Tetrahedron Vol. 40, No. 20, pp. 3945 to 3948, 1984
Printed in the U.S.A.

0040-4020/84 $3.00 + .00

The Effect of Fluorine Substituents on the Structure of Cyclopropane. The Structure of 4,4,8,8-Tetrafluorotricyclo-$(5.1.0.0^{3,5})$octane.

WILLIAM R. DOLBIER, JR.

Department of Chemistry, University of Florida, Gainesville, FL 32611

MARIA ODANIEC, EWA GOMULKA, MARIUSZ JASKOLSKI and HENRYK KORONIAK

Faculty of Chemistry, A. Mickiewicz University,
ul. Grunwaldzka 6, 60-780 Poznan, Poland

(*Received in USA* 23 *July* 1984)

Abstract: The first x-ray structure determination of a fluorine-substituted cyclopropane is reported. The title compound was synthesized via bis difluorocarbene addition to 1,4-cyclohexadiene and its structure determined via x-ray crystallographic techniques. Its cyclopropane bondlengths (1.552 and 1.452 Å) are very similar to those reported earlier in a microwave study of the parent 1,1-difluorocyclopropane, while its cyclohexane ring is virtually planar.

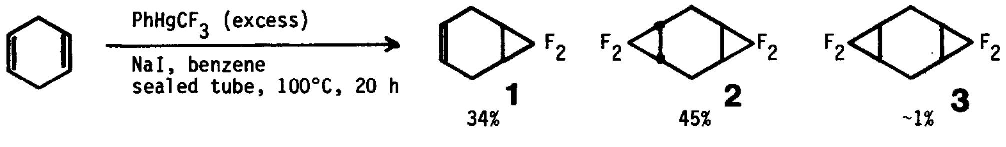
The structures of gem-difluorocyclopropanes and the relationship of such structures to their thermal reactivity have been subjects of much theoretical and experimental interest in recent years. In spite of such interest, there have been in fact very few actual experimental determinations of structure of fluorine-substituted cyclopropanes. A microwave study of 1,1-difluorocyclopropane[1] provided the initial evidence for a dramatic bond lengthening of the C_2-C_3 bond, which is opposite to the CF_2 group. Such lengthening of this bond, when combined with the observed, also dramatic shortening of the C_1-C_2 bonds was consistent with our experimental observation that the C_2-C_3 bond is weakened by 8-9 kcal/mole relative to the parent hydrocarbon.[2]

The microwave structure determinations of cis-1,2,3-trifluorocyclopropane[3] and perfluorospiropentane[4] have been reported, as have partial structures of 1,1,2,2-tetrafluorocyclopropane,[5] cis- and trans-1,2-difluorocyclopropane.[6] Structure determinations have also been made for a number of other substituted cyclopropanes, such as amino,[7] nitro,[8] cyano,[9] 1,1-dichloro[10] and 1,1-dibromo-trans-2,3-diphenylcyclopropane.[11] Recent theoretical studies on the effect of substituents on the structure of cyclopropane indicate that one can calculate such structures with reasonable accuracy.[12] Fluorine substituents, particularly gem-difluoro substituents, appear to have the most dramatic effect upon the structure of cyclopropane.

We wish to report at this time the first x-ray structure determination of a gem-difluorocyclopropane species, that of anti-4,4,8,8-tetrafluorotricyclo$(5.1.0.0^{3,5})$octane 2.

Synthesis.

The title compound was synthesized as shown below, by the addition of difluorocarbene to 1,4-cyclohexadiene using the Seyferth carbene precursor, phenyl trifluoromethylmercury.[13]



Products **1**, **2** and **3** were isolated via preparative glpc, and their ^{1}H,^{19}F and ^{13}C NMR spectra were consistent with their assigned structures. **1**: ^{1}H ($CDCl_3$, TMS, 300 MHz) δ 5.56 (s, 2H), 2.36-2.18 (m, 4H), 1.69-1.63 ppm (m, 2H); ^{19}F ($CDCl_3$, upfield from $CFCl_3$ in ppm) ϕ 127.7 (AB, J_{FF} = 155.2, J_{FH} = 14.2 and 2.3 Hz), 154.2 ppm (AB, J_{FF} = 155.2, J_{FH} < 1 Hz); ^{13}C ($CDCl_3$, downfield from TMS in ppm) δ 122.67 (s, $C_{3(4)}$), 16.7 (s, $C_{2(5)}$) 16.5 (t, $C_{1(6)}$, J_{CF} = 10 Hz), 115.53 (t, C_7, J_{CF} = 285.6 Hz). **2**: ^{1}H δ 1.91 (br. s, 4H), 1.52 (br. s, 2H), 1.47 (br. s, 2H); ^{19}F ϕ 127.9 (AB, J_{FF} = 158 Hz, J_{FH} = 14.1 Hz), 152.3 ppm (AB, J_{FF} = 158 Hz); ^{13}C δ113.3 (t, $C_{4(8)}$, J_{CF} = 113.3 Hz), 14.6 (t, $C_{1(3,5,7)}$, J_{CF} = 10.1 Hz), 6.6 ppm (s, $C_{2(6)}$); mp 68-69°C. **3**: ^{19}F ϕ 126.7 (AB, J_{FF} = 150 Hz, J_{FH} = 13.4 Hz), 154 ppm (AB, J_{FF} = 150 Hz), ^{13}C δ 113.7 (t, $C_{4(8)}$, J = 288.1 Hz), 17.5 (t of d, $C_{1(3,5,7)}$, $^{2}J_{CF}$ = 12.1, $^{4}J_{CF}$ = 5.5), 6.5 ppm (t, $C_{2(6)}$, $^{3}J_{CF}$ = 3.8 Hz); mp 52-53°C.

