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SYNTHESIS AND PROPERTIES OF 9,10-DIPHENYLBICYCLO[6.2.0]DECAPENTAENES. A NEW SYNTHESIS OF THE NOVEL CONJUGATED SYSTEM FROM A VALENCE ISOMER

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It has attracted an appreciable interest whether conjugated fused-ring system with two 4n π electron rings, which thus have overall 4n+2 π electrons, reflect the instability of their component antiaromatic rings or the stability of their overall 4n+2 π electrons.[1] The first three hydrocarbons of such systems are butalene 1, bicyclo[6.2.0]decapentaene 2, and octalene 3. Although simple HMO calculations predict these compounds to be aromatic,[2] Dewar's PMO method[3] or recent Randić's concept of conjugated circuit[4] leads to a conclusion that they are non-aromatic or rather antiaromatic. Experimental investigations on 1 which is an elusive transient substance and on a benzo-derivative of 3 have revealed that they are actually non-aromatic.[1,5,6] However, as far as steric factors are concerned, destabilizing strain energy of planar 2 would be expected to be smaller than that of planar 1 and 3, and accordingly 2 might be better compound to test the question experimentally. Some fairly simple derivatives of 2, 2b∼2f, have been synthesized as red, thermally stable, but air sensitive substances.[7] While the UV spectra of them seem to suggest some delocalization of π electrons, the PMR spectra show rather unusual phenomena to be explained: the four-membered ring proton of 2b appears at appreciably low field of δ 7.66 which is about 1 ppm lower than that of dimethylenecyclobutenes, whereas the eight-membered ring protons do at rather olefinic region of δ 6.12.

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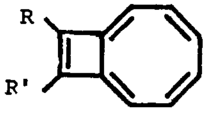

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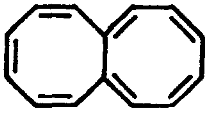
2a: R=R'=H
2b: R=H, R'=CH_3
2c: R=Cl, R'=CH_3
2d: R=H, R'=O-t-Bu
2e: R=R'=O-t-Bu
2f: R=Cl, R'=O-t-Bu



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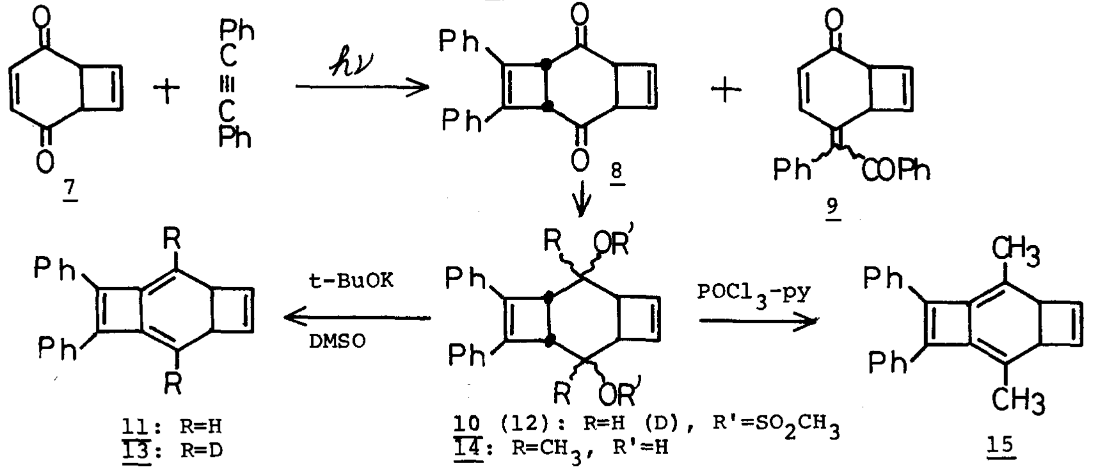
In order to elucidate the π-electron structure of the system of 2, we started investigations on the system exploring a new synthetic method. Here, we describe the syntheses and properties of 9,10-diphenylbicyclo[6.2.0]decapentaenes 4∼6.

