J. Am. Chem. Soc. **1998,** *120,* 2932−2938

Effect of Fluorine Substitution on the Energies of Small Ring Compounds

Kenneth B. Wiberg* and Manuel Marquez

Contribution from the Department of Chemistry, Yale University, New Haven, Connecticut 06520-8107

Received May 2, 1997. Revised Manuscript Received January 13, 1998

Abstract: The effect of fluorine substitution on the energies of small ring compounds has been examined via ab initio calculations at the MP2/6-31G*, MP2/6-311+G*, and B3LYP/6-311+G* theoretical levels, along with correction for differences in zero-point energies. The introduction of a fluorine into a cyclopropane ring leads to destabilization, which results from the higher s character in the orbitals forming the bonds to a substituent. On the other hand, this is not seen with cyclopropene. The effect of 3-substituents on cyclopropene was examined by studying cyclopropenone, cyclopropenethione, methylenecyclopropene, and 3,3-difluorocyclopropene. The stabilization was largest and about equal with the $=$O and $=$S substituents. Smaller effects were observed with $=CH_2$ and F_2 substituents. The nature of the effects was studied making use of electron density difference maps. The structures and energies of the series of C_4H_4 and C_4F_4 derivatives were studied at the above theoretical levels. In most cases, fluorine substitution led to stabilization with respect to but-3-en-1-yne, but with tetrahedrane there was considerable destabilization. Fluorine substitution leads to destabilization of cyclobutyne with respect to cyclobutene.

1. Introduction

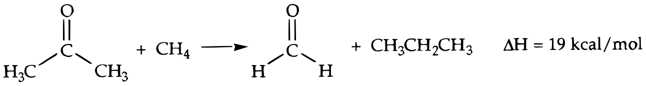
There has been considerable interest in the effect of fluorine substitution on the energies of small ring compounds.[1] If stabilization is found, it will have significant consequences for the synthesis of the more highly strained compounds. Very few experimental thermochemical data are available for the compounds of interest, and therefore, we have examined a number of these compounds via ab initio calculations. Geometry optimizations were carried out at the MP2/6-31G* and B3LYP/6-311+G* theoretical levels that introduce correction for electron correlation using different methods.[2,3] Additional calculations were carried out at the MP2/6-311+G* level using the MP2/6-31G* geometries. The zero-point energies were in most cases calculated using MP2/6-31G* and were scaled by 0.96.[4] In the case of the C_4F_4 compounds, this level of theory was not practical, and the zero-point energies were calculated using HF/6-31G* and scaled by 0.893.[5] The total energies and zero-point energies are available as Supporting Information.

Changes in relative energies usually result from changes in electron density distributions. These changes were examined in several different ways. Electron density difference maps provide direct information about the detailed nature of the changes in electron density differences. The charge distribution also was examined using Bader's atoms in molecules approach (AIM)[6] and using the Weinhold−Reed natural bond order (NBO)[7] analysis. In addition, bond orders were obtained using Fulton's sharing indices.[8]

2. Substituent Effects for Cyclopropanes and Cyclopropenes

The effect of replacing hydrogens at CH_2 groups by fluorine is conveniently examined using the isodesmic reactions shown in Table 1. There is generally good agreement among the several theoretical models. The rms deviation between the MP2/6-31G* and MP2/6-311+G** energies was 1.9 kcal/mol, and between MP2 and B3LYP at 6-311+G** was 1.8 kcal/mol.

Reaction 1 shows that fluorine prefers to be attached to a carbon bearing other carbons rather than hydrogens. The energy change is close to that found for the transfer of a carbonyl group from acetone to formaldehyde:[9]



$$(CH_3)_2C{=}O + CH_4 \longrightarrow H_2C{=}O + CH_3CH_2CH_3 \qquad \Delta H = 19\ \text{kcal/mol}$$

In this case, an electron density plot for acetone minus formaldehyde shows that methyl substitution leads to an increase in π-electron density at the carbonyl oxygen, probably arising

---

[1] Rahman, M. M.; Secor, B. A.; Morgan, K. M.; Shafer, P. R.; Lemal, D. M. *J. Am. Chem. Soc.* **1990**, *112*, 5986. Zhang, Y.; Smith, J.; Lemal, D. M. *J. Am. Chem. Soc.* **1996**, *118*, 9454. Lindner, P. E.; Correa, R. A.; Gino, J.; Lemal, D. M. *J. Am. Chem. Soc.* **1996**, *118*, 2256.

[2] Moller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.

[3] Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. Stephens, P. J.; Delvin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623.

[4] Cf. Wiberg, K. B.; Thiel, Y.; Goodman, L.; Leszczynski, J. *J. Phys. Chem.* **1995**, *99*, 13850.

[5] Pople, J. A.; Head-Gordon, M.; Fox, D. J.; Raghavachari, K.; Curtiss, L. A. *J. Chem. Phys.* **1989**, *90*, 5622.

[6] Bader, R. F. W. *Atoms in Molecules. A Quantum Theory*; Clarendon Press: Oxford, 1990.

