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THE X-RAY DETERMINATION OF THE CONFORMATIONS OF 2,7-DIMETHYL- AND 2,7-DIPHENYL-4,5-BENZOTROPONE

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The crystal structures of the title compounds were determined by X-ray analysis. In spite of overcrowding of the carbonyl oxygen atom and the substituents, the seven-membered rings are nearly planar. There is observed bond alternation in the seven-membered ring, especially the significant elongation of the single bonds neighboring to the carbonyl.

It has been believed that tropone is aromatic as a result of the contribution from the dipolar ionic structure in which the seven-membered ring constitutes a 6π electron system. Recently, Bertelli *et al.*1) and Dewar *et al.*2) have suggested from molecular orbital consideration that tropone is not regarded as an aromatic compound but as polyolefinic. In fact, the crystal structures of several tropone derivatives 3,4,5) show, more or less, bond alternation in the seven-membered rings. It should be, however, noted that the predicted bond lengths do not agree quantitatively with those observed and, in spite of the large deformation of inner-ring angles, the seven-membered ring is almost planar. The latter exhibits a remarkable contrast to the boat form of the antiaromatic azepine system.6) Thus, more extensive investigations are needed for discussing the nature of tropone system. We have studied the crystal structures of several benzotropones7,8,9) and revealed that annelation of two benzene rings makes the conformation of tropone nucleus a deep boat form.7) This is compatible with a general idea that annelation of benzene diminishes the aromaticity of tropone.10) On the other hand, single annelation results in only a slight deviation from the planarity of the seven-membered ring.8,9) Among monobenzotropones, the molecule of 4,5-benzotropone (III) is approximately planar in crystal,8) and its high dipole moment (4.70 D)11) might indicate the contribution from an ionic structure similar to tropone. The dipole moment for 2,7-disubstituted 4,5-benzotropones is considerably reduced from that of the parent compound (III);11,12) 3.67 D for 2,7-dimethyl derivative (I) and 3.69 D for 2,7-diphenyl derivative (II). The present work has been undertaken to determine in detail the structures of I and II and to examine the

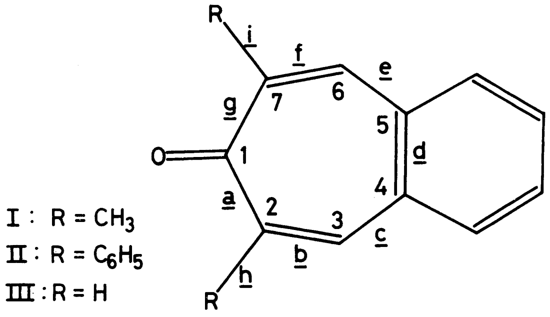

Fig. 1. Numbering of atoms and designation of bonds.

effect of the bulky substituents on the benzotropone system. Numbering of atoms and designation of bonds are shown in Fig. 1.

Crystal data of I and II are listed in the Table. For both crystals, multiple-film equi-inclination Weissenberg photographs were taken about the b and c axes, using Cu-Kα radiation. Intensities were measured by the TV densitometer.[13)]

Table. Crystal data.

Compound	I	II
Chemical formula	$C_{13}H_{12}O$	$C_{23}H_{16}O$
Melting point	84.5°	119.5°
Space group	$Pbca$	$P2_1$
Cell dimensions	a = 19.750(3) Å b = 13.448(3) Å c = 7.422(2) Å	a = 10.683(6) Å b = 16.536(4) Å c = 10.055(5) Å β = 111.88(5)°
Density measured	1.241 $g.cm^{-3}$	1.238 $g.cm^{-3}$
calculated	1.244 $g.cm^{-3}$	1.243 $g.cm^{-3}$
Number of molecules in the unit cell	8	4 (two molecules per asymmetric unit)
Absorption coefficient for Cu-Kα radiation	6.11 cm^{-1}	5.89 cm^{-1}
Number of reflections	2117 (880)*	3582 (284)*

(*Number in parentheses is that of unobserved reflections.)

Brief accounts of structure determination of I and II are as follows.

I: All non-hydrogen atoms were easily found out from the E map using 172 reflections with the signs determined by the symbolic addition procedure.[14)] The positional and anisotropic thermal parameters of the atoms were refined by the least-squares method, including isotropic hydrogen atoms found on the difference map. The final R factor was 0.067 for the observed reflections.