Photoaddition of diphenylacetylene to bicyclo[4.2.0]octa-3,7-diene-2,5-dione 7[8] in benzene or methylene chloride gave [2+2] adduct 8 and a ca 1:1 geometric mixture of conjugated diketone 9[9] in about 30% and 35% yield, respectively. The configuration of 8 is probably anti from a steric point of view, though the spectral data (Table) do not allow to conclude.

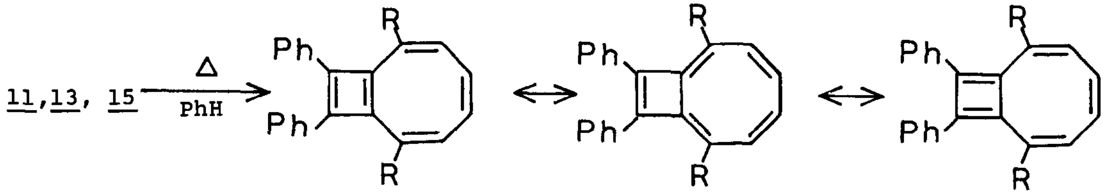
Adduct 8 was converted into a mixture of dimesylate 10 by reduction with LiAlH$_4$ in THF and subsequent mesylation of the resulting diol mixture with CH$_3$SO$_2$Cl in pyridine. Treatment of 10 with three molar amount of t-BuOK in DMSO at room temperature for 15 min gave, in 28% overall yield from 8, the tetraene 11 as a deep yellow, moderately stable, crystalline substance. Using LiAlD$_4$ at the reduction, dideuterio compound 13 was also prepared via dimesylate 12. Reaction of 8 with CH$_3$MgI and subsequent dehydration of diol 14 by POCl$_3$ in pyridine gave dimethyl compound 15 in 29% overall yield.



When heated at 100°C in benzene in a nmr tube sealed under argon atmosphere, 11 cleanly underwent an electrocyclic ring opening to yield the expected compound 4 (t$_{1/2}$=90 min) as red, thermally stable, but somewhat air sensitive, crystalline substance. In crystal state, 11 could be stored over a month in a refrigerator without appreciable change. Similarly, dideuterio compound 5 and dimethyl compound 6 were obtained in high yields from 13 and 15, respectively. Differing from red color of 4 and 5, dimethyl compound 6 is deep yellow.

Activation parameters for the ring opening of 11 were determined by means of PMR spectroscopy to be $Ea = 30.0 \pm 0.3$ kcal/mol and $A = 1.93 \times 10^{14}$ sec^{-1}. The value is 11.3 kcal higher than that of bicyclo[4.2.0]octatriene 16→cyclooctatetraene 17 isomerization[10], which is a reasonable consequence because the ring opening would initially produce the particular canonical form 4A containing antiaromatic cyclobutadiene (and cyclooctatetraene).

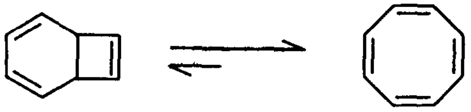
Some spectral data of the products are listed in the Table. The PMR comparison of 4 and 5 allows us to assign the signals at δ 6.30 and 6.70 to C-3$\sim$6 and C-2,7 protons, respectively. On the data of 4$\sim$6, it is interesting to note



4A R = H
5A R = D
6A R = CH_3

B

C



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17

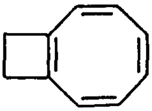

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Table. M.p., PMR, and UV data of the products[11]

