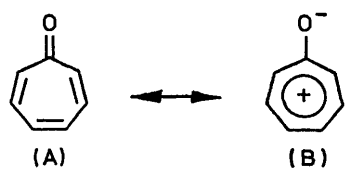
The Crystal and Molecular Structure of 3-Azidotropone

By D. W. J. CRUICKSHANK, G. FILIPPINI, and O. S. MILLS*†

(*Departments of Chemistry*, †*University of Manchester* M13 9PL *and U.M.I.S.T.*)

Summary 3-Azidotropone contains an accurately planar seven-membered ring although the individual carbon–carbon bonds show alternation in lengths.

As part of an extensive study of the structure of tropones, metal π-complexes thereof, and related compounds, we have undertaken the *X*-ray analysis of 3-azidotropone (I). Preliminary bond length data for 4,5-benzotropone[1] (II) and dibenzotropone[2] (III) indicate both an alternation of carbon–carbon distances and non-planarity of the tropone nucleus. Electron diffraction analysis[3] of tropone itself, and the *X*-ray analyses of 2-chlorotropone[4] (IV) and of tropolone[5](V), on the other hand, suggest a planar seven-membered ring. Although earlier suggestions that the participating form (B) was important enough to induce both planarity and aromaticity into tropone, recent calculations[6,7] suggest an almost total lack of resonance stabilisation and predict that the bond lengths will correspond alternately to near single and near double bonds.



(A) (B)

In anticipation of a study of tropone itself (the structure evaluation of which is not simple[8]), we chose to examine (I) because of the absence of resonance implication such as in (II) and (III), lack of heavy-atom influence as in (IV), and inability to form hydrogen bonds, whether inter- or intramolecular, as in (V).

Crystal data:—$C_7H_5N_3O$, $M = 147{\cdot}1$, orthorhombic, $a = 14{\cdot}280$, $b = 12{\cdot}786$, $c = 7{\cdot}757$ Å, $U = 1416$ Å^3, $D_c = 1{\cdot}38$, $Z = 8$, space group *Pbca* (D_{2h}^{15}, No. 61) by systematic absences, four-circle diffractometer[9] data, 841 reflexions with $F_o > 2\sigma$(counting statistics). Structure solution by symbolic addition method, least-squares refinement with anisotropic parameters, R 6·5%.

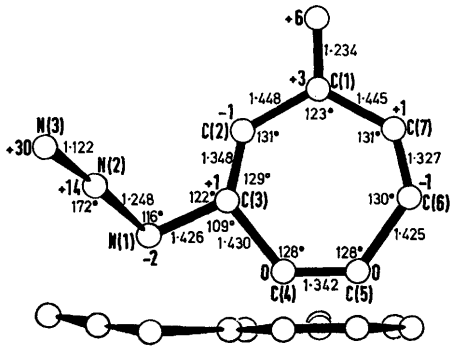


FIGURE. *Bond lengths and angles in 3-azidotropone (e.s.d. 0·009 Å). Deviations of atoms from the least-squares plane defined by atoms* C(2)–C(7) *are given in hundredths* A.

The molecule (see Figure) is planar within the estimated standard deviations of the ring carbon atoms. The bond lengths vary, however, between 1·327 and 1·448 Å (e.s.d. 0·009 Å). The ring exhibits, to a close degree, *mm* symmetry although the azido-group does introduce a small, though noticeable, perturbation of this symmetry. The azido-group is not coplanar with the seven-ring, no doubt due to the unfavourable N–H contacts which would then arise and this non-planarity suggests that the azido-group is not conjugated with the π-system of the ring. The shape and linear dimensions of the azido-group are similar to a previous determination.[10] The inequality of the angles C(2)–C(3)–N(1) and C(4)–C(3)–N(1), 122 and 109°, respectively, is presumed due to steric effects.

(*Received, December 1st, 1971; Com.* 2057.)

[1] T. Hata, H. Shimanouchi, and Y. Sasada, *Tetrahedron Letters*, 1969, 753.
[2] H. Shimanouchi, T. Hata, and Y. Sasada, *Tetrahedron Letters*, 1968, 3573,
[3] K. Kimura, S. Sazuki, M. Kimura, and M. Kubo, *J. Chem. Phys.*, 1957, **27**, 320.
[4] E. J. Forbes, M. J. Gregory, T. A. Hamor, and D. J. Watkin, *Chem. Comm.*, 1966, 114.
[5] H. Shimanouchi and Y. Sasada, *Tetrahedron Letters*, 1970, 2421.
[6] (a) D. J. Bertelli and T. G. Andrews, jun., *J. Amer. Chem. Soc.*, 1969, **91**, 5280; (b) D. J. Bertelli, T. G. Andrews, jun., and P. O. Crews, *J. Amer. Chem. Soc.*, 1969, **91**, 5286.
[7] M. J. S. Dewar and N. Trinajstić, *Croat. Chem. Acta*, 1970, **42**, 1.
[8] M. J. Barrow and O. S. Mills, personal communication.
[9] D. B. G. Edwards, K. Bowden, J. Standeven, and O. S. Mills, *Computer Bulletin*, 1966, **10**, 54.
[10] A. Mugnoli, C. Mariani, and M. Simonetta, *Acta Cryst.*, 1965, **19**, 367.