Application of Linear Free Energy Relationships to Calculated Stabilization Energies of Strained and Unsaturated Molecules

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Abstract: Ab initio molecular orbital calculations with the 4-31G basis set have been performed on substituted ethylenes, cyclopropanes, benzenes, and acetylenes. Isodesmic stabilization energies have been compared with corresponding experimental data based upon $\Delta H_f^{\circ}(g)$ and very good agreement is observed. Additionally, the calculated stabilization energies have been correlated with substituent constants with both the Taft dual substituent parameter (DSP) equation and Topsom's triple substituent parameter approach. Comparisons of the sensitivities of the four molecular systems to σ- and π-substituent effects are made in light of the ionization potentials and electron affinities of the parent hydrocarbons. Substituted ethylenes and benzenes are more sensitive to resonance stabilization by substituents. In contrast, substituted acetylenes are more sensitive to effects associated with the σ-bonding electrons. Cyclopropanes are very weak π-acceptors, but their π-donor abilities are calculated to be greater than vinyl compounds by the stabilization energy criterion. There is a strong correlation between the adiabatic ionization potentials of the four parent hydrocarbons and m_R (i.e., ρ_R) for the four corresponding series of substituted molecules (π-acceptor substituents).

Substituents can have dramatic effects on the geometries and stabilities of strained organic molecules.[1] For example, π-electron-withdrawing substituents significantly shorten the C_2–C_3 (distal) bond length of cyclopropanes[2-5] with tangible effects on the tropylidene–norcaradiene[6,7] and semibullvalene[8] equilibria. Geminal difluorocyclopropanes are more labile than alkylated analogues apparently due to increased strain,[10a-c] and the strain energy in hexafluorocyclopropane is about 54 kcal/mol.[10a-c] A destabilization of ca. 5 kcal/mol per fluorine[11] has been assigned when this substituent is attached to cyclopropane, and these data, in reasonable agreement with a calculated value of 5.9 kcal/mol,[10] have been employed to explain the reactivity of perfluoro-tricyclo[3.2.0.0^{2,7}]hept-3-ene.[12] On the other hand, perfluoroalkyl groups such as CF_3 impose considerable stability on strained molecules and the perfluoroalkyl (R_f) effect[13] appears to be kinetic, rather than thermodynamic, in origin.[14] Thus, thermochemical stability sometimes determines reactivity and sometimes does not.

There is a dearth of thermochemical data on substituted strained molecules.[15] Thus, in order to attempt to assess trends in the thermodynamic stabilization, reliance must be placed on suitable calculational techniques. An earlier study, employing minimal basis set ab initio molecular orbital calculations, provided a qualitative view of substituent effects on a variety of strained and unsaturated molecules.[16] It was realized at the time that the STO-3G basis could not discern the subtle structural differences

induced by substituents and, therefore, idealized molecular geometries were employed.[16] Moreover, it is now known that even with the use of isodesmic equations, the STO-3G basis set can seriously miscalculate stabilization energies. For example, the enthalpy of hydrogenation (relative to that of cyclopropane) of 1,1-difluoroethylene is calculated to be too positive by 18.6 kcal/mol while the 4-31G basis set predicts a value too positive by only 1.1 kcal/mol.[10a] This is also consistent with the findings of George et al. in their comparison of basis sets.[17]

The purpose of this study is to present the best available calculational results obtained at the 4-31G level in order to quantitate the effects of substituents on the thermodynamic stabilization energies of substituted cyclopropanes, ethylenes, acetylenes, and benzenes. Although ethylene is not considered conventionally to be strained, its formulation as "cycloethane" and the view of cyclopropane as a mitigated ethylene[18,19] make comparison between these species interesting. Comparisons of acetylenes and benzenes to ethylene and, by extension, cyclopropane are noteworthy since the phenyl series has considerable thermochemical data, allowing comparison of theory and experiment while the dearth of acetylene thermochemical data should allow some interesting predictions which may suggest specific calorimetry experiments in the future. In order to make quantitative comparisons between different types of substituted hydrocarbons, the techniques of correlation analysis have been employed. Durmaz and Kollmar[20] had earlier concluded that analyzing substituent effects on cyclopropanes using SCF MO energies would be "...a very complex task and might in fact be futile". We agree with this, but we hope to obtain an understanding of σ- and π-interactions using the approach employed in the present work. Use of correlation analysis may furnish a means of comparing, for example, the relative conjugating abilities of vinyl and cyclopropyl moieties. In a study of molecular structures, Allen[4,5] concluded on the basis of C-substituent bond lengths that cyclopropyl is about 70% as effective a conjugating group as vinyl with π-acceptor substituents. Durmaz and Kollmar[20] concluded, also on the basis of molecular structure trends, that cyclopropyl has negligible resonance interactions with π-donor substituents. It is interesting to see how these predictions compare with those based upon energy criteria.

Application of correlation analysis to the problem at hand is not as straightforward as one might hope. The Hammett equation and its modifications and extensions consider the perturbation

