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BOND IONICITY AND THE STRENGTH OF CARBON–CARBON BONDS

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Abstract—A simple VB analysis is used to illustrate that the greater stability of geminally disubstituted ethanes and ethylenes compared to their vicinally substituted counterparts is due to the strength of the central C–C bond and not to the stability of the radical and carbene fragments that compose the molecule. The qualitative arguments are supported by MO calculations. The implications to the additivity rules for the estimation of heats of formation are discussed.

In a recent report[1] the linear combination of fragment configurations (LCFC)[2] method was utilized to discuss the effect that donor-acceptor interactions have on the strength of a bond connecting two molecular fragments. It was proposed that the central C–C bond in 1,1-homodisubstituted ethanes and ethylenes is stronger than the corresponding bond in the 1,2-homodisubstituted isomers due to the greater ionic character of the bond in the former set of molecules. The theoretical rationale is illustrated briefly below for 2-methylpropane and n-butane (1,1- and 1,2-dimethylethane). The first step in the analysis is to divide the molecule into two radical fragments through the bond in question. The basis set configurations, which contain

$(CH_3)_2HC$——CH_3		CH_3H_2C——CH_2CH_3	
Donor	Acceptor	Donor	Donor

only the singly occupied orbitals of the radical fragments, are shown in Scheme 1. The relative energies of the DA, the D_1D_2, and the charge transfer configurations, D^+A^-, D^-A^+, $D_1{}^+D_2{}^-$, can be calculated empirically on the basis of eqns (1)–(4). Here, (I) represents the ionization potential,

$$E_{DA} = E_{D_1D_2} = 0 \tag{1}$$

$$E_{D^+A^-} = I_{\cdot CH(CH_3)_2} - A_{\cdot CH_3} + C \tag{2}$$

$$E_{D^-A^+} = I_{\cdot CH_3} - A_{\cdot CH(CH_3)_2} + C \tag{3}$$

$$E_{D_1{}^-D_2{}^+} = E_{D_1{}^+D_2{}^-} = I_{\cdot CH_2CH_3} - A_{\cdot CH_2CH_3} + C \tag{4}$$

(A) the electron affinity, and (C) the coulomb attraction between the two charged fragments in the ionic configurations. The ground state, ψ_1, and two excited states, ψ_2 and ψ_3, result from the interaction of the neutral and the ionic configurations (Fig. 1). This interaction was suggested[1] to be more stabilizing in the case of the 1,1-isomer than in the case of the 1,2-isomer because of the relatively lower energy of the D^+A^- configuration compared to the linear combination of $D_1{}^-D_2{}^+$ and $D_1{}^+D_2{}^-$ and the greater overlap integral of ϕ_D and ϕ_A as compared to that of ϕ_{D_1} and ϕ_{D_2}. This proposal is supported by the fact that 2-methylpropane is more stable than n-butane and that unsymmetrically substituted molecules are generally more stable than their symmetrically substituted counterparts.[1]

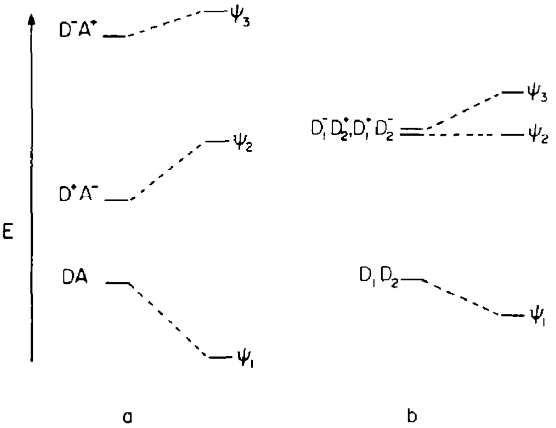
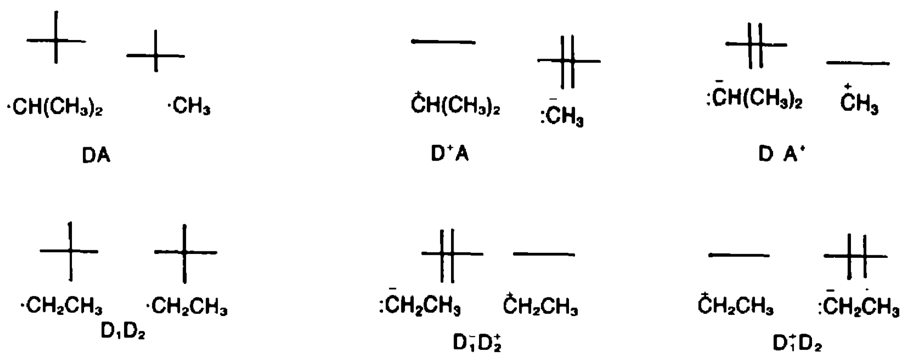