X-Ray Structure Determination

Single crystals were obtained by slow sublimation at 25°C. X-Ray diffraction data were collected from a well-formed crystal with dimensions 0.5 x 0.4 x 0.4 mm, with the specimen sealed in a glass capillary because of volatility. The crystals are orthorhombic, *Cmca*, with a = 7.2029 (6), b = 8.6597 (6), c = 11.9478 (8) Å, V = 745.26 (9) $Å^3$, μ (Cu k α) = 13.3 cm^{-1}; D_x = 1.605 gcm^{-3} for Z = 4 which requires that the molecules have a 2/*m* (C_{2h}) symmetry. 317 unique reflections were measured of which 266 had $I \geq 1.96\ \sigma\ (I)$ and were considered observed. The structure was solved by direct methods and refined by least-squares techniques (with counter weights) to an R value of 0.036. The final refinements included anisotropic non-H atoms, isotropic H atoms and an empirical isotropic extinction parameter x, used to correct the calculated structure factors according to $F_c^1 = F_c\ (1 - x\ F_c^2/\sin\theta)$, which converged at 35 (6) · 10^{-7}. All calculations were performed using SHELX[14] and local programs.[15] Final positional and thermal parameters are given in Table I.[16]

Table I. Final Fractional Coordinates and Thermal Parameters.

atom	x/a	y/b	z/c	U_{11}/U_{iso}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	-0.1077(3)	0.5464(2)	0.1011(1)	0.043(1)	0.049(1)	0.042(1)	0.0047(9)	0.0048(9)	-0.0042(8)
C(2)	-0.2186(4)	0.5	0.0	0.037(2)	0.078(2)	0.047(2)	0.0	0.0	0.000(1)
C(3)	0.0	0.4339(3)	0.1636(2)	0.050(2)	0.051(2)	0.041(2)	0.0	0.0	0.003(1)
F(1)	0.0	0.4330(3)	0.2773(1)	0.073(1)	0.114(2)	0.042(1)	0.0	0.0	0.0170(9)
F(2)	0.0	0.2851(2)	0.1293(1)	0.072(1)	0.047(1)	0.092(1)	0.0	0.0	0.0090(8)
H(1)	-0.160(4)	0.624(2)	0.147(2)	0.061(6)					
H(2)	-0.300(4)	0.585(3)	-0.024(2)	0.075(7)					

Structure

The molecules are located at the crystallographic 2/*m* special positions with the central six-membered ring being *exactly planar*, and the two cyclopropane rings being *anti*. A stereoscopic thermal-ellipsoid view of the molecule with numbering of the asymmetric-unit atoms is shown in Fig. 1.[17] Bond distances and angles are given in Table II.

Table II. Bond Distances (Å) and Angles (°).

C(1)-C(1')	1.552(4)	C(2)-C(1)-C(3)	121.3(2)	C(1)-C(2)-H(2')	107(1)
C(2)-C(1)	1.503(2)	C(2)-C(1)-C(1')	122.1(2)	C(1)-C(2)-C(1'')	115.8(3)
C(3)-C(1)	1.452(3)	C(1')-C(1)-C(3)	57.7(2)	H(2)-C(2)-H(2')	106(4)
C(3)-F(1)	1.359(3)	C(2)-C(1)-H(1)	117(1)	C(1)-C(3)-C(1')	64.6(3)
C(3)-F(2)	1.352(3)	H(1)-C(1)-C(1')	113(1)	C(1)-C(3)-F(1)	121.2(2)
C(1)-H(1)	0.95(2)	C(3)-C(1)-H(1)	113(1)	C(1)-C(3)-F(2)	118.9(2)
C(2)-H(2)	0.98(2)	H(2)-C(2)-C(1)	110(1)	F(1)-C(3)-F(2)	107.3(2)

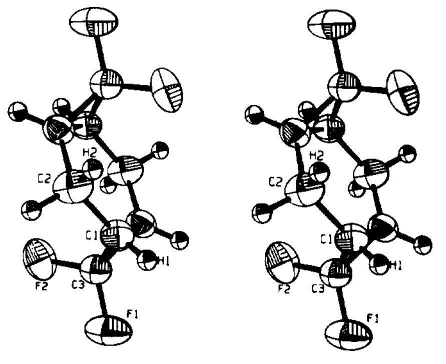


Fig. 1
Thermal-ellipsoid stereoscopic view of the title molecule. Non-H atom ellipsoids have been drawn at 50% probability level.[17] H-atom spheres are on arbitrary scale.

