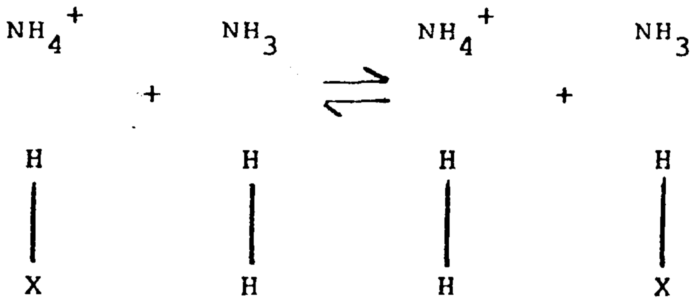
we can show by combining equations 2) and 3):

$$4)\quad \log k/ko = -(m_I \sigma_I/2.303RT + m_R \sigma_R/2.303RT + \delta'/2.303RT)$$

Therefore by comparing equations 1) and 4), it can be seen that the constants obtained by the correlation analysis here (m_I, m_R, and δ'), are directly related to the traditional sensitivity parameters of eq. 1).

Topsom has calculated theoretically his three constants using ab initio molecular orbital studies.[110] Topsom suggests that a substituent's electronegativity effect is not important if the reaction center is separated from the substituent by more than two carbons, as would be the case in meta and para substituted benzoic acids and pyridines. Since in the molecules studied here, the substituent is directly bonded to a carbon involved in the π system, and we are directly analyzing this interaction, the electronegativity parameter σ_X was taken into account. Topsom and coworkers have shown that the electron population at the hydrogen atom attached to various substituents (H-X) can directly provide values for the electronegativity parameter. These studies were done at the 6-31G*//6-31G* level.[110,115]

Marriott and Topsom [110,111,112] have studied the field effect parameter (σ_F) at the 4-31G level with standard geometries by two methods. The first involves the energy change for the proton-transfer equilibria of isolated molecules, thereby avoiding any electronegativity (through-bond) effects:



The second method involves the polarization of the electron population in hydrogen molecules by an isolated H-substituent molecule:

Both methods gave results that were found to be linearly related to established σ_I constants. The σ_F parameters used here are based on the second method alone, as listed in the more recent and more complete compilation of ref. 111.

The theoretical values for σ_Ro are taken from work by Marriott and Topsom,[26] in which the calculated atomic electron population ($\Sigma\Delta q_{\pi}$) of monosubstituted ethylenes was studied at the 4-31G//4-31G level. An excellent correlation between these electron populations and experimental σ_Ro values was found, and the values listed here were taken from this line. Note that for a particular substituent, if there are two possible conformations, the most stable conformation (according to the theoretical energies in this work) was used to find σ_R^o. The following line was found here between Charton's σ_R values and the theoretical σ_R^o values:

5) (n=10) $\sigma_R^o = 0.74\ \sigma_R + 0.03$ $R^2=0.98$ $R=0.99$

Standard error = 0.04

From this line various substituent constants were calculated where the theoretical value was not available. All constants are listed in Table V.2.

As mentioned, Topsom and coworkers have shown that the theoretically-calculated σ_F values are linearly related and virtually identical to experimentally found σ_I values.[110,111,112] In this work, Charton's σ_I was compared to Topsom's σ_F from ref. 111, and a satisfactory correlation was found:

6) (n=19) $\sigma_I = 1.00\ \sigma_F + 0.03$ $R^2=0.94$ $R=0.97$

Standard error = 0.05

From this line the σ_I was calculated for CHO and σ_F was calculated for NC since they were unavailable.

TABLE V.2

SUBSTITUENT CONSTANTS

X	σ_I[g]	σ_R[g]	σ_X[h]	σ_F[f]	σ_R^o[i]
H	0.0	0.0	0.0	0.0	0.0
F	0.54	-0.48	0.52	0.47	-0.29
Cl	0.47	-0.25	0.24[a]	0.44	-0.16[c]
Br	0.47	-0.25			
I	0.40	-0.16			
CH_3	-0.01	-0.16	0.17	-0.01	-0.09
OMe	0.30	-0.58	0.44	0.29	-0.42
OH	0.24	-0.62	0.43	0.30	-0.41
NH_2	0.17	-0.80	0.33[b]	0.15	-0.57
OAc	0.38	-0.23	0.46	0.41	-0.14[c]
vi	0.11	-0.15	0.18	0.04	0.00
HCC-	0.29	-0.04	0.28	0.17	-0.02
nPr	-0.01	-0.16			-0.09[c]
phenyl	0.12	-0.11		0.06	-0.05[c]
OEt	0.28	-0.57			-0.39[c]
CH_2Cl	0.17	-0.08			-0.03[c]
CH_2Br	0.20	-0.10			-0.04[c]
CH_2I	0.17	-0.09			-0.03[c]
Et	-0.01	-0.14			-0.07[c]
t-Bu	-0.01	-0.18		-0.01	-0.10[c]
OBu	0.28	-0.58			-0.40[c]
CN	0.57	0.08	0.31	0.45	0.08
NC	0.63	0.02[d]	0.43[b]	0.60[e]	0.05[c]
CHO	0.25[e]	0.20[c]	0.14	0.22	0.18
COMe	0.30	0.20	0.14	0.19	0.20
CO_2Me	0.32	0.11	0.19	0.25	0.11[c]
NO_2	0.67	0.10	0.40	0.66	0.18
CF_3	0.40	0.11	0.17	0.42	0.03
CO_2Et	0.30	0.11			0.11[c]
CO_2H	0.30	0.11	0.18	0.27	0.11[c]

a) 6-31G*//3G result from Topsom, ref. 115. b) Ref. 115 c) Calculated by eq. 5). d) Exner, ref. 116 e) Calculated from eq. 6). f) From ref. 111, note that there are also values listed in ref. 110 that are slightly different (see text). g) Charton, ref. 109 unless noted otherwise. h) Ref. 110, unless noted otherwise. i) Ref. 26, Marriott and Topsom, unless noted otherwise.

CHAPTER VI

SUBSTITUENT EFFECT DEPENDENCE ON ELECTRONIC PARAMETERS

Charton has shown that if only electrical effect parameters (Taft's or Topsom's parameters used in this work) are necessary to describe the stabilization energy of the four series of molecules (substituted vinyl, ethynyl, cyclopropyl, and phenyl), then the stabilization energy of any one set must be a linear function of any other two sets.[117]

The following is Charton's derivation of this conclusion: If Q_1 and Q_2 are different functions of the field and/or inductive effect (σ_I) and the resonance effect (σ_R), we may write:

1) $Q_{1x} = (L_1 \sigma_{\lambda x}) + (D_1 \sigma_{\delta x}) + h_1$

2) $Q_{2x} = (L_2 \sigma_{\lambda x}) + (D_2 \sigma_{\delta x}) + h_2$

where L_1 not equal to L_2 , D_1 not equal to D_2
(L used to connotate localized, D used to connotate delocalized)

If some quantity Q is correlated with Q_1 and Q_2 we have:

3) $Q_x = a_1 Q_{1x} + a_2 Q_{2x} + a_o$

From equations 1) and 2) it follows:

$$
\begin{aligned}
4)\quad Q_x &= a_1(L_1\sigma_{\lambda x} + D_1\sigma_{\delta x} + h_1) + a_2(L_2\sigma_{\lambda x} + D_2\sigma_{\delta x} + h_2) + a_o \\
&= (a_1L_1 + a_2L_2)\sigma_{\lambda x} + (a_1D_1 + a_2D_2)\sigma_{\delta x} + a_1h_1 + a_2h_2 + a_o \\
&= L\,\sigma_{\lambda x} + D\,\sigma_{\delta x} + h
\end{aligned}
$$

where

$$L = (a_1L_1 + a_2L_2);\quad D = (a_1D_1 + a_2D_2);\quad h = (a_1h_1 + a_2h_2 + a_o)$$

The above conclusion then follows from equations 4) and 3).

If equation 3) is obeyed, then two electrical effect parameters are sufficient to account for the stabilization energy. Also, by comparison of the dual-substituent parameter tests of the various possible arrangements of sets of data, one set that is not as good as the others would become visible.

Table VI.1, A)-C) lists the results of the four possible correlations using Charton's test for the methyl, ethyl, and isopropyl stabilization energies respectively.
Correlations involving the methyl and ethyl stabilization energies are the most meaningful because more data is available and the calculated total energies of the substituted methyl and ethyl groups are generally more accurate than the substituted isopropyl group, due to the degree of geometry optimization. Correlations involving the methyl model of stabilization energy are superior to those of the ethyl model. This is due to the fact that the substituted methyl group lends itself to easier geometry optimization, which results in more accurate

theoretically calculated energies.

Very good correlations are reported in Table VI.1, A) with the methyl stabilization energies. The only suspect correlation is 4), with $R^2=0.84$. The correlations of Table VI.1, B), with the ethyl stabilization energies, show two satisfactory correlations and two poor correlations. Notice that both of the poor correlations, 2) and 4), involve the combination of the stabilization energies of the substituted ethynyl and cyclopropyl groups. Note also that this combination was in the one suspect correlation of Table VI.1, A). It could be concluded, therefore that these two series of data sets desire improvement. It is not surprising that the cyclopropane series should stick out since the majority of substituted cyclopropane 4-31G total energies were calculated in this work either by using geometries calculated at a different basis set or with a limited amount of manual geometry optimization (see Chapt. II). The reason that the substituted acetylene series is an anomaly is that its stabilization mechanism is fundamentally different than the other 3 series. This will be discussed further. Even though only 6 of the 13 substituted acetylenes have been fully optimized, it is felt that these energies are not the problem. This is because substituted acetylene is a small system which allows easy calculation of a "good" geometry.

Note in Table VI.1, A) and B), that the vinyl and ethynyl substituents fall off the line of correlation 3) by an amount close to or greater than the standard deviation. This is most likely due to the fact that the majority of available 4-31G energies of molecules with these two substituents used in the calculation of stabilization energies were not fully geometry optimized, but rather either a standard geometry, or one optimized at a lower calculational level was used (see Chapt. II). It is felt that 1-butyne, styrene, and vinyl acetylene are in the most need of geometry optimization (see Tables III.2, III.4, III.5 and Chapt. IV).

Other information available from these correlations are the similarity or dissimilarity of the various systems. However, the sensitivity parameters can only be taken qualitatively for this purpose since we have already shown that the cyclopropyl data set is relatively poor, and therefore correlations involving this data set will naturally have a low dependence on it. Note that in correlation 1) in Table VI.1, A)-C) the phenyl group appears to be very similar to the vinyl group. Note also the relatively low dependence on the cyclopropyl group as predicted. In correlations 2)-4) note the generally low dependence on the ethynyl group and the good agreement between some combination of two of the other three groups (a slope close to unity). This data leads to the conclusion that the phenyl, vinyl, and cyclopropyl electronic systems are affected similarly by various substituents, while the ethynyl system is affected differently.

TABLE VI.1[a]

	n	R^2	R	Std. Error	a_1	a_2	a_o
			A) METHYL STABILIZATION				
1)[b]	9	0.99	1.00	1.11	0.97	0.42	-1.41
2)[c]	9	0.99	1.00	1.53	1.28	0.09	0.27
3)[d]	13	0.94	0.97	4.12	1.43	-0.13	-3.93
4)[e]	13	0.84	0.92	4.91	0.79	0.33	3.01
			B) ETHYL STABILIZATION				
1)[b]	8	0.94	0.97	0.91	0.21	0.69	-0.58
2)[c]	8	0.63	0.80	2.18	1.32	0.03	1.17
3)[d]	12	0.95	0.97	2.84	1.11	0.01	-2.02
4)[e]	12	0.78	0.88	5.04	1.55	0.22	2.62
			C) ISOPROPYL STABILIZATION				
1)[b]	5	0.98	0.99	0.74	0.16	0.70	-0.41
2)[c]	5	0.80	0.89	2.47	2.44	-0.33	2.03
3)[d]	5	0.98	0.99	0.82	0.77	0.01	-0.64
4)[e]	7	0.88	0.94	4.55	-1.60	0.60	3.20

a) All stabilization energies calculated at 4-31G level. All possible substituents (points) employed.

b) (phenyl-X) = a_1(cyclopropyl-X) + a_2(vinyl-X) + a_o

c) (phenyl-X) = a_1(cyclopropyl-X) + a_2(ethynyl-X) + a_o

d) (phenyl-X) = a_1(vinyl-X) + a_2(ethynyl-X) + a_o

e) (vinyl-X) = a_1(cyclopropyl-X) + a_2(ethynyl-X) + a_o

CHAPTER VII

CORRELATION ANALYSIS WITH SUBSTITUENT CONSTANTS

Through the use of Charton's test of dependence on electronic parameters, it is clear that any one of the four sets of theoretical stabilization energies can be described by Hammett-type substituent constants. Table VII.1 lists the dual substituent parameter tests using Charton's compendium of Taft constants and Table VII.2 contains the triple substituent parameter tests using Topsom's constants for the methyl, ethyl, and isopropyl stabilization energies respectively. Note that π-donating substituents and π-accepting substituents are separated. This is done because both effects are stabilizing ones (as outlined in Chapt. I), and hence the correlation constants would be of opposite sign. Note that we do not include either the vinyl or ethynyl substituents in the correlations. The reason these substituents cannot be included becomes obvious if we consider substituted ethylene. One of the systems would be 1,3 butadiene, with the substituent being the same as the strained species. The existing substituent constants for the vinyl group cannot be used because there will obviously be no electrostatic effect. Any stabilization occurs via the resonance effect. Equivalently, the "substituent" in 1,3 butadiene (or diacetylene) is both an electron donor and an electron acceptor. Remember also that we have shown in Chapt. V that Charton's σ_I constants are actually field effect constants. Therefore whenever we refer to the inductive effect of the DSP approach (Table VII.1), we will state as follows: Inductive (field) effect. Remember as outlined in Chapt. V that this is part of the overall electrostatic effect.

