sulfenyl)-β-CD (**2a**): IR (KBr) 1150, 1080, 1030, 945, 825, 755 cm^{-1}; ^1H NMR (400 MHz, Me_2SO-d_6) δ 1.134 (s, *t*-Bu, 9 H), 1.231 (s, *t*-Bu, 9 H) 3.13–3.93 (m), 4.46–4.56 (m, prim OH, 5 H), 4.81–4.94 (m, C_1-H, 7 H), 5.71–5.96 (m, sec-OH, 14 H), 7.16–7.32 (m, aromatic, 8 H).[17]

2,6-*O*-Dodecakis(*tert*-butyldimethylsilyl)-A,B-bis(*tert*-butylsulfenyl)-β-cyclodextrin (3c). Bis-(*tert*-butylsulfenyl)-β-cyclodextrin (**2c**) was treated with *tert*-butyldimethylsilyl chloride and dry imidazole dissolved in dry DMF similarly to that of **2a**. Purification was achieved by repeated (at least twice) silica gel column chromatography by using $CHCl_3$ as an eluent: IR (KBr) 3460 (br), 2960, 2940, 2900, 2860, 1475, 1365, 1260 ($SiCH_3$), 1160, 1140, 1095, 1045, 860, 840, 785 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.01–0.08 (m, MeSiO–C_6, 30 H), 0.12–0.19 (m, MeSiO–C_2, 42 H), 0.84–0.89 (m, *t*-BuSiO–C_6, 45 H), 0.89–0.96 (m, *t*-BuSiO–C_2, 63 H), 1.315 (s, *t*-BuS, 9 H), 1.337 (s, *t*-BuS, 9 H), 2.83–4.13 (m, 42 H), 4.41–4.57 (m, HO–C_3, 7 H), 4.82–4.91 (m, C_1–H, 7 H). Anal. Calcd for $C_{122}H_{254}O_{33}S_2Si_{12}$: C, 54.63; H, 9.54. Found: C, 54.61; H, 9.67.[17]

