

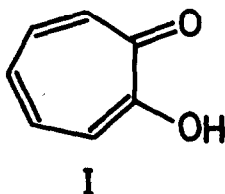
AN X-RAY STRUCTURE ANALYSIS OF TROPOLONE

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Since the non-benzenoid aromatic compounds with seven-membered ring were synthesized, the structure of its principal member, tropolone(I), has been



studied by several physico-chemical methods (1,2,3).

The crystal structure analyses have been carried out for its hydrochloride (4), sodium salt (5) and metal complexes such as cupric tropolone (6) and ferric tropolone (7), but for tropolone itself there was only

unpublished two-dimensional work so far (8). In connection with the recent study on a reevaluation of aromatic character of tropolone (9) and from our general interests to the non-benzenoid aromatic compounds, the present three-dimensional analysis was undertaken in order to reveal the detailed structure of tropolone itself.

Crystals of tropolone are monoclinic, with four molecules in a unit cell of the dimensions $a = 7.15$, $b = 12.19$, $c = 7.11$ Å and $\beta = 99.0^\circ$; the space group is $P2_1/c$. The intensity data were recorded on multiple-film equi-inclination Weissenberg photographs using $\text{CuK}\alpha$ radiation and measured visually. The 1214 independent reflections were obtained. The structure was solved by the symbolic addition method (10) and positional and anisotropic thermal parameters of non-hydrogen atoms were refined by the least-squares method. At this stage the discrepancy factor was 0.12 for the observed reflections.

The crystal structure projected down the c axis is shown in the Figure together with the distances and angles. Estimated standard deviations are

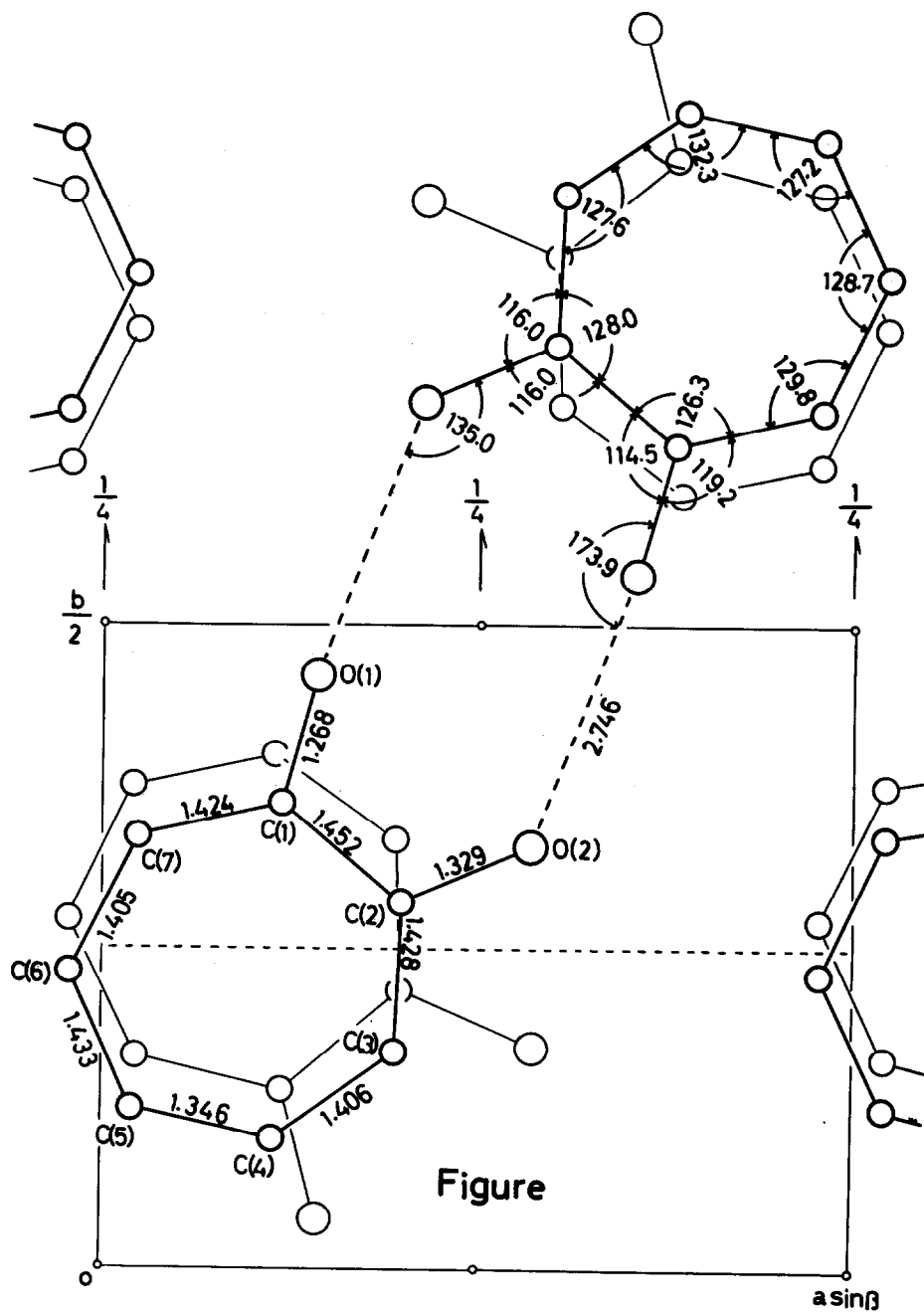
0.008 Å for lengths and 0.5° for angles. The molecule is almost planar, and the intermolecular hydrogen bonds join adjacent molecules together as dimers. The possibility of dimer formation was suggested by the two-dimensional X-ray work and by infrared study (1), and the present work confirms this suggestion.

The carbon-carbon bond lengths, apart from the C(1)-C(2) bond, show no apparent bond alternation as reported for some tropone derivatives (11,12,13). The average value is 1.407 Å, which agrees with the standard aromatic value of 1.392 Å (14). The C(1)-C(2) bond length of 1.452 Å is significantly longer than the other C-C lengths as reported in sodium tropolonate (5) and ferric tropolone (7), but the difference between the C(1)-C(2) and the other C-C lengths is smaller in tropolone itself than in the derivatives mentioned above. On the other hand, in tropolone hydrochloride (4) no such long C(1)-C(2) is observed, and it has been suggested that a net positive charge would distribute over the whole ring. Significant difference between the two C-O bond lengths shows that the hydrogen atom is bonded to O(2) rather than O(1). This is supported by the O...O-C angles shown in the Figure. Both values of C(1)-O(1) length, 1.268 Å and C(7)-C(1)-C(2) angle, 126.3°, are greater than the corresponding values in any tropone derivatives so far reported (11,12,13). The present result suggests that tropolone would not merely be 2-hydroxytropone, but would be more stabilized by the contribution of 6 π -electron system.

The possibility of existence of disorder in the crystal packing seems to be unlikely, considering the normal thermal parameters which show no marked anisotropy, a satisfactory R value and the hydrogen bonding scheme.

Further refinements are in progress, and a detailed account of this work will be published in the near future.

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