Tetrahedron Letters No. 11, pp 847 - 850, 1976. Pergamon Press. Printed in Great Britain.

PENTACYCLO[$8.6.0.0^{1,5}.0^{2,9}.0^{6,11}$]HEXADECA-3,7,13,15-TETRAENE, A NOVEL CAGE HYDROCARBON FROM A CYCLOOCTATETRAENE DIMER

Eiji Ōsawa

Department of Chemistry, Faculty of Science, Hokkaido University

Sapporo 060, Japan

Henning Henke* and Gerhard Schröder

Institut für Anorganische Chemie* und Institut für Organische Chemie der Universität Karlsruhe (TH), D 7500 Karlsruhe, Kaiserstrasse 12, Germany (BRD)

(Received in Japan 9 January 1976; received in UK for publication 3 February 1976)

Recently Staley et al.[1] reported that treatment of tricyclic syn-"2+2"dimer of cyclooctatetraene (1)[2] with KNH_2 in liquid ammonia at -78°C gave a fused 10π aromatic dianion. In contrast, action of potassium t-butoxide upon (1) in DMSO at 55°C for two days afforded an isomeric colorless crystalline hydrocarbon (2), mp 53°, in 77% yield. Upon catalytic hydrogenation, (2) absorbed four moles of hydrogen. (2) shows a highly complex proton nmr spectrum at δ 6.2-5.2 (8H) and 3.7-1.7 (8H). ^{13}C nmr spectrum has sixteen peaks. These data indicate (2) to be a pentacyclic tetraene of low symmetry. The structure of (2) was established by an X-ray analysis.

Single crystals suitable for X-ray analysis could be grown from ethyl acetate/isopropanol solution. The crystal data derived from X-ray photographs and from the angular settings of 17 reflexions in a diffractometer are as follows: monoclinic, a = 6.422(2), b = 12.145(3), c = 14.346(4) Å, β = 97.75(2)°, calculated density D_x = 1.248 gcm^{-3} with Z = 4, D_m = 1.245 gcm^{-3} (obtained by flotation), systematic absences for the reflexions (h0ℓ) with ℓ = odd and (0k0) with k = odd, space group $P2_1/c$.

Despite the low melting point a total of 1030 independent reflexions could be measured on a Picker-FACSI-diffractometer (MoKα radiation with λ = 0.7107 Å, Table. Interatomic Distances (σ = 0 003 Å) and Bond Angles (σ = 0.2°)

1 - 2 = 1.547 Å	2 - 9 = 1 617 Å	6 - 11 = 1.549 Å	11 - 12 = 1.548 Å
1 - 5 = 1.575	3 - 4 = 1 325	7 - 8 = 1 326	12 - 13 = 1.504
1 - 10 = 1 537	4 - 5 = 1 507	8 - 9 = 1.486	13 - 14 = 1.333
1 - 16 = 1.489	5 - 6 = 1 578	9 - 10 = 1 563	14 - 15 = 1 472
2 - 3 = 1.491	6 - 7 = 1.510	10 - 11 = 1 513	15 - 16 = 1 341
3....8 = 2.903 Å	4...7 = 2.823 Å		

2 - 1 - 5 = 101.4°	1 - 5 - 4 = 103.3°	1 - 10 - 9 = 89 6°
2 - 1 - 10 = 91.6	1 - 5 - 6 = 104 2	1 - 10 - 11 = 104.2
2 - 1 - 16 = 120.4	4 - 5 - 6 = 114.2	9 - 10 - 11 = 117 5
5 - 1 - 10 = 104.5	5 - 6 - 7 = 111.8	6 - 11 - 10 = 100.2
5 - 1 - 16 = 113.9	5 - 6 - 11 = 102 1	6 - 11 - 12 = 111.1
10 - 1 - 16 = 121.2	7 - 6 - 11 = 107.1	10 - 11 - 12 = 109.9
1 - 2 - 3 = 105.7	6 - 7 - 8 = 118.9	11 - 12 - 13 = 115.0
1 - 2 - 9 = 87.3	7 - 8 - 9 = 119 3	12 - 13 - 14 = 125 3
3 - 2 - 9 = 116.4	2 - 9 - 8 = 114.7	13 - 14 - 15 = 128.3
2 - 3 - 4 = 110.3	2 - 9 - 10 = 88.1	14 - 15 - 16 = 130 0
3 - 4 - 5 = 112.4	8 - 9 - 10 = 113.3	1 - 16 - 15 = 128 1

graphite monochromator, $\omega - 2\theta$ scan in the range $4^\circ < 2\theta < 40^\circ$, 937 reflexion intensities with $I > 3\sigma$ significantly different from zero) The structure was solved with the aid of direct method using a highly automated version of MULTAN[3] All carbon maxima appeared in the corresponding E-map

Hydrogen positions were obtained from a difference Fourier synthesis. Least-squares refinements of all coordinates and of anisotropic thermal parameters for the carbon atoms converged at an R-value of 3.6 % (calculated for the 937 F_o's with associated intensities $I > 3\sigma$). The hydrogen atoms were restricted to isotropic temperature motion with B-values adopted from their nearest carbons.

