Tetrahedron Letters No. 12, pp 1045 - 1048, 1974. Pergamon Press. Printed in Great Britain.

THE MOLECULAR STRUCTURE OF 1,6-METHANO[10]ANNULEN-11-ONE

Shô Itô and Yoshimasa Fukazawa

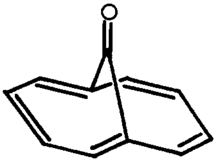
Department of Chemistry, Tohoku University

Sendai 980, Japan

(Received in Japan 24 December 1973; received in UK for publication 8 February 1974)

In the previous paper (1) we have described a two-step synthesis of 1,6-methano[10]annulen-11-one from tropone. This compound, having the p-orbital of the carbonyl group approximately perpendicular to the peripheral 10π-electron system, failed to exhibit appreciable π-π interaction between them. We present here the result of an X-ray structural analysis, which was undertaken in order to establish the precise geometry of this interesting compound, to compare it with those of 1,6-methano[10]annulene derivatives (2, 3) with sp^3 carbon bridge, and, if possible, to detect a small interaction of the two π-systems which may have escaped previous measurements.

1,6-Methano[10]annulen-11-one I (colorless prisms from cyclohexane, m.p. 183-185°) crystallizes in the orthorhombic systems, space group $P2_12_12_1$ (positive piezoelectricity test) with cell dimensions $\underline{a}=10.473$, $\underline{b}=13.339$, $\underline{c}=6.145$ Å, Z=4. In spite of its synthetic origin, I crystallized in the non-centrosymmetric space group due to the presence of a plane of symmetry in the molecule.



I

A total of 860 independent structure factors were collected by Rigaku's automatic diffractometer using Cuk$\underline{\alpha}$ radiation for the structure determination and refinement. Normalized structure factors |E| were computed.

The structure was solved by use of the symbolic addition procedure (4). Four two-dimensional reflections were chosen to specify the origin and enantiomorph and two more reflections for unknown symbols were added for phase determination. Application of Σ_2 relationships failed to give the expected values for these unknowns. Only one set out of sixteen (eight for three-dimensional (every 1/4π), and two (0 and π)

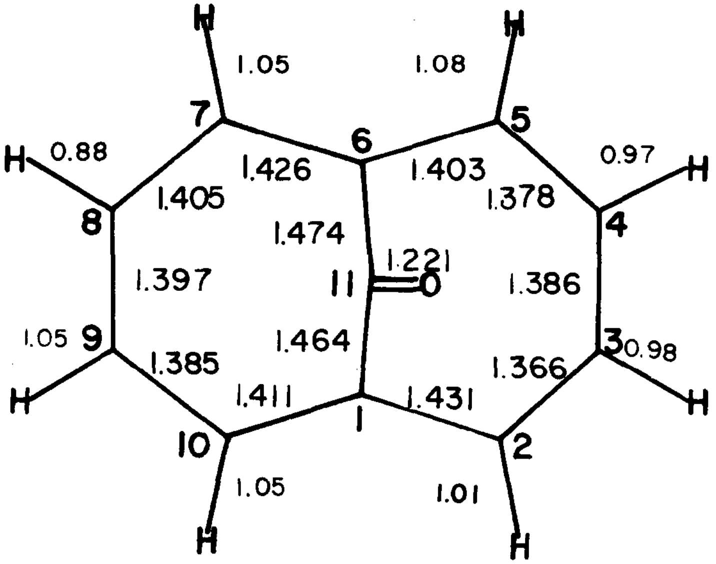


Fig. I. Bond Distances in I

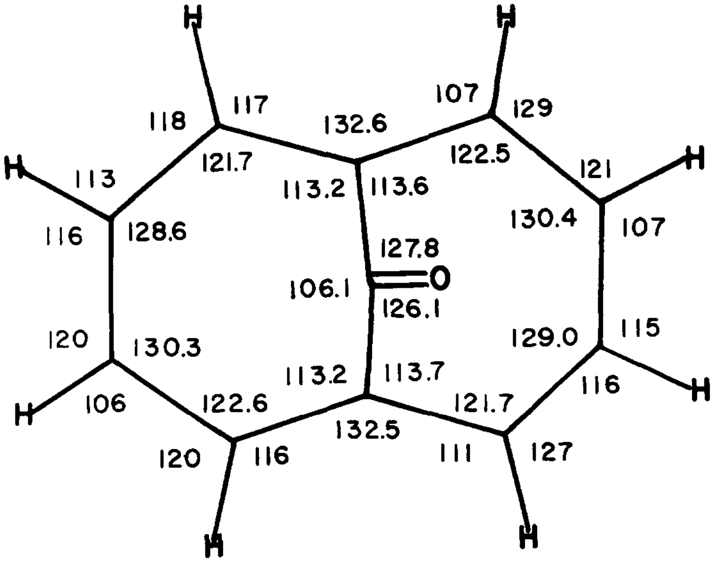


Fig. II. Bond Angles in I

Table I. Dihedral Angles of Least Square Planes in I and II (in degree)

θ	AA'	AB	A'B'	BB'	AB'	A'B	AC	A'C	BC	B'C
I	2.42	13.20	15.77	34.77	18.25	18.62	91.00	89.32	72.65	72.40
II	4.50	18.23	12.98	35.53	17.25	22.60				

for two-dimensional reflections for these unknowns) gave the lowest R_k in the phase calculations by the tangent formula and this gave the correct structure in the E-map synthesis. Refinement was carried out by least squares calcurations, the anisotropic temperature factors being used in the last several cycles. The hydrogen atoms were then found by a difference fourier synthesis and were included in further refinement with isotropic temperature factors. The final R factor for all observed reflections was 4.7%.

