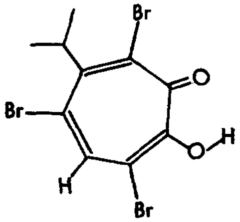
Tetrahedron Letters No. 9, pp 741 - 744, 1972. Pergamon Press. Printed in Great Britain.

CROWDED TROPOLONES. I. THE MOLECULAR STRUCTURE OF 3,5,7-TRIBROMOHINOKITIOL

Shô Itô and Yoshimasa Fukazawa
Department of Chemistry, Tohoku University, Sendai,
and Yoichi Iitaka
Faculty of Pharmaceutical Sciences, University of Tokyo, Tokyo,
Japan

(Received in Japan 18 December 1971; received in UK for publication 27 January 1972)

The molecular structure of tropolone and some of its derivatives has been described by several authors (1-8) both in the crystal and vapor phases, and a planar heptagon has been concluded for the tropolone ring in all cases. Furthermore, the detailed study (8) revealed the absence of bond fixation in tropolone. However, by increasing the number of substituents on tropolone ring, the resulting intramolecular repulsion between them may cause the deformation and/or bond fixation in the ring. In order to see the possibility and also, if it is the case, to understand the way a molecule minimizes the strain, we have commenced an X-ray crystallographic investigation on one of the most heavily substituted tropolone, 3,5,7-tribromohinokitiol.



I

3,5,7-Tribromohinokitiol (I), $C_{10}H_9O_2Br_3$ (9), m.p. 90-91°, crystallized from methanol, belongs to the triclinic system, the space group $P\bar{1}$, with two molecules in a unit cell of dimensions, $a=6.48$ Å, $b=9.63$ Å, $c=9.98$ Å, $\alpha=94.5°$, $\beta=105.9°$, $\gamma=93.1°$.

Three-dimensional intensity data for $0k\ell$-$3k\ell$ and $h0\ell$-$h5\ell$ reflections were collected from the equi-inclination Weissenberg photographs taken with Cu Kα radiation, and intensities were estimated by visual comparison with the calibrated intensity scale. A total of 2684 independent structure factors were evaluated for this analysis. The Patterson synthesis and two cycles of calculation of Fourier synthesis with the use of the heavy atom method revealed the whole structure. The final R-factor after blockdiagonal matrix least squares refinement was 0.09. The standard deviations of positional parameters averaged 0.0011 Å for Br, 0.0075 Å for O and 0.0083 Å for C.

The molecular structure viewed along the b axis is shown in Fig. 1 with the interatomic distances. Two types of C-C bonds with different bond lengths appear alternatively as in the case of tropone derivatives (10). Average value for the shorter bonds (C_2-C_3, C_4-C_5, C_6-C_7) is 1.353 Å, slightly longer than the normal C=C bond distances, and that for the longer bonds (C_1-C_2, C_3-C_4, C_5-C_6 and C_7-C_1) is 1.443 Å, which is in between sp^2-sp^2 (11) (1.466 Å) and benzenoid bond lengths (12) (1.392 Å). Two C-O bond lengths also differ each other. All of these observations revealed a sizable bond fixation in the molecule.

Thus, though designated conventionally as 4-isopropyl-3,5,7-tribromotropolone, the compound actually exists as 2-hydroxy-6-isopropyl-3,5,7-tribromotropone in the crystalline state. The interatomic distances between the adjacent substituents are much shorter than the sums of respective van der Walls radii. The substituents on the heptagon therefore suffer considerable steric deformation.

Bond angles shown in Fig. 2 also revealed the angular deformation. Interior angles of the seven-membered ring vary from 121° to 131°. At C_6 where its substituent isopropyl group is held between two bromine atoms, the interior angle is the smallest. Bending the bond of substituents is also observed. Of the two external angles associated with each substituent, the one facing to the larger substituent at adjacent carbon has always larger values.

As average value (127.3°) for the interior angle is slightly smaller than that in a regular heptagon, a bent seven-membered ring being implied, the planarity of the molecule was therefore calculated, and the result is shown in Fig. 3. Clearly, the tropolone ring is in a twisted boat form; C_2, C_3, C_6 and C_7 lie approximately in a plane forming the bottom part, while C_3, C_4, C_5 and C_6 are in another plane constructing the stern part. The angle between these two planes is 18.8° and that between the bottom plane and the bow part (C_2, C_1 and C_7) of this boat is 19.2°. This is the first instance of a boat form of tropolone ring being detected, although similar deformation has been observed in tropones (13). Out of plane deformation of substituents was also observed: The isopropyl group at C_6 and the bromine atom at C_7 are off the plane C_5-C_6-C_7-C_1, the C_8 down (-0.129 Å) and Br_7 up (0.305 Å), making the internal rotation angle of 10°. The plane O_2-C_2-C_3-Br_3 makes an angle of 5.0° with the plane C_1-C_2-C_3-C_4.