There are many conclusions that can be drawn from these correlations. First of all, note that the correlation constant of Topsom's electronegativity effect (m_X) is almost always positive, and is always positive for correlations involving methyl stabilization (Table VII.1). Since we would expect correlations of methyl stabilization energies to be the most consistent, this is evidence that the substituent electronegativity effect is a stabilizing one. Note that this is in contrast to the prediction of Dill, et al.,[1] as outlined in Chapt. I. A possible explanation of this is that if a substituent withdraws electron density through the exocyclic-ring bond, it is lowering the energy of the π and π^* MO's, thereby reducing strain and imparting stabilization on the system. Note also that the sign of the field effect constant, whether it be m_I or m_F, is negative. Several exceptions to this are the m_I values for the methyl stabilization model (Table VII.1, A)). The reason for this is the inflated dependence on the resonance effect as compared to the inductive (field) effect in the correlations with methyl stabilization energies as opposed to those of ethyl or isopropyl stabilization energies. This means that field effect donors are stabilizing and acceptors are destabilizing. Note that this follows the diagram of Dill, et al.,[1] for through-bond (electronegativity) effects (see Fig. I.2 and

I.3), except this is a through-space effect. It is interesting to note that there is a similar energy difference between the delocalized σ MO's of cyclopropane and propane ($3a_1$ vs. $5a_1$) as there is between the localized σ MO's used in Figs. I.2 and I.3 (see Fig. I.1). Therefore, perhaps Figs. I.2 and I.3 can be used to illustrate a substituent's field effect, with the delocalized MO's used in place of the localized MO's. This model does not work for substituted ethylene, however, because the $3a_g$ MO of ethylene is higher in energy than the $5A_1$ MO of propane (Fig. I.1). It is proposed that the field effect may work in this manner, but it is probably a complex interaction of several molecular orbitals. Also, the correlation parameters of both Charton's and Topsom's resonance effect constants (m_R and m_Ro) show that whether a substituent is π-electron donating or withdrawing, that this is a stabilizing effect.

Observing the DSP correlations with Charton's constants, notice that in general in the transition from methyl to ethyl to isopropyl stabilization energies, the stabilization energies depend more on the inductive (field) effect and less on the resonance effect. This is because in general stabilization energies decrease in magnitude through the methyl, ethyl, and isopropyl model series. Remember that for the vinyl and cyclopropyl substrates, the isopropyl model of stabilization energy should be the best model, since it involves a homodesmotic equation as opposed to an isodesmic equation for the methyl and ethyl models. However it should be noted that the correlations with the methyl and ethyl stabilization energies can tell us more because there is more data and that data is in general better. Similarly, for the triple substituent approach, there is the same general trend. In this case, however, to compensate for the decreasing stabilization energies in the transition from the methyl to ethyl or isopropyl models, there is a decrease in magnitude of stabilizing effects and an increase in destabilization effects.

It is obvious that correlations involving the π-donating substituents are very successful, whether it be for the double or triple constant approach. Likewise, it is also obvious that correlations involving the π-accepting substituents are very poor. It has been shown that this cannot be the fault of the calculated energies by the correlations of theoretical with experimental stabilization energies (Chapt. IV). The failure of these correlations, then, must lie with the mechanism of the substituent-strained system conjugation.

Note that in general, the π-donating substituents interact through donation of lone pair electrons (F,OMe,OH,NH_2). These substituents would have no molecular orbital of π^* type. Note however, that among the π-accepting substituents, there are many with π systems that would have such an orbital (CHO,COMe,CO_2Me,CN,NC). It might be suggested, then that a possible reason for the failure of correlations with π-accepting substituents is because such substituents would have another interaction with the ring, that is, the π^* MO of the substituent with the π orbital of the strained system. It is interesting to note that the correlations with π-accepting substituents depend more on the resonance effect as compared to the inductive (field) effect than correlations with π-donating substituents (Table VII.1).

Notice that the correlations involving π-accepting substituents done with the triple parameter approach are much improved over the dual parameter approach. This may not be due only to the extra freedom in the correlation, but also because of consideration of the electronegativity effect. Note that correlations with π-donors depend very little on the electronegativity parameter as compared to π-acceptors. It is not clear why this is the case, but in the mechanism of π-electron donation, the resonance and electronegativity effects are opposed, while in π-electron acceptance, the two mechanisms are in concert. Therefore, what we are observing is the opposite of what we would expect. For instance, in the case of a π-donating substituent, electron density is being built up in the strained system, and therefore we might expect it to give up electon density through the electronegativity effect more readily. Nevertheless, this consistent trend is evidence of the importance of the electronegativity effect in these systems. These correlations are still not successful, however, which still supports the idea of an extra resonance effect.

We can also see that the vinyl, cyclopropyl, and phenyl systems are very similar in their stabilizing or destabilizing effects with substituents because the relative proportions of the inductive (field) and resonance correlation parameters are very similar. The ethynyl system is very different. Notice that this system depends much more on the electrostatic effects than the other systems. The reason for this has been given by Dill, et al.[1] That is, the split between the σ and π type MO's in acetylene is greater than that in the other systems. The σ-type MO's are much lower in energy than in the other systems, and hence more dependence on these orbitals in the stabilization mechanisms (see Fig. I.1).

We can also see from the correlation constants that the vinyl group is a better π-electron acceptor than cyclopropyl and phenyl, but not as good as ethynyl. This can be seen by the m_R or m_Ro values of the correlations with π-donors or acceptors. Note also that in Table VII.1 all resonance effects are larger than the inductive (field) effects except for substituted ethynyl and the one case of substituted cyclopropyl for π-donors with ethyl stabilization. Table VII.1 also reveals that ethylene and acetylene are better π-acceptors than donors, and cyclopropane and benzene are better π-donors than acceptors.

It is worthwhile to look at the relationships between conjugation parameters and experimental ionization potentials and electron affinities of the parent hydrocarbons. For example in Table VII.3 a comparison is made using data based upon methyl stabilization energies. There is a very high correlation (R^2=0.98, n=4) between the m_R (π-acceptors) and adiabatic ionization potentials of the hydrocarbons. The correlation with vertical ionization potentials is not as good. The reason is, in part, due to the broadness of the cyclopropane band which introduces a large difference between adiabatic and vertical IP's unlike the case for ethylene, acetylene and benzene. Obviously, another aspect of uncertainty is the fact that Jahn-Teller distortions are expected in the radical cations and anions of cyclopropane and benzene. The relationship between vertical EA's (adiabatic values are not available) and m_R (π-donors) is not quite as straightforward. The small value for m_R correlates with the large negative electron affinity of cyclopropane, but after that the relationship breaks down.

Table VII.4 lists correlations of methyl and ethyl stabilization energies using the Taft resonance effect constants that apply where there is extra π-electron demand or donation to the substituent by the substrate. These were attempted here because of the direct conjugation between substituent and strained ring system. There were no dramatic differences from the correlations of Table VII.1. It seems that the correlations involving π-donors were somewhat worsened, and that those with π-electron acceptors were somewhat improved. This is hard to substantiate however, since we are using less points.

TABLE VII.1

	n^k	R^2	R^k	Std. Error	mI^k	$m_R{}^k$	δ'^k
			A) METHYL STABILIZATION				
vi-X							
(π-donors)	6	0.97	0.99	1.07	-4.36	-17.62	0.73[a]
(π-acceptors)	8	0.21	0.46	3.09	4.44	13.77	0.86[b]
	5	0.83	0.91	1.38	3.17	21.54	0.01[c]
cPr-X							
(π-donors)	6	0.98	0.99	0.44	1.39	-7.07	0.42[a]
(π-acceptors)	5	0.88	0.94	1.18	3.11	25.16	0.16[d]
HCC-X							
(π-donors)	6	0.94	0.97	2.68	-47.49	-20.87	2.02[a]
(π-acceptors)	8	0.24	0.49	7.76	-15.89	7.17[h]	2.49[b]
Ph-X							
(π-donors)	6	0.996	0.998	0.33	-0.70	-13.52	0.05[a]
(π-acceptors)	4	0.99	0.99	0.47	0.13	31.69	-0.06[e]
			B) ETHYL STABILIZATION				
vi-X							
(π-donors)	6	0.99	0.996	0.47	-15.27	-17.10	0.15[a]
(π-acceptors)	8	0.13	0.36	2.50	0.80	11.19	0.36[b]
cPr-X							
(π-donors)	6	0.95	0.97	0.57	-9.49	-6.51[i]	-0.17[a]
(π-acceptors)	5	0.90	0.95	0.90	-1.32	24.24	0.25[d]
HCC-X							
(π-donors)	6	0.96	0.98	2.78	-58.45	-20.28	1.48[a]
(π-acceptors)	8	0.30	0.54	8.10	-19.57	4.84[j]	2.45[b]
Ph-X							
(π-donors)	6	0.95	0.98	0.96	-11.58	-12.96	-0.54[a]
(π-acceptors)	4	0.90	0.95	1.21	-3.26	26.16	0.15[e]
			C) ISOPROPYL STABILIZATION[f]				
vi-X	5	0.96	0.98	1.38	-20.44	-15.71	0.25[g]
cPr-X	5	0.85	0.92	1.66	-14.36	-5.40	-0.05[g]
HCC-X	5	0.94	0.97	4.39	-63.12	-19.09	1.60[g]
Ph-X	5	0.92	0.96	1.59	-16.16	-12.07	-0.39[g]

a) Substituents: H, F, Me, OMe, OH, NH_2
b) Substituents: H, CN, NC, CHO, COMe, CO_2Me, NO_2, CF_3
c) Substituents: H, CN, CHO, COMe, NO_2
d) Substituents: H, CN, NC, COMe, NO_2
e) Substituents: H, CN, CHO, NO_2
f) Only enough data to correlate π-donors.
g) Substituents: H, F, Me, OH, NH_2
h) Note inconsistency of sign of this value with that of $m_R{}^o$ (Table VII.2, A)).
i) Note that it is unusual for m_I to be greater than m_R.
j) Note inconsistency of sign of this value with that of $m_R{}^o$ (Table VII.2, B)).
k) n = number of pts., R = correlation coefficient, for others see Chapt. V.

TABLE VII.2[a]

	n	R^2	R	Std. Error	m_X	m_F	m_{R^o}	δ'
A) METHYL STABILIZATION								
vi-X								
(π-donors)	6	0.99	0.997	0.59	15.98	-14.55	-18.73	-0.10
(π-acceptors)	8	0.67	0.82	2.25	38.25	-21.36	16.52	1.24
cPr-X								
(π-donors)	6	0.999	0.999	0.14	7.58	-3.37	-7.03	0.02
(π-acceptors)	5	0.99	0.99	0.56	41.45	-26.23	29.10	-0.09
HCC-X								
(π-donors)	6	0.996	0.998	0.87	33.89	-77.77	-20.80	0.09
(π-acceptors)	8	0.70	0.84	5.42	96.93	-80.51	-14.92	5.50
Ph-X								
(π-donors)	6	0.98	0.99	0.84	2.67	-0.79	-16.96	0.14
(π-acceptors)	4	1.00	1.00	----	41.40	-30.83	40.48	----[b]
B) ETHYL STABILIZATION								
vi-X								
(π-donors)	6	0.99	0.99	0.70	7.03	-20.19	-21.53	-0.05
(π-acceptors)	8	0.81	0.90	1.31	36.10	-23.70	12.69	0.74
cPr-X								
(π-donors)	6	0.98	0.99	0.38	-1.41	-9.03	-9.81	0.07
(π-acceptors)	5	0.97	0.98	0.73	42.23	-31.15	24.78	0.12
HCC-X								
(π-donors)	6	0.99	0.997	1.23	25.55	-84.01	-23.35	0.14
(π-acceptors)	8	0.71	0.85	5.77	94.69	-82.83	-18.54	5.00
Ph-X								
(π-donors)	6	0.95	0.97	1.21	-6.32	-6.44	-19.73	0.19
(π-acceptors)	4	1.00	1.00	----	78.14	-57.00	34.55	----[b]
C) ISOPROPYL STABILIZATION[c]								
vi-X	5	1.00	1.00	0.09	8.06	-27.56	-20.41	0.01
cPr-X	5	0.97	0.99	1.03	0.35	-16.81	-8.70	----[d]
HCC-X	5	1.00	1.00	0.23	29.07	-92.63	-22.11	0.02
Ph-X	5	0.99	0.997	0.63	-2.61	-15.40	-18.59	0.04

a) Same substituents employed for each correlation as in Table VII.1.

b) Not valid, perfect line with four points.

c) Only enough data for correlations with π-donors.

d) F-level or tolerance level not sufficient for program to calculate constant.

