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AN UNSYMMETRICAL TRISDEHYDRO[18]ANNULENE

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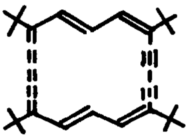
Strong diamagnetic ring current observed in symmetrical dehydroannulenes containing acetylenic and cumulenic linkages ('acetylene-cumulene'-dehydroannulenes) (1) such as tetrakisdehydro[18]annulene (I) (2) and bisdehydro[18]-annulene (II) (3) seemed to suggest that the resonance between the equivalent valence-bond structures ($I_a \leftrightarrow I_b$) plays an important role in the delocalization of π-electrons in the ring system. On the other hand, a very strong paramagnetic ring current has been observed even in an unsymmetrical trisdehydro[16]annulene (III) (4), for which no equivalent Kekulé-structures can be written. Consequently, the preparation of an unsymmetrical [18]- and a symmetrical [16]-annulenes of 'acetylene-cumulene'-type seemed to be of interest with regard to the comparison of their tropicity with those of the symmetrical (I or II) and the unsymmetrical (III) analogues.



Ia

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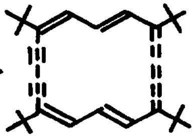
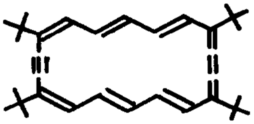
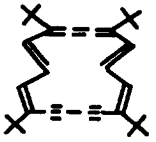


Ib



II



III

In this communication, we wish to report the preparation and magnetic properties of unsymmetrical 3,7,12,18-tetra-*t*-butyl-1,8,10-trisdehydro[18]-annulene (XI).

The reaction product (VI) of the lithio derivative of 3-*t*-butyl-2-penten-4-ynal dimethyl acetal (IV) (5) with the ketone (V) (6) was treated with acetic acid in water-dioxane to give the hydroxyaldehyde (VII), pale yellow solid, 77.6%, mp 40.6∿41.7°C, Mass (m/e) 380 (M^+), 2,4-dinitrophenylhydrazone, reddish brown crystals, mp 104.6∿106.3°C (7). The aldol condensation of VII with pinacolone gave ethynylhydroxy ketone (VIII), yellow solid, 74.2%, Mass (m/e) 462 (M^+), which gave pale yellow crystals, mp 120.6∿121.0°C, on standing a hexane solution in a refrigerator for 3 months. Treatment of VIII with lithium acetylide-ethylenediamine complex yielded the acyclic glycol (IX), pale yellow solid, 86%, mp 48.2∿50.3°C, Mass (m/e) 431 (M^+-*t*-Bu). The acyclic glycol (IX)