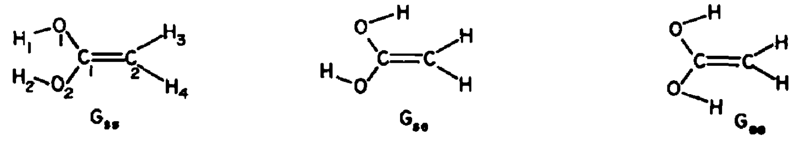
Fig. 1. Configuration interaction diagram for (a) 1,1-dimethylethane, and (b) 1,2-dimethylethane.

The analysis outlined above points to an interaction between the two submolecular fragments as an explanation for the relative stability of the two isomers. This proposal is in conflict with the concept of additivity of group thermochemical properties for the estimation of heats of formation.[3] This popular[4] idea is based on the assumption that a given submolecular fragment makes a constant contribution to the heat of formation of any molecule that contains it (steric effects are considered and accounted for).

In this report the results of semi-empirical and ab-initio MO calculations are combined with a compilation of experimental data in order to show that: (a) The greater stability of the 1,1-disubstituted ethanes and ethylenes relative to the 1,2-isomers is a result of a stronger central C–C bond in the former isomers and not to the stability of the fragments themselves. (b) There is a consistant failing of the additivity rules for the estimation of heats of formation in certain predictable cases involving symmetrical vs unsymmetrical substitution.



Scheme 1.



Scheme 2.

Table 1. Extended Huckel C–C bond energies (kcal/mole) of substituted ethylenes ($C_2H_2X_2$) and ethanes ($C_2H_4X_2$)[a,b]

Substituent (X)	$X_2C{=}CH_2$	t-XHC=CXH	$X_2HC{-}CH_3$	$XH_2C{-}CXH_2$
CH_3	164	160	70	68
NH_2	196	171	70	63
OH	208	183	88	83
F	226	197	96	89

[a] Standard geometry assumed see: J. A. Pople and D. L. Beveridge, *Approximate Molecular Orbital Theory*. McGraw-Hill, New York, 1970.

[b] The least sterically hindered conformer was always chosen.

Table 2. Ab-initio optimized geometries[a] and energies of 1,1-difluoroethylene.

	Basis Set	
	STO-3G	4-31G
r_{CC} (Å)	1.3185	1.3009
r_{CF} (Å)	1.3507	1.3426
$<$FCC	124.50°	125.08°
Total Energy (a.u.)	−272.00065	−275.38125

[a] The C–H bond length and the $<$HCC bond angle were held at the constant values of 1.07 Å and 120°, respectively.

Table 3. Ab-initio total energies (a.u.)[a] of various carbene fragments.

		Basis Set	
Carbene	Conformer[b]	STO-3G	4-31G
CH_2	—	−38.43107	−38.86348
CHF	—	−135.89575	−137.58446
CF_2	—	−233.36210	−236.30187
CHOH	ee	−112.26965	−113.59686
	ss	−112.27435	−113.60104
	se(e)	−112.26936	−113.59662
	se(s)	−112.27470	−113.60137
$C(OH)_2$	ee	−186.10540	−188.32632
	ss	−186.11081	−188.33327
	se	−186.11261	−188.33677

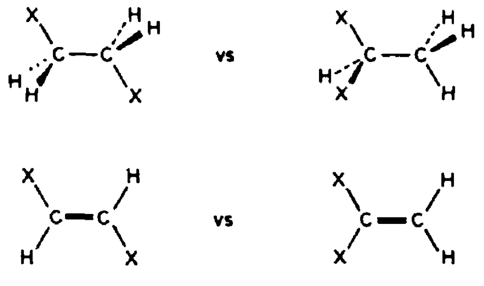
[a] The $^3B_1$ configuration of the carbenes were computed with a spin-restricted open-shell version of the Gaussian 76 series of programs.

[b] See Scheme 2.