(1) Greenberg, A.; Liebman, J. F. "Strained Organic Molecules"; Academic Press: New York, 1978; pp 325–341.
(2) Hoffmann, R. *Tetrahedron Lett.* **1970,** 2907–2910.
(3) Hoffmann, R.; Stohrer, W. D. *J. Am. Chem. Soc.* **1971,** *93,* 6941–6948.
(4) Allen, F. H. *Acta Crystallogr., Sect. B* **1981,** *B37,* 890–900.
(5) Allen, F. H. *Acta Crystallogr., Sect. B* **1980,** *B37,* 81–96.
(6) Ciganek, E. *J. Am. Chem. Soc.* **1965,** *87,* 652–653, 1149–1150.
(7) Wehner, R.; Gunther, H. *J. Am. Chem. Soc.* **1975,** *97,* 923–924.
(8) Paquette, L. A.; Volz, W. E. *J. Am. Chem. Soc.* **1976,** *98,* 2910–2917.
(9) Dolbier, W. R., Jr.; *Acc. Chem. Res.* **1981,** *14,* 195–200.
(10) (a) Greenberg, A.; Liebman, J. F.; Dolbier, W. R., Jr.; Medinger, K. S.; Stancke, A. *Tetrahedron* **1983,** *39,* 1533–1538. However, the value of 80 kcal/mol for strain in c-C$_3$F$_6$ is based on an unsuitable group increment, see ref 10b and 10c. (b) Liebman, J. F.; Dolbier, W. R., Jr.; Greenberg, A., submitted for publication. (c) Smart, B., personal communication, submitted for publication.
(11) O'Neal, H. E.; Benson, S. W. *J. Phys. Chem.* **1968,** *72,* 1866–1887.
(12) Dailey, W. P.; Lemal, D. M. *J. Am. Chem. Soc.* **1984,** *106,* 1169–1170.
(13) Lemal, D. M.; Dunlap, L. H., Jr. *J. Am. Chem. Soc.* **1972,** *94,* 6562–6564.
(14) Greenberg, A.; Liebman, J. F.; Van Vechten, D. *Tetrahedron* **1980,** *36,* 1161–1166.
(15) Pedley, J. B.; Rylance, J. "Sussex-N.P.L. Computer Analysed Thermochemical Data: Organic and Organometallic Compounds"; University of Sussex: Sussex, England, 1977.
(16) Dill, J. D.; Greenberg, A.; Liebman, J. F. *J. Am. Chem. Soc.* **1979,** *101,* 6814–6826.

(17) George, P.; Trachtman, M.; Brett, A. M.; Bock, C. W. *J. Chem. Soc., Perkin Trans 2* **1977,** *8,* 1036–47.
(18) See ref 1, Chapter 2.
(19) (a) Charton, M. In "The Chemistry of Alkenes"; Zabicky, J., Ed.; Interscience Publishers: London, 1970; Vol. 2, pp 511–610. (b) de Meijere, A. *Angew. Chem., Int. Ed. Engl.* **1979,** *18,* 809–826.
(20) Durmaz, S.; Kollmar, H. *J. Am. Chem. Soc.* **1980,** *102,* 6942–6945.

MO Calculations with the 4-31G Basis Set

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Table I. Calculated and Experimental Stabilization Energies of Substituted Ethylenes (Vinyl-X[a])

X	methyl		ethyl		isopropyl	
	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	-5.1	0.6
CH$_3$	4.3	5.4	3.2	2.8	2.6	0.6
OMe	10.9	12.3	6.1	6.9		3.3
OH	10.6	11.9	6.6	6.3	1.9	2.2
NH$_2$	13.3	13.3	11.2	9.7	8.0	6.2
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	3.3	4.8	2.4	1.7		0.2
NC	5.8		2.8			
CHO	6.4	6.9[e]	4.5	4.0[e]		2.2[e]
COMe	3.9	10.5	2.4	7.2		6.9
CO$_2$Me	8.0	11.9	2.0	9.5		8.0
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	5.9		9.2		8.7	
CH$_2^+$	30.0	23.3	23.3	14.6		10.5
vi	7.8	8.8	8.0	6.2		4.7
HCC–	3.9	5.9	3.3	3.1		1.1

[a] All energies in kcal/mol. [b] 4-31G calculated energies used. [c] Experimental heats of formation used. [d] All ΔH_f°(g) values from ref 13. [e] If ΔH_f°(g) of vi-CHO estimated by Hegedus (Hegedus, V. J.; Harrison, A. G. *Int. J. Mass Spectrom. Ion Phys.* **1979**, *30*, 293–306) is used, stabilization energy would be overestimated as compared to the value listed. [f] ΔH_f°(g) for vi-NO$_2$ that was estimated here was used, not Shaw's value.

induced in a reaction center Y by a substituent X through a hydrocarbon framework G, i.e., X–G–Y. The present study examines directly the interaction G–X. Fortunately, a set of calculated substituent parameters has become available which should be directly applicable to the present model.[21–23] Additionally, another series of potentially relevant substituent constants based upon the ionization potentials of monosubstituted benzenes has also been proposed.[24] In the present study, the dual-substituent parameter (DSP) equation of Taft[25] has been employed as have the σ_X, σ_F, and σ_{R^0} constants obtained by Topsom[21–23] in order to quantitate σ- and π-effects on stabilization energies.

Methodology

Calculations in this study have been obtained with the GAUSSIAN 70 program series[26] and the 4-31G basis set.[27] Where geometry-optimized 4-31G/4-31G data are available in the chemical literature, these have been employed in the present study. For molecules in which only non-optimized data are available, the 4-31G optimized structures of the hydrocarbon and substituent were combined and then further optimized by varying the framework-substituent bond length and substituent conformation as well as other selected features such as the ring bond lengths in cyclopropanes. The phenyl series was taken from the literature and is based upon idealized geometries. In all cases, the total energies employed are the lowest (best) to have been reported. Isodesmic eq[28] 1 and 2 have been employed in order to assess "methyl stabilization" and "ethyl stabilization" energies, respectively. Although comparison of cyclopropyl

Table II. Calculated and Experimental Stabilization Energies of Substituted Cyclopropanes (Cyclopropyl-X[a])

X	methyl		ethyl		isopropyl	
	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	5.3		-1.1		-6.2	
CH$_3$	2.7	4.2	1.6	1.6	1.0	-0.6
OMe	5.3		0.5			
OH	5.9		1.9		-2.7	
NH$_2$	6.5	6.6	4.4	3.0	1.2	-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	4.5	1.8	1.3		-0.1
NC	3.4		0.5			
CHO						
COMe	6.6	7.0	5.0	3.6		3.4
CO$_2$Me		6.1		3.9		2.2
NO$_2$	4.5		0.8			
CF$_3$						
Li	-2.1		2.9		6.2	
BH$_2$	6.1		9.4		8.9	
CH$_2^+$	33.7		27.1			
vi	2.7	(-0.6)[e]	2.9	(-3.2)[e]		
HCC–	1.7		1.0			

[a] All energies in kcal/mol. [b] 4-31G calculated energies used. [c] Experimental heats of formation used. [d] Note that Hopkinson et al. (Hopkinson, A. C.; McKinney, M. A.; Lien, M. H. *J. Comput. Chem.* **1983**, *4*, 513–523) found the strain energies of cyclopropane, c-Pr-F, c-Pr-CN, and c-Pr-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/mol. Note that the stabilization for c-Pr-F in this work is in good agreement, and that the same order of stabilization appears for this work with the ethyl model. [e] This value was not included in correlations for reason explained in the Appendix: we do not believe that conjugation of vinyl and cyclopropyl is destabilizing.