TABLE VII.3

A) π-ACCEPTORS

parent hydrocarbon	m_R	hydrocarbon IP(adiab.)	IP(vert)
vi-X	13.8	10.51eV[a]	10.51eV[b]
HCC-X	7.2	11.40[a]	11.40[b]
cPr-X	25.2	9.7[c]	10.53[d]
Ph-X	31.7	9.25[a]	9.25[b]

B) π-DONORS

parent hydorcarbon	m_R	hydrocarbon EA(vert.)[e]
vi-X	-17.6	-1.78eV
HCC-X	-20.9	-2.6
cPr-X	-7.1	-5
Ph-X	-13.5	-1.15

a) G. Bieri, F. Burger, E. Heilbronner, J. P. Maier Helv. Chim. Acta. 1977, 60, 2213-33. b) Assumed to be virtually equal to adiabatic IP's. c) Value approximated from those in R. D. Levin, S. G. Lias "Ionization Potential and Appearance Potential Measurements, 1971-1981" NSRDS-NBS 71, National Bureau Standards, U.S. Dept. of Commerce, Oct. 1982. d) H. Basch, M. B. Robin, N. A. Kuebler, C. Baker, D. W. Turner J. Chem. Phys. 1969, 51, 52-66. e) Values obtained from K. D. Jordan and P. D. Barrow, Accounts Chem. Res., 11, 341-348 (1978) except for cyclopropane which was obtained from K. D. Jordan , personal communication to A. Greenberg.

TABLE VII.4[a]

	n	R^2	R	Std. Error	m_I	m_R+	
				A) METHYL STABILIZATION			
vi-X	6	0.94	0.97	1.61	2.68	-11.56	1.39
cPr-X	6	0.95	0.98	0.64	4.22	-4.65	0.68
HCC-X	6	0.94	0.97	2.62	-39.37	-14.04	2.66
Ph-X	6	0.97	0.99	0.86	4.67	-8.92	0.53
				B) ETHYL STABILIZATION			
vi-X	6	0.98	0.99	0.80	-8.55	-11.40	0.72
cPr-X	6	0.98	0.99	0.34	-7.01	-4.47	0.00
HCC-X	6	0.96	0.98	2.49	-50.68	-13.84	2.03
Ph-X	6	0.96	0.98	0.84	-6.56	-8.74	-0.15

a) All substituents π-donors: H, F, Me, OMe, OH, NH_2. Substituent constants from ref. 109. σ_R value for Me used as σ_R^- (-0.16).

TABLE VII.5[a]

	n	R^2	R	Std. Error	m_I	m_R-	
				A) METHYL STABILIZATION			
vi-X	6	0.53	0.73	2.45	0.35	10.98	0.82[b]
cPr-X	4	1.00	1.00	0.00	-3.65	18.77	0.00[c]
HCC-X	6	0.37	0.61	8.49	-23.05	8.85	3.60[b]
Ph-X	4	1.00	1.00	0.06	-1.89	12.81	-0.01[d]
				B) ETHYL STABILIZATION			
vi-X	6	0.63	0.79	1.34	-2.12	8.28	0.55[b]
cPr-X	4	0.84	0.92	1.52	-6.29	15.51	0.29[c]
HCC-X	6	0.40	0.63	9.12	-25.62	6.34	3.32[b]
Ph-X	4	0.84	0.92	1.54	-4.78	10.14	0.27[d]

a) All substituents π-acceptors. Substituent constants from ref. 109.

b) Substituents: H, CN, CHO, COMe, CO_2Me, NO_2

c) Substituents: H, CN, COMe, NO_2

d) Substituents: H, CN, CHO, NO_2

CHAPTER VIII

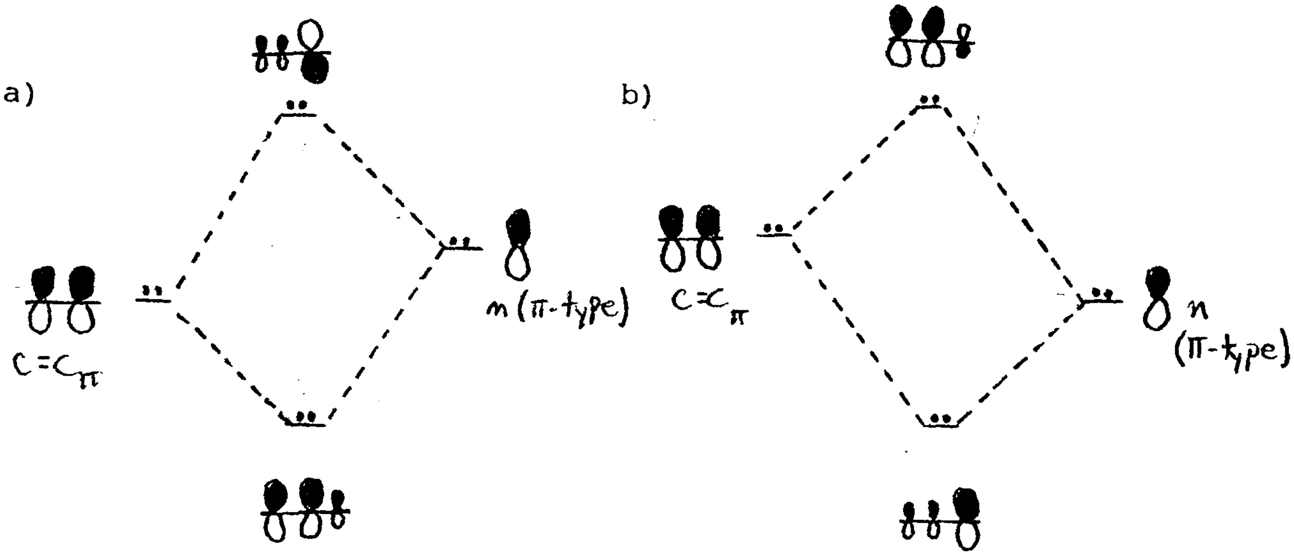
INTERPRETATION OF PHOTOELECTRON SPECTROSCOPY

Any attempt at correlating photoelectron spectroscopy results with thermochemical stabilization is bound to be fraught with difficulty, since the former is a one-electron property and the latter an all-electron property. For example, attempts at analyzing charges in the highest energy orbitals with stabilization energies is problematic since small changes in the remaining orbital energies can be significant. It is also not clear exactly what models should be employed (e.g., F atom + vinyl radical, HF + ethylene, CH_3F + ethylene?). A simple illustration of this problem is furnished by equating the split (2.94 eV)[118] between the two bonding π combinations (ψ_1 and ψ_2) of 1,3 butadienes with the energy difference of β calculated by the simple Hückel molecular orbital technique. This value is fairly consistent with the value of 3.02 eV[181] for β using benzene. However, the resonance energy in benzene, when taken as 2β would be 139 kcal/mol instead of the corresponding experimental value of 36 kcal/mol. Nevertheless, one should obtain some clear measures of the extent of π and σ interactions between hydrocarbon moiety and substituent even if these cannot be readily translated to stabilization energies by themselves.

A literature search concerning the photoelectron spectra of substituted vinyl compounds and their acyclic analogues was completed. This data is very useful because it can reveal the energies of certain electrons of ethylene and of a substituent with and without significant conjugation, that is, when the substituent is bonded to the vinyl group, and when it is bonded to methane or ethane. This data can therefore help reveal by what mechanism stabilization or destabilization of the substituted olefin is occurring. Furthermore, one might generally expect a correlation of π (or π -like) donor properties of hydrocarbon moieties to reflect ionization potentials. Similarly, electron affinities might indicate the relative π acceptor abilities of ethylene, acetylene, cyclopropane, and benzene (see Table VII.3 and Chapt. VII).

Rabalais[3] has pointed out that a substituent with a nonbonding electron pair (π-electron donor) will interact with the ethylene π orbital to form a bonding and an antibonding pair of orbitals (Fig. VIII.1).

Fig. VIII.1



In case a), the substituent π-type pair is higher in energy than the ethylenic π-electron pair, and the bonding pair is localized on the ethylene group. In case b) the substituent π-type electrons are lower in energy than the ethylenic π electron pair, and the bonding pair is localized largely on the substituent. Rabalais terms this the resonance effect.

Superimposed on the above is the substituent inductive (electronegative) effect which if withdrawing, will lower the energy of ethylenic π electron pair and raise the energy of the substituent π electron pair. If the substituent is electropositive, the opposite effect will occur. It can be seen then, that when concerned with the effects on the energy levels of the ethylenic π and substituent π electron pairs the inductive and resonance effects can be opposed or in the same direction.

Also superimposed on the above is the interaction of the substituent π-electons with ethylene's π^* orbital as previously mentioned in the discussion of substituent electronic effects. Note that we will refer to Rabalais' definition of the resonance effect as the resonance effect, and to the HOMO-LUMO interaction as such in the discussion of individual substituent photoelectron spectra. Naturally, both mechanisms are part of the overall resonance effect.

The above electronic effects also hold for the case of a

π-electron acceptor substituent, ie., one with a low-lying π LUMO. The only diffference here is in the direction of the HOMO-LUMO interaction. However, a two-orbital, two-electron interaction is stabilizing while a two-orbital, four-electron interaction would, to the zeroth order, have no associated stabilization.

Through construction of MO diagrams using IP's of π or π-type MO's, possible mechanisms of stabilization or destabilization will be outlined for various substituents. Table VIII.1 lists the vertical ionization potentials (IP_v). The first column lists the IP_v of the $C{=}C_\pi$ MO for unsubstituted ethylene and various substituted ethylenes. The second column lists the IP_v of the substituent's π-type electron pair when unconjugated with ethylene (e.g. in CH_3X) and when conjugated with ethylene in the vinyl derivative. Each substituent will be discussed in turn.

Note also that net stabilization or destabilization of the vinyl system with the substituent cannot be predicted from the following MO diagrams since these are the net of the resonance and electronegative (inductive) effects, and do not take into account the substituent field effect.

Furthermore, there are photoelectron spectra available for substituents not evaluated here, namely CO_2H and CO_2Me (see ref. 3, 128, 132). The reason for this is that for these substituents, the occupied MO's are not readily characterizable as either $C{=}C_\pi$ or substituent "π-type". This was discerned by investigating the MO's of the appropriate molecules in ref. 2.

TABLE VIII.1
VERTICAL IONIZATION POTENTIALS OF π-TYPE ELECTRONS FOR SUBSTITUTED ETHYLENE AND METHANE[a]

		$C=C_\pi$	substituent π-type e^- pair	
	$C=C_\pi$	10.52^b		
1)	Me-F		13.35^c	
	vi-F	10.56^d	13.80^d	
2)	Me-Cl		11.29^e	
	vi-Cl	10.01^f	11.67^f	
3)	Me-Br		10.53^e	
	vi-Br	9.83^f	10.93^f	
4)	Me-OMe		10.01^g	
	vi-OMe	9.14^h	12.13^h	
5)	CH_3-CH_3		12.1^m	
	vi-Me	9.88^i		
6)	Me-OH		10.95^e	
	vi-CH_3	9.88^i		
	vi-CH_2OH	10.16^i	10.93^i	
	vi-OH	9.14^o		
7)	Me-NH_2		9.58^e	
	vi-CH_2NH_2	10.04^i	9.44^i	
8)	Me-SCH_3		8.7^n	
	vi-SCH_3	11.0^n	8.45^n	
		$C=C_\pi$	nN	$C\equiv N_\pi$
9)	Me-CN		13.12^j	12.19^j
	vi-CN	10.92^j	13.02^j	12.36^j
		$C=C_\pi$	nO	$C=O_\pi$
10)	Me-CHO		10.21^k	12.36^k
	vi-CHO	10.94^l	10.11^l	14.00^l

a) All numbers in units of electron volts. b) Ref. 119
c) Ref. 120 d) Ref. 121 e) Ref. 122 f) Ref. 123
g) Ref. 124 h) Ref. 125 i) Ref. 3 j) Ref. 126; average of available values used. k) Ref. 127 l) Ref. 128
m) Ref. 129 n) Ref. 130 o) Ref. 53, adiabatic IP.

