An *ab initio* Study of the Stability of the Symmetrical and Unsymmetrical Difluoroethylenes relative to Ethylene and Monofluoroethylene

By **Charles W. Bock**, Department of Chemistry, Philadelphia College of Textiles and Science, Philadelphia, Pennsylvania 19144, U.S.A.
Philip George,* Department of Biology, University of Pennsylvania, Philadelphia, Pennsylvania 19147, U.S.A.
Gilbert J. Mains, Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74074, U.S.A.
Mendel Trachtman, Department of Chemistry, Weizmann Institute of Science, Rehovot, Israel

Ab initio calculations of the total molecular energy (E_T), charge population, and dipole moments for ethylene, monofluoroethylene, *cis*- and *trans*-1,2-difluoroethylene, and 1,1-difluoroethylene have been carried out using a (7,3) basis set with full geometry optimization, and (7,3), (7,3,1), and (9,5) basis sets using recent experimental geometries. We confirm the finding of Kollman, who used partial geometry optimization at the STO-3G level and earlier experimental geometries, that 1,1-difluoroethylene is more stable than either of the 1,2-isomers, in accord with the behaviour of 1,1- and 1,2-disubstituted ethylenes in general as noted by Epiotis *et al.* The stability of the difluoroethylenes is examined in terms of ΔE_T, and where possible the corresponding reaction heat $(\Delta H^\circ_0)_{zpe}$, for the disproportionation reaction difluoroethylene + ethylene $\longrightarrow$ 2 monofluoroethylene. The closed shell molecular species $CH_2=CH_2$ and $CH_2=CHF$ are thus utilized as a composite molecular energy baseline to assess destabilization or stabilization effects, in contrast to the procedure followed by Epiotis *et al.* and by Whangbo *et al.* which involves open shell molecular fragments. This alternative approach, using the disproportionation reaction, leads to the conclusion that the slightly greater stability of the *cis*- relative to the *trans*-isomer, $(\Delta H^\circ_0)_{zpe} = +1.08$ kcal mol^{-1}, is due to *lesser destabilization* in the *cis*-isomer, since ΔE_T for both disproportionation reactions is substantially negative lying in the range -6 to -8 kcal mol^{-1}.

THE 1,2-dihalogenoethylenes differ from the corresponding alkyl substituted ethylenes in that the *cis*- is more stable than the *trans*-isomer. This finding, now thoroughly established experimentally,[1,2] is contrary to expectation based on a simple electrostatic bond–dipole model in which the negatively charged fluorine atoms, being closer together in the *cis*-isomer, would be presumed to have a destabilizing action. In this context the stability of the unsymmetrical 1,1-isomer in relation to either of the symmetrical 1,2-isomers is particularly significant because the simple electrostatic bond–dipole model would of course suggest that the unsymmetrical isomer would be the least stable since the negatively charged fluorine atoms would be even closer together than in the *cis*-structure.

At present these stability comparisons can not be made entirely using experimental data. ΔH_f^0 at 298 K is known for the 1,1-isomer, but for neither the *cis*- nor for the *trans*-1,2-isomer, and some fundamental vibrational frequencies have not yet been determined which would be essential if a vigorous comparison is to be made throughout between the energy values at the bottom of the potential wells.

Several mechanisms have been proposed to account for the stability relationships of the dichloroethylenes, *e.g.* the resonance structure approach of Pitzer and Hollenberg,[3] the lone pair interaction theory of Epiotis *et al.*,[4] and the influence of the C–X bonding orbital as X becomes more electronegative which has been emphasized by Kollman.[5] Furthermore Epiotis *et al.* have noted that the 1,1-disubstituted ethylenes are in general more stable than either of the 1,2-isomers when the substituents are identical.[4c]

Ab initio studies have been made in the case of the fluoroethylenes to explore the structure–stability relationships using various quality basis sets and a variety of geometries, *e.g.* standard geometry, partial optimization, or matched geometries with the same bond lengths and angles chosen for a pair of isomers.[4b,5,6] The primary purpose of the present calculations is to evaluate total molecular energies for ethylene, mono-, and di-fluoroethylenes in (7,3) and (9,5) basis sets with various contractions using either fully optimized geometry or the best experimental geometry, and thence calculate reaction heats. We shall focus attention on the heat for the disproportionation reaction (1) which by regarding

$$\text{Difluoroethylene} + \text{Ethylene} \longrightarrow 2\ \text{Monofluoroethylene} \qquad (1)$$

the bonding energy in ethylene and monofluoroethylene as a composite molecular energy baseline enables one to assess stabilization or destabilization in terms of an energy that is readily accessible to both rigorous theoretical study and experimental evaluation. No fluorine–fluorine interaction of any kind can be invoked for monofluoroethylene, hence with this composite baseline, a positive value for ΔH^0 is to be identified with stabilization in the difluoroethylene, a negative value of ΔH^0 with destabilization. A value of ΔH^0 close to zero would be indicative of no special bonding interactions in the difluoroethylene of any significance.

Kollman made use of this disproportionation reaction (1) in the case of 1,1-difluoroethylene,[5] and we will compare his *ab initio* reaction heats with ours later. After commenting in more detail on the calculation techniques employed, we discuss the geometry and dipole moments predicted for the various fluoroethylenes, and go on to present the reaction heats evaluated for the *cis–trans* isomerization and disproportionation reaction. Finally ΔH^0 values at 298 K for other substituted ethylenes are calculated from ΔH_f° data in the literature to see whether, in terms of the corresponding composite

TABLE 1

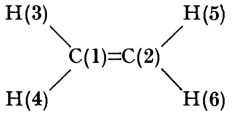
Total molecular energies [a]

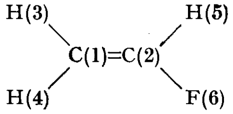
Molecule	(7,3) [b,c]	(7,3) [b,d]	(7,3,1) [d,e]	(9.5) [d,f]	(9,5) [d,g]
$\mathrm{CH_2{=}CH_2}$	−77.943 55	−77.940 07	−77.952 42	−78.009 42	
$\mathrm{CH_2{=}CHF}$	−176.646 00	−176.641 78	−176.666 65	−176.859 25	
cis-CHF=CHF	−275.335 11	−275.332 20	−275.369 00	−275.698 48	−275.716 44
trans-CHF=CHF	−275.337 60	−275.334 10	−275.369 53	−275.699 60	−275.717 08
$\mathrm{CH_2{=}CF_2}$	−275.353 85	−275.352 79	−275.394 57	−275.708 52	−275.728 36