Table III. Calculated and Experimental Stabilization Energies of Substituted Acetylenes (Ethynyl-X[a])

X	methyl		ethyl		isopropyl	
	ΔE_{stab}[b]	ΔH_{stab}[c]	ΔE_{stab}[b]	ΔH_{stab}[c]	ΔE_{stab}	ΔH_{stab}[c]
H	0.0	0.0	0.0	0.0	0.0	0.0
Cl	2.3					
F	-12.8		-19.2		-24.2	
CH$_3$	8.6	7.6	7.6	5.0	7.0	2.8
OMe	0.3		-4.5			
OH	0.7		-3.4		-8.0	
NH$_2$	11.5		9.4		6.2	
OAc						
CH$_2^-$	50.6		46.0			
O$^-$	55.0		51.7		45.3	
NH$_3^+$	-17.5		-22.8		-26.8	
CN	2.1		1.2			
NC	-1.2		-4.2			
CHO	1.7		-0.1			
COMe	2.0		0.5			
CO$_2$Me	2.3		-3.7			
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	7.6	1.6		-2.5
vi	8.3	8.1	8.6	5.5		4.0
HCC–	6.8	8.1	6.2	5.3		3.3

[a] All energies in kcal/mol. [b] 4-31G calculated energies used. [c] Experimental heats of formation used.

derivatives, for example, with the corresponding isopropyl derivatives is perhaps more germane,[16,29] there are many more calculational and thermochemical data for methyl and ethyl derivatives. Analogously calculated isopropyl stabilization energies have, however, been included. Thermochemical data, ΔH_f°(g) are mostly from one compendium.[15]

(21) Topsom, R. D. *Acc. Chem. Res.* **1983**, *16*, 292–298.

(22) Marriot, S.; Topsom, R. D., *J. Am. Chem. Soc.* **1984**, *106*, 7–10.

(23) Marriot, S.; Topsom, R. D. *THEOCHEM* **1984**, *106*, 277–286.

(24) Charton, M. In "The Chemistry of Functional Groups, Supplement C"; Patai, S., Rappoport, Z., Ed.; J. Wiley & Sons, Inc.: New York, **1983**; Chapter 8.

(25) Ehrenson, S.; Brownlee, R. T. C.; Taft, R. W. *Prog. Phys. Org. Chem.* **1973**, *10*, 1–80.

(26) Hehre, W. J.; Lathan, W. A.; Ditchfield, R.; Newton, M. D.; Pople, J. A. "Quantum Chemistry Program Exchange"; Indiana University: Bloomington, Indiana; Program No. 236.

(27) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724–728.

(28) Hehre, W. J.; Ditchfield, R.; Radom, L.; Pople, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 4796–4801.

(29) Fuchs, R. *J. Chem. Educ.* **1984**, *61*, 133–136.

Table IV. Calculated and Experimental Stabilization Energies of Substituted Benzenes (Phenyl-X^a)

X	methyl		ethyl		isopropyl	
	$\Delta E_{stab}{}^b$	$\Delta H_{stab}{}^c$	$\Delta E_{stab}{}^b$	$\Delta H_{stab}{}^c$	$\Delta E_{stab}{}^b$	$\Delta H_{stab}{}^c$
H	0.0	0.0	0.0	0.0	0.0	0.0
Cl		5.7		0.8		-2.2
F	7.8	8.5	1.4	5.1	-3.7	2.4
CH$_3$	1.3	5.5	0.2	2.9	-0.4	0.7
OMe	6.2	9.8	1.4	4.4		0.8
OH	7.5	12.4	3.4	6.8	-1.2	2.7
NH$_2$	9.8	11.3	7.7	7.7	4.5	4.0
OAc						
CH$_2^-$	42.7		38.2			
O$^-$						
NH$_3^+$		8.7		2.2		-3.9
CN	1.2	3.7	0.3	0.6		-0.9
NC						
CHO	5.3	6.8	3.5	3.9		2.1
COMe		6.4		3.0		2.8
CO$_2$Me		8.4		6.0		
NO$_2$	2.5	3.5	-1.2	-0.7		-4.6
CF$_3$		2.0				
Li						
BH$_2$						
CH$_2^+$	43.3		36.6			
vi	-1.3^d	7.1	-1.0^d	4.5		3.0
HCC-	3.1	7.0	2.5	4.2		2.2

^{a}All energies in kcal/mol. ^{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.

Where other data sources are employed these are discussed in the relevant table.

$$RX + CH_4 = CH_3X + RH \qquad (1)$$

$$RX + C_2H_6 = C_2H_5X + RH \qquad (2)$$
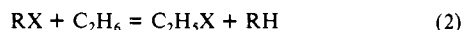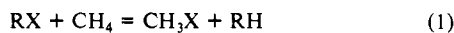
Results

Total energies calculated at the 4-31G level as well as standard gas-phase enthalpies of formation are available in supplementary tables. Tables I–IV list stabilization energies based upon 4-31G calculations and the corresponding stabilization enthalpies based upon values of $\Delta H_f{}^\circ(g)$. Despite the fact that the energies are for hypothetical vibrationless molecules and the enthalpies are at 298 K, the isodesmic calculated stabilization energies are close to the experimental stabilization enthalpies. Table V lists correlations between experimental and theoretical stabilizations. They are generally good with the largest errors introduced when the charged substituents CH$_2^+$, O$^-$, and NH$_3^+$ are employed. Without these charged substituents the standard error is usually under 2 kcal/mol. The correlations are best for methyl stabilizations. The relatively poor correlations for phenyl derivatives reflect our use of a published data series having idealized geometries and not further optimized. This is also apparent from the fact that almost all calculated stabilization energies in the phenyl series (Table IV) are lower than the experimental values, whereas no such trend is seen for the other three substituted hydrocarbons (Tables I–III).