Amylolysis of Bis(phenylsulfenyl)-β-cyclodextrin with Taka-amylase. To a solution of A,D-bis(phenylsulfenyl)-β-cyclodextrin (**6b**) (25 mg, 1.9×10^{-5} mol) in 0.3 mL of dimethyl sulfoxide was added 2.7 mL of 0.2 N sodium acetate buffer (pH 5.5) containing 0.01 M calcium chloride and 25 mg of Taka-amylase. After the mixture was incubated at 40 °C for 10 days, the enzyme was denaturated by the addition of 1.0 mL of 3 N aqueous ammonia. The supernatant obtained by centrifugation of the mixture was evaporated to dryness in vacuo. To the resultant residue were added 4 mL of a 1% aqueous $NaBH_4$ mixture and the mixture was stirred overnight at room temperature. The reaction mixture was acidified to pH 3–4 by the addition of 2 N hydrochloric acid and then filtered by using a membrane filter (Toyo, Membrane Filter 0.45-μm type NC). The crude product in the filtrate was purified by reversed-phase column chromatography by using a gradient elution (from 0–30% aqueous ethanol with 300 mL of water and 300 mL of 30% aqueous ethanol to give **8** (9 mg, 2.1×10^{-5} mol, 54%). A,C-bis(phenylsulfenyl)-β-cyclodextrin (**5**) (25 mg, 1.9×10^5 mol) was hydrolyzed with the amylase, followed by the reduction with a similar procedure to that of the A,D isomer to give 10 mg (2.3×10^{-5} mol, 60%) of **8**. A,B-Bis(phenylsulfenyl)-β-cyclodextrin (**2d**) (110 mg, 8.35×10^{-5} mol) was treated with Taka-amylase at 40 °C for 12 days. After the usual workup, in a similar way to the reaction of **5** or **6b**, the residue obtained by evaporation of the supernatant was dissolved in 30 mL of 10% aqueous ethanol and purified by reversed-phase column chromatography with a gradient elution (from 20% to 50% aqueous ethanol using 400 mL of 20% aqueous ethanol and 400 mL of 50% aqueous ethanol), giving hydrolyzed compound **7a** (42 mg, 6.1×10^{-5} mol, 73%). **7a** was reduced as described above, giving **7b** (38 mg, 5.5×10^{-5} mol) after the usual chromatographic separation with a gradient elution (from 15% to 50% aqueous ethanol using 300 mL of 15% aqueous ethanol and 300 mL of 50% aqueous ethanol). **7a**: FAB MS, *m/e* (relative intensity) 711 ($[M + Na]^+$, 0.82%), 688 (M^+, 0.68), 509 (**9**, 4.6), 255 (**10**, 57). **7b**: ^1H NMR (400 MHz, Me_2SO-d_6) δ 2.93–3.58 (m), 3.63–3.78 (m, 5 H), 3.98–4.07 (m, 1 H), 4.40–4.52 (m, OH, 4 H), 4.547 (d, J = 5.1 Hz, OH, 1 H), 4.892 (d, J = 3.7 Hz, $C_{1'}H$ or $C_{1''}H$, 1 H), 5.032 (d, J = 5.1 Hz, OH, 1 H), 5.099 (d, J = 3.7 Hz, $C_{1'}H$ or $C_{1''}H$, 1 H), 5.234 (d, J = 5.9 Hz, 1 H), 5.580 (d, J = 6.4 Hz, OH, 1 H), 5.633 (d, J = 2.9 Hz, OH, 1 H), 5.671 (d, J = 6.1 Hz, OH, 1 H), 7.09–7.39 (m, aromatic 10 H); ^{13}C NMR (100 MHz, Me_2SO-d_6) δ 35.04, 35.13 ($C_{6'}$, $C_{6''}$), 62.57, 62.80 (C_1, C), 67.10, 67.18, 69.34, 69.99, 71.44, 71.57, 71.86, 72.37, 72.45, 72.72 (C_2, $C_{2'}$, $C_{2''}$, C_3, $C_{3'}$, $C_{3''}$, $C_{4''}$, C_5, $C_{5'}$, $C_{5''}$), 82.68, 83.38 (C_4, $C_{4'}$), 100.19, 101.16 ($C_{1'}$, $C_{1''}$), 125.24, 125.29, 127.76, 128.02, 128.66, 128.80, 137.08 (aromatic C); FAB MS, *m/e* (relative intensity) 713 ($[M + Na]^+$, 0.59%), 690 (M^+, 0.17), 509 (**9**, 2.8), 255 (**10**, 37). **8**: ^1H NMR (100 MHz, Me_2SO-d_6) δ 2.9–4.1 (m), 4.2–4.7 (m, OH, 5 H), 4.7–5.1 (m, OH, $C_{1'}H$, 2 H), 5.20 (d, J = 6 Hz, OH, 1 H), 5.48 (d, J = 6 Hz, OH, 1 H), 7.0–7.5 (m, aromatic 5 H); ^{13}C NMR (25 MHz, MeSO-d_6) δ 35.1 ($C_{6'}$), 62.5, 62.8 (C_1, C_6), 70.1, 71.1, 71.3, 72.0, 72.3, 72.8 (other C atoms), 83.4 (C_4), 1 00.6 ($C_{1'}$), 125.2, 127.7, 128.8, 137.4 (aromatic C atoms); FAB MS, *m/e* (relative intensity) 475 ($[M + K]^+$, 0.63%), 459 ($[M + Na]^+$, 6.5), 437 ($[M + H]^+$, 0.14), 255 (**10**, 12).

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Registry No. **1**, 96761-39-6; **2a**, 80781-23-3; **2b**, 95475-29-9; **2c**, 96761-40-9; **2d**, 95475-68-6; **2e**, 96761-41-0; **3a**, 96791-14-9; **3b**, 96791-15-0; **3c**, 96791-16-1; **5**, 95475-67-5; **6b**, 95475-66-4; **7a**, 96761-42-1; **7b**, 95475-30-2; **8**, 96761-43-2; β-cyclodextrin, 7585-39-9; *m*-benzenedisulfonyl chloride, 585-47-7; *p-tert*-butylthiophenol, 2396-68-1; sodium *p-tert*-butylthiophenolate, 54166-35-7; Taka-amylase, 9001-19-8.

Composite Parameter Method: Application to Calculated Stabilization Energies of Strained and Unsaturated Molecules

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Ab initio molecular orbital calculations at the 4-31G level have been employed to obtain methyl stabilization energies of monosubstituted ethylenes, ethynes, cyclopropanes, and benzenes. A technique called the composite parameter method is developed and applied to correlations between methyl stabilization energies of the four classes of substituted hydrocarbons. The technique establishes the consistency and utility of the data set and also shows that the pattern of stabilization energies in ethynes is markedly different from those of the other three molecular classes.