II: The space group $P2_1$ was inferred from systematic extinction and the values of $\langle|E|\rangle$ and $\langle|E^2-1|\rangle$. In the course of the symbolic addition procedure, seven symbols initially designated were eliminated and all 187 phases which were determined were either 0 or π. Therefore, the refinement by $\Sigma 2$ relation was performed with the provisional space group $P2_1/m$ and 500 reflections with phases obtained were used for the E synthesis. The E map with the extra mirror symmetry could be resolved by the consideration of possible bond lengths and angles, and all 48 non-hydrogen atoms were located. After several cycles of least-squares refinement with anisotropic thermal parameters of the atoms, including isotropic hydrogen atoms, the R factor was reduced to 0.073 for the observed reflections.

Molecular dimensions in I and II are shown in Figs. 2 and 3, respectively, where the crystallographically independent molecules of the latter are represented by II-1 and II-2. There are no significant differences between the corresponding bond lengths in II-1 and II-2. Moreover, the lengths of chemically equivalent bonds, such as a and g, in each molecule are equal to each other within the experimental error. The C=O bond length is 1.227 Å in I, which is in good agreement with those in the related

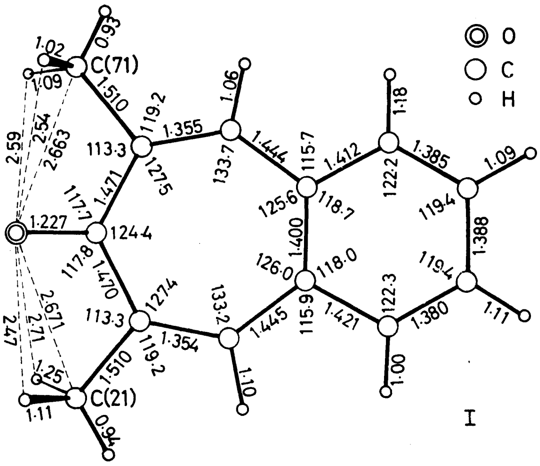

Fig. 2. The structure of I. The standard deviations in the distances and angles are 0.004-0.005 Å for C-C and C-O, 0.03-0.04 Å for C-H and O...H, and 0.3° for C-C-C and C-C-O.

compounds; 1.228 Å in III, 1.23 Å in 2,3-benzotropones,[9)] 1.232 Å in dibenzo[b,f]-tropone, 1.225 Å in tropolonyl p-chlorobenzoate,[5)] 1.234 Å in 3-azidotropone.[3)] This is consistent with the fact that the C=O stretching frequency in the infra-red spectrum of I is nearly equal to those of III and 2,3-benzotropone.[15)] However, the C=O bond in II (1.216 Å) is slightly, but not significantly, shorter than those mentione above. There is definite bond alternation in the seven-membered rings of the compounds. The average length of the formal double bonds (b and f) and that of the formal single bonds (c and e) in I are 1.355 Å and 1.445 Å, respectively, in good agreement with those in II (1.354 Å and 1.447 Å). These averages are close to those in III. On the other hand, the single bonds neighboring to the carbonyl group (average of a and g is 1.471 Å in I and 1.484 Å in II) are remarkably longer than the single bonds (c, e) and also than the corresponding bonds (a, g) in III (1.446 Å).

As seen from Fig. 2, the methyl hydrogens are locked by the oxygen atom, and the average O...H distance is 2.58 Å, nearly equal to the sum of the van der Waals radii. The average O...H(phenyl) distance in II is 2.63 Å, as a result of the torsion of the

