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STRUCTURE OF SOLID DI-9-PENTACYCLO[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]NONYL ETHER ("COATES' ETHER"). BOND SHORTENING IN AN ECLIPSED BICYCLOPROPYL

Sushil Srivastava, S. Chang, J. Lauher,* G. Jenner, and W. J. le Noble*
Department of Chemistry, State University of New York
Stony Brook, New York 11794, U.S.A.

Summary: The X-ray diffraction pattern of the title compound shows the length of the bicyclopropyl bond to be 1.488 ± 0.005 Å, comparable to the C_2C_3 bond length of 1,3-butadiene.

In our synthesis of Coates' alcohol used in connection with the companion study,[1] the last step was the silver perchlorate catalyzed isomerization of 9-homocubanol as described by Paquette et al.[2] In our hands, ^{1}H NMR suggested the presence of variable amounts (to 50%) of another component apparently not observed by these authors. This was isolated as a white solid by chromatography (silica gel, benzene-pentane, mp. 73°). Its NMR spectra are very similar to those of the alcohol, and only the methine ^{13}C and ^{1}H resonances (101.89 and 3.90δ, respectively) differ significantly. An elemental CH analysis, the IR spectrum, and the dry conditions used (anhydrous benzene and freshly prepared silver perchlorate) suggested that the compound could be the title ether; but since the mass spectrum gave essentially m/e = 117 alone and did not show the parent peak, an X-ray diffraction study was undertaken. The results of such a study were considered to be of potential interest for an additional reason: relatively little is known about conjugation and about the connecting bond in bicyclopropyls.[3]

Thus, while the Walsh model for cyclopropanes permits the accommodation of a remarkably large number of varied chemical facts[4] (including the bisected conformation of cyclopropanes conjugated with a double bond), it does not render obvious what might be the best conformation for bicyclopropyls.[5] One way of studying this question is to assay the bond lengths of polycyclic instances in which the two rings are rigidly held at various dihedral angles. The member whose structure we contribute here is of special interest in that this angle should be zero, or close to it.

The crystal used was grown in pentane. We collected 2431 unique intensities on a CAD-4 diffractometer with Mo Kα radiation (λ = 0.71073 Å). The crystal data are: monoclinic, space group $P2_1/c$, a = 10.889(3), b = 9.610(6), c = 11.874(3)Å, β = 94.76(9), Z = 4, Dc = 1.344 g/cm^{-3}. The structure was solved by direct methods with 942 intensity data [$I>3\delta(I)$] and refined with the full matrix least square method. The final R value was 0.036 and Rw was 0.040. An ORTEP drawing is shown in Figure 1.

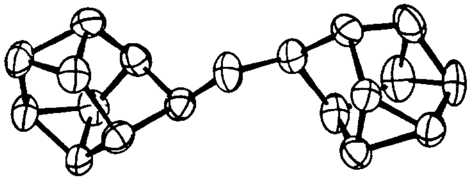

Figure 1

It is found that the bicyclopropyl

connecting bonds have an average length of 1.488 ± 0.005 Å; they are the shortest in the molecule. They are clearly significantly shorter than the other carbon-carbon bonds exocyclic to the cyclopropanes (1.523 ± 0.002 Å), and this is so in the face of eclipsing, and of a tensile strain which is obvious even in the building of a ball-and-stick model. This value is virtually the same as that of the C_2C_3 length in (*s*)-1,3-butadiene.[6] The cyclopropyl bonds themselves average 1,501 ± 0.003 Å in length, and the bonds leading to the ether carbons average 1.533 ± 0.004 Å. The data also confirm that the dihedral angle θ between the cyclopropyl rings equals zero within experimental error. Our result agrees closely with those (1.49 Å) known in *anti*-*cis*, *cis*-2,2^1 -dibromobicyclopropyl[7] ($\theta = 180°$), and in the parent bicyclopropyl[8] ($\theta = 180°$).

It is tempting to conclude that the short bond indicates conjugation. Moreover, one can argue that the standard against which bond shortening should be gauged is not the length of the single C-C bond (1.540 Å), but one corrected for hybridization. If we do so, using the 1.523 Å result for the exocyclic bonds noted above, the standard would be 1.540 - 2(0.017) = 1.504 Å; the effect would then indeed be much diminished. We note that such corrections[9] would also drastically reduce the evidence in support of conjugation between double bonds (allylic C-C bonds have an average length of 1.507 Å), and that conjugation, however strongly supported by spectral evidence, would not be clearly reflected in structural factors.

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References and Footnotes

1. See preceding paper in this issue.
2. L. A. Paquette, J. S. Ward, R. A. Boggs, and W. B. Farnham, *J. Am. Chem. Soc.*, *97*, 1101 (1975).
3. Gleiter and Paquette have recently contributed PE spectral data and appropriate calculations for a number of bicyclopropyls (J. Spanget-Larsen, R. Gleiter, K. Gubernator, R. J. Ternansky, and L. A. Paquette, *J. Org. Chem.*, *47*, 3082 (1982)). Such data are of course more informative about energy levels than about structural details.
4. W. J. le Noble, "Highlights of Organic Chemistry," Marcel Dekker Inc., New York, N.Y., 1974; cf. p. 202 ff.
5. J. Spanget-Larsen, R. Gleiter, M. R. Detty, and L. A. Paquette, *J. Am. Chem. Soc.*, *100*, 3005 (1978).
6. D. J. Marais, N. Sheppard, and B. P. Stoicheff (*Tetrahedron*, *17*, 163 (1962)) quote 1.476 Å for *s*-C_2C_3 on the basis of IR-Raman; A. Almenningen, O. Bastiansen, and M. Traetteberg (*Acta Chem. Scand.*, *12*, 1221 (1958)) report 1.483 Å on the basis of electron diffraction.
7. G. Schrumpf and F. Suesse, *Chem. Ber.*, *105*, 3041 (1972).
8. J. Eraker and C. Romming, *Acta Chem. Scand.*, *21*, 2721 (1967).
9. Pro and con literature is referred to by J. March, "Advanced Organic Chemistry," 2nd Ed., McGraw-Hill, N.Y., 1977; p. 32 f.
10. For a discussion of the cyclopropyl group ability to conjugate with double bonds and its relation to X-ray results, see F. H. Allen, *Acta Cryst.*, *B36*, 81 (1980) and *B37*, 890 (1981). Concerning bicyclopropyls, he writes that he has extracted a number of additional examples of variable degrees of refinement from the X-ray literature; they show "significant clustering" at 1.48-1.50 Å.

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