[a] All energies in a.u. [b] The (7,3) basis set of Roos and Siegbahn [7] was contracted to ⟨5,3⟩ as ⟨3,1,1,1,1;1,1,1⟩. Three uncontracted s functions with exponents 4.9000, 0.8200, and 0.1800 were used on the hydrogen atoms. [c] Completely optimized geometry, see Table 2. [d] Experimental geometry.[11,21] [e] The (7,3) basis set of Roos and Siegbahn [7] was contracted to ⟨4,2⟩ as ⟨4,1,1,1;2,1⟩ and single d_{xy}, d_{xz}, and d_{yz} functions with exponents $\alpha = 0.80$ were included on the carbon and fluorine atoms. Three uncontracted s-functions with exponents 4.9000, and 0.8200, and 0.1800 were used for the hydrogen. [f] The (9,5) basis set of Dunning [12] for carbon and fluorine was contracted to ⟨6,1,1,1;4,1⟩. Four s functions were placed on each hydrogen atom contracted to double zeta as suggested in ref. 12. [g] Same basis set as in note *f*, but contracted to ⟨4,1,1,1,1,1;3,1,1⟩. The contractions of the s functions on the hydrogen atoms were kept at double zeta quality as in note *f*.

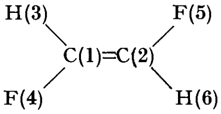
TABLE 2

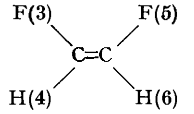
Geometries [a,b]



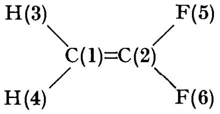


	Experiment [21]	STO-3G *	4-31G *	(7,3) [22]	Experiment [11]	(7,3)
C(1)=C(2)	1.336	1.306	1.316	1.315	1.333	1.305
C(1)–H(3)	1.103	1.082	1.073	1.072	1.085	1.068
C(1)–H(4)	1.103	1.082	1.073	1.072	1.090	1.069
C(2)–H(5)	1.103	1.082	1.073	1.072	1.076	1.067
C(2)–H(6)	1.103	1.082	1.073	1.072		
C(1)F						
C(2)F					1.348	1.369
⟨CCF					120.98	121.8
⟨CCH(3)	120.7	122.2	122.0	121.9	123.92	120.0
⟨CCH(4)	120.7	122.2	122.0	121.9	121.41	121.4
⟨CCH(5)	120.7	122.2	122.0	121.9	127.70	126.3





	Experiment [11]	STO-3G [5]	4-31G [6]	(7,3)	Experiment [11]	STO-3G [5]	4-31G [5]	(7,3)
C(1)=C(2)	1.329	1.326	1.304	1.303	1.331	1.326	1.302	1.303
C(1)–H(3)	1.080	(1.07) [c]	1.066	1.064				
C(1)–H(4)					1.084	(1.07) [c]	1.063	1.064
C(2)–H(5)								
C(2)–H(6)	1.080	(1.07) [c]	1.366	1.064	1.084	(1.07) [c]	1.063	1.064
C(1)F	1.344	1.357		1.367	1.335	1.358	1.362	1.364
C(2)F	1.344			1.367	1.335			1.364
⟨CCF	119.33	123.0	119.5	119.3	123.72	124.2	122.6	122.0
⟨CCH(3)	129.25	121.9	126.0	126.1				
⟨CCH(4)					121.56	120.5	123.7	124.0
⟨CCH(5)								



	Experiment [11]	(7,3)
C(1)=C(2)	1.316	1.300
C(1)–H(3)	1.075	1.065
C(1)–H(4)	1.075	1.065
C(2)–H(5)		
C(2)–H(6)		
C(1)F		
C(2)F	1.324	1.341
⟨CCF	125.34	125.4
⟨CCH(3)	120.37	119.9
⟨CCH(4)	120.37	119.9
⟨CCH(5)		

[a] Bond lengths in Å and bond angles in degrees. [b] Additional experimental data on the fluoroethylenes can be found in refs. 32 and B. Bak, D. Christensen, L. Hansen-Nygaard, and J. Rastrup-Andersen, *Spectrochimica Acta*, 1958, **13**, 120; W. Edgell, P. A. Kinsey, and J. W. Amy, *J. Amer. Chem. Soc.*, 1957, **79**, 2691; and H. W. Morgan and J. H. Goldstein, *J. Chem. Phys.*, 1959, **30**, 1025. [c] Held fixed during the optimization.[5]

* W. H. Latham, L. A. Curtis, W. J. Hehre, J. B. Liole, and S. A. Pople, *Progr. Phys. Org. Chem.*, 1974, **11**, 175.

molecular energy baselines, both destabilization and stabilization are common features in this kind of structure.

BASIS SETS AND EXPERIMENTAL DATA

Several different basis sets and contractions were employed in this study giving the total molecular energies listed in Table 1. First the (7,3) basis set of Roos and Siegbahn[7] for carbon and fluorine, contracted to ⟨3,1,1,1,1;1,1,1⟩[8-10] was used to carry out complete geometry optimizations on ethylene, fluoroethylene, *cis-* and *trans*-1,2-difluoroethylene, and 1,1-difluoroethylene. This basis set is sufficiently small to allow an economical complete geometry optimization of the three four-heavy atom difluoroethylene molecules considered, and the contraction was chosen to allow maximum flexibility in the valence shell. Next, several calculations at the experimental geometries[11] were performed using the (7,3) basis set contracted as above, a (7,3,1) set contracted to ⟨4,1,1,1;2,1;1⟩, and a (9,5) basis set[12] contracted to ⟨6,1,1,1;4,1⟩, and to ⟨4,1,1,1,1,1;3,1,1⟩. These latter, more complete, basis sets were used to check any basis set dependence of our conclusions.

