

THE DIELS-ALDER ADDITION OF DICYANOACETYLENE TO [8](2,5)FURANOPHANE;
THE SYNTHESIS OF A PADDLANE

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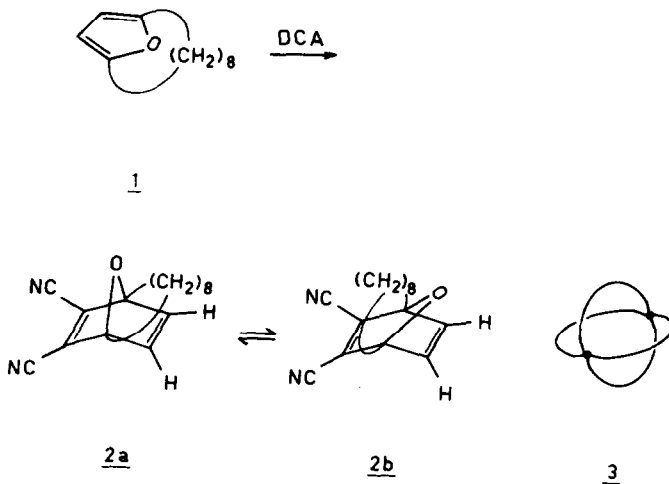
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Structures, that contain tetravalent carbon with the four neighbouring atoms in or close to a plane passing through this carbon ("planar carbon"), are intriguing to us from a preparative point of view.¹

Calculations show that "planar carbon" will be thermodynamically less stable than tetrahedral carbon.² The synthesis of the doubly-bridged structure 2 as described below was planned with the following idea in mind: a reversible reaction - the Diels-Alder addition - might enable us to establish the extent to which the "planarity" is possible.³

Addition of [8](2,5)furanophane (1)⁴ to an excess of dicyanoacetylene (DCA) at room temperature gave the Diels-Alder adduct 2 in 80% yield.



The structure assignment of 2 (mp 138.5-140°) was based on the elemental analysis⁵, molecular weight and spectroscopic properties. Nmr (CDCl₃): δ 7.01 (s, 2), δ 2.2 (m, 4) and δ 1.4 (m, 12); uv max (96% C₂H₅OH) 300 m μ (ϵ 1220)⁶; ir (KBr) 2215 cm⁻¹ (CN). Mass spectrum m/e 254, M⁺, 1%; m/e 228, (M- C₂H₂)⁺, 6%; m/e 178, (M- NC-C \equiv C-CN)⁺, 52%; m/e 94, C₆H₆O⁺, 100%. The adduct of 2,5-dimethylfuran and dicyanoacetylene was synthesized for comparison; its spectroscopic properties resembled those of 2.^{5,7}

The nmr spectrum of 2 is temperature dependent. At -100° we observe two singlets at about δ 7.0 (figure 1). These are most probably due to different conformers frozen out on the nmr time scale. It is clear, however, that nmr by itself cannot differentiate between the possible conformational transitions that can be invoked to explain the spectrum.⁸

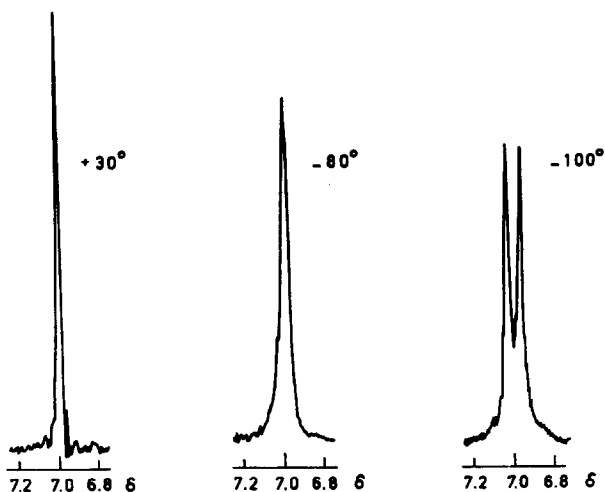


Figure 1. Low field part of the nmr spectrum of a CD₂Cl₂ solution of 2 at about +30, -80 and -100°.

The synthesis of 2 provides us with an example of a compound belonging to the class of tricyclic systems of the general structure 3. Complex polycyclic systems containing the structural unit 3 have been known for about twenty years.⁹ However, we are aware of only two communications^{1a,b} describing some-mutually closely related-examples of 3 as a simple tricyclic system. Recent attempts by Hahn *et al.*^{1d} to synthesize tricyclics like 3 (called "paddlanes" by these authors) were unsuccessful and resulted in the formation of polycyclic compounds (called "double paddlanes").

