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AN X-RAY DETERMINATION OF THE STRUCTURE OF 4,5-BENZOTROPONE

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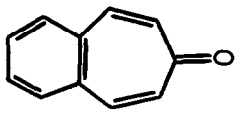
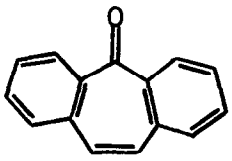
A number of works on 4,5-benzotropone (I) have been done from the physical and organic chemical point of view.



(I)



(II)

Recently, the properties of (I) have been re-examined in comparison with those of [4,5-c]furotropone and it has been suggested that aromatic character of (I) is less than that so far estimated for it (1). Among the condensed tropone derivatives, dibenzo[b,f]tropone (II) is found to be non-planar due to the steric interaction between the oxygen and the nearest neighbouring hydrogen atoms (2). In the molecule (I), however, such steric effect would not be expected; this low aromaticity should be related to other structural factors. In order to reveal these, it is necessary to obtain the detailed molecular geometry of (I).

4,5-Benzotropone (I) crystallizes in a monoclinic space group $P2_1/c$, with four molecules in a unit cell of dimensions; a=6.30, b=7.77, c=17.25Å and β= 100.3°.

Multiple-film equi-inclination Weissenberg photographs were taken for the layer lines from 0 to 4 about the a axis and from 0 to 5 about the b, using Cu-

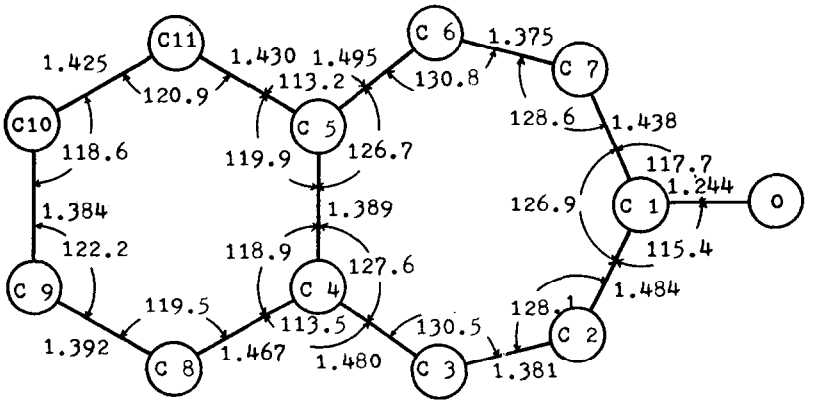
Kα radiation and the integrated intensities were estimated visually against a standard scale. The independent reflections from 1396 planes were recorded.

The phase determination was made by the symbolic addition method; the phases of 105 reflections were obtained. The first E-map gave an outline of the crystal structure. The positional and thermal parameters of non-hydrogen atoms so obtained were refined by least-squares method. Anisotropic temperature factors were applied. After five cycles of refinement, the discrepancy factor, $R=\sum||F_o|-|F_c||/\sum|F_o|$, was reduced to 0.126 for the observed reflection.

The bond lengths and angles at this stage are shown in Fig.1. The molecule could be roughly regarded as planar except for two atoms; O displaces by 0.2 Å and C(1) by 0.1 Å from the mean plane. The intermolecular contacts being normal, it seems that these displacements are not caused by intermolecular interaction. The apparent bond alternation exists in the seven-membered ring. However, the present observed bond lengths do not seem to agree well with those predicted by H.M.O. method (3).

Further refinements are in progress. A detailed account of this work will be presented in the near future.

Fig. 1.



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