TABLE 3

Dipole moments[a] of *cis*-1,2-difluoroethylene and 1,1-difluoroethylene

Basis set			*cis*-1,2-Difluoroethylene	1,1-Difluoroethylene
Carbon and fluorine	Hydrogen	Geometry	Exp. value = 2.42 ± 0.32[32]	Exp. value = 1.366 ± 0.02[b]
(7,3) →⟨3,1,1,1,1;1,1 1⟩	(3)→⟨1,1,1⟩	Exp.	3.10	1.71
(7,3) →⟨3,1,1,1,1;1,1,1⟩	(3)→⟨1,1,1⟩	Opt.	3.36	1.83
(7,3,1)→⟨4,1,1,1;2,1;1⟩	(3)→⟨1,1,1⟩	Exp.	2.62	1.22
(9,5) →⟨6,1,1,1;4,1⟩	(4)→⟨3,1⟩	Exp.	3.55	2.31
(9,5) →⟨4,1,1,1,1,1;3,1,1⟩	(4)→⟨3,1⟩	Exp.	3.47	2.25
(9,5) →⟨4,1,1,1,1,1;2,1,1,1⟩	(4)→⟨3,1⟩	Exp.	3.47	

[a] Dipole moments in Debyes. [b] A. Roberts and W. F. Edgell, *J. Chem. Phys.*, 1949, **17**, 742.

ΔH_f^0 ($H_{298}^0 - H_0^0$) and the assignments of fundamental vibrational frequencies used to calculate experimental values for the reaction heats at 0 K corrected for zero-point energy contributions are given in refs. 13—17.

RESULTS

A *Geometry*.—In Table 2 we list the geometries of ethylene, fluoroethylene, *cis-* and *trans*-1,2-difluoroethylene, and 1,1-difluoroethylene found using the (7,3) basis set. Similar C=C and C–F bond lengths were reported earlier by Bak *et al.*[18] (omitting the *trans*-isomer) with partial geometry optimization at the (7,3) level but contracted to ⟨4,2⟩. For comparison where possible we have included in Table 2 results of optimizations at the widely used STO-3G[19] and 4—31G[20] levels. The electron diffraction results of Carlos *et al.*[11] are also given. The following points may be noted. (1) The C=C double bond lengths for ethylene and the fluoroethylenes predicted at the STO-3G, 4—31G, and (7,3) levels are significantly smaller than the electron diffraction (r_g) values. This is only to be expected since equilibrium bond lengths (r_e) from either theory or based on experiment are in general smaller than the r_g bond lengths obtained from electron diffraction.[21] Furthermore, it has been shown recently that the *sp*-limit C=C double bond length for ethylene may be as low as 1.320 Å.[22] The 4—31G and (7,3) basis sets also predict C–H bond lengths shorter than the electron diffraction values. (2) For *cis-* and *trans*-1,2-difluoroethylene the 4—31G and (7,3) basis sets find that the C=C double bond length decreases by *ca.* 0.012 Å from that in ethylene. The experimental difference is smaller by *ca.* 0.007 Å. (3) The (7,3) basis set finds the C=C double bond length in 1,1-difluoroethylene to be 0.003 Å shorter than in *cis-* and *trans*-1,2-difluoroethylene, only about one-fifth of the experimental value. (4) The (7,3) basis set finds the C=C double bond length in fluoroethylene to be 0.002 Å larger than in *cis-* and *trans*-1,2-difluoroethylene, in good agreement with the experimental difference. (5) The STO-3G, 4—31G, and (7,3) basis sets all find the C–F bond lengths to be too long. However, the (7,3) basis set correctly predicts the observed decrease in the C–F bond length in going from fluoroethylene to *trans-*, to *cis*-1,2-difluoroethylene and finally to 1,1-difluoroethylene. Both the 4—31G and (7,3) basis sets find smaller differences in the C–F bond lengths between *cis-* and *trans*-1,2-difluoroethylene than does experiment. (6) Both the 4—31G and (7,3) basis sets find the CCH bond angles in *cis*-1,2-difluoroethylene to be larger than in the *trans*-isomer but not to the extent found experimentally. (7) The (7,3) basis set accurately reproduces the large CCF angle observed experimentally in 1,1-difluoroethylene, and also reproduces the HCF angle but to a lesser extent the HCH angle in monofluoroethylene.

B *Dipole Moments*.—In Table 3 we list the dipole moments of *cis*-1,2- and 1,1-difluoroethylene. If only *s*- and *p*-functions are included, the dipole moments of both compounds are significantly larger than experiment, a result already noted by Binkley and Pople[6] in the case of the *cis*-structure. The dipole moments of both these molecules are brought into much better agreement with experiment by including *d*-functions on the heavy atoms.

cis–trans *Isomerization and Disproportionation Reaction Heats*.—As noted in the Introduction the main purpose of this paper is to use the reaction heat for the disproportionations (2) and (3) as an energy indicative of stabilization,

$$cis\text{- (or } trans\text{-) } CHX{=}CHX + CH_2{=}CH_2 \longrightarrow 2CH_2{=}CHX \quad (2)$$

$$CH_2{=}CX_2 + CH_2{=}CH_2 \longrightarrow 2CH_2{=}CHX \quad (3)$$

destabilization, or their absence, in the difluoroethylenes. We have not therefore attempted to improve upon the value predicted for the *cis–trans* isomerization. However, as shown in Table 4A, ΔE_T calculated from the E_T values listed in Table 1 compares very favourably with other *ab initio* calculations.[4b,5,6] Small negative values are obtained with (7,3), (7,3,1), and (9,5) basis sets, *i.e.* −1.56 to −0.34 kcal mol^{-1}, like most of those reported, although the highest quality calculation of Binkley and Pople[6] gives a small positive ΔE_T of +0.24 kcal mol^{-1}, similar to the experimental value of +1.08 kcal mol^{-1}.[2] The agreement between theory and experiment is much the same for the *cis–trans* isomerization of but-2-ene, see Table 4B, *i.e.*, the calculated values are *ca.* 1 kcal mol^{-1} more negative. In

TABLE 4

Calculated reaction heat for the *cis–trans* isomerization of 1,2-difluoroethylene [experimental values ΔH^0_{298} $+0.93$, $(\Delta H^0_0)_{\mathrm{zpe}}$ $+1.08$ kcal mol^{-1}] and but-2-ene [experimental values ΔH^0_{298} -1.05 ± 0.24, $(\Delta H^0_0)_{\mathrm{zpe}}$ -1.03 kcal mol^{-1}]

