The Structure of 2-Chlorotropone

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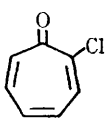
ACCURATE molecular dimensions have been recorded for the sodium salt of tropolone[1] and for tropolone hydrochloride.[2] We now report an *X*-ray structure determination for 2-chlorotropone (I).



(I)

Crystals grown by sublimation are orthorhombic, space group $Pna2_1$ with $a = 12{\cdot}43$, $b = 12{\cdot}57$, $c = 4{\cdot}01$ Å and four molecules in the cell. Intensities were estimated visually from equi-inclination Weissenberg photographs. Of the 760 reflections recorded with Cu–$K\alpha$ radiation, 170 were too weak to be measured and were assigned half the minimum observable intensity.

The structure was solved by Fourier methods and refined by least-squares to an *R*-value of 0·107. Hydrogen atoms were located from a difference Fourier and were included in the refinement with isotropic thermal parameters. Anisotropic parameters were refined for the heavier atoms. The bond lengths resulting from the analysis are shown in the Figure. The five C–H bonds vary from 1·03 to 1·21 Å (mean 1·11 Å). Standard deviations are approximately 0·02 Å for C–C and C–O, 0·01 Å for C–Cl, and 0·15 Å for C–H. The seven-membered ring is planar to within the limits of experimental error. The maximum deviation of a carbon atom from the mean plane is 0·014 Å and of a hydrogen atom 0·21 Å. The chlorine atom lies close to this plane but the oxygen is displaced by 0·07 Å.

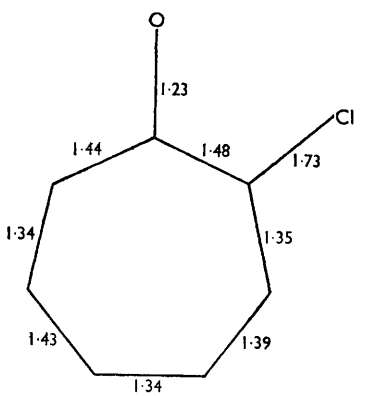


FIGURE. *Experimental bond lengths.*

The π-electron system is partially delocalised, carbon–carbon double-bond lengths compare with 1·334 Å for an olefinic bond, and carbon–carbon single bonds compare with 1·48—1·50 Å for the C_{sp^2}–C_{sp^2} single bond.[3,4] Indeed this latter value agrees nicely with our C-1–C-2 bond length (1·48 Å) which suggests that this bond is hardly included in the π-electron delocalisation. Conjugation then stems from C-2 round to C-1 and on to the oxygen and is obviously sufficient to give a virtually planar structure.[5]

In the tropolone anion[1] the difference between short and long bond lengths is less marked, indicating a more extensively delocalised π-bond system. But here again the C-1–C-2 bond length (1·49 Å) is that of a normal C_{sp^2}–C_{sp^2} single bond and is much longer than the other C–C bonds. It is only in the tropolonium cation[2] that this bond (1·39 Å) becomes fully engaged in the π-bond system, so that π-electron delocalisation is most extensive here and least in 2-chlorotropone.

This picture of 2-chlorotropone is fully in accord with its known properties. Its limited ability to undergo substitution reactions and its ease of rearrangement to benzenoid compounds point to its limited aromatic character when measured against tropolones.

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[1] Y. Sasada and I. Nitta, *Acta Cryst.*, 1956, **9**, 205; R. Shiono, *ibid.*, 1961, **14**, 42.
[2] Y. Sasada and I. Nitta, *Bull. Chem. Soc. Japan*, 1957, **30**, 62.
[3] D. W. J. Cruickshank and R. A. Sparks, *Proc. Roy. Soc.*, 1960, *A*,**258**, 270.
[4] L. Pauling, "The Nature of the Chemical Bond", 3rd Edn., Cornell University Press, Ithaca, 1960.
[5] It is notable that an almost strain-free structure can be made from Dreiding models such that the ring is markedly boat-shaped.