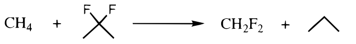
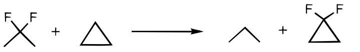
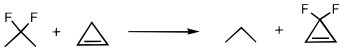
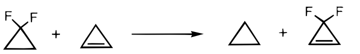
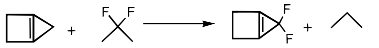
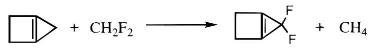
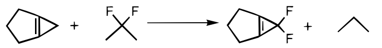
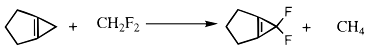
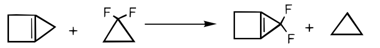
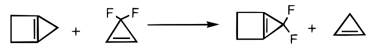
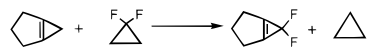
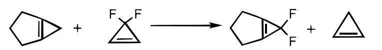
[7] Reed, A. E.; Weinstock, R. B.; Weinhold, F. A. *J. Chem. Phys.* **1985**, *83*, 735. Reed, A. E.; Weinhold, F. A.; Curtiss, L. A. *Chem. Rev.* **1988**, *88*, 899.

[8] Fulton, R. L. *J. Phys. Chem.* **1993**, *97*, 7516. Fulton, R. L.; Mixon, S. T. *J. Phys. Chem.* **1993**, *97*, 7530.

[9] The experimental change in enthalpy at 25 °C is 18.7 kcal/mol (Pedley, J. B. *Thermochemical Data and Structures of Organic Compounds*; Thermodynamics Research Center: College Station, TX, 1994; Vol. 1) and the calculated enthalpy difference at 0 K is 18.9 kcal/mol (MP2/6-311+G**).

S0002-7863(97)01413-3 CCC: $15.00

Table 1. Isodesmic Reaction Energies for Estimating Fluorine Substitution Effects

		ΔH (kcal/mol)		
		MP2	MP2*	B3LYP
[1]		20.6	18.3	16.3
[2]		13.3	14.2	11.2
[3]		3.6	4.2	1.9
[4]		-9.7	-10.0	-9.3
[5]		6.3	8.2	5.4
[6]		-14.2	-10.0	-10.9
[7]		4.9	6.4	3.3
[8]		-15.7	-11.8	-13.0
[9]		-7.0	-6.0	-5.9
[10]		2.7	4.0	3.4
[11]		-8.4	-7.8	-8.0
[12]		1.3	2.2	1.3

MP2=M2/6-31G*//MP2/6-31G*, **MP2***=MP2/6-311+G*//MP2/6-31G*, **B3LYP**=B3LYP//6-311+G*//B3LYP//6-311+G*

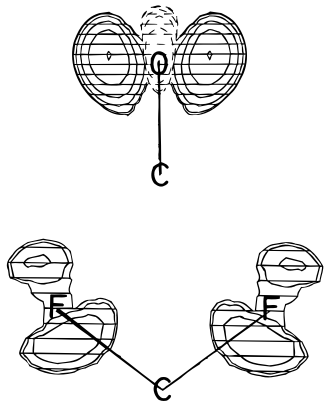
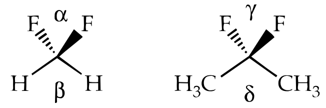


Figure 1. Electron density difference plots: (top) acetone minus formaldehyde; (bottom) 2,2-difluoropropane minus methylene fluoride. The contour level is 0.001 e/au^3.

from the out of plane methyl hydrogens (Figure 1).[10] A similar plot for the electron density difference on going from difluoromethane to 2,2-difluoropropane (Figure 1) shows that there is transfer of electron density to the C−F σ bonds of the latter, but there does not appear to be any π character to the transfer. Thus, despite the similar energy changes, the details of the intramolecular interactions that lead to charge transfer are different. In addition, the amount of charge transfer is small in both cases as can be seen by comparing Figure 1 and Figure 4 (discussed below) where the contour level (0.001 e/au^3) is the same for both plots. The AIM population analysis leads to the same conclusion, with only a 0.004 e increase in electron population at the fluorine on going from difluoromethane to 2,2-difluoropropane.



	α	β	γ	δ
geometric angle	108.4	113.8	105.2	116.8
bond path angle	103.7	121.1	101.3	123.1

Figure 2. Calculated structures of difluoromethane and 2,2-difluoropropane.

If charge transfer to the fluorine is not the major component of the stabilization of 2,2-difluoropropane, what other factors are involved? An important clue is provided by the structures of the halide and of methylene fluoride (Figure 2). The F−C−F bond angle in difluoropropane is unusually small (calcd 105.2°, obsd[11] 106.1°) despite the expected coulombic repulsion between the negatively charged fluorines. The more appropriate angle for a theoretical study is the bond path angle,[12] defined as the angle between the bond paths at the carbon nucleus. This angle is 101.3°, indicating that the bond is bent.[13] A similar examination of methylene fluoride found the calculated geometrical F−C−F angle to be 108.4°, and the bond path angle to be 103.7°.