RESULTS AND DISCUSSION

The computational results presented here were obtained at the extended Huckel[5] and *ab-initio* MO levels. The latter were carried out with both the STO-3G[6] and the 4-31G[7] basis sets contained in the Gaussian 70[8] and Gaussian 76[9] series of programs.

The energies of the central carbon–carbon bonds of the substituted ethanes and ethylenes shown below were computed by taking the difference of the total energies of the molecule and the appropriate carbene or radical fragments. The fragments were computed in the geometry of the molecule that they comprise. The carbene fragments were assumed to have a $^3B_1$ electronic configuration as that is the lowest energy configuration that would result directly from the homolytic cleavage of a double bond.



X = CH_3, NH_2, OH and F

The extended Huckel results are presented in Table 1. The *ab-initio* studies, which were restricted to the

Table 4. Ab-initio optimized geometries and energies of 1,1-dihydroxyethylene

	Conformer[b]		
	G_{ss}	G_{se}	G_{ee}
r_{cc} (Å)	1.3195	1.3258	1.3316
$r_{C_1-O_1}$ (Å)	1.3999	1.3833	1.3866
$r_{C_1O_2}$ (Å)	1.3999	1.3943	1.3866
$<O_1C_1C_2$	120.61°	126.11°	126.44°
$<O_2C_1C_2$	120.61°	124.98°	126.44°
$<H_1O_1C_1$	106.65°	103.47°	105.09°
$<H_2O_2C_1$	106.65°	106.15°	105.09°
STO-3G			
Total Energy (a.u.)	−224.75510	−224.76476	−224.76240
4-31G[c]			
Total Energy (a.u.)	−227.40286	−227.41788	−227.41169

[a] The O–H and C–H bond lengths and the $<H_3CH_4$ bond angle were kept at the constant values of 0.9899 Å, 1.07 Å and 120°, respectively. The other geometric parameters were optimized with the STO-3G basis.

[b] See Scheme 2.

[c] A single 4-31G computation at the STO-3G optimized geometry.

Table 5. Ab-initio C–C bond energies (kcal/mole) of substituted ethylenes ($C_2H_2X_2$)

Substituent (X)	Basis set			
	STO-3G		4-31G	
	$X_2C{=}CH_2$	t-XHC=CXH	$X_2C{=}CJ_2$	t-XHC=CXH
OH[a]	142[b]	133	139	128
	139[c]	128	137	125
	134[d]	124	129	123
F[a]	130	122	136	126

[a] The energies of the 1,2-isomers were reported in: J. R. Larson, N. D. Epiotis and F. Bernarki, *J. Am. Chem. Soc.* **100**, 5713 (1978); N. D. Epiotis, S. Shaik, J. R. Larson and F. Bernarki, *Tetrahedron* 33, 3275 (1977).

[b] The ee conformer

[c] The se conformer

[d] The ss conformer

difluoro and dihydroxy ethylenes with the latter molecules studied in three different conformations (Scheme 2), are summarized in Tables 2–5.

The geometries for the 1,2-isomers are taken from Ref. 10*a* for 1,2-difluoroethylene and Ref. 10*b* for 1,2-dihydroxyethylene.

An examination of the extended Huckel results presented in Table 1 reveals that at this level of theory the C–C bonds of the geminally substituted isomers are stronger than the corresponding bonds of the vicinally substituted isomers. This is found to be true regardless of the nature of the substituent or whether a single or a double carbon–carbon bond is involved. The largest difference is found for difluoroethylene where the carbon–carbon bond of the 1,1-isomer is found to be 29 kcal stronger than that of the 1,2-isomer. The *ab-initio* results found in Table 5 support these findings. For example, the carbon–carbon bond in 1,1-diffuoroethylene was found to be 8–10 kcals stronger than the corresponding bond of the vicinally substituted isomer. The carbon–carbon bond energy in 1,1-dihydroxyethylene was found to be stronger than that of the 1,2-isomer regardless of the conformation of the OH groups or the basis set used.