1) F

Note that for fluorine we might not expect a strong resonance effect since the nonbonding electron pair on fluorine is much lower in energy than the π electron pair of ethylene. Since fluorine is electronegative, we might expect that the ethylenic π electron pair would be somewhat stabilized and the fluorine nonbonding electron pair somewhat destabilized. In fact the π electron pair of ethylene is slightly stabilized due to the electronegative effect, but the nonbonding pair of fluorine is also stabilized, and by a much larger amount than ethylene's electrons. Stabilization is due to the HOMO-LUMO interaction of fluorine's nonbonding pair and ethylene's low-lying π^* MO, which is also lowered in energy by fluorine's elctronegative effect. Ethylene's π electrons are only slightly stabilized because of the opposing resonance and electronegative effects. This results in stabilization by the resonance effect of fluorine on the vinyl group, and net stabilization would depend on the magnitude of the field effect. As Chapter III indicates, there is no stabilization imparted by fluorine on ethylene as compared to ethane.

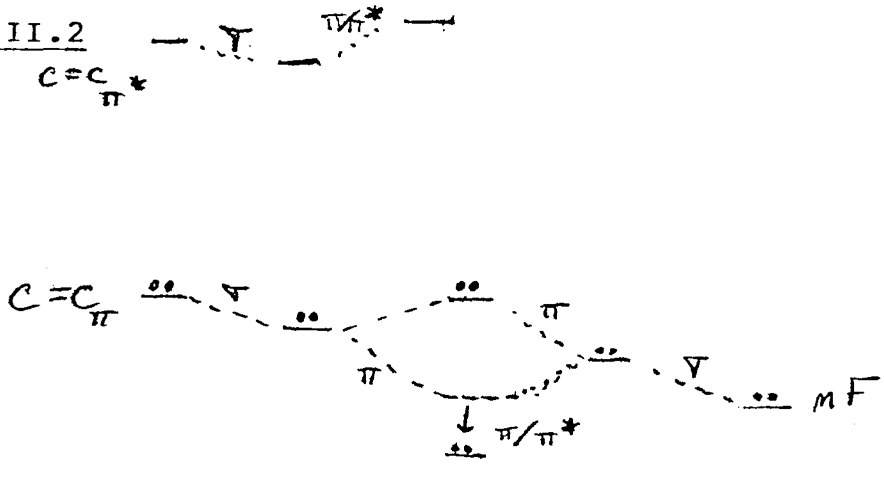
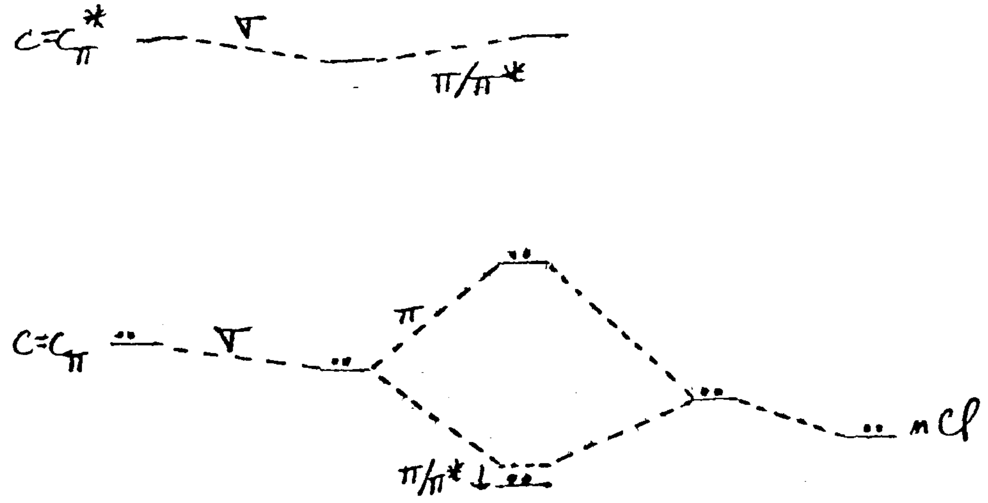


Fig. VIII.2

2) Cl

The mechanism of the electronic effects chlorine has on ethylene naturally should be very similar to fluorine. Since the IP_v of the Cl nonbonding pair is closer to the IP_v of the π electron pair of ethylene than fluorine's, one might expect a stronger resonance effect. This is not necessarily true, however, because chlorine, being a second row element, does not have p orbitals of the proper size for maximum overlap with ethylene's π orbital. The π orbital of ethylene is destabilized because chlorine is much less electronegative than fluorine (see Topsom's electronegativity parameters). Notice also that chlorine's nonbonding eletron pair is not as stabilized as fluorine's because the HOMO-LUMO interaction will be weaker due to this asymmetry. This would result in either less stabilization or more destabilization of the vinyl system than when substituted with fluorine (see Fig. VIII.3). In fact, this is what is observed (see Table III.2).

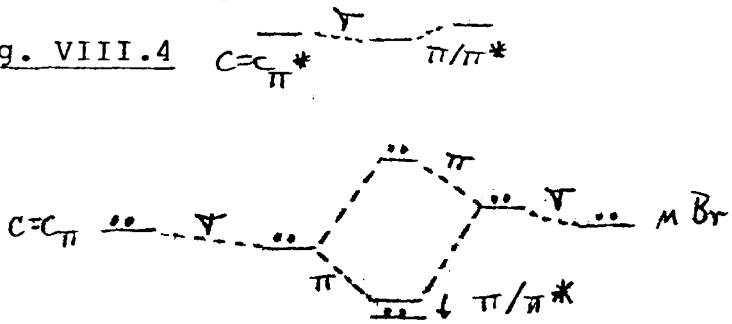
Fig. VIII.3



3) Br

The nonbonding electron pair on bromine is extremely close in energy to that of ethylene's π electron pair, which should result in a very strong Rabalais-type resonance interaction, and does. Note that ethylene's π MO is significantly destabilized (more than with Cl) despite the electronegativity effect. Bromine's nonbonding pair is also stabilized, by about the same amount as chlorine's, due to the π^*-n (HOMO-LUMO) interaction. This stabilization would be much greater than that for chlorine, were it not for the fact that Br has 4p orbitals as compared to chlorine's 3p orbitals. The net result would be less stabilization or more destabilzation of the system than with chlorine (see Fig. VIII.4). Note that Fig. VIII.4 is confusing because it appears that after the electronegativity effect (∇), the nBr MO should be destabilized, and the $C{=}C_\pi$ MO should be stabilized. It must be kept in mind however, that the Rabalais-type π interaction, the elctronegativity effect, and the HOMO-LUMO interaction occur simultaneously.

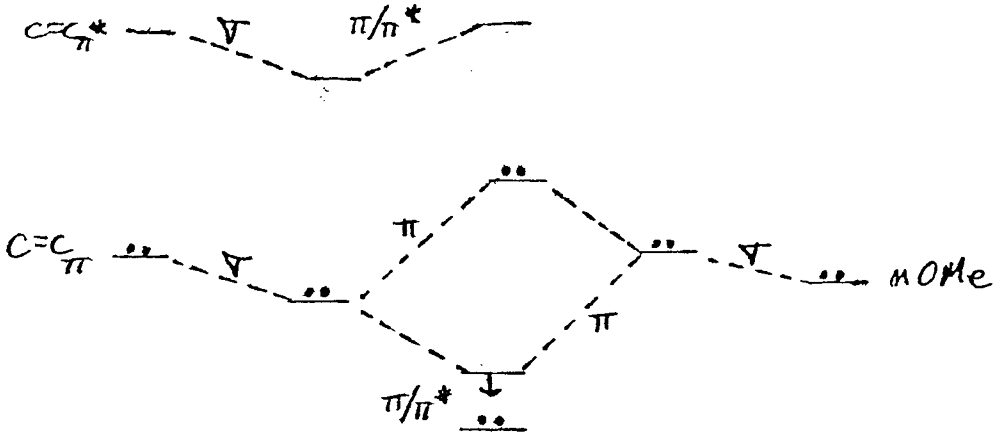
Fig. VIII.4



4) OMe

For the methoxy group, we would expect a good resonance interaction , since the nonbonding electron pair on oxygen is close in energy to ethylene's π-type MO. The experimental ethyl stabilization in methyl vinyl ether is 6.9 kcal/mol (Table III.2), reflecting this strong interaction. Since the nonbonding pair is higher in energy than the π MO, we would expect ethylene's π MO to be stabilized and methoxy's nonbonding pair to be destabilized. Methoxy's inductive effect is weaker than a halogen's, but would also further stabilize ethylene's π MO and destabilize oxygen's nonbonding pair. In fact, however, oxygen's nonbonding pair is stabilized by 2.12eV; while ethylene's π electron pair is destabilized by 1.37eV. This is due to methoxy's very favorable interaction with ethylene's π LUMO, which would be much stronger than a halogen's because in addition to an energy similar to ethylene's π electron pair, the oxygen nonbonding pair is also of a proper symmetry for overlap. Ethylene's electron pair is then destabilized and not stabilized because the oxygen nonbonding pair is stabilized. Note that ethylene's electron pair is not destabilized as much as methoxy's is stabilized. This is due to the extra stabilization methoxy enjoys in conjugation with the π LUMO. Note that the stabilization of the system is significantly greater than it is when conjugated with fluorine (see Table III.2).

Fig. VIII.5

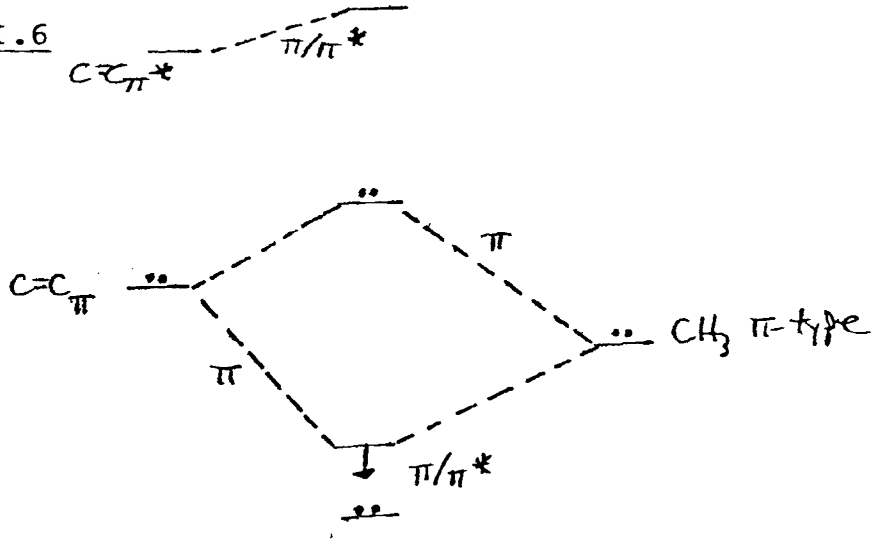


5) Me

Rabalais[3] has discussed the photoelectron spectra of propylene. The electrons occupying the CH_3 π-type orbital are somewhat lower in energy than the π electron pair of ethylene, and hence destabilization of ethylene's π electrons by the resonance effect. The CH_3 group is also very slightly electropositive in comparison to the vinyl group (see Topsom's electronegativity parameters, Table V.2), and so this effect would be in the same direction as the resonance effect.

Resonance stabilization would come from the interaction of the CH_3 π-type MO with ethylene's π LUMO. The energy of CH_3's π-type MO probably would lie somewhere between the energy of the nonbonding electron pairs of fluorine and methoxy. One might arrive at this conclusion since the 4-31G ethyl stabilization of propylene lies between that of vinyl fluoride and methyl vinyl ether (Table III.2). This is in fact the case, as can be seen when comparing the IP_v's of π-type MO's for the methyl substituted compounds. Remember that it is believed that ΔH_{stab} for vinyl fluoride is believed to be faulty (Chapt. IV).

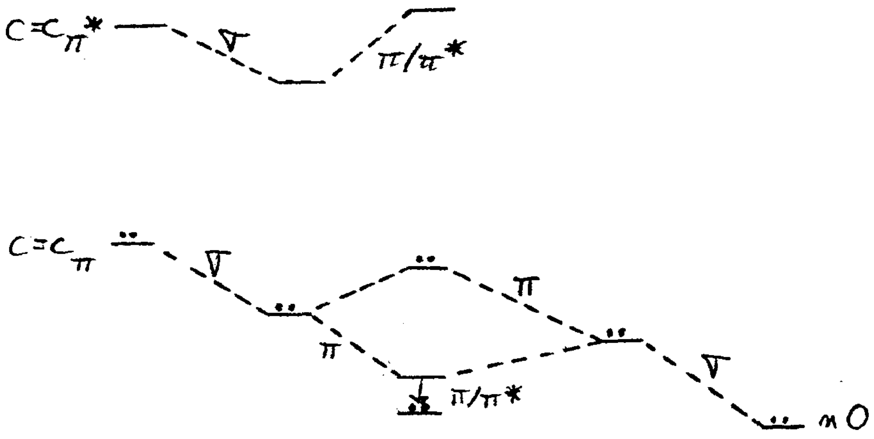
Fig. VIII.6



6) OH and CH_2OH

Vinyl alcohol does not exist as a stable entity (the keto form is preferred), but Rabalais studied the photoelectron spectra of allyl alcohol. For this case then, propene was used as the substrate instead of ethylene. Note that in conjugation, the oxygen nonbonding electon pair is destabilized by .02eV, and the propene π electron pair is stabilized by .28eV. Since oxygen's nonbonding electron pair is lower in energy than propene's π electron pair, we would expect the π electron pair of propene to be destabilized by the resonance effect, but since the oxygen is separated from the π system the inductive effect dominates and the propene π electrons are slightly stabilized. The nonbonding pair of oxygen is not destabilized by an equal amount because of conjugation with propene's π^* MO. An MO diagram of vinyl alcohol would probably be very similar to that of vinyl methyl ether.