It is known that electronegative atoms such as fluorine prefer to be bonded to orbitals that have high p character.[14] The difluoropropane FCF bond path angle of 101.3° corresponds to about 84% p character. The calculated C−C−C geometrical angle increased to 116.8°, with a bond path angle of 123.1° corresponding to about 64% p character. (The C−C−C geometrical angle in propane is 112.4°).[15] As the p-character in the orbital forming the H_3C−C bond decreases, and the s character increases, the carbon becomes more electronegative, and a methyl group may then donate electron density via the σ bonds. This leads to charge transfer from the methyl group to the central carbon, decreasing its positive charge and resulting in stabilization of the central carbon. Whereas the AIM population analysis found a negligible change in the F electron population on going from methylene fluoride to 2,2-difluoropropane (0.004 e), the positive charge at the central carbon decreased by 0.1 e.

The F−C−F bond path angle for methylene fluoride (103.7°) corresponds to 81% p character. The NBO analysis also gives an estimate of the p-character of the bond orbital from carbon to fluorine, and it is 78% p for methylene fluoride and 81% p for difluoropropane. Thus, although the values are slightly different, both AIM and NBO predict a 3% increase in p character for the C−F bond on going from methylene fluoride to difluoropropane.

Reaction 2 indicates that fluorine prefers to be attached to propane rather than to cyclopropane. This is to be expected since a fluorine prefers to be bonded to an orbital with high p character. The CH bonds in propane are formed using ~sp^3 carbon orbitals whereas those in cyclopropane use ~sp^2 carbon orbitals.[16] Although the fluorine substitution may somewhat

---

[10] Wiberg, K. B.; Murcko, M. A. *Tetrahedron* **1997**, *53*, 10123.

[11] Takeo, H.; Sugie, M.; Matsumura, C. *J. Mol. Struct.* **1995**, *352/353*, 267.

[12] Runtz, G.; Bader, R. F. W.; Messer, R. R. *Can. J. Chem.* **1977**, *55*, 3040.

[13] Wiberg, K. B. *Acc. Chem. Res.* **1996**, *29*, 229.

[14] Bent, H. *Chem. Rev.* **1961**, *61*, 275.

[15] Lide, D. R., Jr. *J. Chem. Phys.* **1960**, *33*, 1514.

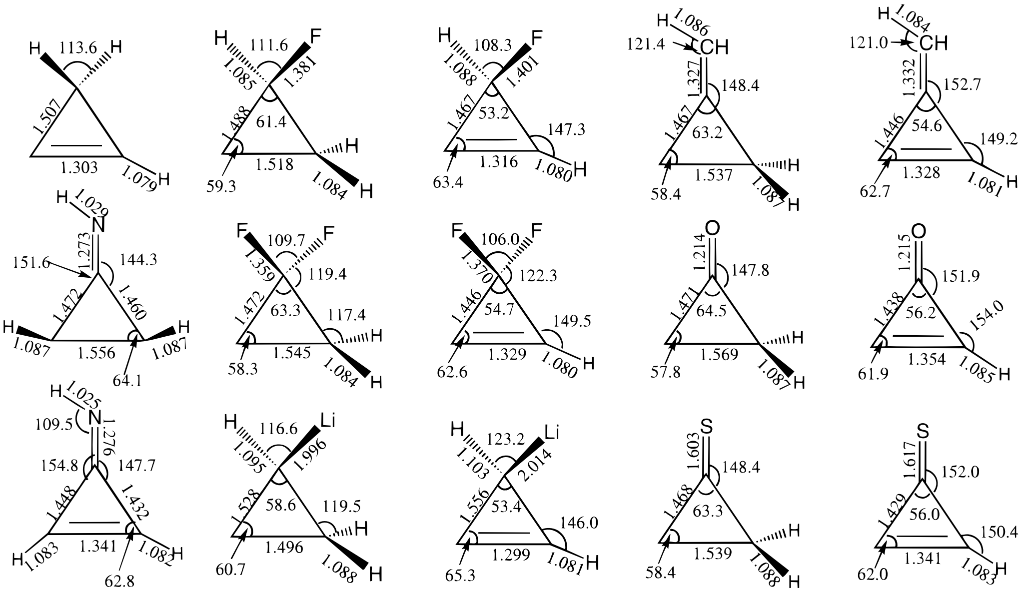


Figure 3. Calculated structures of cyclopropane and cyclopropene derivatives.

modify the cyclopropane orbitals, the increased s character in the cyclopropane C—H bonds will destabilize attached fluorines.

However, reaction 3 shows that this effect almost disappears with cyclopropene. Further, reactions 4, 6, 8, and 11 show that fluorine prefers to be bonded to cyclopropene rather than cyclopropane by about 10 kcal/mol. Ring size has a relatively small effect on the relative energies.

This raises the question of which substituents will stabilize cyclopropene. Some relevant isodesmic reactions are shown in Table 2, and the calculated structures of the compounds are summarized in Figure 3.[17] Reaction 13 is not surprising since it is known that cyclopropenone is significantly stabilized. For example, whereas cyclopropanone is essentially completely hydrated in aqueous solution, cyclopropenone is not hydrated.[18] The stabilization of cyclopropenone is believed to result from the polarization of the carbonyl group and the development of some cyclopropenium ion character.[19]

The replacement of ═O by ═NH leads to a similar but smaller energy change as would be expected for going from O to the less electronegative NH.

