X-Ray Determination of the Conformations of 5-Chloro-2,3-benzotropone and 5,7-Dibromo-2,3-benzotropone

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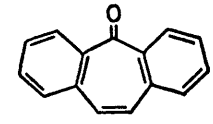
Summary Crystal structure analysis of the title compounds shows that the seven-membered rings in 2,3-benzotropone derivatives are nearly planar, though slight but significant deviations from planarity are observed.

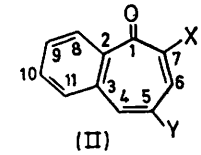
IT is generally assumed that annelation of benzene rings should lead to a loss of aromaticity of tropone,[1] and, in support of this, the seven-membered ring adopts the boat form in dibenzo[*b*,*f*]tropone (I).[2] On the basis of an n.m.r. study,[3] however, the planar form seems to be more favoured for 2,3-benzotropone (IIa). The present work has been undertaken to determine in detail the conformations of seven-membered rings in 2,3-benzotropones; the tropones (IIb) and (IIc) were studied.

Crystals of (IIb), m.p. 95—96°, are monoclinic, space group $P2_1/c$, $a = 6{\cdot}45$, $b = 3{\cdot}88$, $c = 35{\cdot}05$ Å; $\beta = 95{\cdot}7°$; $U = 873$ Å^3; $Z = 4$; $D_m = 1{\cdot}35$, $D_c = 1{\cdot}38$ g/cm^3; μ(Cu-K_α) = 31·3 cm^{-1}. Multiple-film equi-inclination Weissenberg photographs were taken about the *a* and *b* axes, using Cu-K_α radiation. 1709 independent reflexions were recorded, of which 725 were too weak to be measured.

Crystals of (IIc), m.p. 163°, are orthorhombic, space group $P2_12_12_1$, $a = 14{\cdot}39$, $b = 17{\cdot}10$, $c = 4{\cdot}01$ Å; $U =$



(I)



(II)

a, X = Y = H
b, X = H, Y = Cl
c, X = Y = Br

987 Å^3; $Z = 4$ 4; $D_m = 2{\cdot}11$, $D_c = 2{\cdot}11$ g/cm^3; μ(Cu-K_α) = 112·4 cm^{-1}. Weissenberg photographs were taken about the c axis, and precession photographs were taken for interlayer scaling. 1118 independent reflexions were recorded, of which 203 were too weak to be measured.

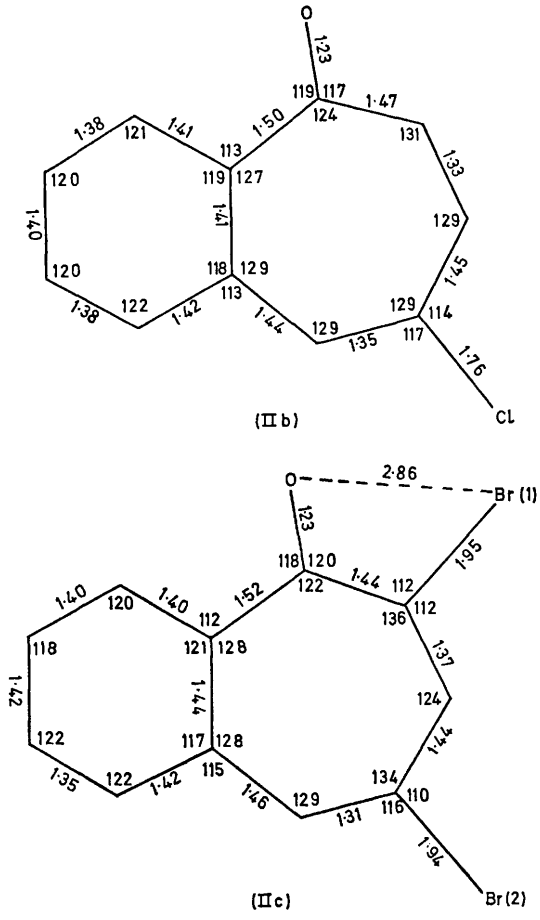


FIGURE. *Bond lengths and angles for* (IIb) *and* (IIc). *E.s.d.s are:* (IIb), 0·009 Å *for* C–Cl, 0·012 Å *for others*, 0·65° *for* ∠C–C–Cl, 0·8° *for others;* (IIc), 0·017 Å *for* C–Br, 0·026 *for others*, 1·2° *for* ∠C–C–Br, 1·7° *for others*.

The intensity data of both crystals were measured visually, and their structures were solved by the heavy-atom method. Positional and anisotropic thermal parameters of all non-hydrogen atoms were refined by least-squares, and contributions from hydrogen atoms were included. The final R value was 0·077 for (IIb) and 0·064 for (IIc), for the non-zero reflexions.

The bond lengths and angles obtained (Figure) show that there is a definite bond alternation in the seven-membered rings; the observed bond lengths are generally in good agreement with those predicted by SCF MO calculation for (IIa),[4] except for C(1)–C(2) (predicted, 1·464 Å) and C=O (predicted, 1·259 Å). The seven-membered rings in (IIb) and (IIc) are nearly planar, but detailed examination shows that they take a shallow boat form. It is interesting to compare the planarity of the seven-membered rings in terms of angles, α, β, and γ, where α is the dihedral angle between the plane (i) defined by atoms C(2,3,6,7) and the plane (ii) of atoms C(1,2,7), β is that between the plane (i) and the plane containing atoms C(3,4,5,6), and γ is the angle between the C=O bond and plane (ii). α, β, and γ are 12°, 3°, and 3° in (IIb); 6°, 1°, and 1° in (IIc); 37°, 20°, and 6° in (I), so clearly the seven-membered rings in (IIb) and (IIc) are more nearly planar than that in (I). This may be of importance in estimating the order of the annelation energy. The seven-membered ring in (IIc) is more nearly planar than that in (IIb), though the intramolecular non-bonded O · · · Br(1) distance in the former is rather short (2·86 Å). It is also interesting that all the C=O bonds in (I), (IIb), and (IIc) tend to be equatorial rather than axial with respect to the seven-membered ring, as in tricarbonyltroponechromium[5] and 4,9-methano[11]annulenone.[6]

The shortest intermolecular Br · · · Br contact in (IIc) is 3·717 Å. Such short Br · · · Br contacts are found in bis-(*m*-bromobenzoyl)methane (3·689 Å)[7] and in 1,4-dibromocycl[3,2,2]azine (3·59 Å).[8] In (IIb), the shortest Cl · · · Cl distance is 3·464 Å; a similar distance is observed in 1,2,3,4-tetrachlorobenzo[*g*]sesquifulvalene (3·39 Å).[9]

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