It is worthwhile to compare the stabilization enthalpies and energies from Tables I–IV with two recent findings. Schulman et al.[30] found that the 6-31G*(SCF) energy difference of 5.2 kcal/mol favoring 1,3,5-cycloheptatriene over norcaradiene decreased to 1.5 kcal/mol for the 7-cyano isomers (corresponding 4-31G(SCF) values, 4.8 and 0.9 kcal/mol; corresponding experimental values[31] 6.2 and 2.0 kcal/mol). They found that the isopropyl stabilization energy in 7-cyanonorcaradiene was only 1.1 kcal/mol and that most of the change in equilibrium concentrations was due to destabilization (ca. 2.9 kcal/mol) in the cycloheptatriene. The rather small 6-31G* isopropyl stabilizations in 7-cyanorcaradiene and cyanocyclopropane (2.0 kcal/mol) still

seem to be a bit larger than the experimental value for cyanocyclopropane (Table II). Doering et al.[32] discussed the stabilization enthalpy in enamines and found stabilization to be about 6 kcal/mol greater for NH$_2$ than for H. This value is somewhat lower than the experimental ethyl stabilization of vinylamine (9.7 kcal/mol, Table I), but the apparent discrepancy might arise from the absence of "saturation effects" in vinylamine, the simplest possible enamine.

Table VI lists the substituent constants employed in this study. Values for the Taft dual substituent parameters were taken from Charton's compendium,[33] and values for σ_X, σ_F, and σ_{R^0} are taken from Topsom's work.[21-23] We note a good correlation between Topsom's σ_{R^0} and Taft's σ_R according to eq 3. This is expected, but we emphasize this relationship since this equation has been employed to calculate values of σ_{R^0}, when missing, from σ_R and to calculate one σ_R value from σ_{R^0}. Similarly, a plot of Taft's σ_I values from the Charton compendium against Topsom's σ_F is summarized in eq 4. One can see that the experimental "inductive

$$\sigma_{R^0} = 0.74\sigma_R + 0.03 \quad (n = 10, R^2 = 0.98) \qquad (3)$$

$$\sigma_I = 1.00\sigma_F + 0.03 \quad (n = 19, R^2 = 0.94) \qquad (4)$$

effect" constant is virtually identical with the field effect constant derived theoretically with a model avoiding through-bond effects.[21-23] This relationship was employed to derive a value for σ_I from σ_F as well as a value for σ_F from σ_I in Table VI.

In attempting to employ isodesmic stabilization energies or enthalpies to obtain correlations with substituent constants, it is assumed that isodesmic entropies of reaction are negligible and this is true with some readily understandable exceptions.[34] Another point that must be addressed is that both π-donors and π-acceptors can cause stabilization. Thus, one must treat them separately or in terms of an analogue of the DSP equation in which there are separate terms for π-donating and π-accepting substituents. This is different from the case where, for example, one plots π-charge at the β-carbon of a substituted olefin against σ_R where π-donors yield negative charges and π-acceptors yield positive charges. Since the π-donors and π-acceptors are separated, most of the attempted correlations will involve only 6–8 data points, including hydrogen. It is certainly recognized that the practice of employing 6–8 data points with two independent parameters (Taft DSP approach) or three independent parameters (Topsom procedure) weakens the statistically based arguments made in the present work. Nevertheless, the conclusions, which may be considered semiquantitative, are an improvement over purely qualitative conclusions.[16]

Table VII lists correlations of methyl, ethyl, and isopropyl stabilization energies, respectively, using the Taft DSP approach. A number of points are apparent: (a) correlations of π-donors appear to be considerably better than correlations of π-acceptors; (b) acetylenes behave differently compared to ethylenes, cyclopropanes, and benzenes in that their stabilization energies are much more sensitive to σ_I than to σ_R, all other correlations of methyl and ethyl stabilizations with the exception of the ethyl stabilizations of cyclopropanes (π-donor substituted) have $m_R > m_I$, this is consistent with qualitative observations by others[35] and a quantitative approach based upon the "Composite Parameter Method";[36] (c) the m_I values all become more negative in going from methyl to the ethyl to the isopropyl series, the changes for all four hydrocarbon classes are about equal for π-donor substituents while a different equality is seen for π-acceptor substituents; (d) the dependence on σ_R for both π-donors and acceptors weakens in going from methyl to ethyl to isopropyl stabilizations, however, the changes are much smaller than those for σ_I; (e)

(30) Schulman, J. M.; Disch, R. L.; Sabio, M. L. *J. Am. Chem. Soc.* **1984**, *106*, 7696–7700.

(31) See unpublished data of Anet and Miura in Table IV of ref 30.

(32) Doering, W. v. E.; Birladeanu, L.; Andrews, D. W.; Pagnotta, M. *J. Am. Chem. Soc.* **1985**, *107*, 428–432.

(33) Charton, M. *Prog. Phys. Org. Chem.* **1981**, *13*, 119–251.

(34) Liebman, J. F.; Hyman, A.; Laydon, L.; Stevenson, T., Greenberg, A., unpublished results.

(35) Furet, P.; Hallak, G.; Matcha, R. L.; Fuchs, R. *Can. J. Chem.*, submitted for publication, personal communication from R. Fuchs.

(36) Charton, M.; Greenberg, A.; Stevenson, T. A. *J. Org. Chem.*, in press.