There is a dearth of thermochemical data for substituted strained molecules (e.g., cyclopropanes)[1,2] and even for unsaturated molecules such as acetylenes.[3] Thus, for the present at least, attempts to investigate thermochemical

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stabilization or destabilization must rely to some extent upon calculational techniques.[2,3] The reliability of such techniques in calculating stabilization energies has already been examined.[4] The present paper considers the relationship between calculated stabilization energies of four molecular systems: substituted ethylenes, ethynes, benzenes, and cyclopropanes. One might anticipate that isodesmic[5-7] stabilization energies for these four systems should show similar substituent dependencies. For example, for reasonably small substituents, all four carbon frameworks should not introduce steric terms. All four molecular systems are capable of both "localized" (inductive, electrostatic field) and "delocalized" (resonance) effects especially in light of the well-known behavior of cyclopropane as a mitigated olefin.[8] A treatment termed the "composite parameter method" has been developed in order to check the consistency in a parameter, such as stabilization energy, between three or more molecular systems. It allows a check of the self-consistency of the input data for the parameter. Additionally, the particular relationships calculated provide insight into the similarities or dissimilarities between molecular systems. The present paper examines "methyl stabilization" energies of substituted ethylenes, acetylenes, cyclopropanes, and benzenes and their correlations with the composite parameter method.

Composite Parameter Method

Consider the quantities Q_1 and Q_2 which are different functions of the electrical effect substituent constants σ_λ, representing the "true" localized (field and/or inductive) effect, and σ_δ, representing the "true" delocalized (resonance) effect. We may write

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

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

with

$$L_1 \neq L_2 \text{ and/or } D_1 \neq D_2 \quad (3)$$

Let some quantity of interest Q be correlated with Q_1 and Q_2. The correlation equation is

$$Q_X = a_1Q_{1X} + a_2Q_{2X} + a_0 \quad (4)$$

From eq 1 and 2,

$$Q_X = L\sigma_{\lambda X} + D\sigma_{\delta X} + h \quad (5)$$

where

$$L = a_1L_1 + a_2L_2,\ D = a_1D_1 + a_2D_2,\ h = a_1h_1 + a_2h_2 + a_0 \quad (6)$$

This result is a special case of a more general relationship. Consider a set of composite parameters κ_i which are linear functions of the "pure" parameters ζ_j,

$$\kappa_i = \sum_{i=1}^{m}\sum_{j=1}^{n}(a_{ij}\zeta_j + a_{i0}) \quad (7)$$

Thus, for example, when $m = n = 3$, eq 8–10 are obtained.

$$\kappa_1 = a_{11}\zeta_1 + a_{12}\zeta_2 + a_{13}\zeta_3 + a_{10} \quad (8)$$

$$\kappa_2 = a_{21}\zeta_1 + a_{22}\zeta_2 + a_{23}\zeta_3 + a_{20} \quad (9)$$

$$\kappa_3 = a_{31}\zeta_1 + a_{32}\zeta_2 + a_{33}\zeta_3 + a_{30} \quad (10)$$

If some quantity Q is a linear function of κ_i

$$Q = \sum_{i,k=1}^{p} b_k\kappa_i + b_0 \quad (11)$$

then it follows from the above that

$$Q = \sum_{l=1}^{q} c_l\zeta_l + c_0 \quad (12)$$

Thus, in general, if some quantity is a linear function of "pure" independent variables it is also a linear function of composite independent variables which are themselves a linear function of the appropriate "pure" independent variables. That is why it is not necessary to have "pure" parameters, each representing only a single effect, in order to carry out correlation analysis for predictive purposes. Correlations based on "pure" parameters would obviously lend themselves to interpretation most readily.

In the context of the present work, correlation of Q_X with composite parameters is useful in determining whether or not the composite parameters used do in fact contain all of the pure parameters required to provide a good model of Q.

