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CROWDED TROPOLONES. II.

THE MOLECULAR STRUCTURES OF 3,7-DIBROMO- AND 5,7-DIBROMOHINOKITIOL

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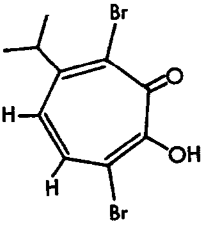
In the previous paper (1) on the molecular structure of 3,5,7-tribromohinokitiol (I), we have reported that the heptagon with 6 substituents in a row minimizes the internal strain in rather complicated manner. In order to gain more information on the way a tropolone ring release the strain, we have extended the X-ray analysis to two less crowded tropolones, 3,7-dibromohinokitiol (II) and 5,7-dibromohinokitiol (III), both with 5 substituents on heptagon.

3,7-Dibromohinokitiol (II), $C_{10}H_{10}O_2Br_2$ (2), m.p. 133-134°, crystallized from methanol, belongs to orthorhombic system, the space group is Pbca, with 8 molecules in a unit cell of dimensions a=13.487 Å, b=14.505 Å, c=11.095 Å.



II

Three-dimensional intensity data were collected on an automatic diffractometer with ω -2θ scanning technique using MoKα radiation. Total of 1064 reflections with the intensities greater than the twice of their standard deviations was obtained. The structure was solved by the heavy atom method. The final R-index after the least-squares refinement was 0.078 (3).

The molecular structure viewed along the c axis is shown in Figs. 1 and 2 with interatomic distances and bond angles. The tropone type bond alternation (4) was again observed with shorter bonds (average length: 1.353 Å) and longer bonds (1.433 Å). Two C-O bonds also have different bond lengths. Thus

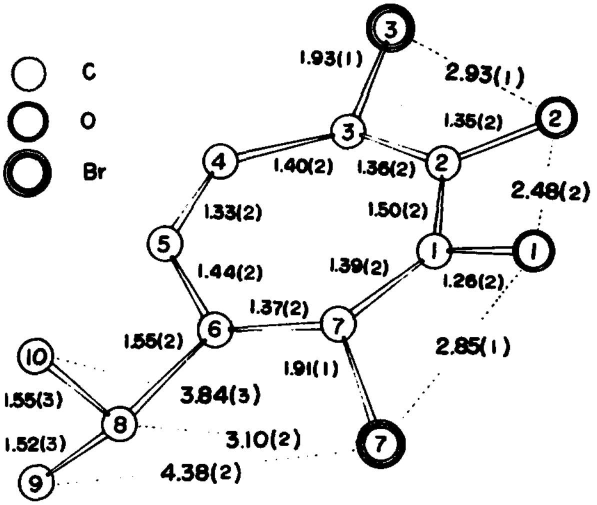


Fig. 1. Molecular geometry of II viewed along the c axis with interatomic distances. Standard deviations x10^2 Å in parentheses.

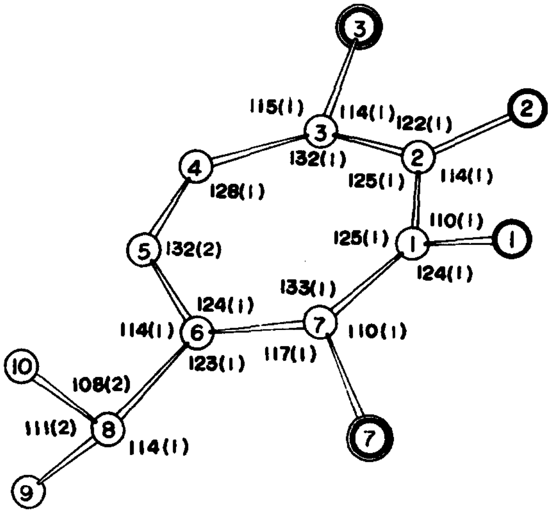


Fig. 2. Molecular geometry of II viewed along the c axis with bond angles. Standard deviations (°) in parentheses.

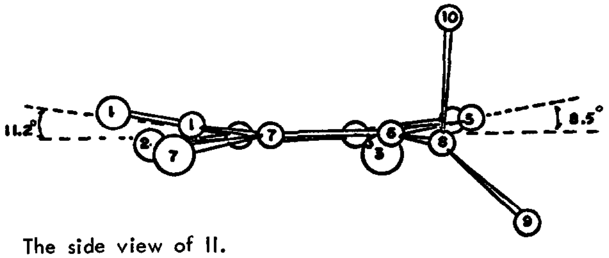


Fig. 3. The side view of II.