The replacement of the oxygen in cyclopropenone by sulfur leads to the surprising observation that it is stabilized by about the same amount. Whereas oxygen is considerably more electronegative than carbon, leading to strong polarization in the sense $C^{+}-O^{-}$ for both the σ and π systems,[20] carbon and sulfur have similar electronegativities.[21] A calculation of the charges at carbon and sulfur found a small polarization in the sense $C^{-}-S^{+}$. In view of this, how can C═S lead to the same stabilization of a cyclopropene ring as C═O?

The charges derived from population analyses are not well suited to the detailed study of substituent effects because they represent averages, either over a set of orbitals as in the NPA analysis, or over specific volumes of space as in the AIM analysis. Therefore, we prefer to examine the change in electron density distribution on going from one compound to another. Some examples are shown in Figure 4. Here are shown the changes that occur on going from cyclopropene to the substituted cyclopropene. The cyclopropene derivatives have essentially the same ring structure, and in each case, an average geometry was taken for the cyclopropene ring, and a geometry optimization for the remaining internal coordinates was carried out at the B3LYP/6-311+G** level. The wavefunctions for cyclopropene were calculated using the same geometry. The electron density distribution about each compound was calculated for a $15 \times 15 \times 15$ au three-dimensional array. Then, for each substituted cyclopropene, the density distribution for cyclopropene was subtracted from it, and a 3D plot was constructed using the 0.001 e/au^3 contour. Dashed lines indicated a loss of electron density, and solid lines indicate a gain in electron density on going from cyclopropene to its derivative.

The first plot (A) shows the difference between cyclopropenone and cyclopropene. Here, it can be seen that in the ketone, electron density is taken from the C═C bond. The side view shows that much of the difference is derived from the π-bond. However, the front view shows that much of the density is also taken from the bent σ bond. Thus, both the σ and π components of the C═C appear to be involved. At the same time, the C—C single bonds gain some electron density. This is the change that is expected for the development of some cyclopropenium ion character in cyclopropenone.

The electron density difference between cyclopropenethione and cyclopropene (Figure 4, B) is similar to that found for cyclopropenone. The similarity is more clearly shown by the

---

(16) Coulson, C. A.; Moffitt, W. *J. Chem. Phys.* **1947**, *15*, 151; *Phil. Mag.* **1949**, *40*, 1.

(17) The calculated structures are in good agreement with the experimental structures. Cyclopropene (Å): C═C = 1.295(1), C—C = 1.507(1) (Stigliani, W. M.; Laurie, V. W.; Li, J. C. *J. Chem. Phys.* **1975**, *62*, 1890.). Cyclopropenone: C═C = 1.354(3) , C—C = 1.428(5) , C═O = 1.206(6) (Staley, S. W.; Norden, T. D.; Taylor, W. H.; Harmony, M. D. *J. Am. Chem. Soc.* **1987**, *109*, 7641). Methylenecyclopropene: C═CH^2 = 1.332(6) , C—C = 1.441(6) , C═C = 1.312 (Norden, T. D.; Staley, S. W.; Taylor, W. H.; Harmony, M. D. *J. Am. Chem. Soc.* **1986**, *108*, 7912). Cyclopropanone: C1—C3 = 1.475(17), C2—C3 = 1.575(12), C═O = 1.191(21) (Pochen, J. M.; Baldwin, J. E.; Flygare, W. H. *J. Am. Chem. Soc.* **1969**, *91*, 1896). 1,1-Difluorocyclopropane: C1—C2 = 1.464(2), C2—C3 = 1.553(1), C—F = 1.358(2) (Perretta, A. T.; Laurie, V. W. *J. Chem. Phys.* **1975**, *62*, 2469). 1,1-Difluorocyclopropene: C—C = 1.438 (7), C═C = 1.321(1), C—F = 1.365(5) ((Ramaprasad, K. R.; Laurie, V. W.; Craig, N. C. *J. Chem. Phys.* **1976**, *64*, 4832).

(18) Breslow, R.; Ryan, G. *J. Am. Chem. Soc.* **1967**, *89*, 3073.

(19) Cf. Krebs, A. W. *Angew. Chem., Int. Ed. Engl.* **1964**, *4*, 10. Eicher, T.; Weber, J. L. *Top. Curr. Chem.* **1975**, *57*, 1.

(20) Wiberg, K. B.; Hadad, C. M.; Rablen, P. R.; Cioslowski, J. *J. Am. Chem. Soc.* **1992**, *114*, 8644.

(21) Allred, A. L.; Rochow, E. G. *J. Inorg. Nucl. Chem.* **1958**, *5*, 264.

