

The Crystal and Molecular Structure of 4,9-Methano[11]annulenone

By D. W. HUDSON and O. S. MILLS*

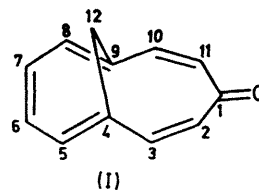
(Department of Chemistry, University of Manchester, Manchester M13 9PL)

Summary The structure of the title compound shows alternation of bond lengths and the carbonyl group occupies the position *syn* to the bridging methano group.

ALTHOUGH the crystal structure of tropone itself has not yet been reported, the currently held view is that it is flat and this is supported by electron diffraction studies. Nevertheless, preliminary bond-length data for 4,5-benzotropone¹ and for 2-chlorotropone² show alternation of bond lengths. Recently the preparation of an analogue of tropone has been reported in the bridged annulene series,³ namely 4,9-methano[11]annulenone (I). We have determined the structure of (I) for comparison with tropones, bridged[10]- and bridged[14]-annulenes. We believe this to be the first reported determination of any annulenone.

Crystal data: C₁₂H₁₀O. *M* = 170.2, orthorhombic, *a* = 12.64(6), *b* = 8.46(8), *c* = 16.81(4) Å, *U* = 1800 Å³, space group *Pbca* by systematic absences, *Z* = 8. The structure

is based on 1580 independent reflexions collected on a Hilger and Watts four-circle computer-controlled diffractometer.⁴ 971 intensities were > 3σ (counting statistics). Solution was by direct methods; *R* = 7.4%.



Formally (I) bears the same relationship to methano[10]-annulene (II) as does tropone to benzene. Our determination of (I) shows that the C(4)-C(9) distance, 2.31 Å, is greater than the comparable one⁵ in (II) by approximately 0.05 Å and thus there is evidence neither for a tricyclic

formulation nor for homoaromaticity. In the material which we analysed, the carbonyl group occupies the *syn* rather than the *anti* position with respect to the bridging group. The alternation in bond lengths (Figure), is more marked than that which occurs in (II) and suggests that (I)

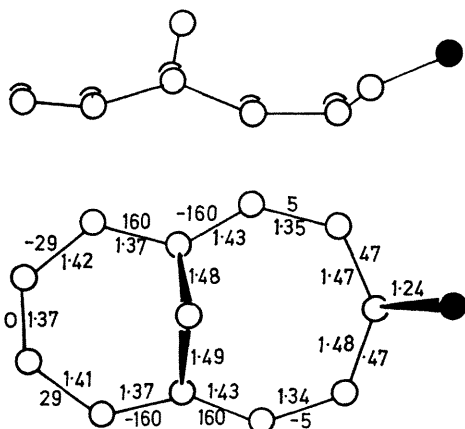


FIGURE. Elevation and plan of 4,9-methanol[11]annulene. C—C bond lengths are contained within the plan, torsion angles without.

is less aromatic than (II). Our observations are to be compared with the prediction that annulenes are expected to be aromatic if they contain a $(4n+3)$ -membered ring.⁶ In spite of differences in alternation of bond lengths and the incorporation of an additional carbon atom into the [11]annulene, the overall shapes of (I) and (II) have much in common. One major difference is that the bridging group, symmetrically placed with respect to the two rings in (II), is displaced towards the larger ring in (I). Thus the dihedral angle between the planes defined by atoms C(3), C(4), C(9), and C(10) and by C(4), C(9), and C(10) is 105° whereas that between the latter plane and that defined by atoms C(4), C(5), C(8), and C(9) is 117° . Although C(1) is formally sp^2 -hybridised, as are all of C(1)—C(11), the oxygen atom is not coplanar with atoms C(1), C(2), and C(11) but is displaced 0.23 \AA out of that plane away from the bridging methylene group. Only the atoms C(4) and C(9) have bond angles within 2° of the 120° associated with sp^2 -hybridisation. All the remainder exceed 123° ; the largest, at C(2) and C(11), are 132° . The molecule has an idealised plane of mirror symmetry shown by the values of the torsion angles (Figure).

We thank Professor E. Vogel for a sample of (I).

(Received, December 2nd, 1970; Com. 2084.)

¹ T. Hata, H. Shimanouchi, and Y. Sasada, *Tetrahedron Letters*, 1969, 753.

² E. J. Forbes, M. J. Gregory, T. A. Hamor, and D. J. Watkin, *Chem. Comm.*, 1966, 114.

³ W. Grimme, J. Reisdorff, W. Jünemann, and E. Vogel, *J. Amer. Chem. Soc.*, 1970, **92**, 6335.

⁴ D. B. G. Edwards, K. F. Bowden, J. Standeven, and O. S. Mills, *Computer Bulletin*, 1966, **10**, 54.

⁵ M. Dobler and J. D. Dunitz, *Helv. Chim. Acta*, 1965, **48**, 1429.

⁶ E.g. G. M. Pilling and F. Sondheimer, *J. Amer. Chem. Soc.*, 1968, **90**, 5610; A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," Wiley, New York, 1961, ch. 10.