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Preliminary Note

The crystal structure of hexafluorotropone at −50 °C

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X-Ray analyses [1, 2], dipole moment and NMR measurements [3] and theoretical calculations [3, 4] indicate that tropone possesses only very limited aromatic character and that it can be adequately represented by the cycloheptatrienone form (A) with bond lengths corresponding alternately to near-double and near-single bonds. We have determined the crystal structure of hexafluorotropone [5] to assess the effect on the bonding and on the geometry of the ring of replacing the hydrogen atoms of tropone by highly electronegative fluorine substituents.

Crystals grown by sublimation are monoclinic, space group $P2_1/n$ with $a = 5.76$, $b = 9.12$, $c = 13.23$ Å, $\beta = 93.1°$ and $Z = 4$. Intensities were measured with a Stoe two-circle computer-controlled diffractometer within the range $0.1 < \sin\theta/\lambda < 0.57$. The structure was solved by direct methods and refined by least-squares analysis to an R value of 5.0% for the 614 reflections considered to be observed $[I > 2.5\sigma(I)]$. Bond lengths and angles are shown in Figure 1. Bond lengths corrected for thermal effects on the basis of rigid-body motion [6] are shown in parentheses. Estimated standard deviations are *ca.* 0.007 Å for lengths and 0.5° for angles. Chemically-equivalent (but crystallographically-independent) bonds and angles agree to well within the limits of experimental error.

The seven-membered ring is accurately planar. The maximum deviation of a carbon atom from the mean plane is 0.007 Å. The oxygen atom lies close to this plane (deviation 0.004 Å) and the maximum deviation of a fluorine atom is 0.023 Å.

The carbon–carbon formal double bonds have lengths close to the accepted value for a pure double bond (1.335 Å) [7]. The formal single bonds fall into two categories, C(1)—C(2) and C(1)—C(7) with mean length 1.443 (1.452) Å, and C(3)—C(4) and C(5)—C(6), mean length 1.400 (1.408) Å, only slightly longer than the accepted aromatic value [7]. The C(1)—C(2) and C(1)—C(7) lengths are in close agreement with the lengths of the corresponding bonds in tropone [2], as is the formal double bond C(4)—C(5). The other

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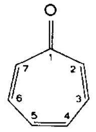

(A)

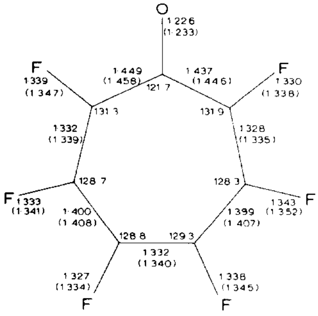

Fig. 1. Experimental bond lengths and angles. Lengths corrected for the effects of thermal motion are in parentheses.

C—C lengths are *ca.* 0.025 Å shorter than the corresponding bonds in tropone. Thus bonds where both carbon atoms carry a fluoro substituent are slightly shorter than might be expected on the basis of measurements of hydrocarbon systems (standard length of a double bond 1.335 Å and of a C(sp^2)—C(sp^2) pure single bond 1.48 Å). A similar shortening of the double bond in fluoroethylenes has been reported [8] from microwave spectroscopic studies, and in the crystal structure [9] of pentafluorobenzoic acid the mean aromatic bond length is *ca.* 0.01 Å shorter than in comparable hydrocarbon derivatives. The C—O bond is significantly shorter in hexafluorotropone than in tropone where its length is 1.258 Å. The C—F bond lengths average 1.335 (1.343) Å in good agreement with previous measurements [7 - 9] for this type of bond.

The overall picture, therefore, seems to be that the degree of π-electron delocalisation within the ring is not affected to a great extent by the fluoro substituents, but that the carbonyl oxygen atom is involved to a somewhat lesser extent in the fluoro compound. However, unlike the situation in the fluoro compound, the carbocyclic ring of tropone deviates slightly, but significantly, from planarity, adopting a boat-like conformation [2]. A similar, but more pronounced, deviation from planarity has been observed in the crystal structure of hexachlorotropone [10]. The higher stability of hexafluorotropone relative to hexachlorotropone is consistent with the planarity of the ring system in the former compound.

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1 D. J. Watkin and T. A. Hamor, J. Chem. Soc. (B), (1971) 2167.
2 M. J. Barrow, O. S. Mills and G. Filippini, J. Chem. Soc. (Chem. Commun.), (1973) 66.

3 D. J. Bertelli and T. G. Andrews, Jr., J. Amer. Chem. Soc., 91 (1969) 5280; D. J. Bertelli, T. G. Andrews, Jr. and P. O. Crews, ibid., 5286.
4 M. J. S. Dewar and N. Trinajstic, Croat. Chem. Acta, 42 (1970) 1.
5 D. J. Dodsworth, C. M. Jenkins, R. Stephens and J. C. Tatlow, J. Chem. Soc. (Chem. Commun.), (1972) 803.
6 D. W. J. Cruickshank, Acta Crystallogr., 9 (1956) 754; V. Schomaker and K. N. Trueblood, ibid., B24 (1968) 63.
7 Chem. Soc. Special Publ., No. 18, Chemical Society, London, 1965.
8 V. W. Laurie, J. Chem. Phys., 34 (1961) 291.
9 V. Benghiat and L. Leiserowitz, J. Chem. Soc. (Perkin Trans. II), (1972) 1778.
10 R. P. Dodge, R. J. Sime and D. H. Templeton, private communication to K. V. Scherer, Jr. cited in J. Amer. Chem. Soc., 90 (1968) 7352.