Basis set	Reference	Geometry	$E_T(trans) - E_T(cis)$/kcal mol^{-1}
A 1,2-Difluoroethylene			
STO-3G [a]	4*b*	Partially optimized	-0.24
4-31G [a]	4*b*	Partially optimized STO-3G	-0.52 [b]
4-31G	4*b*	Partially optimized	-1.29
4-31G	6	Standard	-1.04
4-31G	6	Optimized	-1.32
4-31G (RMP2)	6	Standard	-0.71
6-31G	6	Standard	-0.89
6-31G (RMP2)	6	Standard	-0.52
6-311G	6	Standard	-0.20
6-31G *	6	Standard	-0.23
6-311G *	6	Standard	$+0.26$
(7,3)	This paper	Optimized	-1.56
(7,3)	This paper	Experimental [c]	-1.19
(7,3,1)	This paper	Experimental [c]	-0.34
(9,5) [d]	This paper	Experimental [c]	-0.70
(9,5) [e]	This paper	Experimental [c]	-0.40
B But-2-ene			
STO-3G	26	Optimized	-1.67
4-31G	26	Optimized at 4-31G level	-1.68

[a] Additional values of the isomerization heat can be calculated from a series of E_T values in ref. 5 which refer to geometries with the same bond lengths and angles in the two isomers. We note that some of the STO-3G values are positive. [b] Value given in ref. 4*b* is -0.63 kcal mol^{-1}. [c] See ref. 9. [d] $(9,5) \rightarrow \langle 6,1,1,1;4,1 \rangle$ for carbon and fluorine. [e] $(9,5) \rightarrow \langle 4,1,1,1,1,1;3,1,1 \rangle$ for carbon and fluorine.

the present context it is the overall similarity between the values obtained with the various basis sets that is important because it would suggest that the results reported below for the disproportionation reactions are just as reliable.

Before proceeding to discuss the results for the difluoroethylenes in terms of the composite molecular energy baseline, we note that an alternative approach has been discussed in the literature to account for the exothermicity that characterizes the disproportionation reaction when the substituents are identical, and the difference in stability between the unsymmetrical and symmetrical isomers.[4] For example, CH_2=CHF is envisaged as the union of the two different molecular fragments CH_2· and CHF·, the 1,1-difluoro isomer as the union of the two different fragments CH_2· and CF_2· but the *cis*- and *trans*-1,2-isomers, by their very nature, as the union of the two identical molecular fragments, CHF·. These molecular fragments are then considered as electron donors, D, or electron acceptors, A. The unsymmetrical 1,1-isomer is thus a D–A (or A–D) combination, whereas the *cis*- and *trans*-1,2-isomers are D–D or A–A combinations. By analogy with the Woodward–Hoffman rules for the kinetic behaviour of organic reactions, Epiotis *et al.* propose that a D–A combination will be stabilized relative to a D–D or an A–A combination and that the difference in stability (electronic energy) will increase as the donor–acceptor property of the two fragments from which the 1,1-isomer is made is enhanced relative to that in the 1,2-isomer fragments. These authors have marshalled experimental evidence for these structure–stability relationships, and have shown, along with other theoretical calculations, how the linear combination of fragment configuration (l.c.f.c.) method can be applied to the problem. The utilization of molecular fragments in this way amounts to the adoption of a different baseline from which the stabilization or destabilization of the 1,1- and 1,2-difluoroethylenes can be assessed. Other fragmentation processes have also been considered in the literature, *e.g.* $F_2C_2H_2$ was disected into FF and C_2H_2 by Epiotis and Yates [4d] and into F and FC_2H_2 by Whangbo *et al.*[23] This molecular fragment approach has been explored quite extensively by these authors, although some of their conclusions differ.[4,23] However, the composite molecular energy baseline approach has received less attention,[5] so we shall now consider it further.

First, it is of interest to examine the data for dialkyl derivatives, to get some idea of the magnitude destabilization or stabilization can have. ΔH^0_{298} Values are presented in Table 5, along with values for the *cis–trans* isomerization. It can be seen that ΔH^0_{298} for disproportionation of the *trans*-isomer is zero to within experimental error for all the CH_3, CH_3CH_2, $CH_3CH_2CH_2$, and $(CH_3)_2CH$ substituted compounds. This strongly suggests that no special interaction effects of any kind are present in these *trans*-CHX=CHY structures. Only for the two derivatives in which $(CH_3)_3C$ is one of the substituents is there any significant departure from zero. The reaction heat in these cases apparently takes on a small negative value, which would be indicative of slight destabilization. On the other hand for the *cis*-isomers there is slight destabilization to the extent of *ca.* 1 kcal mol^{-1} throughout the entire series of CH_3, CH_3CH_2, $CH_3CH_2CH_2$, and $(CH_3)_2CH$ derivatives, and then for the mono-$(CH_3)_3C$ substituted derivatives it increases abruptly to *ca.* 5 kcal mol^{-1} (see Table 5, column b).

TABLE 5

ΔH^0_{298} For the disproportionation reactions of *trans*- and *cis*-1,2-dialkylethylenes: A, *trans*-CHX=CHY + CH_2=CH_2 $\longrightarrow$ CH_2=CHX + CH_2CHY; B, *cis*-CHX=CHY + CH_2=CH_2 $\longrightarrow$ CH_2=CHX + CH_2=CHY; and for the *cis–trans* isomerization C, *cis*-CHX=CHY $\longrightarrow$ *trans*-CHX=CHY

Substituents		$\Delta H^0{}_{298}$/kcal mol^{-1} [13]		
X	Y	A	B	C
CH_3	CH_3	$+0.10$ ±0.60	-0.96 ±0.60	-1.05 ±0.24
CH_3	CH_3CH_2	$+0.07$ ±0.72	-0.79 ±0.72	-0.86 ±0.43
CH_3CH_2	CH_3CH_2	$+0.33$ ±0.84	-1.29 ±0.84	-1.63 ±0.62
CH_3	$CH_3CH_2CH_2$	0.00 ±1.05	-0.38 ±0.98	-0.38 ±0.69
CH_3	$(CH_3)_2CH$	$+0.50$ ±0.86	-0.45 ±0.79	-0.96 ±0.60
CH_3	$(CH_3)_3C$	-0.93 ±0.86	-4.80 ±0.93	-3.87 ±0.60
CH_3CH_2	$(CH_3)_3C$	-1.34 ±1.00	-5.71 ±1.29	-4.37 ±1.05

This contrast in behaviour is, of course, reflected in the reaction heats for the *cis–trans* isomerization (see Table 5, column c). Steric hindrance has been advanced to account for the small decrease in stability of *cis*-but-2-ene with respect to *trans*-but-2-ene, and there are independent thermodynamic data which support this explanation.[24]

Evidently, destabilization of a similar nature and magnitude is present in all the *cis*-isomers in Table 5 where the carbon atoms attached to the double bond carbons are CH_3–, –CH_2–, or $>$CH–. Serious steric hindrance when $(CH_3)_3C$ is the substituent is widely accepted.[25] Reaction heats calculated for the disproportionation of *trans*- and *cis*-but-2-ene from total molecular energies reported in the literature using the STO-3G, 4—31G, 6—31G, and 6—31G* basis sets [26–31] are in good agreement with experiment (see Table 6A) although not quite so good as that found for the isomerization reaction (see Table 4B).