In order to further investigate the above phenomena the thermodynamics of the following isodesmic reactions were examined (Table 6).

$$X_2C + H_2C \longrightarrow 2XHC \tag{5}$$

$$X_2C = CH_2 \longrightarrow tHXC = CXH \tag{6}$$

$$X_2HC + H_3C \longrightarrow 2XH_2C \tag{7}$$

$$X_2HC\text{–}CH_3 \longrightarrow XH_2C\text{–}CXH_2 \tag{8}$$

Inspection of Table 6 reveals that reactions 5 and 7 are generally exothermic while reactions 6 and 8 are generally endothermic. Reactions 5 and 7 are always found to be more exothermic or less endothermic than reactions 6 and 8, respectively. The stronger carbon–carbon band of the 1,1-isomers is a direct result of this fact, e.g. in the case of the 4-31G calculation of difluoroethylene, reaction 5 is found to be exothermic by 2 kcal and reaction 6 is endothermic by 8 kcal, hence, the carbon–carbon bond of the 1,1-isomer is 10 kcal stronger than that of the 1,2-isomer. Therefore, it is clear that the well documented[1] superiority of geminal vs vicinal substitution in disubstituted ethanes and ethylenes is intimately connected with the greater strength of the C–C bond in the 1,1-isomers and is not due to the stability of the fragments which actually favor the 1,2-isomers.[11] This latter conclusion is supported by the recently published ab-initio results shown below.[12] These results

Table 6. Computed energetics of reactions 5–8

Substituent					ΔH (kcal/mole)				
(X)		5			6		7		8
	E.H.	STO-3G	4-31G	E.H.	STO-3G	4-31G	E.H.	E.H.	4-31G[a]
CH_3	−4	—	—	+1	—	—	−2	−1	+1
NH_2	−13	—	—	+12	—	—	−4	+3	+6
OH	—	−2[b]	−2	—	+7	+9	+3	+8	+11
	—	−1[c]	+1	—	+10	+13			
	−13[d]	−4	−3	+8	+5	+3			
F	−28	+1	−2	+2	+10	+8	+2	+8	+12

[a] W. J. Hehre and J. Hehre and J. A. Pople, *J. Am. Chem. Soc.* **97**, 6941 (1975); W. A. Lathan, L. Radom, W. J. Hehre and J. A. Pople, *Ibid.* **95**, 699 (1973); L. Radom, W. A. Lathan, W. J. Hehre and J. A. Pople, *Ibid.* **95**, 693 (1973).

[b] The ee conformer

[c] The se conformer

[d] The ss conformer

Table 7. Pi Dissociation energies of selected olefins

Olefin	Pi Dissociation[a] Energy (kcal/mole)	Ref.
1,1-difluorethylene	62.1 ± 1.0	*b*
tetrafluoroethylene	52.3 ± 2.0	*c*
ethylene	59.1 ± 2.0	*d*

[a] The pi dissociation energy is defined as the difference between the first and second bond dissociation energies in converting a saturated system in to an unsaturated one. For ethylene: $D_\pi(C{=}C) = DH°(CH_3CH_2{-}H) - DH°(^{\cdot}CH_2CH_2{-}H)$. For further explanation see: S. W. Benson, *J. Chem. Educ.* **42**, 502 (1965).

[b] J. M. Pickard and A. S. Rodgers, *J. Am. Chem. Soc.* **98**, 6115 (1976).

[c] E. Wu and A. S. Rodgers, *Ibid.* **98**, 6112 (1976).

[d] S. W. Benson, *J. Chem. Educ.* **42**, 502 (1965).

Table 8. Observed and estimated heats of formation[a]

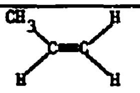
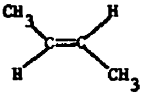
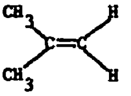
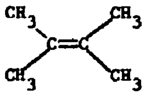
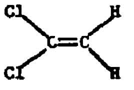
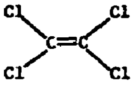
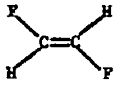
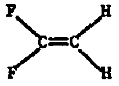
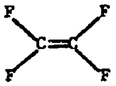
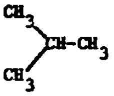
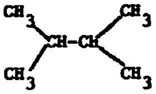
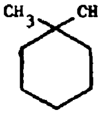
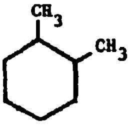
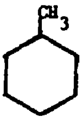
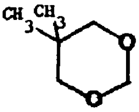
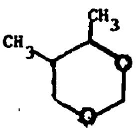
		ΔH_f (kcal)	
Entry	Molecule	Obs.	Est.
a		+ 4.9	+ 4.8
b		− 2.7	− 3.0
c		− 4.0	− 3.6
d		−16.7	−17.6
e		+ 0.3	+ 4.5
f		− 3.6	− 3.6
g		-	−75.2
h		−80.8	−71.5

Table 8 (*Contd*).