It follows from eq 1–6 that if only electrical effect parameters are required to describe ΔH_{stab} or ΔE_{stab} (stabilization enthalpy or energy from an isodesmic reaction, see Scheme I), any one of the data sets must be a linear function of any other two of the sets. Thus, for example, the ΔH_{stab} values must be a linear function of the ΔE_{stab} values for substituted cyclopropanes and acetylenes. Then we may write the equation

$$\Delta H_{stab(GX)} = a_1\Delta E_{stab(G_1X)} + a_2\Delta E_{stab(G_2X)} + a_0 \quad (13)$$

where G is phenyl, vinyl, cyclopropyl, or ethynyl. If eq 13 is obeyed, then two electrical effect parameters are sufficient to account for the data in all three substitution series. If it is not obeyed then either the calculated energies do not reflect the actual energies or factors other than electrical effects are involved in the reaction. In order to provide a valid test only ΔH_{stab} or ΔE_{stab} values considered reliable can be included in the correlation.

It must be noted that a good correlation with eq 13, or other relationships of the same type, is a necessary condition for the dependence of ΔH_{stab} on localized and delocalized electrical effects but it is not sufficient. If, for example, ΔE_{stab} was a function of the delocalized electrical effect and a steric effect,

$$\Delta E_{stab} = a_1\sigma_\delta + a_2\nu_\psi + a_0 \quad (14)$$

where ν_ψ is the "true" steric parameter and ΔH_{stab} is also a function of σ_δ and ν_ψ, then eq 13 must be obeyed. It follows that successful correlation with eq 13 means that ΔH_{stab} is a function of the same "pure" independent variables as are the ΔE_{stab} values. Poor fit to eq 13 implies that one or more factors other than those of which ΔE_{stab} is a function are required to model ΔH_{stab}.

Calculational Techniques

Ab initio molecular orbital calculations have been employed by using the GAUSSIAN 70 Program Series[9] and

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Scheme I

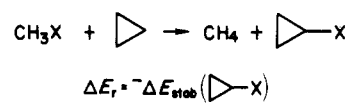

Table I. Methyl Stabilization Energies (Scheme I) Calculated on the Basis of 4-31G Calculations

	methyl stabilization energies, kcal/mol			
	vinyl-X	cyclopropyl-X	ethynyl-X	phenyl-X
H	0.0	0.0	0.0	0.0
F	6.4[a]	5.3	-12.8	7.8
CH_3	4.3	2.7	8.6	1.3
CH_3O	10.9	5.3	0.3	6.2
OH	10.6	5.9	0.7	7.5
NH_2	13.3	6.5	11.5	9.8
CH_2^-	39.6	*b*	50.6	42.7
O^-	38.6	12.0	55.0	*c*
CN	3.3	2.8	2.1	1.2
NC	5.8	3.4	-1.2	*c*
CHO	6.4	*b*	1.7	5.3
$COCH_3$	3.9	6.6	2.0	*c*
CO_2CH_3	8.0	*b*	2.3	*c*
NO_2	4.7	4.5	-18.6	2.5
Li	4.8	-2.1	31.2	3.2
CH_2^+	30.0	33.7	14.2	43.3
$CH{=}CH_2$	7.8	2.7	8.3	-1.3
HCC	3.9	1.7	6.8	3.1
NH_3^+	1.5	6.3	-17.5	*c*

[a] For $CH_3F + CH_2{=}CH_2 \rightarrow CH_4 + CH_2{=}CHF$, $\Delta E_r = -6.4$ kcal/mol. [**Note**: in difluoro derivatives, there is special stabilization associated with geminally substituted difluoroalkyl moieties (e.g., see: Greenberg, A.; Liebman, J. F.; Dolbier, W. R., Jr.; Medinger, K. S.; Skancke, A. *Tetrahedron* **1983** *39*, 1533)]. [b] 4-31G calculations did not converge. [c] 4-31G total energy of phenyl-X not calculated in original ref 12.

the 4-31G basis set.[10] Most of the data are from the literature and are either fully optimized at the HF/4-31G level or semioptimized with the optimum HF/4-31G geometries of a substituent and a hydrocarbon framework which were combined and the resulting structure optimized at the 4-31G level with respect to substituent conformation and the length of the hydrocarbon substituent bond. For the cyclopropanes, the C_1C_2 (C_1C_3) and C_2C_3 bonds were also varied. Although some of the values are not perfectly optimized they are undoubtedly very close to being so and are the best values known to the authors following an extensive literature search.