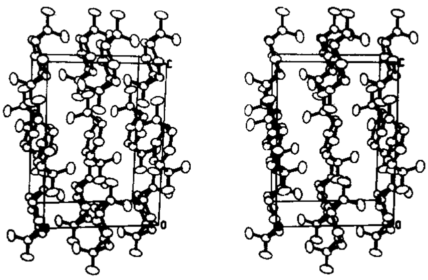
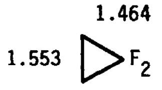
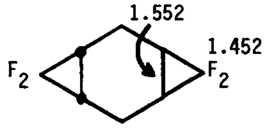


Fig. 2
Stereoscopic view of the arrangement of the molecules in the unit cell.

DISCUSSION

Comparing the observed bond lengths of **2** with those of 1,1-difluorocyclopropane one can see that their respective bond lengths are almost identical. In comparison to the observed C-C bond length of 1.514 Å for unsubstituted cyclopropane,[18] each shows a substantial bond lengthening for the C-C bond opposite to the CF_2 group along with a similarly impressive bond shortening for the adjacent bonds. While the observed bond lengthening not unexpectedly has been shown to give rise to a substantial (i.e. 8-10 kcal/mole) concommitant weakening of the bond to homolytic cleavage,[2] the shortening of the adjacent bond does not seem to be accompanied by an analogous strengthening. Indeed, while ab-initio and force constant calculations imply that this bond should be strengthened, what little kinetic experimental evidence exists indicates a slight weakening (i.e. 1-2 kcal/mole).[2] The effect of substituents, such as fluorine, on the molecular parameters of cyclopropane has already been rationalized effectively.[12] The x-ray structure determination of 4,4,8,8-tetrafluorotricyclo(5.1.0.0^{3,5})-octane presented here is significant in that it (1) corroborates the earlier rather remarkable microwave results on 1,1-difluorocyclopropane and (2) gives evidence that even when incorporated into a more complex molecule, such a gem-difluorocyclopropane entity retains its basic structure.





Acknowledgement. Support of this research in part by the National Science Foundation is acknowledged by WRD with thanks.

References and Footnotes

1. Perreta, A. T.; Laurie, V. W. J. Chem. Phys. **1975**, 62, 2469.
2. Dolbier, W. R. Jr. Acc. Chem. Res. **1981**, 14, 195.
3. Gillies, C. W. J. Mol. Struct. **1976**, 59, 482.
4. Dolbier, W. R. Jr.; Sellers, S. F.; Smart, B. E.; Oberhammer, H. J. Mol. Struct. **1983**, 101, 198.

5. Stigliani, W. M.; Laurie, V. W. 30th Symposium on Molecular Spectroscopy, Paper TFS, Columbus, Ohio, 1975. See also reference 12 (d).

6. (a) Laurie, V. W.; Sengupta, S. K. 32nd Symposium on Molecular Spectroscopy, Paper TGS, Columbus, Ohio 1977; (b) Sengupta, S. G.; Laurie, V. W. 31st Symposium on Molecular Spectroscopy, Paper MS4, Columbus, Ohio, 1976.

7. Harmony, M. D.; Bostrum, R. E.; Hendrickson, D. K.*J. Chem. Phys.* **1975**, *62*, 1599.

8. Mochel, A. R.; Britt, C. O.; Boggs, J. E. *J. Chem. Phys.* **1973**, *58*, 3221.

9. Pearson, R. Jr.; Choplin, A.; Laurie, V. W. *J. Chem. Phys.* **1975**, *62*, 4859.

10. Cole, K. C.; Gilson, D. F. R. *J. Mol. Struct.* **1975**, *28*, 385.

11. Jason, M. E.; Ibers, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 6612.

12. (a) Hoffmann, R. *Tetrahedron Lett.* **1970**, 2907; (b) Gunter, H. *Tetrahedron Lett.* **1970**, 5173; (c) Durmasz, S.; Kollmar, H. *J. Am. Chem. Soc.* **1980**, *102*, 6942; (d) Deakyne, C. A.; Allen, L. C.; Craig, N. C. *J. Am. Chem. Soc.* **1977**, *99*, 3895; (3) Skancke, A. *J. Mol. Struct.* **1977**, *42*, 235.

13. Seyferth, D.; Hopper, S. P. *J. Org. Chem*. **1972**, *37*, 4070.

14. Sheldrick, G. M. SHELX-76, a program for crystal structure determination, Cambridge University, 1976.

15. Jaskolski, M. *4th Symposium on Organic Crystal Chemistry*, Poznan, September 1982, Collected Abstracts, ed. by Z. Kaluski, p. 70.

16. (a) The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lansfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication. (b) Supplementary data available includes the observed and calculated structure factors. See Notice to Authors, *Tetrahedron* **40** (2), ii (1984).

17. Johnson, C. K., ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1976.

18. Jones, W. J.; Stoicheff, B. P. *Can. J. Phys.* **1964**, *42*, 2259.