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A SYMMETRICAL BISDEHYDRO[16]ANNULENE

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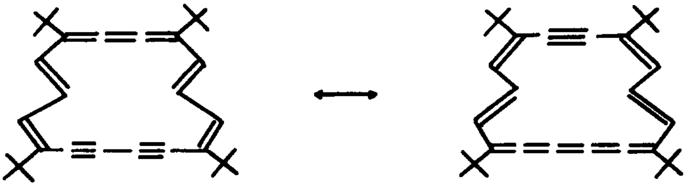
3,7,12,16-Tetra-*t*-butyl-1,8,10-trisdehydro[16]annulene (I) has been proved to sustain a very strong paramagnetic ring current (1), even equivalent valence-bond structures, which seem to have an important role in the π-electron delocalization, can not be written for the annulene (I) and even some preference of structure I_a has been suggested by the ^{13}C NMR spectrum (2). In the preceding paper, we reported the synthesis of an unsymmetrical trisdehydro[18]annulene which showed essentially the same diatropicity as those of symmetrical analogues, 1,8-bisdehydro[18]- (3) and 1,3,10,12-tetrakisdehydro[18]annulenes (4).



I_a I_b

This communication is concerned with the synthesis and paratropicity of 3,7,10,16-tetra-*t*-butyl-1,8-bisdehydro[16]annulene (IX), which can be regarded as a resonance hybrid of the equivalent structures $IX_a \leftrightarrow IX_b$.

The lithio derivative obtained on treatment of the di-*t*-butyl-dienyne ketone (II) (5) with lithium di-*i*-propylamide (-75∿-85°C) was allowed to react with trimethylchlorosilane to yield the trimethylsilyl derivative (III), pale yellow crystals, mp 71.7∿73.8°C, 87.6%. The trienyne ketone (IV) (4) was converted into the lithio derivative (V) by the reaction with lithium diethylamide (-75∿-85°C). Treatment of III with V gave the hydroxy ketone (VI), yellow solid, 51.6% (6). The reaction of VI in tetrahydrofuran with dimethyl sulfate in the presence of powdered potassium hydroxide resulted in the methoxy ketone (VII), yellow solid, 71.1% accompanied with the cleavage of the trimethylsilyl group. The crude cyclic alcohol (VIII) obtained by the cyclization of VII by means of potassium hydroxide in liquid ammonia was chromatographed on silica

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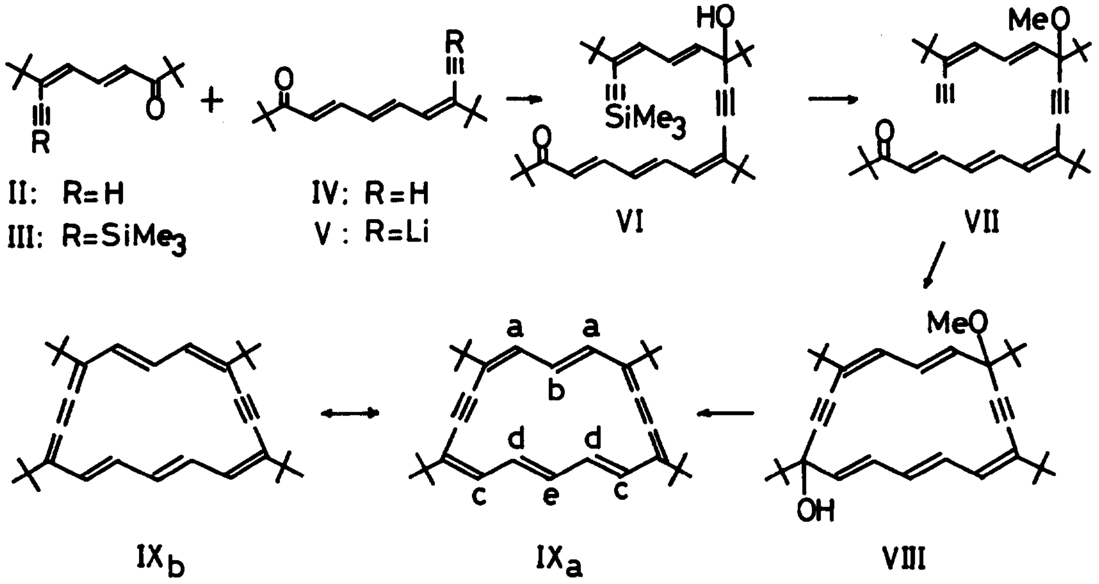
gel. Elution with benzene-hexane (3:7) gave VIII, colorless crystals, mp 253.1∿259.9°C, 3.5%, Mass (m/e) 444 (M^+-OMe), 419 (M^+-*t*-Bu), together with small amount of unidentified cyclic alcohols, mp 276.0∿280.8°C (dec.), colorless crystals, and mp 216.3∿219.9°C (dec.), colorless crystals. The elemental analyses of the unidentified alcohols could not be performed from the lack of materials.