Compds.	M.p. °C	PMR, δ ppm[a)]	UV, λ nm (ε)[b)]
8	144-145	4.13 (2H, s), 4.15 (2H, s) 6.15 (2H, s), 7.2-7.7 (10H, m)	———
11	117-119	3.61 (2H, d, J 3.7 Hz), 5.60 (2H, d, 3.7), 6.21 (2H, s) 6.9-7.3 (6H, m), 7.5-7.8 (4H, m)	248.5 (28300) 262 (25000) 334 (26900)
13	110-111	3.60 (2H, s), 6.20 (2H, s) 6.9-7.3 (6H, m), 7.5-7.8 (4H, m)	———
15	97-98	1.85 (6H, s), 3.47 (2H, s) 6.37 (2H, s), 6.9-7.3 (6H, m) 7.4-7.8 (4H, m)	253 (28200) 257 (27800) 335 (14800)
4	132-133	6.30 (4H, m), 6.70 (2H, m) 7.0-7.3 (6H, m), 7.4-7.7 (4H, m)	239.5 (19200) 329.5 (60700) 420 (790), 448 (640) 482 (410), 536 (200)
5	———	6.30 (4H, s) 7.0-7.3 (6H, m), 7.4-7.7 (4H, m)	———
6	131-133	2.03 (6H, s), 5.98 (4H, s) 6.9-7.3 (10H, m)	238 (15800) 315 (39300), and tailing to ca 450

a) in C_6D_6 at 60 MHz except 8 ($CDCl_3$); b) in cyclohexane

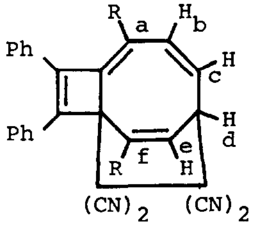
the following features: (i) the chemical shifts of C-3∼6 protons of 4 are about 0.2 and 0.8 ppm lower than those of 2b and 18[12], respectively. (ii) there are considerable substituent effect by the methyls in 6: the UV maxima are blue shifted appreciably with smaller ε and its C-3∼6 protons appear at 0.32 ppm higher field than those of 4 and 5.

Among three non-polar canonical forms conceivable, A∼C, the importance as a resonance contributor would be in the order of B > C ≫ A in view of antiaromaticity of cyclobutadiene and proper structure for pericyclic conjugation. The manifestitation of aromaticity of the system would depend on the degree of contribution of C. Regardless the contribution of C, the structure B would force the eight-membered ring to planar or near planar owing to the planarity of the dimethylenecyclobutene component, increasing strain. Near planarity of

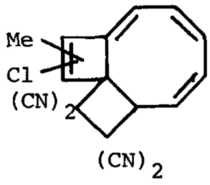
4 is actually suggested by the fairly large half-width (11 Hz) of the C-2,7 proton signals compared with nearly zero coupling between C-1 and C-8 protons of cyclooctatetraene (tub form)[13].

From these results and considerations, we are inclined to say at this stage that there is some delocalization of π electrons at least in 4 as a 10 π aromatic system, and that the DEπ thus gained is at a delicate balance with steric destabilization in (near) planar 4. The considerable substituent effects by the methyls might be largely due to a geometrical change to less planarity resulting from increased steric repulsion rather than their electronic effect.

It has been reported that 2c readily reacted with tetracyanoethylene (TCNE) to give a mixture of [2+2] adducts 19.[7] Similarly 4 smoothly reacted with TCNE, but the product 20 was a [4+2] ([8+2] when the structure C is considered) adduct [m.p. 229°C; δ ($CDCl_3$) 4.04 (1H, dd, J=8.7, 7.0 Hz, Hd), 5.8-6.3 (4H, m, Hb,c,e,f), 6.67 (1H, d, 9.1, Ha), 7.2-7.8 (10H, m); λ (EtOH) 231 (ε 17800), 251 (sh, 15900), 278 (17000), 349 nm (18200)]. The [2+2] structure is definitely ruled out by the PMR spectrum of dideuterio adduct 21 obtained from 5 [δ ($CDCl_3$) 4.04 (dd, J=8.7, 7.0 Hz, Hd), 5.91 (dd, 12.0, 8.7, Hc), 6.20 (d, 7.0, He), 6.28 (d, 12.0, Hb)].



20: R=H
21: R=D



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Further studies on 4∿6 including X-ray analysis as an important clue for aromaticity and attempts of synthesizing the parent compound by the present method are in progress.

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