Against this background we can now proceed to assess the significance of the disproportionation reaction heats for *trans*- and *cis*-1,2-difluoroethylenes calculated from the E_T values of Table 1 (see Table 6B). For *both* isomers the reaction heat is a substantial *negative* quantity, indicative of destabilization. In magnitude the values are greater than those for the structurally hindered $(CH_3)_3C$ compounds in Table 5. Furthermore there is very satisfactory agreement between the values obtained using the various basis sets. The averages are -6.47 and -7.42 kcal mol^{-1} for the *trans*- and *cis*-isomer respectively, with an average deviation in each case of 0.55 kcal mol^{-1}. The sizeable negative energy is thus independent of basis set and geometry employed, and there seems little doubt that similar calculations using the 6—311G* basis set of Binkley and Pople,[6] which gives a small positive ΔE_T for the *cis–trans* isomerization, would likewise give sizeable negative energies for these disproportionation reactions. Hence it appears that if one takes the bonding in ethylene and monofluoroethylene as a composite molecular energy baseline the greater stability of the *cis*- with respect to the *trans*-structure is a consequence not of some direct stabilizing interaction in the *cis*-structure, but of destabilizing interactions in both structures, with the *cis*-structure being the less destabilized.

TABLE 6

Disproportionation reaction heats for A dimethylethylenes and B difluoroethylenes

Reaction	Experimental		Calculated ΔE_T values							
	ΔH^0_{298} [13]	$(\Delta H_0{}^0)_{zpe}$ [13–17]	STO-3G	4-31G	6-31G	6-31G *	(7,3) [a]	(7,3) [b]	(7,3,1) [b]	(9,5) [b,c]
A Dimethylethylenes										
trans-MeCH=CHMe + CH_2=CH_2 → 2MeCH=CH_2	$+0.10$ ± 0.60	-0.31	-1.81	-1.46	-1.75	-2.40				
cis-MeCH=CHMe + CH_2=CH_2 → 2MeCH=CH_2	-0.96 ± 0.60	-1.34	-3.48	-3.14	-3.43	-4.08				
Me_2C=CH_2 + CH_2=CH_2 → 2MeCH=CH_2	$+1.22$ ± 0.62	$+0.59$	-2.03	-1.14	-1.44	-2.08				
B Difluoroethylenes										
trans-FCH=CHF + CH_2=CH_2 → 2CH_2=CHF							-6.93	-5.89	-7.12	-5.95
cis-FCH=CHF + CH_2=CH_2 → 2CH_2=CHF							-8.50	-7.09	-7.45	-6.65
CH_2=CF_2 + CH_2=CH_2 → 2CH_2=CHF	$+1.24$ ± 1.86		$+4.1$	$+1.2$			$+3.26$	$+5.83$	$+8.59$	-0.35

[a] Optimized geometry. [b] Experimental geometry.[11] [c] (9,5)→⟨6,1,1,1;4,1⟩ for carbon and fluorine.

It will be interesting to check these calculated reaction heats when an experimental determination of ΔH_f^0 is made for either isomer. However, ΔH_f^0 values have been determined for the unsymmetrical 1,1-difluoroethylene and for tri- and tetra-fluoroethylene, and ΔH^0_{298} for their disproportionation reactions will now be examined to see what kind of interaction effects are present.

In the case of 1,1-difluoroethylene ΔH^0_{298} has a small

$$CH_2{=}CF_2 + CH_2{=}CH_2 \longrightarrow 2CH_2{=}CHF \tag{4}$$

positive value of 1.24 kcal mol^{-1}. This is almost identical to the value of 1.22 kcal mol^{-1} for the corresponding unsymmetrical dimethylethylene, *i.e.*, 2-methylpropene, which strongly suggests that the bonding in the unsymmetrical difluorostructure involves no special fluorine–fluorine interaction arising from electronic properties associated with fluorine *per se*, *e.g.* the lone pair electrons or electronegativity effects. The experimental uncertainty, however, is rather large for the difluoro compound, such as to make the value lie within the range -0.62 to $+3.10$ kcal mol^{-1} Even so, at the one extreme the value of -0.62 kcal mol^{-1} is of negligible negative magnitude compared with those of the *cis*- and *trans*-isomers, while at the other extreme the value of $+3.10$ kcal mol^{-1} would be indicative of moderate stabilization, not destabilization, as in the case of the *cis*- and *trans*-isomers. The values for the disproportionation reaction heat listed in Table 6B, show that the (7,3) and (7,3,1) basis sets are inadequate to treat this kind of structure, and a basis set of (9,5) quality is needed before acceptable agreement between the calculated and experimental value is achieved. Nevertheless, the E_T values in Table 1 show consistently that the 1,1-isomer is more stable than either the *cis*- or *trans*-isomer, in accord with the observation of Epiotis *et al.*[4d] for unsymmetrical and symmetrical disubstituted ethylenes with identical substituents.

With this knowledge of the bonding in 1,1-difluoroethylene we can proceed to explore the kind of interaction effects present in tri- and tetra-fluoroethylene. ΔH^0_{298} for the disproportionation reactions (5) and (6) of these com-

$$CHF{=}CF_2 + CH_2{=}CH_2 \longrightarrow CH_2{=}CHF + CH_2{=}CF_2 \tag{5}$$

$$CF_2{=}CF_2 + CH_2{=}CH_2 \longrightarrow 2CH_2{=}CF_2 \tag{6}$$

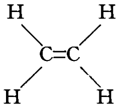
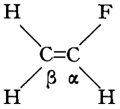
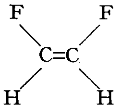
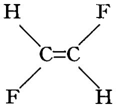
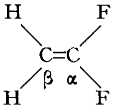
pounds is quite large and negative, -8.48 ± 3.47 and -14.70 ± 2.17 kcal mol^{-1}, respectively. Since there is no evidence for strong interaction effects in 1,1-difluoroethylene, but at most stabilization not exceeding 3.10 kcal mol^{-1}, these quite large and negative disproportion reaction heats point to substantial destabilization in the tri- and tetra-fluoro compounds. These more highly substituted fluoroethylenes share an obvious structural relationship with the *cis*- and *trans*-1,2-derivatives in that they all have at least one fluorine attached at each end of the carbon–

carbon double bond. Hence these additional ΔH^0_{298} values support the contention that destabilization is a characteristic of this particular structural feature.