The methyl stabilization energy, an example of an isodesmic energy, is calculated according to Scheme I (illustrated for cyclopropane but similarly applicable for vinyl, ethynyl, and phenyl systems). Although it has been argued that ethyl stabilization would be a more relevant parameter and isopropyl better still for species such as cyclopropyl and vinyl,[2,7] the use of methyl stabilization has certain advantages. First, thermochemical and fully optimized calculational data are more readily available for methyl than for ethyl and isopropyl derivatives and steric effects and conformational problems are less significant. In addition, by referring all four molecular types to one reference state rather than two reference states (i.e., isopropyl for cyclopropyl and vinyl; *tert*-butyl for ethynyl and phenyl) a comparison can be made between all four systems. Entropy changes have been shown to be negligible for isodesmic reactions.[11] They are thus neglected in this study. Additionally, enthalpy and energy are equated in the present work and differences in zero-point energies and 0–298 K thermal corrections are considered to be negligible.

Table II. Linear Correlations between Calculated (HF/4-31G) Methyl Stabilization Energies and Experimental Methyl Stabilization Enthalpies

corr.	framework	n^a	R^{2a}	R^a	std error	m^a	b^a
	Methyl Stabilization						
1	vinyl	16	0.95	0.97	2.53	1.27	-2.36[b]
2	vinyl	13	0.92	0.96	1.19	0.83	0.42[c]
3	phenyl	10	0.81	0.90	1.54	0.78	-0.86[d]
4	cyclopropyl	6	0.93	0.96	0.81	0.95	-0.55[e]
5	ethynyl	5	0.88	0.94	2.03	1.21	-0.65[f]
6	all four	34	0.91	0.95	2.34	1.26	-2.81[g]

[a] Linear correlation parameters: n = no. of data points, m = slope, b = y intercept, R = correlation coefficient. [b] Substituents: H, F, CH_3, OCH_3, OH, CN, CHO, CO_2CH_3, NO_2, CF_3, CH_2^+, O^-, NH_3^+, C_2H_3, HCC (excludes Cl, $COCH_3$). [c] Substituents: H, F, CH_3, OCH_3, OH, CN, CHO, CO_2CH_3, NO_2, CF_3, C_2H_3, HCC. [d] Substituents: H, F, CH_3, OCH_3, OH, NH_2, CN, CHO, NO_2, HCC (excludes C_2H_3). [e] Substituents: H, CH_3, NH_2, CN, NH_3^+, C_2H_3. [f] Substituents: H, CH_3, CH_2^+, C_2H_3, HCC. [g] Includes H substituents and excludes CH_2CHCl, $CH_2CHCOCH_3$, $C_6H_5CHCH_2$.

Table III. Linear Regressions Comparing Calculated Methyl Stabilization Energies in the Manner of Eq 13[a]

	n	R^2	R	std error	a_1	a_2	a_0
1[b]	12	0.95	0.98	2.83	0.99	0.35	-1.54
2[c]	12	0.96	0.98	2.50	1.25	0.12	-0.68
3[d]	14	0.93	0.96	4.26	1.35	-0.08	-3.98
4[e]	16	0.85	0.92	4.31	0.81	0.34	2.55

[a] All stabilization energies calculated at HF/4-31G level. All possible substituents (points) employed. [b] Phenyl-X = a_1(cyclopropyl-X) + a_2(vinyl-X) + a_0. [c] Phenyl-X = a_1(cyclopropyl-X) + a_2(ethynyl-X) + a_0. [d] Phenyl-X = a_1(vinyl-X) + a_2(ethynyl-X) + a_0. [e] Vinyl-X = a_1(cyclopropyl-X) + a_2(ethynyl-X) + a_0.

Results and Discussion

Calculated 4-31G methyl stabilization energies are listed in Table I. The total energies and comparisons with experimental $\Delta H_f°$ (g) data are provided elsewhere.[12] The 4-31G data on monosubstituted benzenes employed idealized ring geometries while the cyclopropane series data set is not as completely optimized as the vinyl and ethynyl sets.[12] Qualitatively, one sees similarities between the vinyl, phenyl, and cyclopropyl series, with the greatest stabilizations in the first case and the least stabilizations in the last. It is clear that substituted acetylenes behave very differently, showing large destabilizations where substituents are strong σ acceptors (e.g., CF_3, NO_2, NH_3^+).

Table II lists linear correlations between calculated methyl stabilization energies and experimental methyl stabilization enthalpies. Experimental gas-phase enthalpies of formation are almost entirely from one reference source[13] and the source of additional data has been documented elsewhere.[12] The correlations are generally good.

