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PRELIMINARY NOTE

The Crystal Structure of Pentafluorotropolone

J. J. GUY and T. A. HAMOR

Department of Chemistry, University of Birmingham, Birmingham B15 2TT
(Great Britain)

X-Ray crystallographic analyses of tropolone [1] and 4-isopropyltropolone [2] indicate that the π-electron systems of these molecules are partially delocalised, delocalisation extending from the hydroxy-oxygen atom, O(2), round the ring to the carbonyl oxygen atom, O(1). The C(1)-C(2) ring bond is only slightly shorter than a $C(sp^2)-C(sp^2)$ single bond so that it seems to be involved in the delocalisation only to a small extent. The π-electron delocalisation is, however, probably affected by intra- and inter-molecular hydrogen bonding [1,3]. We now report the results of an X-ray crystal structure analysis of the fluorinated analogue, pentafluorotropolone [4].

Crystals grown by sublimation are orthorhombic, space group $P2_12_12_1$ with a = 5.89, b = 6.10, c = 19.67 Å and Z = 4. Intensities were measured with a Stoe two-circle computer-controlled diffractometer within the range $0.1 < \sin\theta/\lambda < 0.7$. The structure was solved by direct methods and refined by Fourier and least-squares calculations to an R value of 3.7% for the 761 reflections used in the analysis [$I > 2.5\sigma(I)$]. Anisotropic temperature factors were used for the heavier atoms and an isotropic temperature factor for the hydrogen atom linked to the hydroxy-oxygen atom.

Bond lengths and angles are shown in Figure 1. Bond lengths corrected for thermal effects [5] are 0.008 - 0.010 Å greater than those in Figure 1. Estimated standard deviations are ca. 0.005 Å for lengths and 0.3° for angles. The O(2)-H bond length is 0.85 ± 0.1 Å and the C(2) - O(2) - H angle 107°. The hydrogen atom is situated approximately equi-distant from the carbonyl oxygen atom of its own molecule and one belonging to a neighbouring molecule at distances of 2.06 and 2.07 Å, indicating a possible

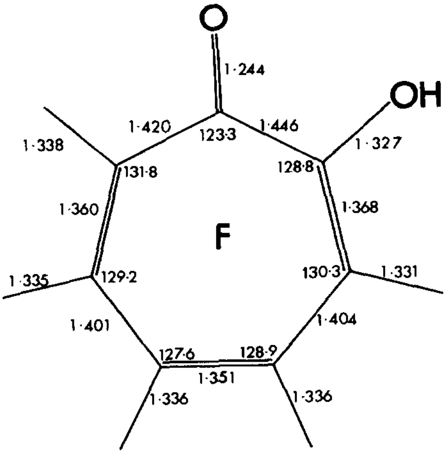

Fig.1. Pentafluorotropolone. Experimental bond lengths (Å) and angles (degrees).

bifurcated hydrogen bond. Similar hydrogen bonding occurs in the crystal structure of tropolone [1].

The seven-membered ring is planar to within the limits of experimental error, the maximum deviation of a carbon atom from the mean plane being 0.011 Å. The carbonyl and hydroxy-oxygen atoms are situated on opposite sides of this plane at distances of 0.037 and 0.012 Å. The maximum deviation of a fluorine atom is 0.059 Å, and the hydrogen atom also lies close to the ring-plane. The whole molecule is thus essentially planar and attempts to describe the carbon skeleton in terms of a shallow boat conformation, as in tropolone and 4-isopropyltropolone [3], are not appropriate. The pattern of bond angle variation within the ring is, however, similar to that observed in tropolone.

Within the ring, bond lengths in pentafluorotropolone follow the trend observed in tropolone. The carbon-carbon formal double bonds average 1.360 Å in length (uncorrected for thermal effects) compared with 1.364 Å in tropolone. Excluding the long C(1)-C(2) bond, of length 1.446 Å, the single bonds average 1.408 Å. In tropolone the C(1)-C(2) bond is 1.454 Å and the mean of the other single bonds 1.404 Å. The C(2)-O(2) length, 1.327 Å, is similar to the corresponding bond length in tropolone (1.333 Å), but the C(1)-O(1) bond is significantly shorter; 1.244 Å in pentafluorotropolone compared with 1.261 Å in tropolone. The carbon-fluorine bonds average 1.335 Å, the same as in hexafluorotropone [6].

The overall picture, therefore, seems to be that the π-electron delocalisation is not greatly affected by the substitution of fluorine for hydrogen, but that in pentafluorotropolone the carbonyl oxygen atom is involved to a somewhat lesser extent in the electron delocalisation. An identical conclusion was reached [6] by comparing bond lengths in the crystal structures of tropone [7] and hexafluorotropone, although the degree of π-electron delocalisation is smaller in these molecules. A possible explanation for the shorter C-O(carbonyl) bond length in the fluoro-compounds is that the fluorine atoms are involved in the electron delocalisation, so that the partial negative charge which in tropone and tropolone is concentrated largely on the carbonyl oxygen atom, is distributed also over the fluorine atoms in the fluorinated analogues.

A slight shortening of carbon-carbon bonds compared with hydrocarbon systems was noted in hexafluorotropone [6]. Such a shortening does not occur in pentafluorotropolone.

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