			ΔH_f (kcal)	
Entry	Molecule		Obs.	Est.
i			-155.0	-155.0
j			-32.2	-32.1
k			-54.0	-54.7
l	$ClCH_2-CH_3$		-26.7	-25.7
m	$ClCH_2-CH_2Cl$		-31.0	-31.2
n	$F-CH_2-CH_3$		-62.5	-61.9
o	FCH_2-CH_2F		-	-103.8
p	Cl_2CH-CH_3		-31.1	-29.0
q	$Cl_2CH-CHCl_2$		-36.5	-35.8
r	CF_3CH_3		-178.2	-169.2
s	CF_3CF_3		-316.8	-316.8
t	$HOCH_2CH_2OH$		-92.4	-92.8
u	$(HO)_2CHCH_3$		-56.2	-56.5
v			-43.3	-42.8
w		trans	-43.0	-43.0
		cis	-41.2	-41.4
x			-37.0	-36.8
y			-100.6	-97.7
z		trans	-98.1	-98.4

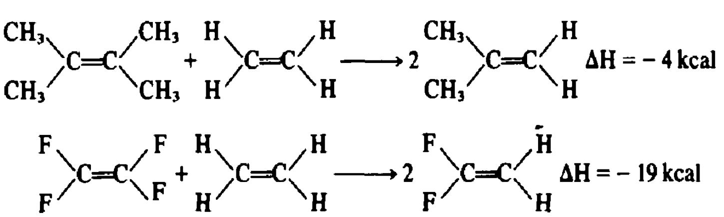
[a] Estimated values were taken from Ref. 3*a*. Observed values were taken from both Ref. 3*a* and 3*b*.

were obtained with an extended basis set and complete geometry optimization of the triplet carbenes.

	Reaction	ΔH (kcal)
No polarization functions	$CH_2 + CF_2 \longrightarrow 2CHF$	−4
	$CH_2 + CCl_2 \longrightarrow 2CHCl$	−5
Optimized d orbitals on Carbon	$CH_2 + CF_2 \longrightarrow 2CHF$	−2
	$CH_2 + CCl_2 \longrightarrow 2CHCl$	−3

In conclusion we find that the pattern of substitution on ethanes and ethylenes has an effect on the strength of the central carbon–carbon bond as predicted in a previous report to be due to an unexpected bond ionicity effect.[1,13] Although the computational methods used here have never been shown to accurately predict the strengths of bonds we maintain that the consistency of the results is very suggestive.

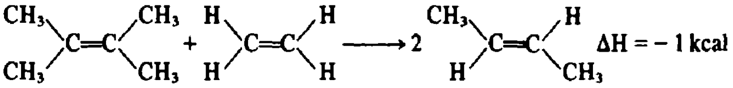
Further evidence is found by examining reactions 9 and 10. The exothermicity of these reactions is consistant with a model that predicts that the central carbon–carbon bond of the geminally disubstituted molecule is stronger than the average of the corresponding bonds in the tetrasubstituted and unsubstituted molecules because the former bond is more ionic. The pi-bond of 1,1-difluroethylene is found to be stronger than that of either ethylene or tetrafluoroethylene.



(9)

(10)

The exothermicity of reaction (9) could be explained in terms of steric repulsions between the cis methyl groups in tetramethylethylene. However, if steric effects are the cause one would expect reaction (11) to be more exothermic than reaction (9).



(11)

Implications to the estimation of thermochemical properties

We now turn our attention to the additivity rules for the estimation of heats of formation. These rules are based on the assumption that after correcting for adverse steric effects a submolecular fragment will contribute equally to the heat of formation of any molecule in which it is found. The results presented here contradict this assumption as they suggest that the interactions between the fragments that comprise a molecule can influence its heat of formation more than the stability of the fragments themselves. Since the interaction between two fragments becomes increasingly more stabilizing as the fragments become better donor-acceptor pairs, it is expected that the additivity rules will breakdown in *predictable* situations, i.e. the stability of unsymmetrically substituted molecules will be underestimated, or the stability of symmetrically substituted molecules will be overestimated, or both. It must be emphasized that we consider these thermochemical additivity relationships very useful and worthwhile, however, it must be realized that just because the rules work reasonably well does not mean that the underlying assumption is correct. The examples presented below illustrate a consistent error which is inherent in that assumption.