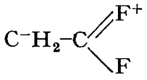
Considerations of Gross Atomic Population and Molecular Geometry of the Mono- and Di-fluoro-substituted Ethylenes relating to their Stability.—The results of a gross atomic population analysis (see Table 7) show that in monofluoroethylene and in the unsymmetrical 1,1-difluoroethylene there is a striking difference between the α- and β-carbon atoms. The β-carbon atoms have a significantly greater electron population, so much so that the carbon atoms are oppositely charged. On the other hand, in the *cis*- and *trans*-1,2-isomers both carbon atoms are positively charged (equally) to a small extent. Beyond this, there are no clear cut trends that distinguish the two sets of structures. In all cases there is withdrawal of electrons from the hydrogen, as there is in ethylene itself, and a build-up of electrons on the fluorine. The *ab initio* calculations of Bak *et al.*[18] using a more contracted (7,3) basis set gave charge distributions in $CH_2{=}CH_2$, $CH_2{=}CHF$, *cis*-$CHF{=}CHF$, and $CH_2{=}CF_2$ very similar to those in Table 7, so our results serve to corroborate and extend their findings. It is of interest to note that the charge separations correspond to what would be expected on the basis of simple resonance theory, and offer a qualitative explanation for the relative stabilities of the symmetrical and unsymmetrical derivatives. It has long been known that compared with alkyl halides the halogen atom in vinyl halides is far less reactive. This has been thought of in terms of the halogen atom being less ' negative ' in the vinyl structure, more ' strongly bonded ' or a combination of both. These features are accounted for by postulating that resonance structures of the type $F^+{=}CH{-}C^-H_2$ lead to partial double bond character in the carbon–fluorine bond.[31] Now in a 1,2-difluoroethylene the corresponding structures $F^+{=}CH{-}C^-H{-}F$ and $F{-}C^-H{-}CH{=}F^+$ might be expected to be somewhat less favoured because of repulsion between C^-H and F in such close proximity. Furthermore, partial double bond formation at both ends of the molecule would require the improbable structure $F^+{=}C^-H\ C^-H{=}F^+$, with no covalent bond at all between the two carbon atoms which are adjacent and carry like charges, a structural feature always regarded to be a destabilizing influence in resonance theory.[31] The corresponding charge separation in the 1,1-difluoroethylene would, however, result in structures (1) and (2)

TABLE 7

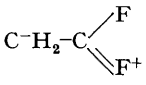
Gross atomic population analysis

Compound	Basis set (7,3,1) [a]	 (9,5) [a,b]
	0.795 6.410=6.410	0.822 6.357=6.357
	0.773 9.386 6.535=5.760 0.779 0.767	0.790 9.313 6.461=5.844 0.796 0.796
	9.375 5.864=5.864 0.761	9.304 5.910=5.910 0.786
	9.391 5.870=5.870 0.739	9.319 5.920=5.920 0.761
	0.751 9.359 6.614=5.165	0.769 0.9288 6.533=5.351

[a] Experimental geometry.[11] [b] (9,5)→⟨6,1,1,1;4,1⟩ for carbon and fluorine.



(1)



(2)

which, like the vinyl fluoride structure $C^-H_2{-}CH{=}F^+$, do not involve the negatively charged carbon being in close proximity to fluorine. On the contrary, attraction between fluorines in such different electronic states in these resonance structures for the 1,1-derivative could be held responsible for any slight stabilizing interaction.

On the other hand it is perhaps equally important to draw attention to the fact that differences in bond length, which would be expected to accompany charge separation of this kind, are not substantiated by experimental data or the theoretical calculations. While the slightly shorter C=C bond length in the 1,1-isomer compared with the *cis*- and *trans*-1,2-isomers (see Table 2) could be taken as indicative of somewhat stronger bonding, and hence relative destabilization of the two symmetrical isomers, the carbon–fluorine bond length is largest in the monofluoroethylene and shorter in the 1,1-isomer, the derivatives in which resonance structures containing $C{=}F^+$ would be regarded as more likely. Although the carbon–fluorine bond is undoubtedly longer still in alkyl fluorides, *i.e. ca.* 1.38 Å,[32] it would appear that significant and very similar charge separation occurs in monofluoroethylene and the 1,1-isomer without the expected systematic changes in the length of the carbon–fluorine bond.

With regard to the approach followed by Epiotis *et al.*[4] we note that even here there are inconsistencies between prediction and experiment. The C=C bond length is shorter in the 1,1- than in the 1,2-isomer, in accord with expectation, whereas the bond length is slightly longer in monofluorethylene than in any of the difluoro derivatives, which would not be indicative of a ' stronger bond ' in the conventional sense as required by the donor–acceptor relationships.

DISCUSSION

Disproportion redistribution reactions have been utilized in many studies of reactivity in physical organic chemistry, inorganic chemistry, thermochemistry, *etc.* too numerous to list in a paper on a single topic. One aspect of these reactions, in certain cases, does, however, call for comment. The disproportionation reaction (7) for 1,2-disubstituted ethylenes comes into the category

$$CHX{=}CHY + CH_2{=}CH_2 \longrightarrow CH_2{=}CHX + CH_2{=}CHY \quad (7)$$

of homodesmotic reactions.[33] This is a type of reaction which has proved to be particularly suitable for the evaluation of conventional ring strain energies in nonconjugated and saturated ring structures [34] and stabilization energies in aromatic structures, because extraneous energy contributions arising from changes in carbon–carbon or carbon–heteroatom bonding or changes in the number of bonded hydrogen or heteroatoms are thereby minimized. The present paper, in effect, extends the use of homodesmotic reactions to evaluate destabilization or stabilization energies in acyclic structures, or to demonstrate that no special interaction effects are present.