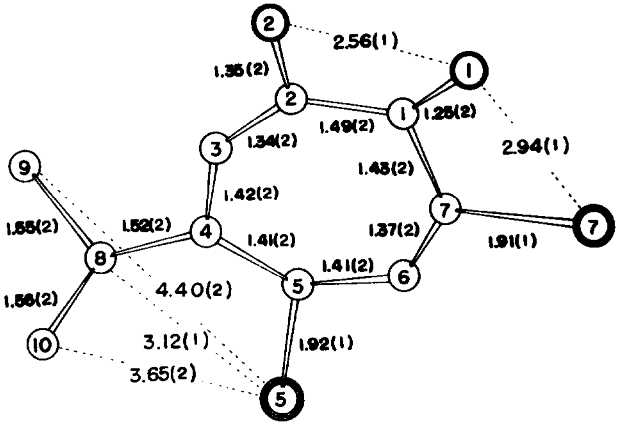


Fig. 4. Molecular geometry of III viewed along the c axis with interatomic distances. Standard deviations x10^2 Å in parentheses.

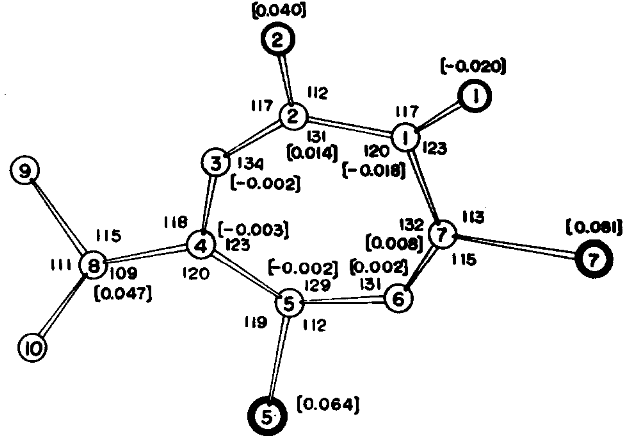
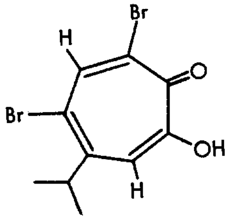


Fig. 5. Molecular geometry of III viewed along the c axis with bond angles (°) and planarity (Å). Standard angular deviations: 1° for all angles. Deviations from the least-squares plane in brankets.

the compound exists in crystalline state as 3,7-dibromo-2-hydroxy-6-isopropyltropone if commonly used numbering system is applied. The tropolone ring is deformed as shown in Fig. 3 by the steric repulsion of five substituents in a row. The calculation reveals that the two sets of atoms, C_2, C_3, C_6 and C_7, and C_3, C_4, C_5 and C_6, are in planes, respectively, forming bottom and stern part of a boat. The angle between these planes is 8.5° and that between bow part (C_2, C_1 and C_7) and the bottom plane is 11.2°. These two angles are almost half of those in (I). The interatomic distances between the adjacent substituents on the heptagon are much shorter than the respective sums of van der Waals radii (5) revealing again the presence of considerable non bonded repulsion. The vertical deformations of the substituents are also observed. In the crystalline state this molecule forms a dimeric pair by the intermolecular hydrogen bond.



III

5,7-Dibromohinokitiol (III), $C_{10}H_{10}O_2Br_2$ (6), m.p. 94-95°, crystallized from ether, belongs to monoclinic system of the space group $P2_1/a$, with 4 molecules in a unit cell of dimensions a=20.900 Å, b=11.118 Å, c=4.877 Å, β=90.04°.

Collection of intensity data, analysis and refinement were carried out in the same way as for II. 1587 Reflections with intensities greater than the twice of their standard deviations were evaluated and the final R-index was 0.077 (7).

As the five large substituents are devided in two parts by hydrogen atoms in this compound, the steric repulsion between each substituent must be smaller than that of (II). The molecular structure viewed along the *c* axis (Figs. 4 and 5) with the interatomic distances and bond angles clearly indicates the presence of bond fixation both for C-C and C-O bonds and vertical deformation of each substituent. However, the tropolone ring is completely planar within experimental errors. The compound exists as 5,7-dibromo-2-hydroxy-4-isopropyltropone as commonly called. The same type of intermolecular hydrogen bond as in II was observed also in this case.

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References and Footnotes

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7) The standard deviations of positional parameters are 0.0016 Å for bromine atoms, 0.010 Å for oxygen atoms and 0.011 Å-0.017 Å for carbon atoms.