Table V. Linear Regression of 4-31G Calculated and Experimental Stabilization Energies, $\Delta E_{stab} = m\ \Delta H_{stab}(\text{exptl}) + b$[o]

corr.	framework	n	R^2	R	std error	m	b
			(A) Methyl Stabilization				
1	vinyl[a]	16	0.95	0.97	2.53	1.27	-2.38
2	vinyl[b]	13	0.92	0.96	1.19	0.83	0.41
3	phenyl[c]	10	0.81	0.90	1.54	0.78	-0.86
4	cyclopropyl[d]	6	0.93	0.96	0.81	0.95	-0.55
5	ethynyl[e]	5	0.88	0.94	2.03	1.21	-0.65
6	all four[f]	34	0.91	0.95	2.34	1.26	-2.82
7	all four[g]	29	0.80	0.90	1.52	0.83	-0.12
			(B) Ethyl Stabilization				
8	vinyl[h]	16	0.85	0.92	3.91	1.48	-2.21
9	vinyl[i]	10	0.94	0.97	0.90	1.00	0.67
10	phenyl[j]	10	0.72	0.85	1.43	0.76	-0.75
11	cyclopropyl[k]	6	0.98	0.99	0.34	1.49	-0.31
12	ethynyl[e]	5	0.55	0.74	2.64	1.02	2.44
13	all four[f]	34	0.79	0.89	3.30	1.38	-1.45
14	all four[g]	30	0.46	0.68	2.28	0.74	0.54
			(C) Isopropyl Stabilization				
15	vinyl[l]	7	0.92	0.96	3.65	1.55	-0.06
16	cyclopropyl[m]	4	0.83	0.91	0.98	0.76	1.04
17	all four[n]	15	0.82	0.90	3.80	1.42	-0.08

[a] Substituents: H, F, Me, OMe, OH, CN, NH_2, CHO, CO_2Me, NO_2, CF_3, CH_2^+, O⁻, NH_3, vi, HCC- (omit Cl, COMe). [b] Substituents: H, F, Me, OMe, OH, CN, NH_2, CHO, CO_2Me, NO_2, CF_3, vi, HCC- (omit Cl, COMe, charged substituents). [c] Substitutents: H, F, Me, OMe, OH, NH_2, CN, CHO, NO_2, HCC-. [d] Substituents: H, Me, NH_2, CN, NH_3^+, COMe. [e] Substituents: H, Me, CH_2^+, vi, HCC-. [f] Previous four data sets including H only once. [g] Same as above but lacking charged substituents. [h] Substituents: H, F, Me, OMe, OH, CN, NH_2, CHO, COMe, CO_2Me, NO_2, O⁻, NH_3^+, vi, HCC-, CH_2^+. [i] Same as set 8 less CO_2Me, F, COMe, and charged substituents. [j] Substituents: H, F, Me, OMe, OH, NH_2, CN, CHO, NO_2, HCC. [k] Substituents: H, Me, NH_2, CN, NH_3^+, COMe. [l] Substituents: H, F, Me, OH, NH_2, O⁻, NH_3^+. [m] Substituents: H, Me, NH_2, NH_3^+. [n] Includes phenyl, ethynyl; H used only once. [o] m = slope, n = no. of points, b = y intercept, R = correlation coefficient.

Table VI. Compilation of Taft DSP Constants[33] and Topsom Constants as well as Some Derived Constants (See Eq 3 and 4)

	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
n-Pr	-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 R. Topsom, personal communication. See also ref 21-23. [b] R. Topsom, personal communication, see ref 21-23. [c] Calculated by eq 3. [d] Exner, O. In "Correlation Analysis in Chemistry"; Chapman, N. B., Shorter, J., Eds.; Plenum Press: New York, 1978. [e] Calculated from eq 4. [f] From ref 22, note that there are also values listed in ref 21 that are slightly different. [g] Charton,[33] unless noted otherwise. [h] Reference 21, unless noted otherwise. [i] Reference 23, unless noted otherwise.

methyl, ethyl, and isopropyl stabilization energy correlations give the same ordering of hydrocarbon moiety sensitivities for their interactions with π-donor substituents (hydrocarbon moieties as

π-acceptors); (f) a different ordering given by both ethyl and methyl stabilization energies is found for interactions with π-acceptor substituents (hydrocarbon moieties as π-donors).

Table VIII lists correlations of stabilization energies using the Topsom three-parameter approach. Again one sees better correlations for π-donor substituents than π-acceptor substituents. The m_{R^o} are very similar to values of m_R (Tables VII and VIII) with one exception (HC≡CX, X = π-acceptors). The m_X, m_F sum is generally comparable to m_I except for the previously noted (HC≡CX, X = π-acceptor) case. It is worthwhile noting that m_X values for π-acceptors are larger than those for the π-donors for each hydrocarbon moiety. The absolute values of m_X are larger than those of m_F for all cases except acetylenes substituted with π-donors.

The substituents vinyl, ethynyl, phenyl, and cyclopropyl have not been included in the regression analyses summarized in Table VIII. It is simple to illustrate the rationale of these omissions by considering 1,3-butadiene (i.e., vinyl-substituted ethylene). In contrast to substituents which can be classified as π-donors or π-acceptors, vinyl is neither (or both) in this instance. Thus, employing the DSP constants for vinyl (Table VI) and the values of m_I and m_R in Table VII for vinyl compounds substituted by π-donors, a value of 2.9 kcal/mol is anticipated for the 4-31G methyl stabilization energy. This is significantly lower than the 7.8 kcal/mol 4-31G calculated methyl stabilization energy found in Table I which compares well with the experimental value of 8.8 kcal/mol. The huge discrepancy between the anticipated 4-31G methyl stabilization energy of diacetylene (-10.9 kcal/mol) and the 4-31G calculated value +8.3 kcal/mol, which is in good agreement with the experimental value of +8.1 kcal/mol, has a related origin. In that instance, the substituent constants of the ethynyl group indicate a fairly strong σ-withdrawing effect and a relatively weak π-donating effect. The values of m_I and m_R for acetylenes, as stated previously, indicate a greater sensitivity to σ- than to π-effects. Thus, a strong σ-withdrawer would be a strong destabilizer. However, the symmetry in diacetylene requires the substituent not to behave as a σ-withdrawer.