The disproportionation reaction (8) for unsymmetrical 1,1-disubstituted ethylenes is no longer homodesmotic

$$\mathrm{CH_2{=}CXY + CH_2{=}CH_2 \longrightarrow CH_2CHX + CH_2{=}CHY} \qquad (8)$$

because this structure itself is the smallest that contains the necessary structural element, =CXY, which has to be matched on reactant and product side to satisfy the homodesmotic criteria. The small (positive) ΔH^0_{298} values for both the 1,1-dimethyl and 1,1-difluoro compounds can therefore be attributed to this unavoidable mismatch in bonding in the above disproportionation reaction, and no special interaction effect over and above this need be invoked. Furthermore, as shown in Table 8, this value of *ca.* +1 kcal mol^{-1} is also characteristic of other 1,1-dialkylethylenes in which X = $\mathrm{CH_3}$ and Y = $\mathrm{CH_3CH_2}$, $\mathrm{CH_3CH_2CH_2}$, or $\mathrm{(CH_3)_2CH}$. Only with a larger Y substituent, keeping X = $\mathrm{CH_3}$, does ΔH^0_{298} decrease and take on a small negative value indicative of destabilization (again presumably a steric effect).

TABLE 8

ΔH^0_{298} for the homodesmotic disproportionation reactions of 1,1-dialkylethylenes, $\mathrm{CH_2{=}CXY + CH_2{=}CH_2 \longrightarrow CH_2{=}CHX + CH_2{=}CHY}$

Substituents		
X	Y	ΔH^0_{298}/kcal mol^{-1} [13]
$\mathrm{CH_3}$	$\mathrm{CH_3}$	$+1.22 \pm 0.62$
$\mathrm{CH_3}$	$\mathrm{CH_3CH_2}$	$+0.76 \pm 0.67$
$\mathrm{CH_3CH_2}$	$\mathrm{CH_3CH_2}$	$+0.72 \pm 0.86$
$\mathrm{CH_3}$	$\mathrm{CH_3CH_2CH_2}$	$+1.31 \pm 0.98$
$\mathrm{CH_3}$	$\mathrm{(CH_3)_2CH}$	$+0.93 \pm 0.72$
$\mathrm{CH_3}$	$\mathrm{(CH_3)_2CHCH_2}$	$+0.14 \pm 1.15$
$\mathrm{CH_3CH_2}$	$\mathrm{(CH_3)_2CH}$	-0.12 ± 0.88
$\mathrm{CH_3}$	$\mathrm{(CH_3)_3CCH_2}$	-1.17 ± 0.81

It now remains to be seen how widespread destabilizing interactions may be in substituted ethylenes with a substituent at each end of the double bond, and whether stabilization can also occur. ΔH^0_{298} values for the homodesmotic disproportionation reaction of a variety of substituted ethylenes, calculated from experimental ΔH_f^0 data in the literature [13] are presented in Table 9. Apparently destabilization is by no means restricted to the *cis*- and *trans*-1,2-difluoro compounds, but is also present in the *cis*- and *trans*-dicarboxylic acids, and in the *cis*-dicyano derivative. There is destabilization in tetrachloroethylene as in tetrafluoroethylene. But there are also a number of instances where the sign of $\Delta H_{298}{}^0$ is indicative of stabilization. The *cis*- and *trans*-1,2-dichloroethylenes thus differ from the corresponding difluoro compounds, with ΔH^0_{298} of *ca.* +4 kcal mol^{-1} in contrast to the values calculated for the fluoro compounds of *ca.* −6 to −8 kcal mol^{-1}. Furthermore, stabilizing interactions would appear to be a common property of several prop-1-ene derivatives, $\mathrm{CH_3CH{=}CHX}$, and also 1,1-dichloroethylene and 2-chloropropane for which the disproportionation heats are $+4.80 \pm 1.03$ and $+6.29 \pm 2.92$ kcal mol^{-1}, respectively.

TABLE 9

ΔH^0_{298} for the homodesmotic disproportionation reaction of a variety of substituted ethylenes

Compound	ΔH^0_{298}/kcal mol^{-1}	Interaction
$\mathrm{CHX{=}CHX}$		
trans-$\mathrm{Cl_2}$	$+4.16 \pm 2.89$	Stab.
cis-$\mathrm{Cl_2}$	$+4.28 \pm 2.10$	Stab.
trans-$\mathrm{(COOH)_2}$ [a]	-3.56 ± 1.31	Destab.
cis-$\mathrm{(COOH)_2}$ [a]	-4.45 ± 2.22	Destab.
cis-$\mathrm{(CN)_2}$	-7.41 ± 1.60	Destab.
$\mathrm{CH_3CH{=}CHX}$		
trans-Cl	$+8.89 \pm 2.94$	Stab.
cis-Cl	$+9.80 \pm 2.94$	Stab.
trans-Br	$+0.72 \pm 1.89$	Stab.
cis-Br	$+1.48 \pm 1.86$	Stab.
trans-CN	$+1.91 \pm 1.03$	Stab.
cis-CN	$+3.51 \pm 1.03$	Stab.
trans-$\mathrm{COOCH_3}$ [b]	-5.62 ± 1.15	Destab.
$\mathrm{CHX{=}CX_2}$		
$\mathrm{F_3}$	-8.48 ± 3.47	Destab.
$\mathrm{Cl_3}$	-1.03 ± 3.08	Destab.
$\mathrm{CX_2{=}CX_2}$		
$\mathrm{F_4}$	-14.70 ± 2.17	Destab.
$\mathrm{Cl_4}$	-9.25 ± 1.84	Destab.

[a] ΔH^0_f for acylic acid gas estimated from the value for the liquid taking $\Delta H^0_{\mathrm{evap}}$ to be the same as that for propionic acid, which is likely to be quite reliable since the b.p.s of the two acids are identical (I. L. Finar, ' Organic Chemistry,' Longman, London, 1971, 5th edn., pp. 210, 213). [b] ΔH^0_f for methyl crotonate estimated from ΔH^0_f for the ethyl ester, using the difference between ΔH^0_f for methyl and ethyl acetate.