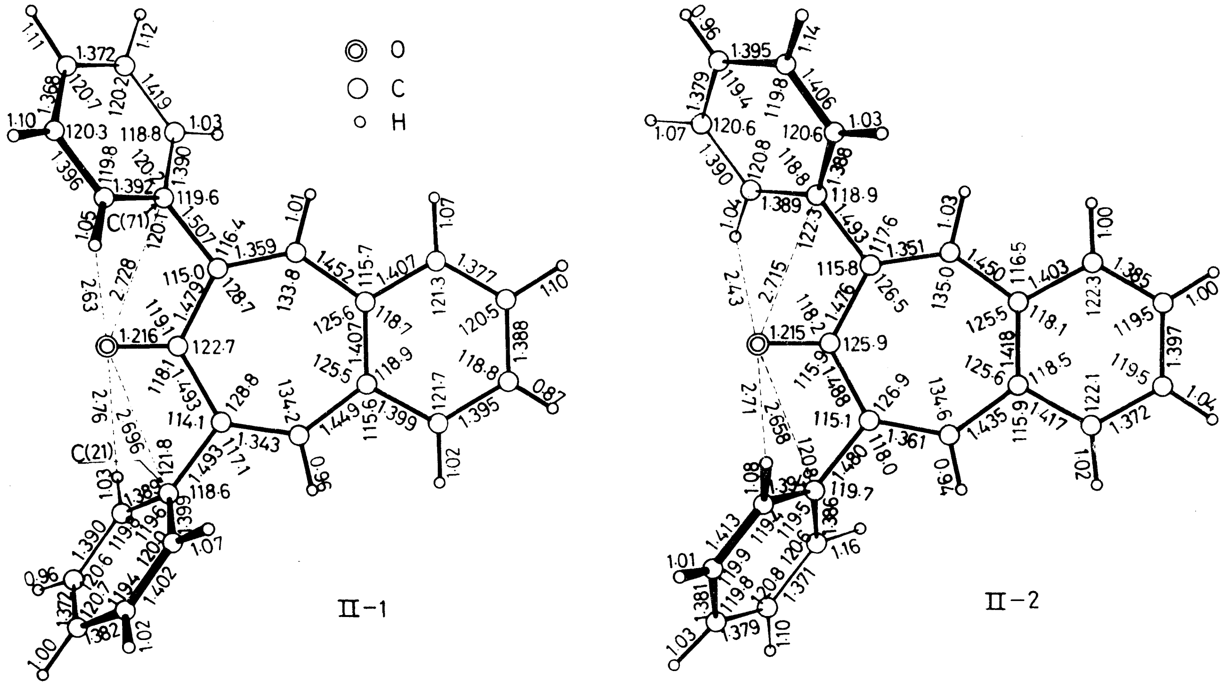

Fig. 3. The structures of II-1 and II-2. The standard deviations in the distances and angles are 0.008-0.011 Å for C-C and C-O, 0.08 Å for C-H, and 0.5-0.7° for C-C-C.

h and i bonds. The torsion angles of these bonds are 63.5° and 49.9° in II-1 and 59.8° and 45.8° in II-2. These angles are significantly different to each other, which might be due to the intermolecular effect. The average torsion angle (54.8°) is of the same order as that of the central C-C bond in 4-acetyl-2'-fluorobiphenyl (50.5°).[16) The h and i bonds are of essentially equal lengths, average being 1.493 Å. This is close to the inter-ring distance in coplanar biphenyl (1.497 Å).[17) The intramolecular O...C contacts are abnormally short, in contrast to the O...H contacts described above. The average distance of O...C(21) and O...C(71) is 2.667 Å in I and 2.699 Å in II.

The seven-membered rings of I and II are nearly planar, but , strictly speaking, they adopt a shallow boat form. In order to compare the planarity of the seven-membered ring, it is convenient to use the two angles α and β, where α is the dihedral angle between the bottom [C(2),C(3),C(6),C(7)] and the bow [C(1),C(2),C(7)] planes, and β is the angle between the bottom and the stern [C(3),C(4),C(5),C(6)]. The values of α and β are 11.5° and 4.7° in I, 7.0° and 2.8° in II-1, and 3.7° and 1.7° in II-2, respectively. The angles in I are somewhat larger than those in III (3.6° and 3.7°). It may be said, however, that the seven-membered rings in these compounds are essentially planar; the fairly rigid planarity of the tropone nucleus is kept even in the present 2,7-disubstituted derivatives. The intramolecular overcrowding in I and in II seems to be mainly relieved by the elongation of the a and g bonds. Therefore, it is suggested that the π electron interaction between the carbonyl group and the other part of the benzotropone is reduced to a considerable extent. This may explain the decrease in dipole moment as mentioned above.

Intermolecular contacts are normal, except for a few short O...H contacts; 2.47 Å in I, 2.45 Å and 2.31 Å in II.

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