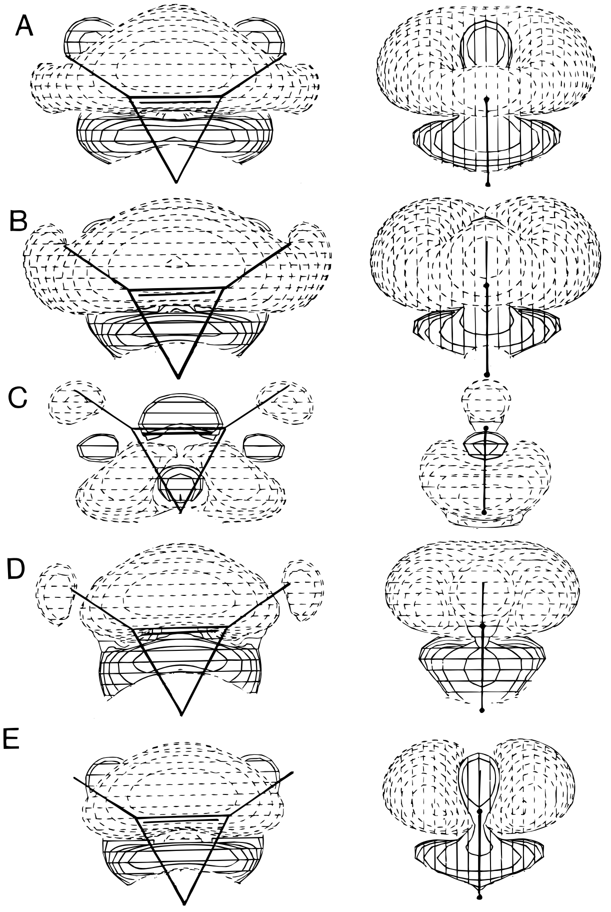


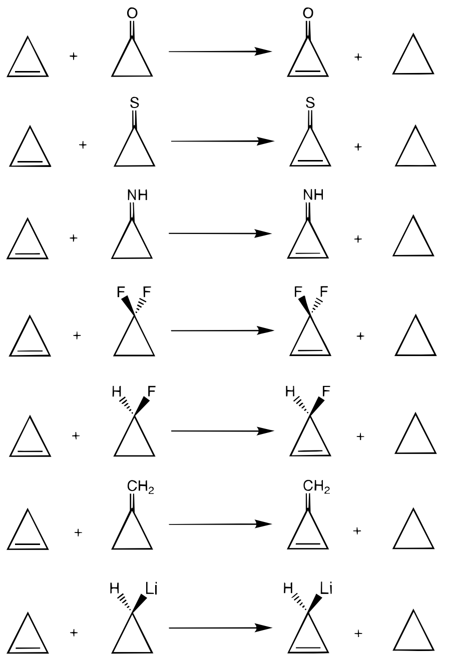
Figure 4. Electron density difference plots for the ring C═C and C−C bonds: (A) cyclopropenone minus cyclopropene; (B) cyclopropenethione minus cyclopropene; (C) cyclopropenethione minus cyclopropenone; (D) 3,3-difluorocyclopropene minus cyclopropene; (E) methylenecyclopropene minus cyclopropene. The left hand views are for the plane of the cyclopropene rings, and the right hand views correspond to a 90° rotation. The contour level is 0.001 e/au^3.

difference between cyclopropenone and cyclopropenethione (Figure 4, C). The side view shows that there is no significant π density difference between the two. These changes in electron density cannot be due to a positive charge being developed at C_3 by the substituent since this is not the case for the C═S group in which there is little difference in electronegativity between the atoms. Rather, it appears that there is a driving force for reducing the electron density associated with the C═C bond, and that it will be donated to any acceptor. It is known, for example, that both C═O and C═S are good π electron acceptors when attached to an amino group, although the details of how the electron density is accepted is somewhat different.[22] Here, the π-charge transfer is mainly to the carbon of the strongly polarized C═O group, and it is to both the C and S of the relatively unpolarized C═S group.

A 3,3-difluoro substitution also leads to a similar change in electron density distribution (Figure 4, D), and this is also the case for methylenecyclopropene (Figure 4, E), although the net shift appears to be smaller. An integration of the region of charge density loss at the C═C double bonds gave about a 0.25 e loss when the ring is substituted by ═O or ═S. The ═CH_2 group leads to about half as large a shift.[23]

The results of these calculations may be compared with the Fulton sharing indices that correctly reproduce the conventional C−C bond orders (i.e. 1.01 for ethane, 1.90 for ethylene, and 2.85 for acetylene) (Table 3).[24] The more stable derivatives that had the largest electron density loss in the double bond

Table 2. Isodesmic Reactions for Substituted Cyclopropenes



	ΔH (kcal/mol)		
	MP2	MP2*	B3LYP
[13]	-22.6	-22.4	-21.8
[14]	-21.5	-20.0	-21.8
[15]	-14.6	-14.6	-14.0
[16]	-9.7	-10.0	-9.3
[17]	-9.2	-9.7	-9.0
[18]	-8.2	-8.7	-9.1
[19]	4.3	3.8	4.0

Table 3. Bond Indices for Cyclopropene Derivatives

compound	C−C index	C═C index
cyclopropene	1.010	1.938
3,3-difluorocyclopropene	1.028	1.793
methylenecyclopropene	1.104	1.781
cyclopropenone	1.099	1.706
cyclopropenethione	1.166	1.678

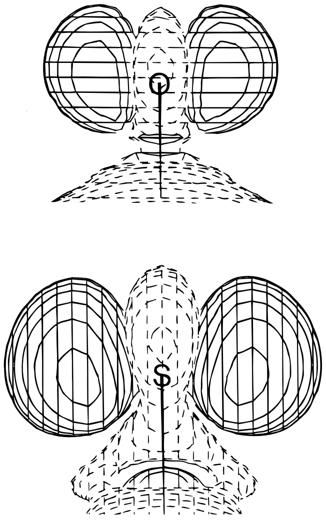


Figure 5. Electron density difference maps for the C═O and C═S bonds: (top) cyclopropenone minus cyclopropanone; (bottom) cyclopropenethione minus cyclopropanethione. The contour level is 0.001 e/au^3. The vertical lines indicate the C−O or C−S bond.