The molecular structure, shown in Fig. I with the interatomic distances, has roughly mm2 symmetry and has no appreciable bond alternation in the peripheral system. This is in agreement with the result of PMR analysis (1) where two vicinal coupling constants are practically identical ($J_{2,3}$=9.22, $J_{3,4}$=9.21). The peripheral bonds connected with the bridge head carbons, C1-C2, C5-C6, C6-C7 and C10-C1, are slightly longer (average value 1.417 Å) than the rest (average value 1.386 Å). This is the trend observed in both 1,6-methano[10]annulene-2-carboxylic acid (II) (average value 1.409 Å (2)) and 11,11-difluoro-1,6-methano[10]annulene (III) (average value 1.43 Å) (3)). The carbonyl bond length (1.221 Å) is somewhat longer than that of the isolated carbonyl group (5), close to those values reported for 9-fluorenones (6). This can not, however, be considered as an evidence for the conjugated effect because there are similar bond lengths reported for isolated ketones (7). The bridging bonds, C1-C11 and C6-C11 (mean value 1.469 Å), are considerably longer than the single bond in C=C-C=O system (1.44 Å) (5) suggesting no conjugation. Therefore, the length may be taken as typical for the C-C bond in an unconjugated C=C-C=O system. Eight C-H bond distances vary from 0.88 Å to 1.08 Å, the average value being 1.01 Å.

Fig. II illustrates bond angles in I and Table I lists the planarity of the molecule for I and II. In the latter, average planes of C2-C3-C4-C5, C7-C8-C9-C10, C1-C2-C5-C6, C1-C6-C7-C10, and C1-C11-C6 are referred to as A, A', B, B' and C, respectively. The ∠C2-C3-C4 and three equivalent angles are larger than ∠C1-C2-C3 and its equivalents, a characteristic feature also observed in II and III. However, I has the largest average value (129.6°) for ∠C2-C3-C4. This is primarily due to the largest bridging angle

∠C1-C11-C6 (originally sp^2) which increases the distance between C1 and C6 (2.348 Å) compared with those in II and III (2.257 Å and 2.22 Å, respectively). At the same time, the bond angle ∠C1-C11-C6 is much smaller than the normal bond angle for carbonyl carbon and in fact similar to that in 5-membered ring (7). The higher frequency observed in the IR spectrum of I (1743 cm^{-1} in KBr and 1749 cm^{-1} in $CHCl_3$) is accounted for by the known bond angle-frequency relationship (8,9). The dihedral angles of the least square plane (Table I) reveal that the peripheral ring is flatter in I than in II, suggesting more delocalization of π-electrons.

Thus, the determination of the precise geometry of I described in this paper revealed no appreciable interaction between the carbonyl group and the peripheral system situated parpendicular to each other, although electrons are delocalized extensively within the latter system. Establishment of the geometry should be useful for the future study of the physical properties of I.

We thank Professor Yoichi Iitaka, University of Tokyo, for his permitting us to use his facilities.

References and Footnotes

1) S. Itô, H. Ohtani, S. Narita and H. Honma, Tetrahedron Letters, 2223 (1972).

2) M. Dobler and J.D. Dunitz, Helv. Chim. Acta, 48, 1429 (1965).

3) C.M. Gramaccioli and M. Simonetta, Tetrahedron Letters, 173 (1971); Acta Cryst., B27, 2231 (1971).

4) J. Karle and I.L. Karle, Acta Cryst., 21, 849 (1965).

5) L.E. Sutton, "Interatomic Distances and Configurations in Molecules and Ions", Special Publications No. 11 and No. 18 (1958 and 1965), The Chemical Society, London.

6) H.R. Luss and D.L. Smith, Acta Cryst., B28, 884 (1972), D.L. Dorset, A. Hybl and H.L. Ammon, Ibid., B28, 3122 (1972).

7) T.N. Margulis, Acta Cryst., 18, 742 (1965). C.S. Gibbons and J. Trotter, J. Chem. Soc., Perkin II, 737 (1972).

8) J.O. Halford, J. Chem. Phys., 24, 830 (1956).

9) The compound quoted in reference 7 has $\nu_{C=O}$ at 1748 cm^{-1} in $CHCl_3$. J.R. Scheffer, J. Trotter, R.A. Wostradowski, C.S. Gibbons and K.S. Bhandari, J. Am. Chem. Soc., 93, 3813 (1971).