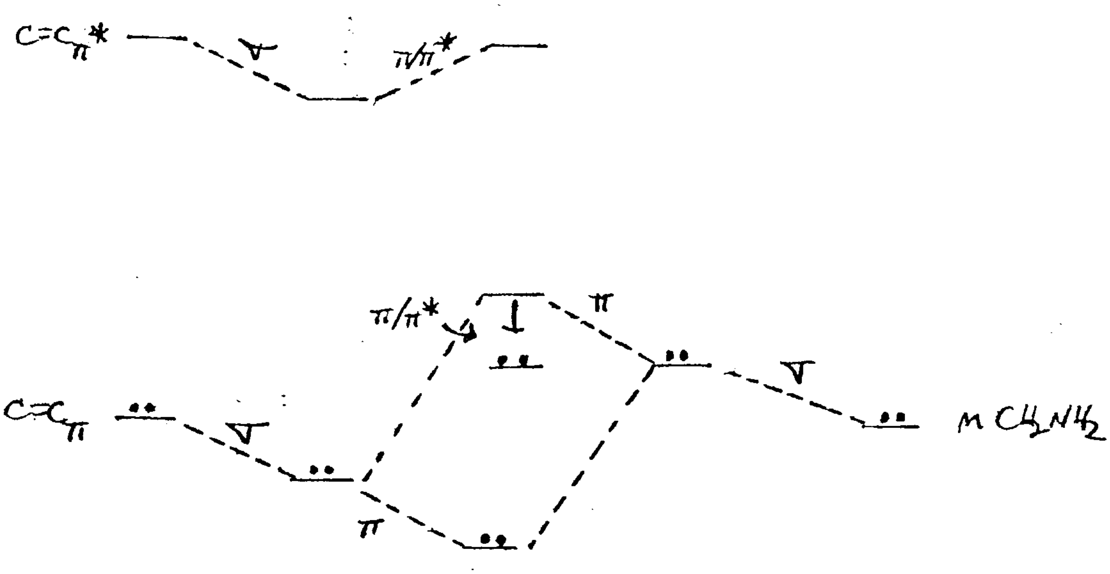
Fig. VIII.7



7) NH_2 and CH_2NH_2

Vinyl amine is a hard molecule to isolate, but was generated by thermal decomposition of cyclobutylamine. Its PES was determined by subtracting that of ethylene. The first two bands are the π combinations: $IP_{\pi 1}$ (adiab.=8.20 eV, vert.=8.65 eV), $IP_{\pi 2}$ (vert, 11.90 eV).[131] The 3.25 eV split indicates substantial interaction. This case was also investigated by Rabalais[3] by observing the PES of the allyl substituent. This case is different than that of allyl alcohol because the substituent nonbonding pair is higher in energy than that of the propene π electron pair. For this reason, both the resonance and inductive effects operate in the same direction, stabilizing the propene π electrons and destabilizing the NH_2 nonbonding pair. The resonance effect must again be weak due to one carbon separation since the stabilization of propene's π electrons is not as much as with alcohol. Since the resonance effect is not important in both cases, the electronegative effect dominates, and the alcohol group stabilizes the propene π orbital more than NH_2 since it is more electronegative. Once again, the substituent's lone pair is not destabilized by the same amount as the propene π electrons are stabilized because of a favorable interaction with propene's π^* MO. Note that the NH_2 lone pair is destabilized more however, than the lone pair of OH. This is due to the slight resonance interaction with the propene π MO, which would tend to destabilize the NH_2 lone pair relative to the OH lone pair.

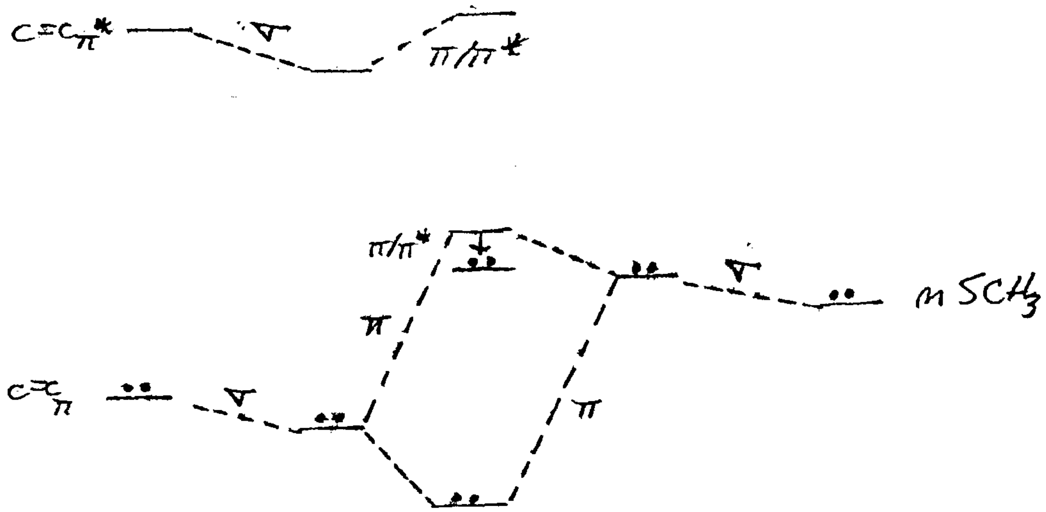
Fig. VIII.8



8) SCH$_3$

One might expect a much weaker π interaction between SCH$_3$ and ethylene than with OMe because in the former a 3p orbital is involved rather than a 2p orbital. This is in fact the case. Evidence of this is the fact that n-π^* (HOMO-LUMO) interaction does not result in overall stabilization of the π-type MO of the substituent as it does in methyl vinyl ether. Through Rabalais-type resonance interaction, the SCH$_3$ π-type MO is destabilized and the C=C$_\pi$ MO is stabilized. Note that the substituent π-type MO is not destabilized through conjugation as much as the C=C$_\pi$ MO is stabilized. This is because of the weak interaction between SCH$_3$ and the low-lying π^* MO.

Fig. VIII.9

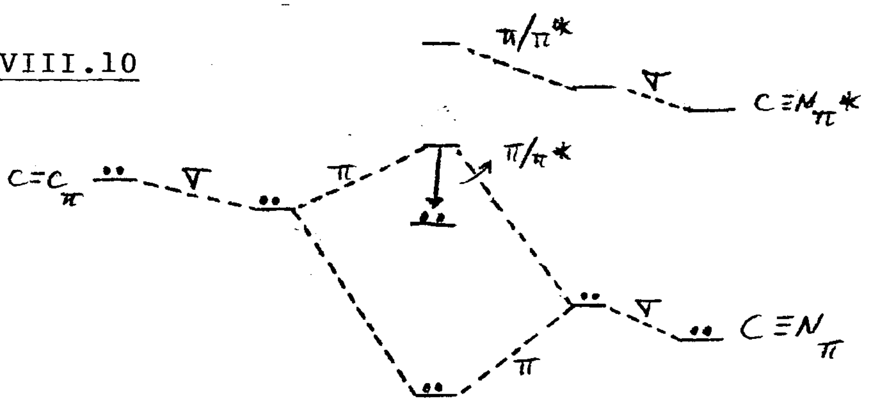


9) CN

This case is more complex than the above substituents because there are three π type MO's that must be considered; the ethylene π MO, two cyano π MO's, as well as the nitrogen nonbonding pair. However, the interactions are very similar to the above, except that now the substituent is the π electron acceptor. The ethylene π MO is affected three ways; it is destabilized by a resonance interaction with the CN π MO, it is stabilized by cyano's electronegativity, and it is stabilized by its interaction with the π^* MO of CN. This results in overall stabilization of ethylene's π MO. The resonance interaction also results in the stabilization of the CN π MO, which is opposed by the electronegativity interaction. Note that ethylene's π MO might be destabilized were it not for the interaction with the π^* MO of CN. The nonbonding electron pair of nitrogen is destabilized because of the increase of electron density it experiences. This can be represented by the canonical structures:

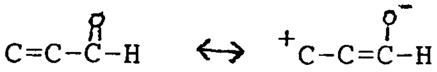
$$C{=}C{-}C{\equiv}N \leftrightarrow {}^{+}C{-}C{=}C{=}N^{-}$$

Fig. VIII.10



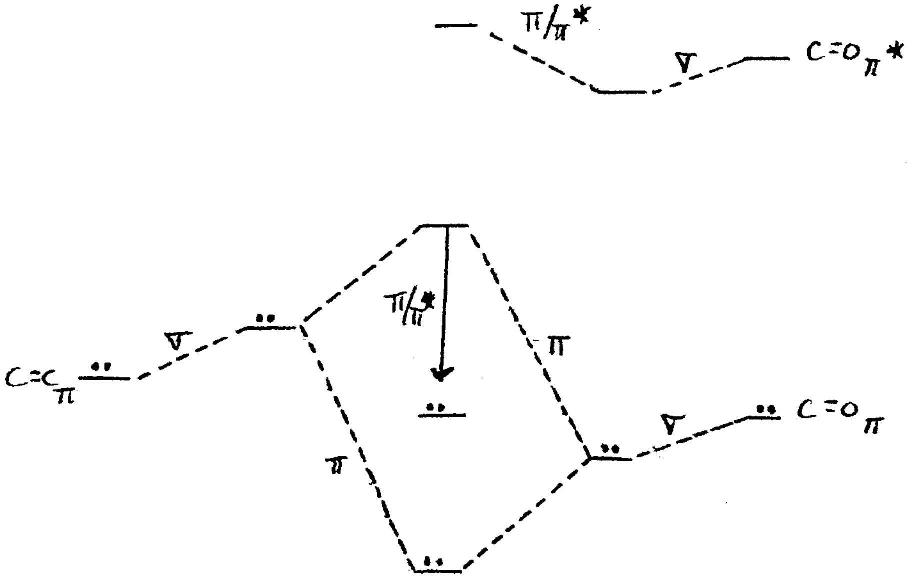
10) CHO

The case of acrolein is very similar to that of acrylonitrile. In this case however, the π MO of ethylene is stabilized less than the π MO of the substituent because the carbonyl π system is not as electronegative as nitrile. The MO of ethylene would be destabilized, were it not for the favorable interaction of it with the π^* MO of the carbonyl. The nonbonding electron pair of the oxygen is destabilized due to the increase in electron density it experiences when the aldehyde group accepts π electrons from the ethylene group. This is represented by the canonical structures:



$$C{=}C{-}\overset{O}{\overset{\|}{C}}{-}H \longleftrightarrow {}^{+}C{-}C{=}\overset{O^-}{\overset{|}{C}}{-}H$$

Fig. VIII.11



It is interesting to compare two relatively simple systems: The substituted ethylenes and substituted acetylenes. While there are photoelectron spectroscopy data on substituted cyclopropanes, these are not as extensive or as easy to interpret. Figure VIII.12 shows the experimental electronic levels attributed to π orbitals in 1,3-butadiene, diacetylene (1,3-butadiyne), and but-3-ene-1-yne. The magnitudes of π splitting are similar for the three compounds although the split in 1,3-butadiene (2.94 eV)[118] is significantly greater than that in diacetylene (2.45 eV).[118] This is a measure of the resonance interaction between sp^2 carbons and between sp carbons. The associated Hückel α parameters for the two molecules (-7.24 for butadiene and -8.65 for diacetylene)[118] are measures of the greater electronegativity of the sp-carbon framework of the latter.

Table VIII.2 lists photoelectron spectral data for monosubstituted acetylenes. In Figure VIII.13 we have compared photoelectron data for the vinyl and ethynyl derivatives having the π-withdrawing substituents CHO and CN. Acetylenes and vinyl compounds provide instructive comparisons. For example, one of the substituent π orbitals mix with the ethylenic π system in acrylonitrile while the other does not. The induced difference betweeen the two cyano π systems can then be crudely taken as due to π interaction alone. The conjugative destabilization of the ethylene π orbital is then taken to be equal in magnitude to the conjugative stabilization of the cyano π'' orbital. The energy change in cyano π' is simply taken as due to the inductive effect of vinyl and assumed to be equal to that for the cyano π''. It is obvious at this point that the vinyl π_{CC} has been significantly stabilized inductively by attachment of cyano. One can obtain a semiquantitative picture for cyanoacetylene if it is assumed that the conjugative interaction is about equal to that in acrylonitrile (recall Figure VIII.12). It becomes apparent that the cyano $\pi'$and π'' orbitals are shifted to lower energy in ethynyl compared to vinyl (both lower than methyl) reflecting the electronegativities of these hydrocarbon frameworks. Furthermore, the ethynyl π orbitals, already lower in energy than the vinyl π orbitals, are less shifted to lower energy than the latter by attachment of cyano.