Discussion

One of the goals of the present study is to relate the thermodynamic stabilizations of substituted strained and unsaturated molecules to relevant properties of the parent hydrocarbons. In this regard, it is worthwhile viewing Table IX which compares

Table VII. Correlation Analysis of Stabilization Energies by the Taft DSP Equation: $\Delta E = m_I \sigma_I + m_R \sigma_R + b$

	n	R^2	R	std error	m_I	m_R	
				(A) Methyl Stabilization			
vi-X							
(π-donors)	6	0.97	0.99	1.07	-4.36	-17.62	0.73[a]
(π-acceptors)	8	0.22	0.47	3.05	4.30	14.35	0.83[b]
	5	0.83	0.91	1.37	3.25	21.38	0.02[c]
c-Pr-X							
(π-donors)	6	0.95	0.98	0.69	1.78	-7.36	0.71[a]
(π-acceptors)	5	0.91	0.95	1.05	2.90	25.98	0.12[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	7.71	-16.08	7.80[h]	2.91[b]
Ph-X							
(π-donors)	6	0.97	0.99	0.82	-4.40	-10.86	-0.25[a]
(π-acceptors)	4	0.98	0.99	0.59	-0.92	28.10	-0.08[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	0.15	0.38	2.30	1.27	10.57	0.01[b]
c-Pr-X							
(π-donors)	6	0.94	0.97	0.63	-9.32	-6.87[i]	0.12[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	0.29	0.54	8.07	-19.15	4.28[j]	2.09[b]
Ph-X							
(π-donors)	6	0.82	0.91	1.56	-6.48	-10.30	-0.84[a]
(π-acceptors)	4	0.90	0.95	1.08	-4.23	21.97	0.14[e]
				(C) Isopropyl Stabilization			
vi-X	5	0.97	0.99	1.09	-22.32	-13.80	-0.01[g]
c-Pr-X	5	0.93	0.97	1.16	-15.88	-4.00	-0.00[g]
HCC-X	5	0.95	0.98	4.04	-65.00	-17.18	1.34[g]
Ph-X	5	0.78	0.88	1.97	-12.69	-7.68	-0.94[g]

[a] Substituents: H, F, Me, OMe, OH, NH$_2$. [b] Substituents: H, CN, NC, CHO, COMe, CO$_2$Me, 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^0} (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 tht of m_{R^0}.

Table VIII. Correlation of Stabilization Energies (kcal/mol) by the Topsom Equation: $\Delta E = m_X \sigma_X + m_F \sigma_F + m_R \sigma_{R^0} + b$

	n	R^2	R	std error	m_X	m_F	m_{R^0}	b
				(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	2.22	37.15	-20.89	17.05	1.24
c-Pr-X								
(π-donors)	6	0.98	0.99	0.54	11.24	-5.31	-5.83	0.09
(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	0.95	0.98	1.32	-3.68	9.09	-15.18	0.14
(π-accpeptors)	4				27.39	-22.55	35.70	
				(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	0.80	0.89	1.25	32.47	-20.82	12.38	0.34
c-Pr-X								
(π-donors)	6	0.92	0.96	0.90	2.07	-11.18	-8.95	0.15
(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	0.87	0.93	1.62	-12.66	3.44	-17.95	0.33
(π-acceptors)	4				63.23	-48.04	28.99	
				(C) Isopropyl Stabilization[c]				
vi-X	5	1.00	1.00	0.45	4.15	-6.71	-19.00	-0.03
c-Pr-X	5	1.00	1.00	0.26	1.16	-18.64	-6.32	0.02
HCC-X	5	1.00	1.00	0.31	25.15	-91.78	-20.70	-0.02
Ph-X	5	0.97	0.98	1.06	-11.96	-5.22	-15.38	0.07

[a] Same substituents employed for each correlation as in Table VII. [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 IX. Relationships of Conjugation Sensitivity Slopes (m_R) to Ionization Potentials and Electron Affinities of Parent Hydrocarbons

(A) π-Acceptors

parent hydrocarbon	m_R	hydrocarbon	
		IP(adiab.), eV	IP(vert), eV
vi-X	14.4	10.51[a]	10.51[b]
HCC-X	7.8	11.40[a]	11.40[b]
c-Pr-X	26.0	9.86[c]	10.60, 11.30[d]
Ph-X	28.1	9.25[a]	9.25[b]

(B) π-Donors

parent hydrocarbon	m_R	hydrocarbon EA(vert),[e] eV
vi-X	-17.6	-1.78
HCC-X	-20.9	-2.6
c-Pr-X	-7.4	-5.29[f]
Ph-X	-10.9	-1.15

[a] Kimura, K.; Katsumata, S.; Achiba, Y.; Yamazaki, T.; Iwata, S. "Handbook of HeI Photoelectron Spectra of Fundamental Molecules"; Japan Scientific Society, Halstead Press: New York, 1981. [b] Value approximated from those in Levin, R. D.; Lias, S. G. "Ionization Potential and Appearance Potential Measurements, 1971-1981", National Bureau Standards, U.S. Dept. of Commerce, Oct. 1982, NSRDS-NBS 71. [c] Lias, S. G.; Buckley, P. J. *Int. J. Mass Spectrom. Ion Proc.* **1984**, *56*, 123-137. [d] Basch, H.; Robin, M. B.; Kuebler, N. A.; Baker, C.; Turner D. W. *J. Chem. Phys.* **1969**, *51*, 52-66. [e] Values obtained from Jordan and Burrow (Jordan, K. D.; Burrow, P. D. *Acc. Chem. Res.* **1978**, *11*, 341-348) Jordan, personal communication to A. Greenberg. [f] Howard, A. E.; Staley, S. J. In "ACS Symposium Series, No. 263, Resonances in Electron-Molecule Scattering Van der Waals Complexes and Reactive Dynamics", Truhlar, D. G., Ed.; ACS: Washington, D.C., 1984, pp 183-192.