---

(22) Wiberg, K. B.; Rablen, P. R. *J. Am. Chem. Soc.* **1995**, *117*, 2201.

(23) The interaction of the CH2 group with the cyclopropane ring has been studied by Norden, T. D.; Staley, S. W.; Taylor, W. H.; Harmony, M. D. *J. Am. Chem. Soc.* **1986**, *108*, 7912. They found opposing σ and π charge shifts and concluded that the interaction led to stabilization on the order of that for butadiene.

Table 4. Relative Energies of C_4H_4 and C_4F_4 Isomers

	C_4H_4				C_4F_4		
compound	HF[a] 4-31G	MP2 6-31G*	MP2 6-311+G*	B3LYP 6-311+G*	MP2 6-31G*	MP2 6-311+G*	B3LYP 6-311+G*
but-3-ene-1-yne	0.0	0.0	0.0	0.0	0.0	0.0	0.0
butatriene	11.6	11.9	12.3	3.0	−3.6	−3.5	−10.2
methylenecyclopropene	36.2	24.7	25.9	23.7	22.6	22.8	20.8
cyclobuta-1,3-diene	45.7	37.5	37.6	39.1	32.0	30.7	30.5
bicyclo[1.1.0]but-1(2)-ene	46.6	45.0	44.5	47.7	16.6	16.3	20.4
2-bicyclo[1.1.0]butylidene[b]	78.2	51.8	51.8	54.9	22.9	20.6	24.2
tetrahedrane	93.8	61.1	61.9	65.2	108.9	108.9	107.0
bicyclo[1.1.0]but-1(3)ene	117.0	63.3	64.0	72.4	14.7	16.8	34.2
cyclobutyne	117.5	80.3	78.1	85.9	43.8	44.5	59.8

[a] Reference 25. [b] The stable structure for cyclobuta-1,2-diene (see text).

region also have the smallest C═C bond index. Thus, the energies, the electron density difference plots, and the sharing indices lead to a consistent picture of the origin of the stabilization of 3-substituted cyclopropenes.

There is also the question of how much of the electron density that is taken from the double bond appears at the carbon vs oxygen of a C═O group, and at the carbon vs sulfur of a C═S group. This was examined by obtaining B3LYP/6-311+G** wavefunctions for cyclopropenone and cyclopropanone using the average C═O bond length, but optimizing all of the other parameters. A cubic array of electron density was created for each compound, and that for cyclopropanone was subtracted from that for cyclopropenone. The difference density is shown in Figure 5A. The same procedure was used for the C═S derivatives, and the corresponding difference density plot is shown in Figure 5B. It can be seen that considerably more π-electron density is transferred to the sulfur than to the oxygen. Thus, the electron density changes for cyclopropenone and cyclopropenethione exactly parallel those for acetamide and thioacetamide,[22] and the stabilization energies are quite similar in the two cases.

3. The C_4H_4 and C_4F_4 Compounds

The C_4H_4 series of compounds present a variety of structural types including several small ring compounds. They have been examined by Hehre and Pople at the 4-31G//STO-3G level.[25] We were interested in seeing how large a change in relative energy might be found on replacing the hydrogens by fluorine. It is now readily possible to study the C_4H_4 compounds at a higher theoretical level than was possible in the previous study. Therefore, both sets of compounds were studied via geometry optimizations at the MP2/6-31G* and B3LYP/6-311G** levels along with single point MP2/6-311G** calculations using the MP2/6-31G* geometries. The relative energies, corrected for the zero-point energy differences (MP2/6-31G* for C_4H_4, HF/6-31G* for C_4F_4), are summarized in Table 4.[26]

In accord with the previous study, but-1-yne-3-ene was the most stable C_4H_4 isomer, and butatriene was the next more stable isomer. However, with the perfluoro derivatives, the relative energies are reversed, probably due to the destabilization of fluorine attached to a CC triple bond. This can be seen in the following isodesmic reaction:

$$\mathrm{HC{\equiv}CF + CH_3CH_3 \rightarrow HC{\equiv}CH + CH_3CH_2F} \quad \Delta H = -12.9\ \mathrm{kcal/mol}$$

A fluorine prefers to be attached to a saturated carbon vs an acetylenic carbon by 13 kcal/mol. When the comparison is made with an vinylic carbon:

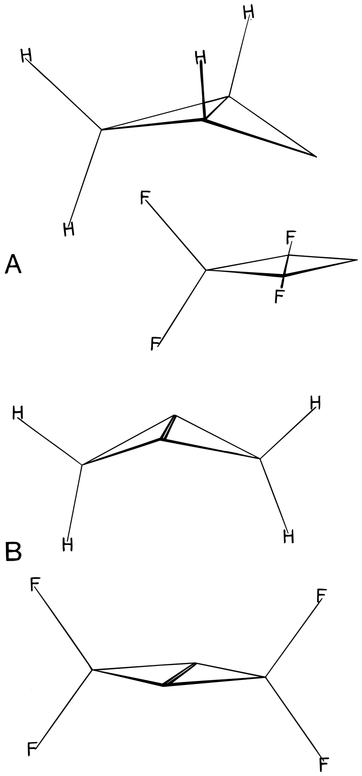


Figure 6. Structures of bicyclo[1.1.0]butenyl-2 and its perfluoro derivative (A), and of bicyclo[1.1.0]but-1(3)-ene and its perfluoro derivative (B).

$$\mathrm{H_2C{=}CHF + CH_3CH_3 \rightarrow H_2C{=}CH_2 + CH_3CH_2F} \quad \Delta H = +3.5\ \mathrm{kcal/mol}$$

a small preference is found for the fluorine to be attached to the ethylenic carbon. This probably results from the polarization of the C═C double bond by the fluorine.[27]

The two sets of MP2 calculations gave essentially the same relative energies. In most cases, there was reasonably good agreement between the MP2 and B3LYP calculations, but with butatriene there was a large difference. Thus, it appears that the B3LYP model leads to significant errors with butatriene. The same conclusion may be reached in the perfluoro series. The following discussion will make use of the MP2 relative energies.

---

[24] The sharing indices were calculated using the B3LYP wavefunctions.

[25] Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 6941.

[26] The total energies and zero-point energies are available as Supporting Information.

[27] Wiberg, K. B.; Rablen, P. R. To be published.

Table 5. Sharing Indices for Some C_4H_4 and C_4F_4 Derivatives

compound	bond	MP2 6-31G*	B3LYP 6-311+G**	sharing index
butatriene	C1=C2	1.3237	1.3150	1.795
	C3=C3	1.2759	1.2656	2.019
butatriene-F4	C1=C2	1.3167	1.3080	1.612
	C2=C3	1.2714	1.2505	2.019
vinylacetylene	C1≡C2	1.2229	1.2058	2.697
	C2−C3	1.4290	1.4224	1.165
	C3=C4	1.3442	1.3382	1.788
vinylacetylene-F4	C1≡C2	1.2152	1.1979	2.479
	C2−C3	1.4140	1.4081	1.129
	C3=C4	1.3392	1.3343	1.513
methylenecyclopropene	H_2C=C2	1.3317	1.3295	1.759
	C2−C3	1.4462	1.4420	1.104
	C3=C4	1.3277	1.3178	1.781
methylenecyclopropene-F4	H_2C=C2	1.3175	1.3117	1.643
	C3−C3	1.4632	1.4580	1.038
	C3=C4	1.3114	1.3033	1.644
cyclobuta-1,3-diene	C−C	1.5666	1.5775	0.973
	C=C	1.3450	1.3333	1.876
cyclobuta-1,3-diene-F4	C−C	1.5790	1.5901	0.870
	C=C	1.3318	1.3184	1.683
bicyclobut-1(2)-ene	C1=C2	1.3589	1.3696	1.583
	C1−C3	1.7909	1.8156	0.569
	C2−C3	1.4373	1.4153	1.293
	C1−C4	1.5148	1.5276	0.936
	C3−C4	1.4812	1.4867	1.092
bicyclobut-1(2)-ene-F4	C1=C2	1.3453	1.3665	1.444
	C1−C3	1.8670	1.9114	0.481
	C2−C3	1.4332	1.4003	1.204
	C1−C4	1.5148	1.5276	0.894
	C3−C4	1.4812	1.4867	0.925
cyclobuta-1,2-diene	C1=C2	1.4320	1.4259	1.307
	C1−C3	1.5998	1.6098	0.693
	C1−C4	1.4985	1.5016	1.009
cyclobuta-1,2-diene-F4	C1=C2	1.4105	1.4012	1.283
	C1−C3	1.8282	1.8448	0.480
	C1−C4	1.5037	1.5059	0.903
tetrahedrane	C−C	1.4770	1.4794	1.025
tetrahedrane-F4	C−C	1.5009	1.4976	0.933
bicyclobut-1(3)ene	C1−C2	1.4886	1.4938	0.998
	C1=C3	1.4121	1.3710	1.617
bicyclobut-1(3)ene-F4	C1−C2	1.5846	1.5055	0.990
	C1=C3	1.4425	1.4316	1.295
cyclobutyne	C1≡C2	1.2754	1.2425	2.514
	C2−C3	1.5781	1.6222	0.844
	C1−C4	1.5152	1.4953	1.048
cyclobutyne-F4	C1≡C2	1.2809	1.2402	2.470
	C2−C3	1.5418	1.5640	0.818
	C1−C4	1.5230	1.5290	0.837

With the exception of tetrahedrane, fluorination was calculated to lead to stabilization relative to butatriene or but-3-en-1-yne. Cyclobuta-1,2-diene is bent, has a relative short C1−C3 distance, and is probably best described as a 2-bicyclo[1.1.0]-butylidene (Figure 6). The same can be said for the perfluoro derivative, except that the latter is almost planar, whereas the former is bent. Tetrahedrane is calculated to be considerably destabilized. Here, both HF/6-31G* and MP2/6-31G* frequency calculations found a pair of degenerate imaginary modes for perfluorotetrahedrane. When the imaginary mode was followed down to the adjacent minimum on the potential energy surface, perfluorocyclobuta-1,3-diene was formed. Tetrahedrane itself is a minimum on the potential energy surface.