In the case of vinyl and ethynyl aldehydes similar reasoning is employed. The subsituent's single π system can now interact with only the π''orbital of acetylene. The induced difference between the alkyne's π' and π''orbitals, which is fairly small, is taken as the conjugative interaction and the π_{CO} is stabilized by an equal amount. For purposes of comparison the conjugative interaction is assumed to be equal to that in acrolein. It again becomes clear that the more electronegative alkyne framework is less lowered in energy than the vinyl framework and has a greater effect on lowering π_{CO} than the latter. There is still a problem here since the γ_R parameters (Chapt. V) for CHO and CN are 0.20 and 0.08 respectively, seemingly opposite to the extent of interactions reported here.

TABLE VIII.2

PHOTOELECTRON SPECTRA OF SUBSTITUTED ETHYNYL
$HC\equiv C\text{-}X$

X	
H	11.40[j]
CH_3	10.54(10.37),14.6(13.91)[a]
$CH_2{=}CH_2$	9.63(C=C),10.61(C≡C),12.01(C C),13.2(γ)[b]
C_6H_5	8.82($\pi\phi$),9.50($\pi\phi$),10.32($C\equiv C_\pi$),11.02($C\equiv C_\pi$)[c]
F	11.50(11.26)π,18.0∇,18.0π_F[d]
Cl	10.63,14.08[e]
Br	10.31,13.00[e]
I	9.94,12.08[e]
SCH_3	10.34(π)[k]
CHO	n'_o10.8(10.70), π''_{CC}11.6(11.57), π'_{CC}11.7, π''_{CO}14.4(13.99)[f]
CO_2H	n'_o10.9, π''_{CC}11.4, π'_{CC}11.9,n''_o12.4, π''_{CO}15.9[f]
CH_2OH	π''_{CC}10.5, π'_{CC}10.9,n''_o11.5[f]
<u>c</u>Pr	9.58($C\equiv C\text{-}\lhd$),10.09($C\equiv C\text{-}\lhd$),11.58($C\equiv C+\triangle$),12.2($C\equiv C+\triangle$)[b]
CN	11.75(11.60,π),13.54(∇),14.18(14.03,π)[a]
NC	(calc.) 11.33(π),11.70(∇),15.33(π)[a]
CO_2CH_3	10.75(18a'),11.2(4a"),11.4(17a'),11.47(3a")[g]
$(Me)_3Si$	π_{CC}10.2(V),9.9(A)[d] and 10.73[h]
CF_3	π12.09(11.96),15.25,15.9[i]
CH_2Cl	10.7(π_{CC}),11.1(π_{CC}),11.7(nCl)[g]

a) Ref. 133 b) Ref. 137 c) Ref. 134 d) Ref. 144
e) Ref. 145 f) Ref. 135 g) Ref. 142 h) Ref. 141
i) Ref. 138 j) Ref. 129 k) Ref. 140

TABLE VIII.3

PHOTOELECTRON SPECTRA OF UNCONJUGATED SYSTEMS

X	CH_3X (n or π)	HX (n or π)
F	13.1(12.54)[a]	16.9[b]
Cl	11.29,11.32[c]	12.75,12.83[c]
Br	10.54,10.86[c]	11.65,11.98[c]
I	9.54,10.17[c]	10.39,11.05[c]
SCH_3	8.7[d]	9.46[e]
CHO	10.3(10.20,n_o)[f] 13.2(12.61) π_{CO}	10.9(10.88,n_o),[g] 14.5(14.09, π_{CO})
CO_2H		10.9(10.70,n_o)[g] 12.1(n_o), π'_{CO}(13.6-15.0)
CH_2OH		10.7(n_o)[g] 10.9(degen.)
CN	π_{CN}12.46(12.21),[h] n_N13.17(13.14)	13.61(π)[e]
NC	n_C11.32(11.27),[h] π_{NC}12.5(12.24)	
CO_2Me		10.99,11.53,13.07,[e] 14.01

a) Ref. 145 b) Ref. 144 c) Ref. 143 d) Ref. 130
e) Ref. 133 f) Ref. 142 g) Ref. 135 h) Ref. 139

FIG. 8.12

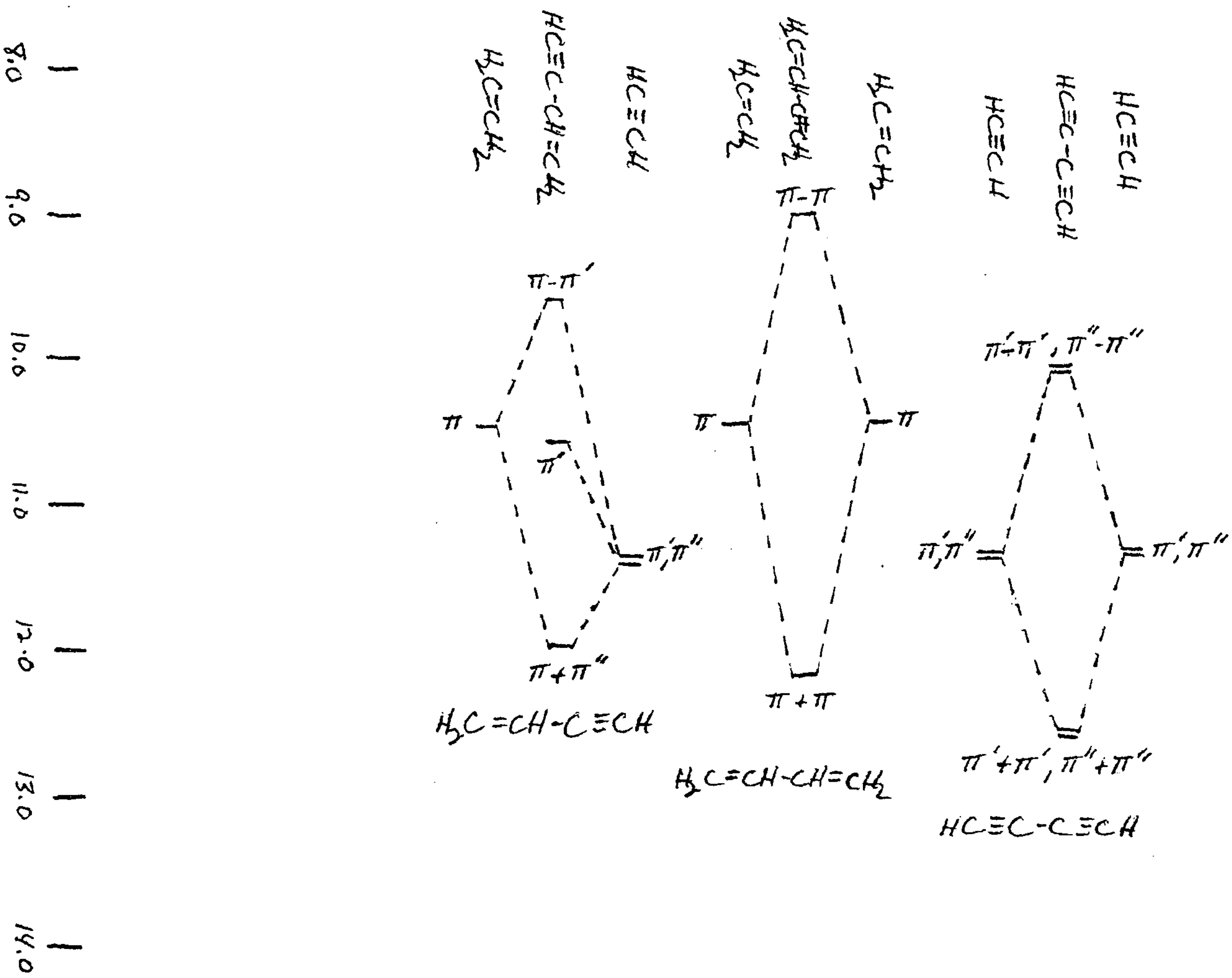
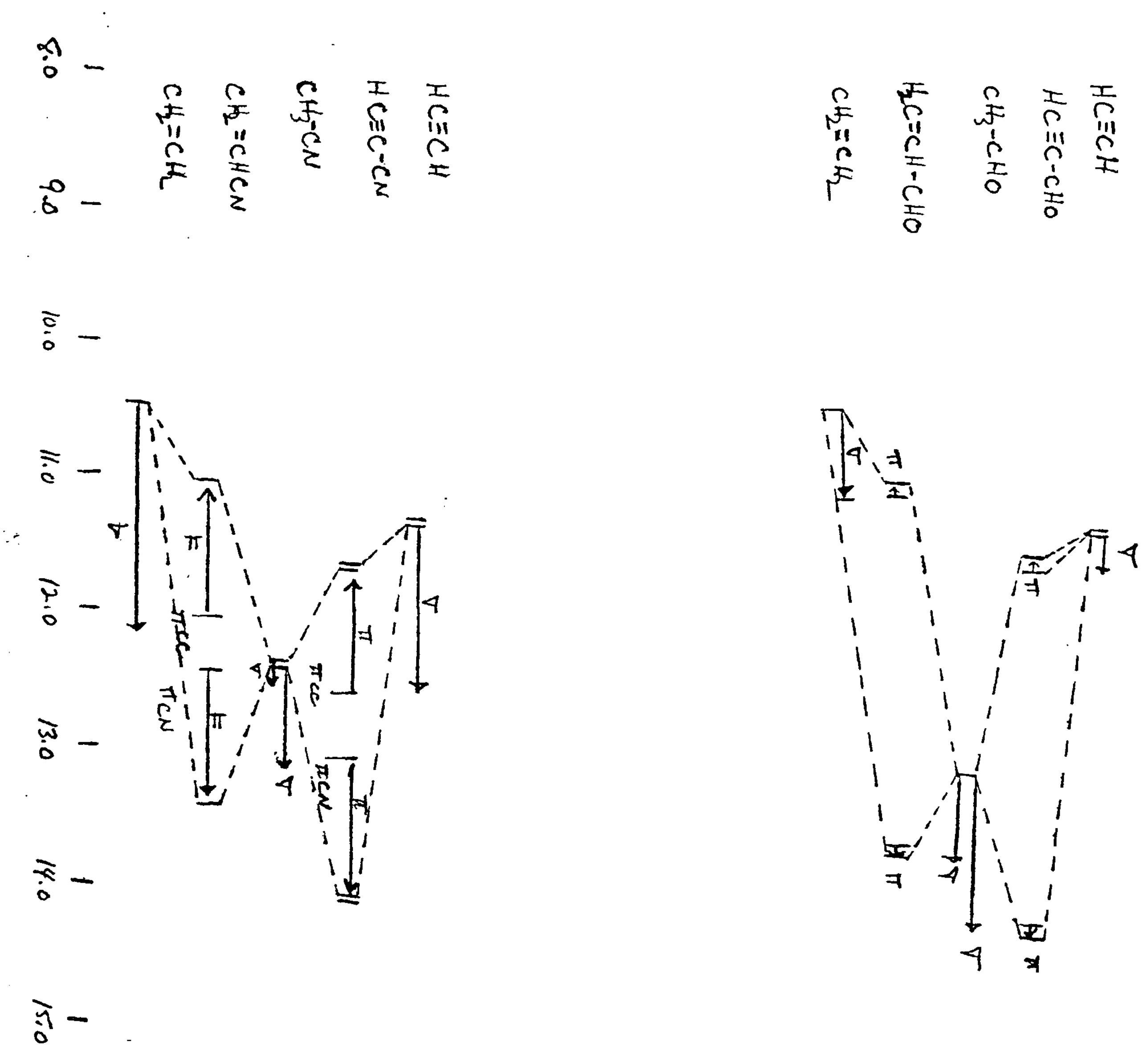

8.0
9.0
10.0
11.0
12.0
13.0
14.0
$H_2C=CH_2$
$HC\equiv C-CH=CH_2$
$HC\equiv CH$
$H_2C=CH_2$
$H_2C=CH-CH=CH_2$
$H_2C=CH_2$
$HC\equiv CH$
$HC\equiv C-C\equiv CH$
$HC\equiv CH$
$\pi-\pi'$
π
π'
π, π''
$\pi+\pi''$
$H_2C=CH-C\equiv CH$
$\pi-\pi$
π
π
$\pi+\pi$
$H_2C=CH-CH=CH_2$
$\pi'-\pi', \pi''-\pi''$
π', π''
π', π''
$\pi'+\pi', \pi''+\pi''$
$HC\equiv C-C\equiv CH$

FIG. 8.13


8.0
9.0
10.0
11.0
12.0
13.0
14.0
15.0
HC≡CH
HC≡C-CN
CH3-CN
CH2=CHCN
CH2=CH2
σ
π
πCC
πCN
HC≡CH
HC≡C-CHO
CH3-CHO
H2C=CH-CHO
CH2=CH2

There is not a great deal of data on the photoelectron spectra of substituted cyclopropanes.[146] The parent compound has the degenerate 3e' π-like orbitals as its HOMO's. Jahn-Teller distortion leads to vertical IP's for the first two peaks of the PE spectrum at 10.53eV and 11.30 eV[147] which corresponds to these MO's. If one assumes that the average value of 10.9 eV approximates a hypothetical vertical IP for the "non-Jahn-Teller-distorted cyclopropane," then one may be able to make comparisons with other monosubstituted cyclopropanes. An interesting comparison is the split between molecular orbitals induced by conjugation of cyclopropane and ethylene[148] compared with the analogous interaction in ethynylcyclopropane[137] (see Fig. VIII.14). The two π combinations in vinyl cyclopropane (vertical IP, 9.2eV and 11.7eV) and the corresponding combinations in ethynyl cyclopropane (vertical IP, 9.58eV and 12.2eV) are split by 2.5eV and 2.6eV respectively, values fairly close to the splits in 1,3-butadiene and diacetylene.