A remarkable feature of the molecule is a very long single bond C2-C9 (1.617 Å), which is among the longest on record for carbon. The lengthening is possibly due to the strong repelent forces which arise between two double bonds oriented face-to-face if they come too close together (here C3-C4 and C7-C8). Similar examples are known.[4]

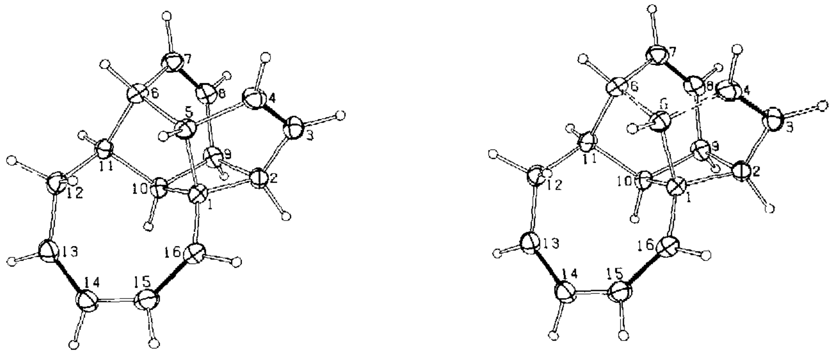
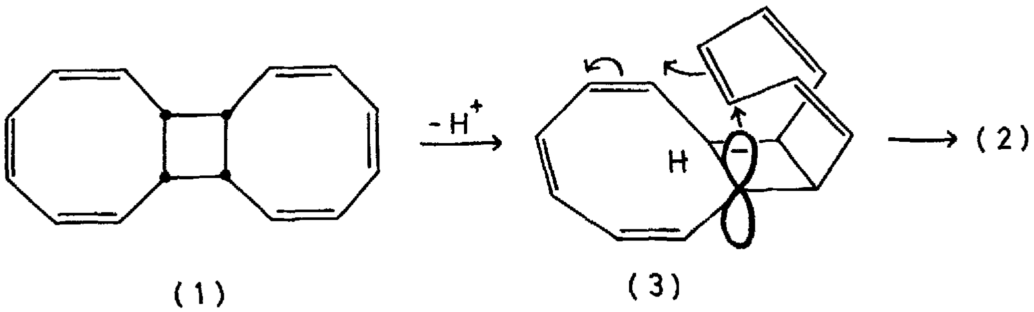


Figure   Stereoscopic View of the Molecule (2) with Thermal-Ellipsoids at the 20% Probability Density Level. (The spheres of hydrogen atoms are on an arbitrary scale. Double bonds are drawn as darkened lines)

Suggested mechanism for the formation of (2) involves abstraction of allylic proton with the base to give an intermediate carbanion (3). As can be seen from the drawing one of the folded conformations of (3) seems especially favorable for the subsequent relocation of bonds. The degree of folding, and consequently the proximity of one of the double bonds to the developing carbanion center, is presumably increased by flattening of the other cyclooctatriene ring due to the sp^2 nature of its allylic carbanion center.[5]



The structure of (2) contains a 1,5-cyclooctadiene unit. The uv-spectrum (cyclohexane) reveals $\lambda_{max}(\varepsilon)$ at 255 nm (5,000). We observe a bathochromic shift of 27 nm with respect to 1,3-cyclooctadiene. (2) has so far refused to close photochemically to a bridged homopentaprismane and resembles hypostrophene[6] in this respect. (2) does not undergo addition reaction with potential dienophiles either, indicating high strain in the cyclooctadiene portion.[5] Further chemistry of (2) is under active investigation and will be reported.

Acknowledgement. The authors express their gratitude to Prof. H. Wondratschek and Dr. B Deppisch for making their diffractometer available, and to Dr. R. Ader of Bruker Corporation, Karlsruhe, for taking ^{13}C nmr spectra E. O. is indebted to the International Science Cooperative Program sponsored by the Japan Society for Promotion of Science, and to the Alexander von Humboldt-Stiftung, Bonn-Bad Godesberg, for support. The support of the Badische Anilin- und Soda-Fabrik AG, Ludwigshafen, is gratefully acknowledged. All crystallographic computing was done on a Univac 1108 at the Rechnenzentrum der Universität Karlsruhe.

REFERENCES AND NOTES

(1) S. W. Staley, G. M Cramer, and A. W. Orvedal, J. Amer. Chem. Soc., 96, 7433 (1974).

(2) G Schröder, "Cyclooctatetraen", Verlag Chemie, Weinheim, 1965.

(3) G. Germain, P. Main, and M. M. Woolfson, Acta Cryst., A 27, 368 (1971).

(4) (a) M. Ehrenberg, Acta Cryst., 20, 177 (1966);
 (b) M. Ehrenberg, ibid., B 24, 1123 (1968);
 (c) J. Gaultier, C. Hauw, J. P. Desvergne, and R. Lapouyade, Cryst. Struct. Commun., 4, 497 (1975).

(5) Empirical force field calculations pertaining to these problems are in progress.

(6) (a) J. S. McKennis, L. Brener, J. S. Ward, and R. Pettit, J. Amer. Chem. Soc. 93, 4957 (1971).
 (b) W. Schmidt and B T. Wilkins, Tetrahedron, 28, 5649 (1972).