The composite parameter method has been employed by using eq 13, where $\Delta E_{stab}(G_1X)$, $\Delta E_{stab}(G_2X)$, and $\Delta E_{stab}(GX)$ are total stabilization energies for a given substituent X for any of the four hydrocarbon systems investigated. That is, one relationship might employ G

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Table IV. Correlation Analysis of Methyl Stabilization Energies (kcal/mol) according to Taft DSP Equation $E = m_I\sigma_I + m_R\sigma_R + b$

	n	R^2	R	std error	m_I	m_R	b
vi-X							
π donors	6	0.97	0.99	1.07	−4.36	−17.62	0.73
π acceptors	8[a]	0.22	0.47	3.05	4.30	14.35	0.83
	5[b]	0.83	0.91	1.37	3.25	21.38	0.02
c-C_3H_5X							
π donors	6	0.95	0.98	0.69	1.78	−7.36	0.71
π acceptors	5	0.91	0.95	1.05	2.90	25.98	0.12
HCC-X							
π donors	6	0.94	0.97	2.68	−47.49	−20.87	2.02
π acceptors	8	0.24	0.49	7.71	−16.08	7.80	2.91
Ph-X							
π donors	6	0.97	0.99	0.82	4.40	−10.86	−0.25
π acceptors	4	0.98	0.99	0.59	−0.92	28.10	−0.08

[a] Substituents: H, CN, NC, CHO, COMe, CO_2Me, NO_2, CF_3. [b] Substituents: H, CN, CHO, COMe, NO_2.

as phenyl, G_1 as cyclopropyl, and G_2 as vinyl. A bilinear regression is performed with substituent data points for which stabilization energies exist for all three substituted hydrocarbons. The mixing coefficients a_1 and a_2 indicate the relative strengths of the relationships of $\Delta E_{stab(GX)}$ to $\Delta E_{stab}(G_1X)$ and $\Delta E_{stab}(G_2X)$. These relationships are displayed in Table III. The first three relationships are very highly correlated, while the fourth relationship is somewhat weaker. Generally, this means that the ΔE_{stab} data sets are comparably good. The phenyl set has a slightly weaker correlation with experiment than the vinyl, cyclopropyl, and ethynyl sets (see Table II) for the reasons stated earlier. It is clear from correlation 1 that phenyl stabilization energies are strongly related to those of cyclopropyl and vinyl (the a_1/a_2 ratio is 2.8). In contrast, when the stabilization energies of phenyl derivatives are correlated with cyclopropyl and ethynyl ($a_1/a_2 = 10$), it is clear that there is virtually no relationship with the latter. The same conclusions are apparent in correlating phenyl with vinyl and ethynyl ($a_1/a_2 = 17$). Relationship 4 does show a significant relationship with ethynyl derivatives, but the correlation is much less reliable and it may thus be the result of this and perhaps the similarity in size allowing these systems to have similar polarizabilities. The nondependence of relations 2 and 3 on ethynyl stabilization energies could arise if the ethynyl data set was of poor quality, but Table II clearly indicates this is not the case. It could happen if the substituent effects in phenyl, cyclopropyl, and vinyl derivatives depended on three factors, all fortuitously showing the same dependence on this factor while ethynyl compounds showed a different dependence on this factor. However, this is not the case since correlation of ΔE_{stab} for HC≡CX with those for all three other groups was very poor ($R^2 = 0.436$). The explanation for these relationships is that the predominant stabilization/destabilization influences in phenyl, vinyl, and cyclopropyl derivatives are different from those in substituted acetylenes. This can be illustrated by the data in Table IV which summarize correlation analysis[12] according to the Taft dual substituent parameter (DSP) equation.[14] Since both π-donor and π-acceptor substituents yield positive stabilization energies, they must be treated separately. Although the n value is therefore very small and the correlations must not be too finely interpreted, one key point stands out. For vinyl, cyclopropyl, and phenyl, the sensitivities to resonance effects (m_R) are greater than the sensitivities to inductive effects (m_I). The reverse is clearly true for the acetylenes. Although n is small for each data set, the cumulative effect is the same. There is an extra factor present (or absent) in the acetylenes relative to the other three series. The sp hybridized carbons must dramatically increase the sensitivity to inductive effects. Thus, the huge calculated stabilization in lithioacetylene, which mimics the stabilization in acetylide ion, is clearly an order of magnitude different from those in the other three series, clearly showing the effect of the sp hybridized orbital. The destabilization in nitroethyne is also almost an order of magnitude greater than for the other three series. Furthermore, as noted elsewhere,[12] the high IP of the parent hydrocarbon acetylene relative to ethylene, cyclopropane, and benzene is consistent with its reduced ability to conjugate with π-acceptor substituents. Thus, in comparison with ethylene, it is much more sensitive to σ effects and much less sensitive to π effects. Additionally, it is also possible that the second π system in the ethynyl series interacts with substituents in a manner different from the other three series. This has been noted qualitatively by others.[3] Furthermore, the electronegative framework may well enhance the π-electron affinity and decrease the π-donor ability of the acetylene framework relative to the sp^2 hybridized carbon frameworks which form the basis for substituent constants.