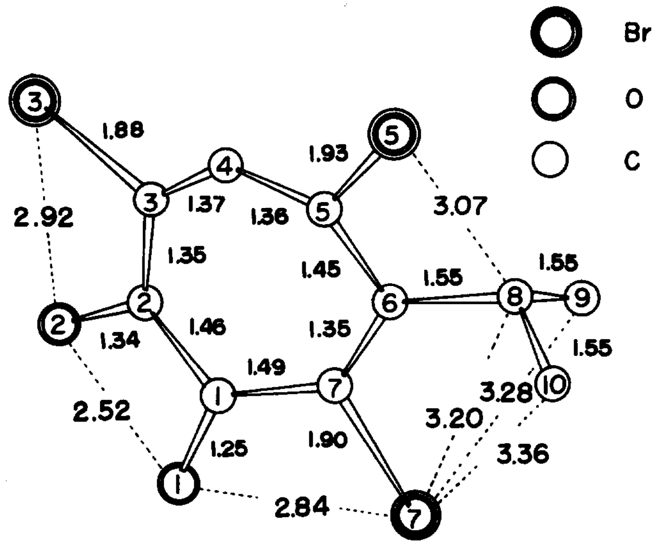


Fig. 1. Molecular geometry of I viewed along the b axis with interatomic distances (Å). Standard deviations: 0.01 Å for all distances.

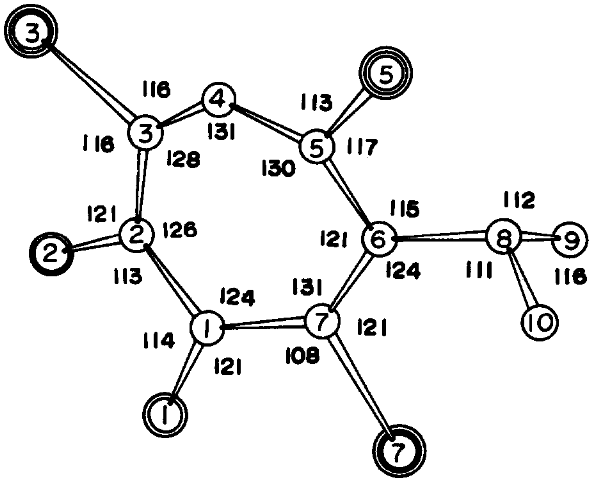


Fig. 2. Molecular geometry of I viewed along the b axis with the bond angles (°). Standard deviations: < 1° for all angles.

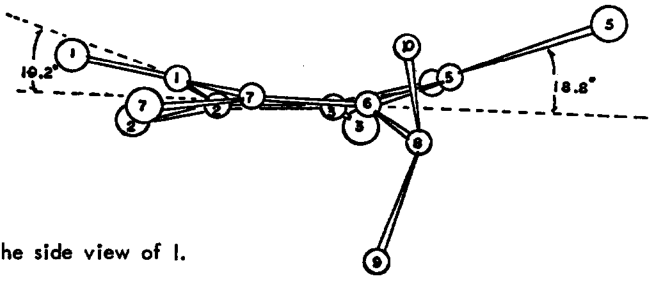


Fig. 3. The side view of I.

The reason for the out of plane displacement of Br_3 is not clear, but that for O_2 might be due to the intramolecular hydrogen bonding with O_1. This view is supported by the facts that O_1 is also bent from the bow plane toward O_2, and that there is no intermolecular hydrogen bonding in the crystalline state. The present investigation clearly indicates that the compound I is deformed in a rather complicated way in order to minimize the steric strain exist between the substituents, and, as the result, the heptagon is distorted and double bonds are fixed probably at the expense of some of resonance energy of the tropolone ring system.

References and Footnotes

1) M. Kimura and M. Kubo, Bull. Chem. Soc. Japan, **26**, 250 (1953).

2) M. Kubo, M. Kimura and K. Kimura, Ibid., **27**, 455 (1954).

3) Y. Sasada, K. Osaki and I. Nitta, Acta Cryst., **7**, 113 (1954), Y. Sasada and I. Nitta, Bull. Chem. Soc. Japan, **30**, 62 (1957).

4) Y. Sasada and I. Nitta, Acta Cryst., **9**, 205 (1956), R. Shiono, Ibid., **14**, 42 (1961).

5) J.M. Robertson, J. Chem. Soc., 1222 (1951), W.M. Macintyre, J.M. Robertson and R.F. Zahrobsky, Proc. Roy. Soc., A **289**, 161 (1965).

6) T.A. Hamor and D.J. Watkin, Chem. Comm., 440 (1969).

7) V.W. Day and J.L. Hoard, J. Am. Chem. Soc., **92**, 3626 (1970), J.J. Park, D.M. Collins and J.L. Hoard, Ibid., **92**, 3636 (1970).

8) H. Shimanouchi and Y. Sasada, Tetrahedron Letters, 2421 (1970), H. Shimanouchi and Y. Sasada, Abstracts of Papers, International Symposium on the Chemistry of Nonbenzenoid Aromatic Compounds, Sendai, Japan, p. 85 (1970).

9) M. Yasunami, K. Takase and T. Nozoe, Tetrahedron Letters, 4327 (1970).

10) E.J. Forbes, M.J. Gregory, T.A. Hamor and D.J. Watkin, Chem. Comm., 114 (1966).

11) L.E. Sutton, "Tables of Interatomic Distances and Configuration in Molecules and Ions, Supplement 1956-1959", The Chemical Society, London (1965).

12) E.G. Cox, D.W.J. Cruickshank and J.A.S. Smith, Proc. Roy. Soc., A **247**, 1 (1958).

13) K.V. Scherer, Jr., J. Am. Chem. Soc., **90**, 7352 (1968), H. Shimanouchi, T. Hata and Y. Sasada, Tetrahedron Letters, 3573 (1968).