In 1968 Wiberg *et al.*^{1c} recognized **3** as a class of compounds in which the bridge-head carbons might approach a square planar configuration. Tricyclic compounds like **2** possess an interesting feature in that the degree of free rotation of the methylene bridge - $(CH_2)_n$ - depends on n . For large n , rotation over all the bridges would be possible, whereas for a relatively small n rotation is inhibited. This conformational behaviour is not unlike that observed for certain cyclophanes.^{4,10} Molecular models of **2** point to facile rotation of the [8] methylene chain over the oxygen bridge only. In the terminology of Hahn, Bohm and Ginsburg^{1d}, the oxygen atom "finds itself within the larger cavity of the molecule".

Although further studies undoubtedly are necessary, the Diels-Alder reaction seems to be a valuable tool for the synthesis of systems related to **2**.

REFERENCES AND NOTES

1. For a number of synthetic approaches to systems related to the "planar carbon" model see:
 - a. T. Mori, K. Kimoto, M. Kawanisi, and H. Nozaki, Tetrahedron Lett., 3653 (1969);
 - b. C.W. Thornber, Chem. Commun., 238 (1973);
 - c. K.B. Wiberg, J.E. Hiatt, and G.J. Burgmaier, Tetrahedron Lett., 5855 (1968);
 - d. E.H. Hahn, H. Bohm, and D. Ginsburg, ibid., 507 (1973);
 - e. H. Wynberg and R. Helder, ibid., 4317 (1971);
 - f. C.F.H. Allen and J.A. VanAllan, J.Org.Chem., 18, 882 (1953);
 - g. P.G. Gassman and R.P. Thummel, J.Amer.Chem.Soc., 94, 7183 (1972);
 - h. C.H. Park and H.E. Simmons, ibid., 94, 7184 (1972);
 - i. K.B. Wiberg and G.J. Burgmaier, ibid., 94, 7396 (1972);
 - j. R.E. Pincock and E.J. Torupka, ibid., 91, 4593 (1969);
 - k. V. Georgian and M. Saltzman, ibid., 4315 (1972).
2. a. H.J. Monkhorst, Chem. Commun., 1111 (1968);
 - b. R. Hoffmann, R.W. Alder, and C.F. Wilcox, Jr., J.Amer.Chem.Soc., 92, 4992 (1970);
 - c. W.A. Lathan, W.J. Hehre, L.A. Curtiss, and J.A. Pople, ibid., 93, 6377 (1971);
 - d. S. Durmaz, J.N. Murrell, and J.B. Pedley, Chem. Commun., 933 (1972);
 - e. R.A. Firestone, ibid., 163 (1973).

3. In this letter we want to draw attention to the preparation of the tricyclic system 2. We realize that its synthesis is only an approach to the synthesis of "planar carbon". However, homologues of 2 could contain "planar carbon" if the methylene bridge could be sufficiently shortened. In this connection the synthesis of the lower homologues of 1 is crucial.
4. H. Nozaki, T. Koyama, and T. Mori, Tetrahedron, 25, 5357 (1969).
5. Correct C, H and N analyses were obtained.
6. For a discussion of the electronic spectra of Diels-Alder adducts of dicyanoacetylene, see R.C. Cookson, J. Dance, and M. Godfrey, Tetrahedron, 24, 1529 (1968).
7. mp 76-76.5°; nmr (CDCl₃): δ 6.99 (s, 2), δ 1.85 (s, 6); uv max (96% C₂H₅OH) 307 mμ (ε 1120)⁶; ir (KBr) 2215 cm⁻¹ (CN). Mass spectrum m/e 172, M⁺, 10%; m/e 146, (M- C₂H₂)⁺, 44%; m/e 96, (M- NC≡C-CN)⁺, 67%; m/e 43, 100%.
8. For some examples of conformational transitions in bridged systems see:
- F. Vögtle, Tetrahedron, 25, 3231 (1969);
 - S. Fujita, S. Hirano, and H. Nozaki, Tetrahedron Lett., 403 (1972);
 - S. Hirano, T. Hiyama, S. Fujita, and H. Nozaki, Chem.Lett., 707 (1972);
 - F. Vögtle, Chem.Ber., 102, 1449 (1969).
9. See ref. 1f for the first examples; other examples are given in ref. 1e and some references cited therein.
10. a. A.T. Blomquist, R.E. Stahl, Y.C. Meinwald, and B.H. Smith, J.Org.Chem., 26, 1687 (1961);
- b. Compare also J.G. Vinter and H.M.R. Hoffmann, J.Amer.Chem.Soc., 95, 3051 (1973).