In looking at ionization potentials and electron spectra of other cyclopropyl compounds it is interesting to make comparisons between the isopropyl and cyclopropyl derivatives (Table VIII.4).

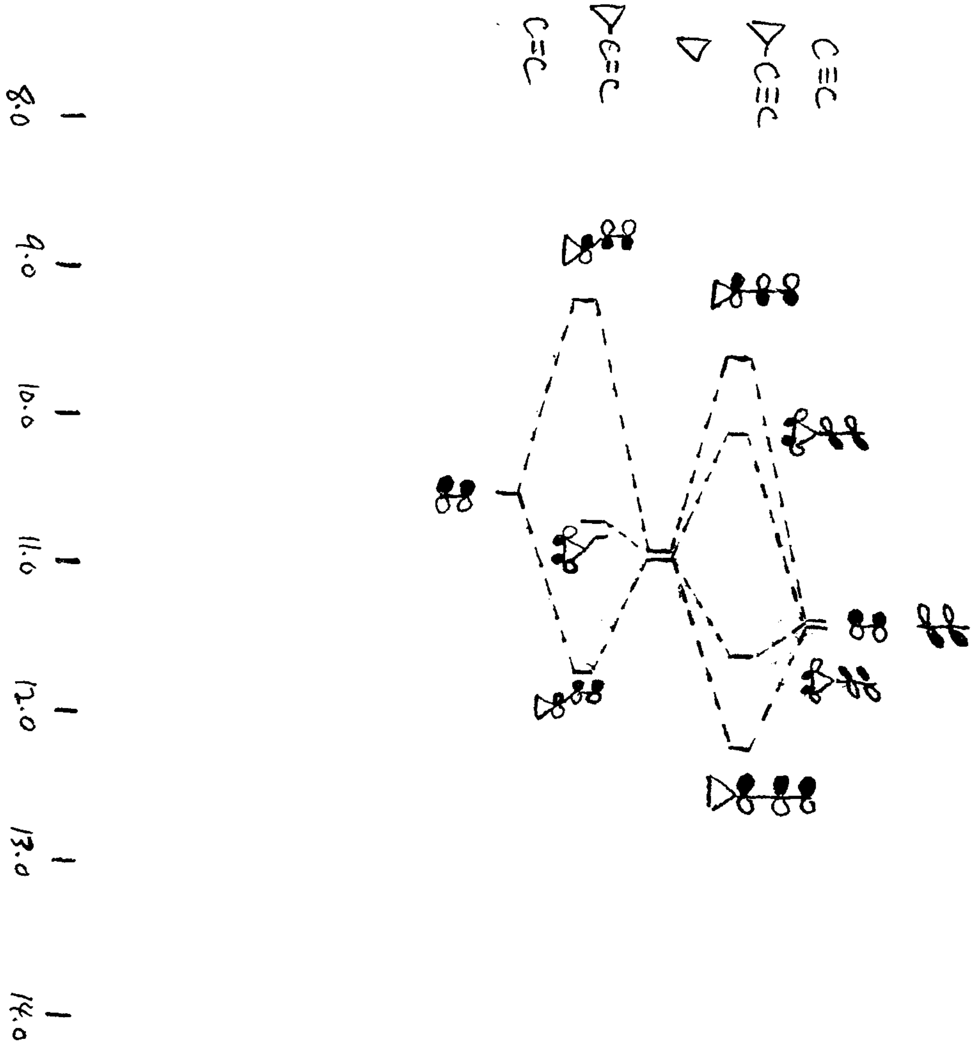
TABLE VIII.4

X	Et-X	iPr-X	cPr-X
H	12.0^a	11.5^a	$10.53, 11.30^b$
CH_3	11.5^a	11.4^a	9.9^a
$CH=CH_2$	9.63^j	$9.53(A)^a$	9.2^c
C CH	10.20^j	$10.10^{a,d}$	9.58^e (CC′)
CN			10.9^f
NH_2	9.50^a	9.31^a	9.41^k
Br	10.28^a	$10.25(est.)^g$	9.66^h
COOH	10.51^a	10.30^a	10.64^i (A?)

a) Ref. 146 b) Ref. 137 c) Ref. 148 d) The value given is vertical for iPrCCH. e) Ref. 147 f) Ref. 119, pp.207-213. g) Use adiabatic value of 10.12 from ref. 149, add difference of 9.66-9.53(vert.-adiab.) for cPr-Br. h) Ref. 149 i) Ref. 150 j) Ref. 129 k) Kimura, K.; Katsumata, S.; Achiba, Y.; Yamazaki, T.; Iwata, S. "Handbook of He I Photoelectron Spectra of Fundamental Organic Molecules"; Japan Scientific Societies Press: Tokyo; Halsted Press: New York, 1981, p. 118, 119.

For example, the vertical ionization potential of bromocyclopropane (9.66eV)[149] can be compared to the value for isopropyl bromide (est. 10.25eV) to give one a feeling for the extent of n-π interaction. Note that it is believed that the value for cyclopropylamine from ref. 119 (7.4 eV) is faulty because this would suggest a much stronger π interaction between NH_2 and the π system of the cyclopropyl group than the vinyl group (see previously).

FIG. 8.14



CHAPTER IX

^{13}C CHEMICAL SHIFTS

Several workers have attempted correlations of the ^{13}C NMR chemical shifts of monosubstituted ethylenes.[151,152] Schraml[156] correlated the ^{13}C chemical shift at C_a and C_b (see Fig. IX.1) with the Q parameter for a limited number of substituents. He argues that bulky substituents or ones with multiple bonds do not fit the correlation. Miyajima, Takahashi, and Nishimoto[152] studied 24 monosubstituted ethylenes. These workers studied the relationships between the and π charge densities on C_a and C_b and the corresponding ^{13}C σ chemical shifts. Since there are small changes in π electron density as compared to the changes in σ electron density on C_a, these workers hold that the chemical shifts for C_a must depend on the substituent inductive effect. They have presented various evidence including a correlation of the σ electron density on C_a vs. the C_a chemical shift. These workers have also correlated the π charge density on C_b vs. σ_π of Tsuno; along with the ^{13}C chemical shift of C_b vs. σ_π; and have thereby shown that δC_b depends only on substituent resonance effects.

Fig. IX.1

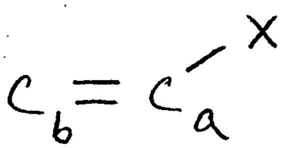


Table IX.1 lists the available data of the ^{13}C chemical shifts for C_a and C_b of monosubstituted ethylenes relative to TMS. Table IX.2 lists these same chemical shifts, relative to H, thereby keeping H as the standard as in all other correlations in this work. Table IX.3, 1) and Fig. IX.2 show the result of the correlation of δC_b with Taft's resonance effect parameter, σ_R. This supports the work of Miyajima, et al., since a satisfactory correlation is obtained. Halogens beyond the first row (Cl, Br, I), as well as the cyano substituent, were left out of the correlation because they fell far off the line. This agrees with findings of Miyajima, et al. It is most likely that the electronegativity effect of the halogens beyond the first row is the major determinant of δC_b, since these substituents will have negligible resonance effects due to poor overlap of their p orbitals with those of ethylene (see section on photoelectron spectroscopy, Chapt. VIII). This is logical because the ^{13}C chemical shift depends on the energy of the delocalized π electrons, and as has been shown, a substituents electronegativity effect can lower the energy of ethylene's π MO. Note that the four halogens seem to form their own line, following a logical order of most to least resonance effect (F-I) as one moves off the line. It is not readily apparent why cyano falls off the line, but note that it falls off in the same direction as the halogens, and therefore perhaps the cyano group has an unusually powerful electronegativity effect. As pointed out by Miyajima, et al.,[152] CN also has an anisotropy effect which may help explain this.

Note also that it appears that π-donating substituents shield C_b and π-accepting substituents deshield C_b relative to H since C_b relative to H is negative for π-donors and positive for π-acceptors. Electronegative electron withdrawl seems to deshield C_b because the halogens Cl, Br, and I increasingly deshield as they exhibit diminishing resonance effect.

Returning to the problem of the chemical shift of C_a, an attempt was made here to correlate δC_a with Charton's compilation of the Taft inductive substituent constant, σ_I, but no correlation was found (Table IX.3, eq. 2)). Eliminating the substituents that fell off the lines in correlations 1), 5) and 7) did not improve the correlation (see correlation 3)). An attempt was also made by use of the dual-substituent parameter approach to correlate the C_a chemical shift with Topsom's σ_X and σ_F (Table IX.3, 4)), with no success. The correlations were tried again with Charton's σ_R constants, now with success. Correlations 5), 6), and 7) of Table IX.3, and Figure IX.3 show the surprising result that δC_a is primarily dependent on the substituent resonance effect. From the lines of correlations 5) and 7) it is obvious that both π electron donors and acceptors deshield C_a by their resonance effect (both a positive or a negative σ_R will give a positive δC_a). It also appears that electronegative withdrawl at C_a causes shielding since for Cl, Br, and I there is increasing shielding. The halogens Cl, Br, and I were left out of correlation 5) for the same reason they were left out of the correlation involving δC_b. It is interesting to note that it appears the halogens deviate in a logical order as they do in correlation 1), and that the deviation seems magnified in comparison to correlation 1). π-electron donors and acceptors were separated because almost all of the substituents deshield C_a relative to H, and therefore since the parameters being tested are all of the same sign, the two classes of substituents must be separated since the resonance effect constants are of different sign. This is analagous to the case of correlations with stabilization energies, where both π donors and acceptors stabilized the ring system through the resonance effect. despite the difference in the direction of flow of the π electrons.

Other substituents that deviate from line 5) are OH and t-butyl, and were not included as were not Cl, Br, and I. Vinyl-alcohol is not a stable molecule (keto form prefered) and there is probably significant error in the evaluation of its chemical shift.[153] The t-butyl substituent unusually deshields C_a, probably due to its steric effect.

Note that correlation 6) is vastly improved by the elimination of CN and NO_2 (eq. 7)). Remember that there was also a problem with the cyano substituent in correlation 1) with the chemical shift of C_b. Note that the cyano and isocyano substituents are the only two among the π-acceptors that shield C_a, and therefore we might conclude that this is due somehow to the triple bond. Note also that once again the cyano group deviates in the same direction as the halogens, implying an unusually strong electronegativity effect. The NO_2 group interestingly deshields C_a more than expected, as does the t-butyl group. We might conclude, therefore, that the bulky oxygen and methyl groups of these substituents have an extra resonance effect on the adjacent carbon. This is not seen for these two substituents in their effect on the chemical shift of the distal carbon.

It can also be seen that the π-accepting substituents depend more on the resonance effect than the π-donating substituents in the chemical shift of C_a (correlation 7) vs. 5)). This agrees with the conclusions in the section on correlations with stabilization energies (Chapt. VII), that the π-acceptors have an extra resonance effect. There is a lot of evidence here why successful correlations with the stabilization energies of π-accepting substituents on strained systems could not be obtained, that is that groups like NO_2 or CF_3 are much different than CN or NC, and both are in turn much different from the carbonyl-containing substituents.

In conclusion, it can be said that despite the fact that electron density does not change much on C_a, its chemical shift is still dependent on the energy of the π electrons. We know that the energy of monosubstituted ethylene's π electrons can change due to the substituents electronegativity and resonance effects.