Whereas bicyclo[1.1.0]but-1(3)-ene is calculated to be puckered, the perfluoro derivative is almost planar (Figure 6). This is probably another manifestation of the stabilization of cyclopropenes by fluorine substitution, and it may be noted that the perfluoro compound has a much lower relative energy than its all-hydrogen analog.

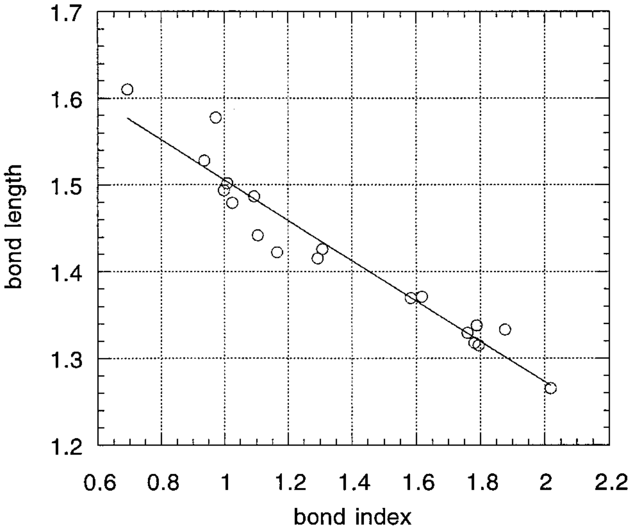
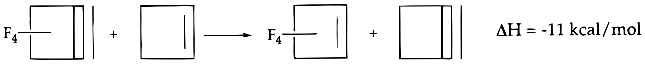


Figure 7. Relationship between bond lengths and bond indices for the C_4H_4 and C_4F_4 derivatives.

The data in Table 4 only provide relative energies for the two series of compounds, and do not directly address the question of whether or not F stabilizes compounds such a cyclobutyne. One way in which to obtain information on this question is to examine the reaction:



It is found to be exothermic, indicating that fluorine substitution destabilizes cyclobutyne relative to cyclobutene.[28] In this connection, it may be noted that perfluoro-2-butyne is similarly destabilized with respect to 2-butyne.[29]

$$HC{\equiv}CCF_3 + C_3H_8 \rightarrow HC{\equiv}CCH_3 + CH_3CH_2CF_3 \quad \Delta H = -14 \text{ kcal/mol}$$

The differences between the C_4H_4 and C_4F_4 series may also be examined using the bond indices. The calculated bond lengths and indices are shown in Table 5. The MP2 and B3LYP bond lengths are in reasonable agreement, and the few known structures in this series[30] lie between the two calculated structures. The general trend is for all of the bond lengths to decrease on fluorine substitution. The sharing indices for the carbon−carbon double bonds decrease substantially on fluorine substitution, suggesting that the electron densities in these bonds are reduced. In view of the results shown above for the cyclopropene derivatives, this should lead to stabilization. It might be noted that for most bonds there is a linear relationship between the C−C bond lengths and the sharing indices (Figure 7).

Conclusions. Fluorine strongly prefers to be bonded to carbon orbitals having high p character. Thus, methyl substitution leads to stabilization of methylene fluoride, whereas fluorine substitution on cyclopropane leads to destabilization. The largest destabilization was found with tetrahedrane.

---

(28) At the MP2/6-311+G* level, the energies of cyclobutene and perfluorocyclobutene are −155.46763 and −551.83013, respectively, and the MP2/6-31G* zero-point energies are 58.5 and 38.3 kcal/mol.

(29) Shobe, D. S. Ph.D. Thesis, Yale, 1994.

(30) Vinylacetylene: CC = 1.215(3) , C=C = 1.344(4), C−C = 1.215-(3) (Fukuyama, T.; Kuchitsu, K.; Morino, Y. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 379). Butatriene: C_1=C_2 = 1.318(10) , C_2=C_3 = 1.283(15) (Almenningenm A.; Bastiansen, O.; Traetteberg, M. *Acta Chem. Scand.* **1961**, *15*, 1557).

On the other hand, small rings having double bonds are stabilized by fluorine substitution, as is found with 3,3-difluorocyclopropene and many of the C_4F_4 cyclic compounds.

Calculations. The ab initio calculations and the NBO calculations were carried out using Gaussian-95.[31] The AIM electron populations and the Fulton sharing indices were calculated using AIM96.[32]

Supporting Information Available: Tables of calculated energies and zero-point energies (4 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

JA971413B

---

(31) M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortis, J. B. Foresman, J. Cioslowski, B. B. Sefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez and J. A. Pople. Gaussian 95, Development Version (Rev. D) Gaussian, Inc., Pittsburgh, PA 1995.

(32) Keith, T. A., Yale University. This is based on PROAIM: Biegler-Konig, F. W.; Bader, R. F. W.; Tang, T.-H. *J. Comput. Chem.* **1982**, *3*, 317.