The contribution that a C–(F)₂ group (using a notation similar to Benson's[3a]) makes to the heat of formation of a molecule could be estimated in either of the two following ways:

$$\text{(a) } C\text{–}(F)_2 = \frac{1}{2}\Delta H_f(C_2F_4) = \frac{1}{2}(-155.0\,\text{kcal}) = -77.5\,\text{kcal}$$

$$\text{(b) } C\text{–}(F)_2 = \Delta H_f(F_2CCH_2) - \frac{1}{2}\Delta H_f(C_2H_4) = (-80.8\,\text{kcal}) - \frac{1}{2}(12.50\,\text{kcal}) = -87.1\,\text{kcal}$$

Because the effect of bond ionicity is inherent in method (b) and not in method (a), the former value is found to be 9.6 kcal more negative than the latter. Using the C–(F)₂ value from (a) we estimate the heat of formation of F_2CCH_2 to be −71.2 kcal (using a C–(H)₂ value of +6.3 kcal), an underestimation of 9.6 kcal. On the other hand, using the C–(F)₂ value from method (b) we estimate the heat of formation of C_2F_4 to be −174.0 kcal, an error of −19.0 kcal. The averaging of values (a) and (b) would only further complicate matters. This inconsistancy in the organo halogen series was noted by Benson *et al.*[3a] and attributed to dipole–dipole interactions. In the following example we point out that the same trend can be found in hydrocarbons, where dipole–dipole interactions are minimized.

The contribution that a C–(CH₃)₂ group makes to the heat of formation of a molecule could be estimated in either of two ways:

$$\text{(c) } \mathrm{C{-}(CH_3)_2} = \frac{1}{2}\Delta H_f[\mathrm{(CH_3)_2CC(CH_3)_2}]$$
$$-1.0\,\text{kcal (correction for steric effects)}^{3a}$$
$$= \frac{1}{2}(-16.7\,\text{kcal}) - 1\,\text{kcal}$$
$$= -9.3\,\text{kcal}$$

$$\text{(d) } \mathrm{C{-}(CH_3)_2} = \Delta H_f[\mathrm{(CH_3)_2CCH_2}] - \frac{1}{2}\Delta H_f[\mathrm{C_2H_4}]$$
$$= -4.0\,\text{kcal} - \frac{1}{2}(12.5\,\text{kcal})$$
$$= -10.3\,\text{kcal}$$

The latter value is more negative because it contains the effect of bond ionicity while the former value does not. Using the $\mathrm{C{-}(CH_3)_2}$ value from (C) the heat of formation of $\mathrm{(CH_3)_2CCH_2}$ is estimated to be -3.0 kcal (using a $\mathrm{C{-}(H)_2}$ value of $+6.3$ kcal) an underestimation of 1.0 kcal. On the other hand, using the $\mathrm{C{-}(CH_3)_2}$ value derived via method (d) the heat of formation of $\mathrm{(CH_3)_2CC(CH_3)}$ is estimated to be -18.6 kcal after adding a $+2.0$ kcal correction for steric effects) an overestimation of the stability by 1.9 kcal.

A comparison of the observed vs estimated heats of formation presented in Table 8 shows that almost without exception the stability of mono-substituted or geminally disubstituted molecules are underestimated while the stability of the corresponding 1,2-disubstituted or tetrasubstituted molecules is generally overestimated. A notable example is a comparison of entries (c) and (d). Here the heat of formation of 1,1-dimethylethylene is in error by $+0.4$ kcal while the heat of formation of tetramethylethylene is in error by -0.9 kcal. Another example is 1,1-difluoroethylene and tetrafluoroethylene, entries (h) and (i). In this case the stability of the former molecule is underestimated by 9.3 kcal, while the estimated value and the observed value for the latter molucule are identical. This occurs because the contribution that a $\mathrm{C{-}(F)_2}$ group makes is defined as $(1/2)\Delta H_f(\mathrm{C_2F_4})$. Although the discrepancies are often very small, they do represent a consistent pattern that users of the estimation procedures should be aware of. This is particularly true if one wishes to determine the relative stability of a symmetrically substituted molecule vs its asymmetrically substituted counterpart.

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