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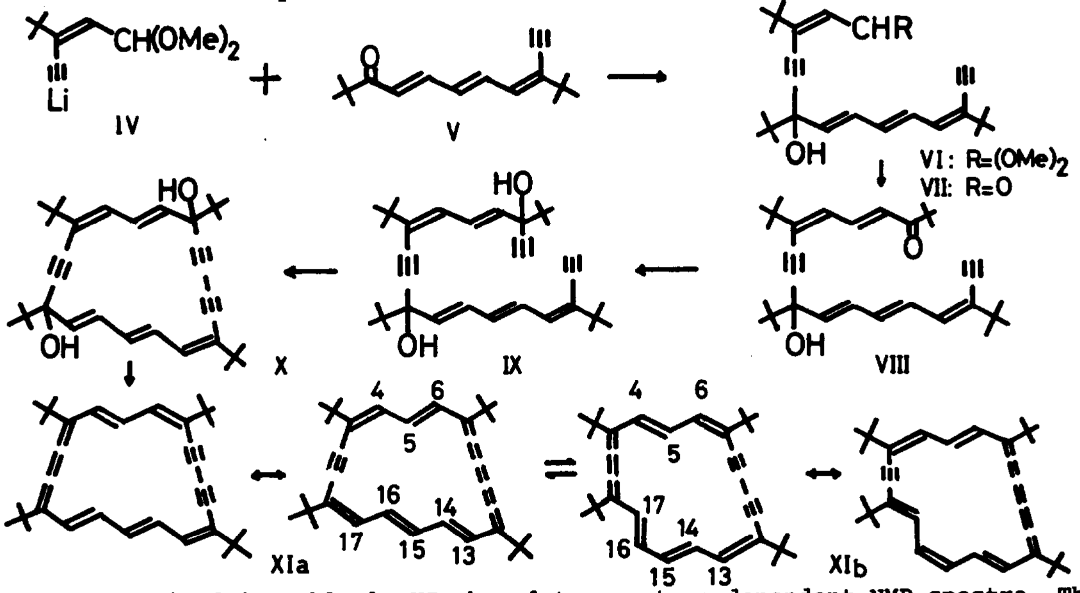
was oxidatively coupled by copper(II) acetate in pyridine-methanol-ether under high dilution conditions. Chromatography of the product on silica gel yielded diastereomeric cyclic glycol (X_a), colorless crystals, 28.5%, mp 114.0∿114.5°C, Mass (m/e) 429 (M^+-*t*-Bu) and X_b, pale yellow solid, 29.6%. An ethereal solution of X_a was mixed at -60°C with a solution of tin(II) chloride dihydrate in the same solvent saturated with hydrogen chloride. The reaction mixture, which had been kept at the same temperature for 20 min., was worked up in the usual way. Chromatography of the product on alumina gave the tetra-*t*-butyltrisdehydro[18]-annulene (XI), brown red crystals, 82%, mp >250°C (dec.). The annulene (XI) forms 1:1 CT complex, purple fine crystals, mp 209°C (dec.), with 2,4,7-trinitrofluorenone. The mass spectrum of the complex exhibits fragmentation pattern of the both components [annulene: m/e 452 (M^+), 395 (M^+-*t*-Bu), 338 (M^+-2×*t*-Bu); trinitrofluorenone: m/e 315 (M^+)]. The unsymmetrical trisdehydro[18]annulene (XI) was found to be less stable than the symmetrical analogues (I and II). XI showed an electronic spectrum related closely with those of I and II.



As summarized in Table 1, XI showed temperature dependent NMR spectra. The signals observed at τ 7.34 and 6.39 in the spectrum at 125°C disappeared at temperature lower than 50°C without essential change of other signals. This fact indicates that some linkage in XI is conformationally mobile. In order to determine the mobile bond, monodeuterated trienyne ketone (V), 2,2,10,10-tetramethyl-9-ethynyl-4,6,8-undecatrien-3-one-4-d, was prepared by the reaction of 3,3-dimethylbutan-2-one-1-d_3 with trimethylsilyl derivative of 4-*t*-butyl-2,4-heptadien-6-ynal (8). The monodeuterated V thus prepared was converted into trisdehydro[18]annulene (XI) deuterated at 17-position according to the above stated reaction sequence. The NMR spectrum of monodeuterated XI measured at 125°C exhibits only a very weak doublet at τ 6.40, thus indicating the conformational mobility of 16,17-*trans*-double bond. Consequently, XI appeared to be an

Table 1. High Temperature NMR Spectra of XI in $CDBr_3$. τ-values (J in Hz)

Temp. °C \ Proton	H^4,H^6	H^5	H^{13}	H^{14}	H^{15}	H^{16}	H^{17}	*t*-Bu
125	0.66 (13)	12.97t (13)	0.88d (12)	11.41dd (12,14.5)	2.24dd (14.5,11)	7.34d (11,15)	6.39d (15)	7.96s 8.06s 8.15s
70	0.58d (13)	13.19t (13)	0.80d (12)	11.86dd (12,14.5)	1.94dd (14.5,11)	7.4 br.	6.4 br.	7.95s 8.02s 8.13s
50	0.55d (13)	13.26t (13)	0.77d (12)	12.08 br.	1.78 br.	*ca.* 6.8 very broad		7.94s 8.01s 8.02s 8.13s
31	0.50d (13)	13.32t (13)	0.71d (12)	12.25 br.	1.68 br.			7.93s 8.00s 8.01s 8.12s
125*	0.66d (13)	12.97t (13)	0.89d (12)	11.39dd (12,14.5)	2.27dd (14.5,11)	7.29d (11)	6.4 v.w.	7.97s 8.05s 8.15s