m_R values for all four substituted systems with adiabatic and vertical ionization potentials of the parent hydrocarbons which, of course, arise from π or π-like molecular orbitals. There is a good correlation ($n = 4$; $R^2 = 0.97$) with the adiabatic ionization potentials which will not be significantly changed even if Jahn-Teller effects in cyclopropane and benzene are corrected for. Comparison of m_R values for substituents which are π-electron donors with vertical electron affinities (Table IXB) does not yield any obvious correlation. The only obvious point is that the lowest m_R corresponds to the cyclopropyl series where the parent hydrocarbon has, by far, the least affinity for electrons. This corresponds to the view[20] that cyclopropyl is a poor π-acceptor and thus shows little conjugation with π-donor substituents. For example, the lowest energy conformer of cyclopropylamine does not have suitable geometry for conjugation between the ring and the amino substituent.[20] This is consistent with the photoelectron spectrum of cyclopropylamine[37] which does not indicate any significant conjugation (IP$_v$(cyclopropylamine) = 9.41 eV; IP$_v$-(isopropylamine) = 9.31 eV). It is also consistent with the observation that cyclopropanes have almost no ability to stabilize attached carbanion centers.[38,39] The point that π-donors produce little stabilization on cyclopropane rings has also been made recently by Clark et al.[40] They note that F has no significant conjugation with the ring and that only strong π-donors such as NH_2 and O^- may stabilize the ring. We agree and quantitate this view by noting that for isopropyl stabilization of π-donor-substituted cyclopropanes (Table VII), the value of m_I (-15.88) is much greater than m_R (-4.00). Clearly, σ-acceptor groups destabilize the ring. After that, the poor correlations may reflect

the fact that adiabatic EA are unmeasurable at present or that the energies of the metastable species measured might not correlate well with the ground-state substituted hydrocarbons.

An unanticipated result of the correlation analysis techniques employed here is the finding in Tables VII and VIII that m_R (m_{R^0}) in cyclopropyl derivatives is larger than that in vinyl derivatives when π-acceptor substituents are considered. This suggests that cyclopropyl is a stronger π-donor than vinyl. While this is consistent with the values of the adiabatic IPs of the two parent hydrocarbons (Table IX), the conclusion is not self-evident when one compares the vertical IPs (Table IX) or considers that the orbital overlap with the substituent may be better for vinyl derivatives.[19] It is inconsistent with most of the comparisons (e.g., UV and IR spectral data) which indicate that the cyclopropyl group interacts with substituents in a manner intermediate between alkyl and vinyl.[19] Furthermore, it is not consistent with Allen's conclusion[4,5] that cyclopropyl is about 70% as effective as vinyl in conjugating π-acceptor substituents. However, on the basis of structural data of cyano- and ethynylcyclopropane, Harmony et al.[41] concluded that cyclopropyl is a stronger π-donor than vinyl.

It is not immediately obvious that substituent effects on energies should exactly parallel substituent effects on molecular geometries, although one would expect an interrelationship. Conjugative interactions of vinyl and cyclopropyl groups, as measured by rotational barriers, have been shown to be about equal for the π-acceptor substituents COF,[42] CHO,[42] BF_2,[42] and NO_2.[43] De Meijere[19b] states that the "...ability of the cyclopropyl group to stabilize a center of positive charge is comparable with, or even greater than, that of the vinyl and phenyl group".

Another interesting trend is the variation in m_I (Table VII) within a related series (e.g., vinyl-X, π-donors) as one goes from methyl to ethyl to isopropyl stabilization. For vinyl, m_I exhibits the values -4.36, -15.27, and -22.32, respectively. Interestingly, the changes for cyclopropyl, ethynyl, and phenyl molecules substituted by π-donor substituents are about the same as for vinyl. The corresponding changes for m_R (Table VII) are very much smaller, e.g., for vinyl-X (X = π-donors) -17.62, -17.10, -13.80. This means that resonance stabilization is fairly independent (within the error limits of our analysis) of the model chosen (methyl, ethyl, isopropyl). However, the inductive effect (destabilizing for the majority of substituents examined which are σ-withdrawers) is highly dependent on the model compound. Thus, σ-withdrawal is most destabilizing when isopropyl is the model and least destabilizing when methyl is the model. The importance of inductive effects in determining stabilizations of cyclopropanes substituted by π-donors was demonstrated by Clark et al.[40] The decreased stabilization in going from methyl stabilization to isopropyl stabilization noted in that paper and here is reflected in the increasingly negative m_I as one goes from methyl to isopropyl. That is to say, σ-withdrawing substituents produce their greatest destabilization relative to isopropyl and this is the dominant substituent effect for π-donors. However, for π-acceptor substituents, conjugation plays a significant and perhaps dominant role. This is easy to understand if one realizes that σ_I is identical with σ_F which is itself a measure of a substituent's ability to induce through-space (dipole–dipole) interactions. Such interactions will be dependent upon the polarizability of the hydrocarbon framework. The isopropyl framework is much more polarizable and can neutralize an induced charge better than the smaller frameworks. The average molecular polarizabilities for propane, ethane, and methane are 6.3, 4.4, and 2.6, respectively.[38] For π-acceptor substituents the charge in m_I in going from methyl to ethyl stabilization energies is only about -3 to -4 instead of ca. -11 as in the case of the π-donors. Similarly, the magnitude of m_I for substituted acetylenes reflects mostly the sp character of the carbon framework but also the low polarizability of acetylene (3.3),[44] which can be compared with those of ethylene

(37) Kimura, K.; Katsumata, S.; Achiba, Y.; Yamazaki, T.; Iwata, S. "Handbook of HeI Photoelectron Spectra of Fundamental Organic Molecules"; Japan Scientific Societies Press: Tokyo (Halsted Press: New York distributors), 1981; pp 117-119.

(38) (a) Perkins, M. J.; Ward, P. *Chem. Commun.* **1971**, 1134. (b) Perkins, M. J.; Ward, P. *J. Chem. Soc., Perkin Trans. 1* **1974**, 667.