TABLE IX.1

^{13}C CHEMICAL SHIFTS (δC) RELATIVE TO TMS[a] (ppm)

	X	δC_a	δC_b
1)	H	123.3	123.3[b]
2)	F	152.1	92.0[c]
3)	Cl	126.1	117.2[d]
4)	Br	114.3	122.4[d]
5)	I	85.4	130.5[e]
6)	Me	136.2	115.9[b]
7)	OMe	153.8	84.6[d]
8)	OH	148.1[h]	
9)	OAc	141.7	96.6[d]
10)	vi	138.1	117.5[f]
11)	Ph	137.7	113.8[d]
12)	OEt	151.8	83.5[d]
13)	CH_2Cl	135.0	118.6[d]
14)	CH_2Br	135.5	119.9[d]
15)	CH_2I	137.5	119.3[d]
16)	Et	140.7	113.3[b]
17)	t-Bu	149.3	109.3[f]
18)	OBu	151.4	82.9[3]
19)	nPr	138.5	114.4[c]
20)	nBu	138.7	114.4[f]
21)	CN	108.2	138.0[d]
22)	NC	119.4	120.6[g]
23)	CHO	138.6	137.6[d]
24)	COMe	137.7	129.5[d]
25)	CO_2Me	129.0	130.2[d]
26)	NO_2	145.6	122.4[d]
27)	CO_2Et	129.7	130.1[d]
28)	CO_2H	128.4	133.0[d]

a) Where chemical shift data was available with CS_2 or benzene as the standard, the following shifts were used for calibration: $\delta CS_2 = 193.7$ ppm; $\delta Ph = 128.7$ ppm. (ref. 154)
b) Ref. 155. c) Ref. 151 d) Ref. 152 e) Ref. 156
f) Ref. 157 g) Ref. 158 h) Ref. 153

TABLE IX.2

^{13}C CHEMICAL SHIFTS RELATIVE TO H^{a} (ppm)

	X	δC_a	δC_b	
1)	H	0.0	0.0	
2)	F	28.8	-31.3	
3)	Cl	2.8	-6.1	
4)	Br	-9.0	-0.9	
5)	I	-38.1	7.0	
6)	Me	12.9	-7.4	
7)	OMe	30.5	-38.7	
8)	OH	24.8		
9)	OAc	18.4	-26.7	
10)	vi	14.8	-5.8	
11)	Ph	14.4	-9.5	
12)	OEt	28.5	-39.8	
13)	CH_2Cl	11.7	-4.7	
14)	CH_2Br	12.2	-3.4	
15)	CH_2I	14.2	-4.0	
16)	Et	17.4	-10.0	
17)	t-Bu	26.0	-14.0	
18)	OBu	28.1	-40.4	
19)	nPr	15.2	-8.9	
20)	nBu^{b}	15.4	-8.9	π-donors
21)	CN	-15.1	14.7	π-acceptors
22)	NC	-3.9	-2.7	
23)	CHO	15.3	14.3	
24)	COMe	14.4	6.2	
25)	CO_2Me	5.7	6.9	
26)	NO_2	22.3	-0.9	
27)	CO_2Et	6.4	6.8	
28)	CO_2H	5.1	9.7	

a) See Table IX.1 for references. b) Substituent constants not available, not included in correlations.

TABLE IX.3

n	R^2	R	Std. Error	equation
1) δC_b vs σ_R[a]				
22	0.95	0.97	3.89	$\delta C_b = 65.49\,\sigma_R - 1.07$
2) δC_a vs σ_I[b]				
27	0.14	0.38	14.36	$\delta C_a = -22.21\,\sigma_I + 16.64$
3) δC_a vs σ_I[c]				
20	0.002	0.04	9.60	------
4) δC_a vs σ_X, σ_F[d]				
15	0.43	0.65	10.40	$\delta C_a = 79.25\,\sigma_X - 45.20\,\sigma_F + 3.24$
5) δC_a vs σ_R, π-donors[e]				
14	0.88	0.94	3.04	$\delta C_a = -38.42\,\sigma_R + 8.24$
6) δC_a vs σ_R, π-acceptors[f]				
9	0.34	0.59	9.66	$\delta C_a = 96.99\,\sigma_R - 4.44$
7) δC_a vs σ_R, π-acceptors[g]				
7	0.93	0.97	1.97	$\delta C_a = 86.59\,\sigma_R - 3.13$

a) Substituents: H, F, Me, OMe, OAc, vi, Ph, OEt, CH_2Cl, CH_2Br, CH_2I, Et, t-Bu, OBu, nPr, NC, CHO, COMe, CO_2Me, NO_2, CO_2Et, CO_2H

b) Substituents: All possible but nBu (no substituent constant).

c) Substituents: Those of b) less Cl, Br, I, t-Bu, NO_2, CN, OH

d) Substituents: H, F, Cl, Me, OMe, OH, OAc, vi, CN, NC, CHO, COMe, CO_2Me, NO_2, CO_2H

e) Substituents: H, F, Me, OMe, OAc, vi, Ph, OEt, CH_2Cl, CH_2Br, CH_2I, Et, OBu, nPr

f) Substituents: H, CN, NC, CHO, COMe, CO_2Me, NO_2, CO_2Et, CO_2H

g) Substituents: Those of f) less CN, NO_2

FIG. IX.2

22 PTS; FROM EQ. 1) OF TABLE IX.3

δC_b vs ∇_R

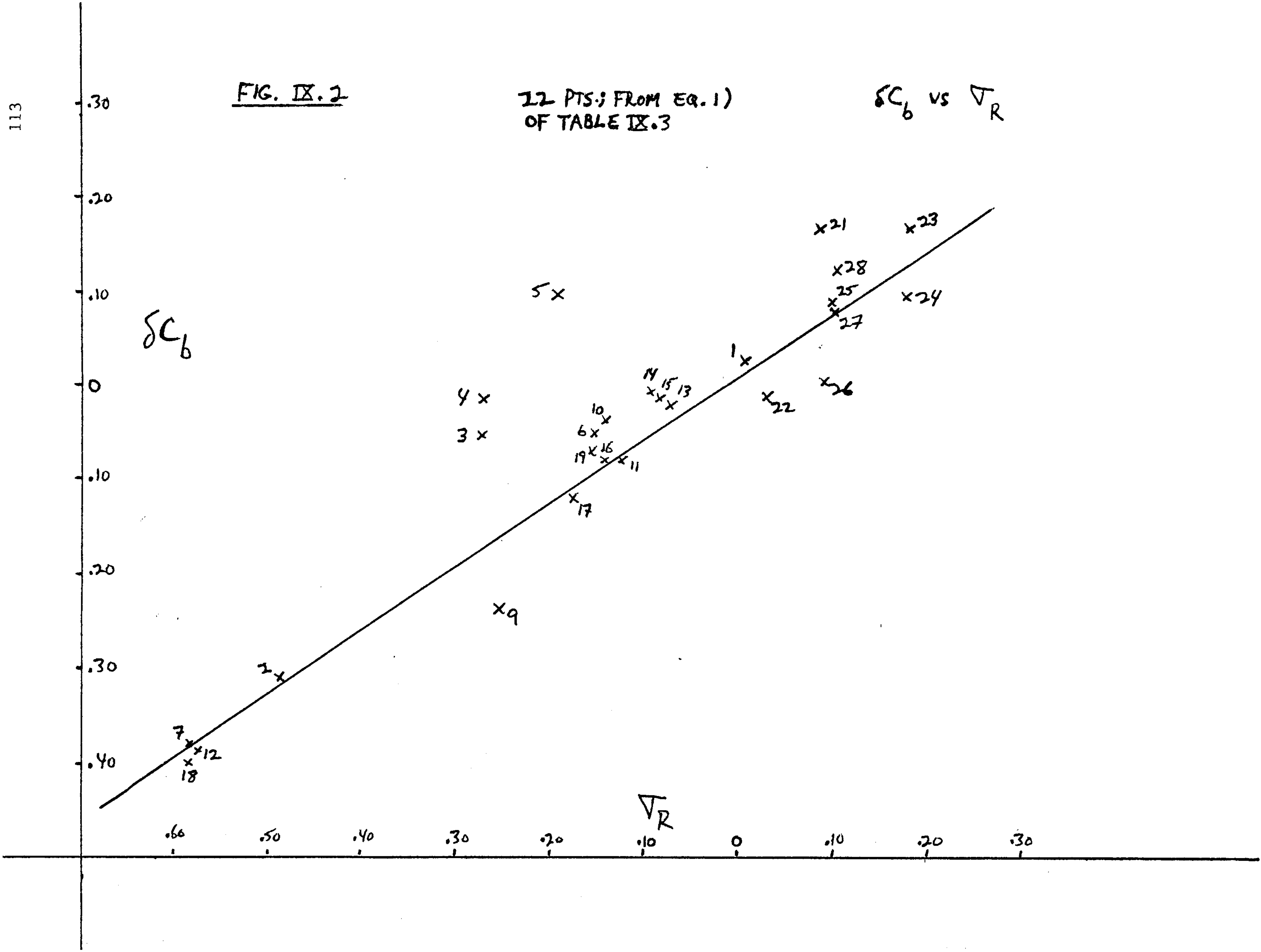
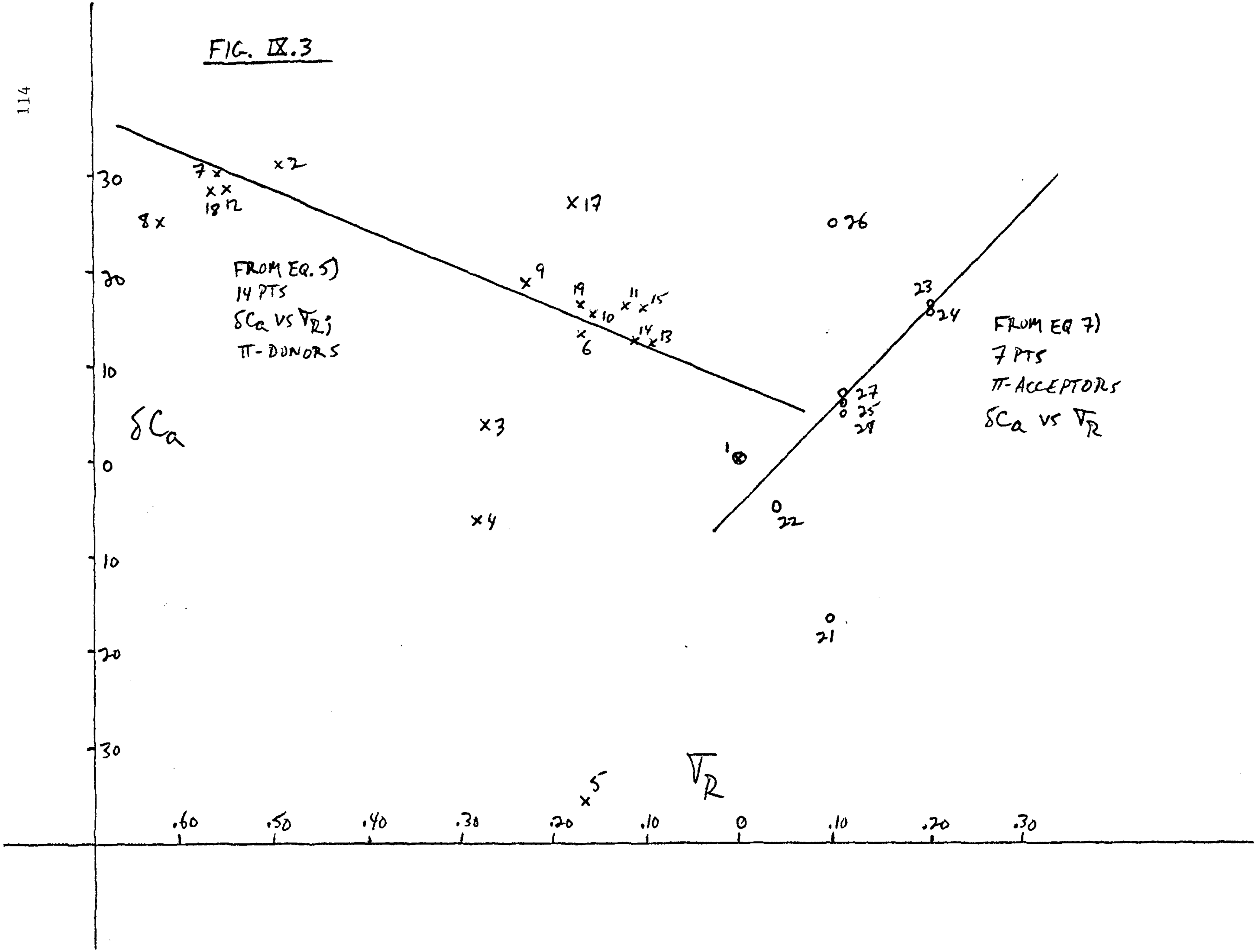


FIG. IX.3


30
20
10
0
10
20
30
δCa
σR
.60
.50
.40
.30
.20
.10
0
.10
.20
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7
2
18
12
8
17
26
9
19
10
11
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6
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13
23
24
27
25
28
3
1
22
4
21
5
FROM EQ. 5)
14 PTS
δCa VS σR;
π-DONORS
FROM EQ 7)
7 PTS
π-ACCEPTORS
δCa VS σR

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