* Monodeuterio-XI. v.w. = very weak signal. br. = broad signal.

equilibrium mixture of nonequivalent conformers (XI_a and XI_b), and the signals at τ 7.43 and 6.39 observed at 125°C seemed to be the averaged values of the chemical shifts of H^{16} and H^{17} at their inner and outer positions, respectively, owing to rapid exchange of the positions. The NMR signals of inner protons observed at low temperature consist of two groups of signals at *ca.* τ 13- and 14-regions, and the parameters are recorded in Table 2. The triplets observed at τ 14.12 and 14.43 at -80°C become progressively broader on elevation of temperature accompanying with low-field shift, and the doublet at τ 13.02 which was observed at -80°C disappeared at -50°C. The pronounced temperature dependency of these signals suggests that the signals should arise from the protons attached to rather flexible part of the annulene skeleton, *i.e.*, 14,15, 16 and 17-positions. The doublet could be assigned to H^{17} in XI_b. The double

Table 2. Chemical Shifts of Inner Protons at Low Temperature. τ-values

	XI_a		XI_b		
	H^5	H^{14},H^{16}	H^5	H^{14}	H^{17}
-80°C	13.02dd or 13.22dd	14.12t or 14.43t	13.22dd or 13.02dd	14.43t or 14.12t	13.02d
-60°C	13.04dd or 13.23dd	14.10t br. or 14.37t br.	13.23dd or 13.04dd	14.37t br. or 14.10t br.	13.05d
-50°C	12.65t or 12.87t	13.65t br. or 13.89t br.	12.87t or 12.65t	13.89t br. or 13.65t br.	

br. = broad signal. Solvent: CS_2-CD_2Cl_2

doublets at τ 13.02 and 13.22 in the spectrum at -80°C were found to be less temperature dependent than the signals of other inner protons, and are assigned to H^5 in XI_a and XI_b, which attached to the rigid part of the annulene perimeter. Disappearance of the doublet at τ 13.02 observed at -80°C on warming to -50°C indicates that the molecule becomes "mobile" at this temperature. The ratio of XI_a: XI_b at non-mobile temperature was estimated to be *ca.* 1:2 comparing the intensity of τ 13-region (H^5 in XI_a, and H^5 and H^{17} in XI_b) with that of τ 14-region (H^{14}, H^{16} in XI_a, and H^{14} in XI_b).

The complex signals of outer protons observed at low temperature could be divided into low-field and high-field portions. The low-field portion was assigned to H^{15}, H^{17} in XI_a and H^{15}, H^{16} in XI_b, which were bound to rather "soft" part of the perimeter of XI, because the multiplet of low-field portion showed a marked broadening on elevation of temperature. On the contrary, the high-field portion was found to be temperature independent, and could be assigned to the protons (H^4, H^6 and H^{13}) attached to the "rigid" part of XI_a and XI_b.

The difference in chemical shifts between the inner and outer protons, $\Delta\tau = \tau_o - \tau_i$, can be regarded as an approximate measure of ring current. The apparent decrease of Δτ-value for the unsymmetrical XI (Δτ14.29 ∿ 11.77 in CS_2 at -80°C; Δτ=12.82 ∿ 10.57 in $CDBr_3$ at 31°C) as compared with those of the symmetrical I (Δτ=14.84 in $CDCl_3$ at 36°C) and II (Δτ=13.46 and 12.96 in $CDBr_3$ at 36°C) seems to be insignificant, if we take into account the difference in ring strain and conformational stability between I, II and XI. This result is consistent with the induction of a very strong paramagnetic ring current in the unsymmetrical III and seems to suggest a minor energy difference between 'butatriene-diacetylene'- and 'acetylene-hexapentaene'-structures (see, the following paper).

References and Note

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