(39) Streitwieser, A., Jr., cited as ref 112 in de Meijere review (ref 19B. above).

(40) Clark, T.; Spitznagel, G. W.; Klose, R.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1984**, *106*, 4412-4419.

(41) Harmony, M. D.; Nandi, R. N.; Tietz, J. V.; Choe, J.-I, Getty, S. J.; Staley, S. W. *J. Am. Chem. Soc.* **1983**, *105*, 3947-3951.

(42) Noe, E.; Young, R. M. *J. Am. Chem. Soc.* **1982**, *104*, 6218-6220.

(43) Skancke, A. *Acta Chem. Scand. A* **1982**, *A36*, 637-639.

(4.2),[39] cyclopropane (6.0),[45] and benzene (10.4).[44]

When one examines the Topsom parameter correlations, similar effects are seen, as expected, in the variation in m_F (Table VIII) as compared to m_I. However, m_X also becomes more negative upon going from methyl to ethyl stabilzation, and this is more difficult to understand.

In any case, it is quite clear that the magnitude of nonresonance stabilization (destabilization) effects is strongly dependent upon the identity of the acyclic model.

Conclusions

Stabilization energies (4-31G) of monosubstituted ethylenes, ethynes, cyclopropanes, and benzenes successfully reproduce the corresponding values based upon experimental $\Delta H_f(g)$. The values can be employed in linear free energy relationships since the entropy changes of isodesmic equations are negligible. Correlations using the Taft dual substituent parameter (DSP) approach as well as Topsom's three parameter approach yield similar conclusions: (a) correlations involving π-donor substituents are superior to those including π-acceptor substituents; (b) stabilization energies of substituted ethylenes, benzenes, and cyclopropanes are more sensitive to resonance rather than inductive interaction with the substituents, in contrast to ethynes where the reverse is true; (c) the sensitivities of the four series of molecules to resonance stabilization involving π-acceptor substituents correlates well with the adiabatic ionization potentials of the parent hydrocarbons,

and this suggests that cyclopropyl is a stronger π-donor than vinyl which contrasts with the more conventional view based upon UV and IR spectral and molecular geometry studies; (d) cyclopropane has the least electron affinity of the four parent hydrocarbons and, thus, it is logical that cyclopropane shows the lowest sensitivity to π-donor substituents and is therefore a very weak π-acceptor, however, no obvious order is apparent for the other three parent hydrocarbons; (e) values of m_R show little variation with the model employed while m_I varies significantly, reflecting the polarizabilities of the model hydrocarbons. Cyclopropane's high π-donor/low π-acceptor ability may combine to make it a poor transmitter of resonance effects.[46]

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Supplementary Material Available: Listing of total energies, level of geometry optimization, and gas-phase enthalpies of formation for substituted methanes, ethanes, 2-propanes, acetylenes, ethylenes, cyclopropanes, and benzenes (12 pages). Ordering information is given on any current masthead page.

(44) Miller, K. J.; Savchik, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 7206–7213.

(45) This value is the average of calculations according to ref 39 based upon alkyl and vinyl carbons.

(46) Trachtenberg, E. N.; Odian, G. *J. Am. Chem. Soc.* **1958**, *80*, 4018–4022.

Lyomesophases of the Diethylammonium Flufenamate–Water System Studied by Deuterium NMR Spectroscopy

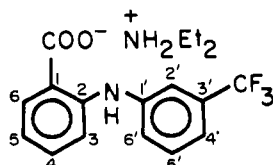**I. Kustanovich,[‡] R. Poupko,*[‡] H. Zimmermann,[†,‡] Z. Luz,[‡] and M. M. Labes[§]**

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Abstract: It was confirmed by using ^{2}H NMR spectroscopy that mixtures of water and diethylammonium flufenamate (DEAF) form lyomesophases in the concentration range 2.5–60 wt % DEAF. Depending on the concentration of the DEAF, two phases are formed with different structural characteristics. In solutions containing below 20 wt % DEAF, the mesophase consists of micellar structures of various shapes that are not well aligned by the magnetic field. Deuterium NMR of deuterated DEAF molecules in this phase exhibit powderlike spectra. At high concentration of DEAF (>20 wt %), monodomain samples are formed which are well aligned by the magnetic field. Deuterium NMR spectra in this phase consist of sharp doublets for each of the various deuterons. The results are consistent with the bilamellar structure for the mesophases as suggested by Eckert and Fischer. The DEAF molecules are highly ordered in the layers and appear to orient with the aromatic rings parallel to the director. In the high concentration range, the order parameter for the DEAF molecules exceeds 0.4.

I. Introduction

In 1981 Eckert and Fischer[1] (EF) have shown that mixtures of diethylammonium flufenamate (DEAF) and water form lyomesophases over a wide range of DEAF concentrations (2.5 to ~60 wt %) and temperatures (up to ~60 °C). The phe-

nomenon is quite unusual since most amphiphiles that are known to form lyomesophases consist of rod-like (or double rodlike)

molecules with well-defined polar heads to which one or two long hydrophobic chains are bonded, e.g., alkali-metal soaps, phospholipids, and other detergents.[2] The structure of the DEAF molecule differs from these amphiphiles in that it consists of two aromatic rings bonded via a polar bridge and substituted on both rings with polar groups. A similar nonconventional amphiphile is the disodium cromoglycate salt which in aqueous solutions also forms lyomesophases.[3] Both of these compounds are remarkable
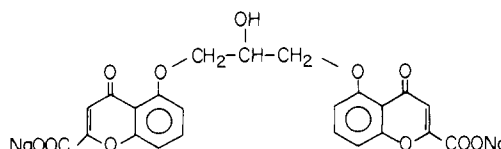
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(1) Eckert, T.; Fischer, W. *Colloid Polym. Sci.* **1981**, *259*, 553.
(2) Wilson, P. A. In "Liquid Crystals and Plastic Crystals"; Gray, G. A., Wilson, P. A., Eds.; Wiley: New York, 1974; Vol 1, pp 60, 199.