Conclusions

The composite parameter approach has been introduced and indicates that linear free energy relationships can be successfully applied to ab initio stabilization energies of molecules in which the same general influences are operative. In the present series of substituted derivatives (vinyl, ethynyl, cyclopropyl, and phenyl), nonbonded repulsions are absent. The approach may be used to indicate whether or not the quality of data is sufficiently good for application. Additionally, it has shown that substituted ethynes are subject to stabilization mechanisms different from those in ethylenes, cyclopropanes, and benzenes.

Registry No. CH_2=CHF, 75-02-5; CH≡CF, 2713-09-9; C_6H_5F, 462-06-6; CH_2=$CHCH_3$, 115-07-1; CH≡CCH_3, 74-99-7; $C_6H_5CH_3$, 108-88-3; CH_2=$CHOCH_3$, 107-25-5; CH≡$COCH_3$, 6443-91-0; $C_6H_5OCH_3$, 100-66-3; CH_2=CHOH, 557-75-5; CH≡COH, 32038-79-2; C_6H_5OH, 108-95-2; CH_2=$CHNH_2$, 593-67-9; CH≡CNH_2, 52324-04-6; $C_6H_5NH_2$, 62-53-3; CH_2=$CHCH_2^-$, 1724-46-5; CH≡CCH_2^-, 31139-07-8; $C_6H_5CH_2^-$, 18860-15-6; CH_2=CHO^-, 64723-93-9; CH≡CO^-, 64066-01-9; CH_2=CHCN, 107-13-1; CH≡CCN, 1070-71-9; C_6H_5CN, 100-47-0; CH_2=CHNC, 14668-82-7; CH≡CNC, 66723-45-3; CH_2=CHCHO, 107-02-8; CH≡C-CHO, 624-67-9; C_6H_5CHO, 100-52-7; CH_2=$CHCOCH_3$, 78-94-4; CH≡$CCOCH_3$, 1423-60-5; CH_2=$CHCO_2CH_3$, 96-33-3; CH≡$CC-O_2CH_3$, 922-67-8; CH_2=$CHNO_2$, 3638-64-0; CH≡CNO_2, 32038-80-5; $C_6H_5NO_2$, 98-95-3; CH_2=CHLi, 917-57-7; CH≡CLi, 1111-64-4; C_6H_5Li, 591-51-5; CH_2=$CHCH_2^+$, 1724-44-3; CH≡CCH_2^+, 21540-27-2; $C_6H_5CH_2^+$, 6711-19-9; CH_2=CHCH=CH_2, 106-99-0; CH≡CCH=CH_2, 689-97-4; C_6H_5CH=CH_2, 100-42-5; CH≡C-C≡CH, 460-12-8; C_6H_5C≡CH, 536-74-3; CH_2=$ChNH_3^+$, 56359-27-4; CH≡CNH_3^+, 64709-59-7; cyclopropyl fluoride, 1959-79-1; methylcyclopropane, 594-11-6; methoxycyclopropane, 540-47-6; cyclopropanol, 16545-68-9; cyclopropylamine, 765-30-0; cyclopropoxide, 72507-73-4; cyclopropanecarbonitrile, 5500-21-0; cyclopropyl isocyanide, 58644-53-4; acetylcyclopropane, 765-43-5; nitrocyclopropane, 13021-02-8; cyclopropyllithium, 3002-94-6; cyclopropylmethylium, 14973-56-9; vinylcyclopropane, 693-86-7; ethynylcyclopropane, 6746-94-7; cyclopropylammonium, 72507-71-2.

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