From another point of view [*] the disproportionation reaction for disubstituted ethylenes with identical substituents can be regarded as an example of the formal reaction (9). In inorganic chemistry with $\mathrm{A_2}$ and $\mathrm{B_2}$

$$\mathrm{A_2 + B_2 \longrightarrow 2AB} \qquad (9)$$

diatomic molecules, the different electronegativities of A and B result in such reactions being exothermic, or, putting it differently, the thermochemical bond energy is greater in the unsymmetrical species AB than in $\mathrm{A_2}$ or in $\mathrm{B_2}$.[31] The exothermicity noted by Epiotis *et al.*[4d] for disubstituted ethylenes is thus a similar structure–stability relationship in an organic setting, although it would appear from the survey that exception may occur, as for instance in the case of the dichloro-derivatives.

We conclude from the above survey, and from the *ab initio* calculations presented earlier in this paper, that, taking ethylene and the monosubstituted ethylene as a composite molecular energy baseline destabilizing and stabilizing interactions are a general property of 1,2-disubstituted ethylenes, and that the problem of accounting for the sign and magnitude of *cis–trans* isomerization

---

[*] We thank a referee for drawing our attention to this general feature.

reaction heats is really part of a more complicated problem of interaction across the carbon–carbon double bond affecting the stability of the molecule with respect to the bonding energy in monosubstituted ethylene and ethylene itself.

[8/509 *Received*, 20*th March*, 1978]

REFERENCES

[1] N. C. Craig and E. A. Entemann, *J. Amer. Chem. Soc.*, 1961, **83**, 3047.

[2] N. C. Craig, L. G. Piper, and V. L. Wheeler, *J. Phys. Chem.*, 1971, **75**, 1453.

[3] K. S. Pitzer and J. L. Hollenberg, *J. Amer. Chem. Soc.*, 1954, **76**, 1493.

[4] (*a*) N. D. Epiotis, *J. Amer. Chem. Soc.*, 1973, **95**, 3007; (*b*) N. D. Epiotis, R. L. Yates, J. R. Larson, C. R. Kirmaier, and F. Bernardi, *ibid.*, 1977, **99**, 8379; (*c*) N. D. Epiotis, J. R. Larson, R. L. Yates, W. R. Cherry, S. Shaik, and F. Bernardi, *ibid.*, p. 7460; (*d*) N. D. Epiotis and R. L. Yates, *ibid.*, 1976, **98**, 461; (*e*) F. Bernardi, W. Cherry, S. Shaik, and N. D. Epiotis, *ibid.*, 1978, **100**, 1352; (*f*) N. D. Epiotis, W. R. Cherry, S. Shaik, R. Yates, and F. Bernardi, ' Structural Theory of Organic Chemistry,' in ' Topics in Current Chemistry, No. 70,' Springer Verlag, New York, 1977.

[5] P. Kollman, *J. Amer. Chem. Soc.*, 1974, **96**, 4362.

[6] J. S. Binkley and J. A. Pople, *Chem. Phys. Letters*, 1977, **45**, 197.

[7] B. Roos and P. Siegbahn, *Theor. Chim. Acta*, 1970, **17**, 209.

[8] S. Skaarup, J. E. Boggs, and P. N. Skancke, *Tetrahedron*, 1976, **32**, 1179.

[9] C. W. Bock, M. Trachtman, P. George, and G. Mains, *J. Mol. Structure*, 1978, **49**, 211.

[10] H. Johansen, *Theor. Chim. Acta*, 1971, **21**, 9.

[11] J. L. Carlos, jun., R. R. Karl, jun., and S. H. Bauer, *J.C.S. Faraday II*, 1974, 177.

[12] T. H. Dunning, jun., *J. Chem. Phys.*, 1970, **53**, 2823.

[13] J. B. Pedley and J. Rylance, ' Sussex-NPL Computer Analyzed Thermochemical Data: Organic and Organometallic Compounds,' University of Sussex, Brighton, 1977.

[14] ' Selected Values of Chemical Thermodynamic Properties,' NBS Technical Note 270–3, U.S. Government Printing Office, Washington, 1968.

[15] ' Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds,' API Research Project 44, Carnegie Press, Pittsburgh, 1953.

[16] T. Shimanouchi, ' Tables of Molecular Vibrational Frequencies. Consolidated Vol. 1,' NSRDS–NBS39, U.S. Government Printing Office, Washington, 1972.

[17] J. E. Kilpatrick and K. S. Pitzer, *J. Res. Nat. Bur. Standards*, 1947, **38**, 191.

[18] B. Bak, C. Kierkegaard, J. Pappas, and S. Skaarup, *Acta Chem. Scand.*, 1973, **27**, 363.

[19] W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, 1969, **51**, 2657.

[20] R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, 1971, **54**, 724.

[21] (*a*) K. Kuchitsu, T. Fukuyama, and Y. Morino, *J. Mol. Structure*, 1968, **1**, 463; (*b*) K. Kuchitsu, *J. Chem. Phys.*, 1966, **44**, 906.

[22] C. W. Bock, P. George, G. J. Mains, and M. Trachtman, *J. Mol. Structure*, 1978, **49**, 215.

[23] M. H. Whangbo, D. J. Mitchell, and S. Wolfe, *J. Amer. Chem. Soc.*, 1978, **100**, 3698.

[24] W. G. Dauben and K. S. Pitzer, ' Conformational Analysis,' in ' Steric Effects in Organic Chemistry,' ed. M. S. Newman, Wiley, New York, 1956, ch. 1.

[25] E. L. Eliel, ' Stereochemistry of Carbon Compounds,' McGraw–Hill, New York, 1962.

[26] W. J. Hehre and J. A. Pople, *J. Amer. Chem. Soc.*, 1975, **97**, 6941.

[27] J. S. Binkley, J. A. Pople, and W. J. Hehre, *Chem. Phys. Letters*, 1975, **36**, 1.

[28] W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, 1971, **93**, 808.

[29] L. Radom, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, 1971, **93**, 5339.

[30] W. J. Hehre and J. A. Pople, *J. Amer. Chem. Soc.*, 1975, **97**, 6941.

[31] L. Pauling, ' The Nature of the Chemical Bond,' Cornell University Press, Ithaca, 1940, 2nd edn., p. 215.

[32] V. W. Laurie, *J. Chem. Phys.*, 1961, **34**, 291.

[33] P. George, M. Trachtman, C. W. Bock, and A. M. Brett, *Theor. Chim. Acta*, 1975, **38**, 121.

[34] P. George, M. Trachtman, C. W. Bock, and A. M. Brett, *Tetrahedron*, 1976, **32**, 317.