The cyclic alcohol (VIII) was treated with tin(II) chloride and tetrahydrofuran saturated with hydrogen chloride resulting in a deep violet solution. However, rapid change of the color of solution into orange brown indicates an unstable nature of the bisdehydro[16]annulene (IX), and the isolation of IX could not be realized. The electronic spectrum of IX in tetrahydrofuran measured at -78°C is shown in Fig. 1. The absorption curve exhibits a very broad absorption band at long wavelength region which is characteristic for [4n]annulene (1,2,7,8). The absorption maximum at short wavelength region could not be observed owing to overlap with the absorption of the cyclic alcohol (VIII).



The cyclic alcohol (VIII) placed in a NMR tube was mixed under argon atmosphere at -80°C with tin(II) chloride and THF-d_8 saturated with deuterium chloride, and the mixture was allowed to warm to -50°C. Resulting deep violet solution was subjected to the NMR measurements. The NMR spectrum indicates an incomplete conversion of the cyclic alcohol (VIII) into the annulene (IX). But, as shown in Table 1 and Fig. 2, the signals due to the annulene (IX) could be clearly discriminated from the signals of VIII. The conformational stability of IX was revealed by the essentially temperature independent NMR

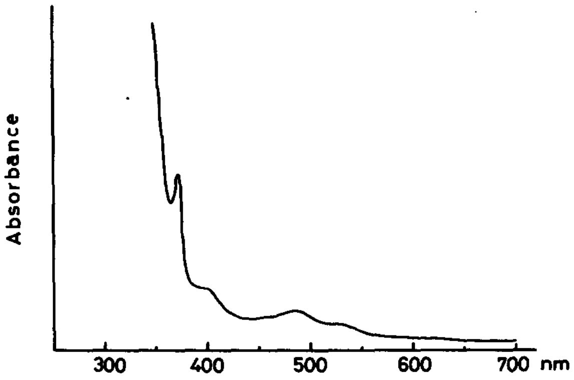


Fig. 1. Electronic spectrum of IX in THF at -78°C

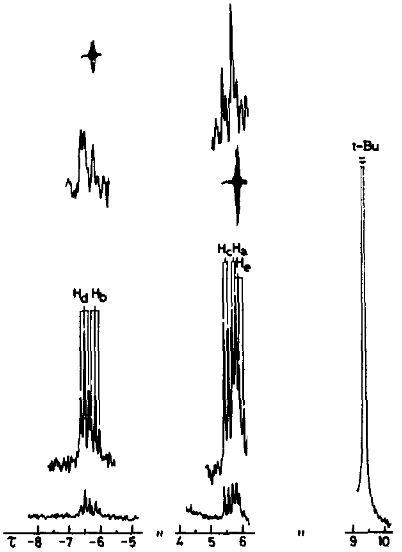


Fig. 2. 100 MHz NMR spectrum of IX in THF-d_8 at -50°C

Table 1. 100 MHz NMR spectrum of IX in THF-d_8 at -50°C. τ-values

Inner protons		Outer protons	
H^d	-6.49 t (J=13.5 Hz)	H^c	5.50 d (J=13.5 Hz)
H^b	-6.15 t (J=13.5 Hz)	H^a	5.75 d (J=13.5 Hz)
		H^e	5.90 t (J=13.5 Hz)
t-Bu	9.34 s,	9.38 s	

Table 2. 100 MHz NMR spectra of IX in THF-d_8. τ-values

	-90°C	-70°C	-40°C	-30°C	-20°C
H^d	-6.63t	-6.53t	-6.31t	-6.28t	-6.26t
H^b	-6.23t	-6.17t	-6.03t	-6.00t	-6.02t
H^c	5.57d	5.55d	5.51d	5.51d	5.46d
H^a	5.80d	5.80d	5.80d	5.81d	5.76d
H^e	5.92t	5.93t	5.95t	5.93t	5.89t
t-Bu	9.38s,9.42s	9.37s,9.41s	9.35s,9.39s	9.36s,9.39s	9.34s,9.38s

J=13.5 Hz

spectra (Table 2).

The difference between the chemical shifts of inner proton (H^d) and outer proton (H^e) was found to be $\Delta\tau$=12.39 (-50°C) being smaller than the value for the unsymmetrical trisdehydro[16]annulene (I) ($\Delta\tau$=12.91 and 12.95 in $CDCl_3$ at 36°C) (1,2,6). Because the highly strained nature of the 16-membered ring in VIII and IX seems to be reflected in the unusually low yield of the cyclization reaction of VII leading to VIII, the low conversion of VIII into IX, and the instability of IX as compared with rather stable I, the minor difference in $\Delta\tau$-values between I and IX should be attributed to the difference of ring strain and/or of planarity.

The present result is consistent with the observation that an unsymmetrical trisdehydro[18]annulene shows almost the same diatropicity as that of symmetrical analogue (9). Thus, it was found that the structural change in both 'acetylene-cumulene'-dehydro[4n+2]- and [4n]annulenes from symmetrical one to unsymmetrical one exerts rather minor influence upon their tropicity. This fact seems to indicate that the energy difference between the non-equivalent valence-bond structures in unsymmetrical 'acetylene-cumulene'-dehydroannulenes, such as I_a and I_b, is not large enough to suppress significantly the delocalization of the π-electron system.

References and Note

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