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PENTAKISDEHYDRO[16]ANNULENO[18]ANNULENE

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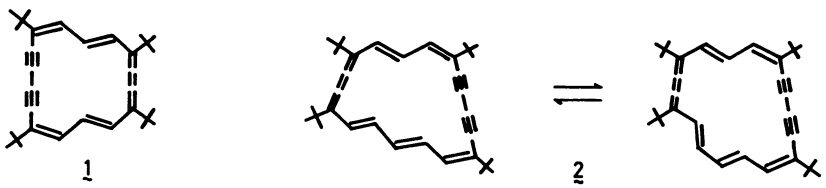
Pentakisdehydro[16]annuleno[18]annulene consisting of a trisdehydro[16]-annulene and a trisdehydro[18]annulene has been synthesized. The ^{1}H NMR spectrum indicates the paratropicity of 16- and diatropicity of 18-membered ring, respectively. The trisdehydro[18]annulene moiety is conformationally mobile and the ^{1}H NMR behavior is described.

Previously we have observed the very strong paratropicity and high conformational stability of the tetra-*t*-butyltrisdehydro[16]annulene (1)[1]. On the other hand, the strongly diatropic tetra-*t*-butyltrisdehydro[18]annulene (2)[2] was found to exist in an equilibrium mixture owing to conformational mobility of a *trans*-double bond. Consequently, the synthesis of an annuleno-annulene consisting of these two antiaromatic and aromatic moieties (1 and 2) seemed to be of considerable interest in view of the effect of annelation on the tropicity of each ring and on the conformational mobility of the aromatic moiety.



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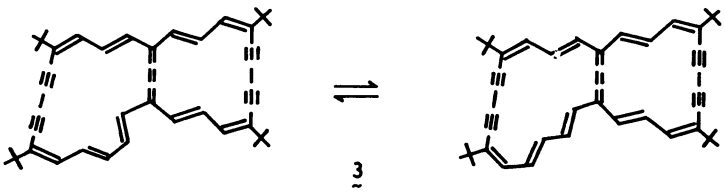
$\tau_i - \tau_o = 12.96 \sim 14.35$ (−80 °C)



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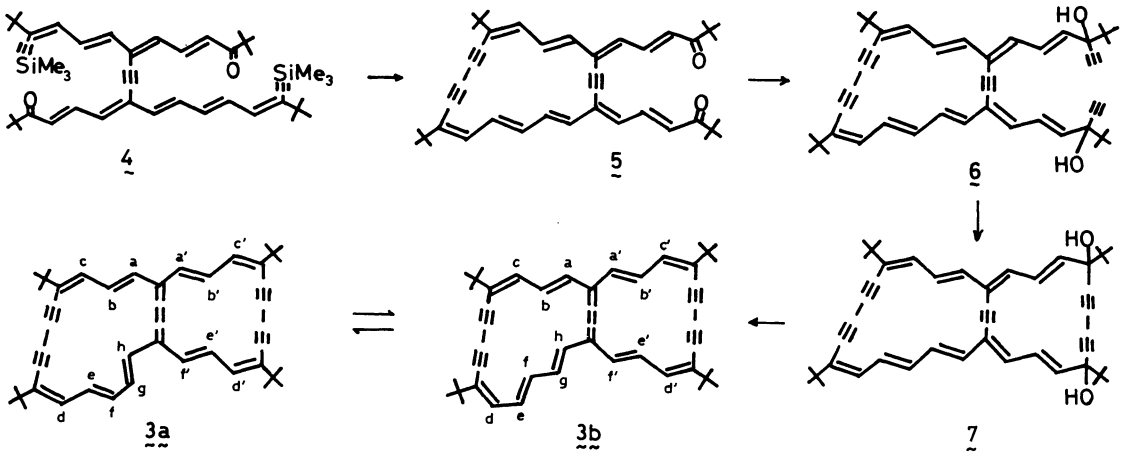
The synthesis of 3 was carried out by the reaction sequence outlined in Scheme. Oxidative coupling of the bis(trimethylsilyl) diketone (4)[3] with copper(II) acetate in pyridine and methanol at 80-90°C afforded the cyclic triyne diketone [5, orange-red crystals, mp *ca.* 210°C (dec.), 61%, Mass(m/e): 586 (M^+)]. The diketone (5) could be bisethynylated with lithium acetylide in THF[4] to give the monocyclic diol [6, yellow viscous oil, 89%, Mass(m/e): 638 (M^+)]. The diol (6) was again oxidized with copper(II) acetate in pyridine-methanol to yield the bicyclic glycol (7, orange-yellow crystals, mp > 280°C (dec.), 36%, Mass(m/e): 636 (M^+)]. Treatment of the bicyclic glycol (7) with tin(II) chloride in ether saturated with hydrogen chloride gave the pentakisdehydro[16]-annuleno[18]annulene (3) in the form of fairly stable deep green crystals (mp > 100°C (dec.), 85%). The absorption curve of the electronic spectrum of 3 (ES: $\lambda_{max}^{pentane}$ 305sh, 320sh, 335, 363, 410sh, 429, 461, 685, 747, 824 nm) is closely related with that of tetrakisdehydro[16]annuleno-[18]annulene (8c)[5].



Scheme

The ^{1}H NMR spectrum of 3 was temperature dependent, as indicated in Figure. The signals at τ 11.73 (triplet) and 11.74 (doublet) in the spectrum at 50°C was assigned to the inner protons H_b and H_h. At the same temperature no signals of the protons H_e and H_f were observed, thus indicating the conformational mobility of the H_e,H_f-*trans*-double bond. On cooling, the signals of 3 caused progressive broadening and the very broad spectrum was observed at 0°C. Further cooling resulted in the appearance of new complex signals. The spectrum at -70°C shows unresolved multiplets at τ -6.8 ∿ -7.2 (inner protons of 16π moiety), τ 1.2 ∿ 2.4 (outer protons of 18π moiety), τ 3.9 ∿ 4.2 (outer protons of 16π moiety), and τ 11.4 ∿ 12.3 (inner protons of 18π moiety). Although the attempts to observe the averaged signal of H_e and H_f at higher temperature were unsuccessful owing to the instability of 3, we have tentatively concluded that the annulenoannulene (3) should exist in an equilibrium mixture of nonequivalent conformers (3a and 3b) on the basis of the above-

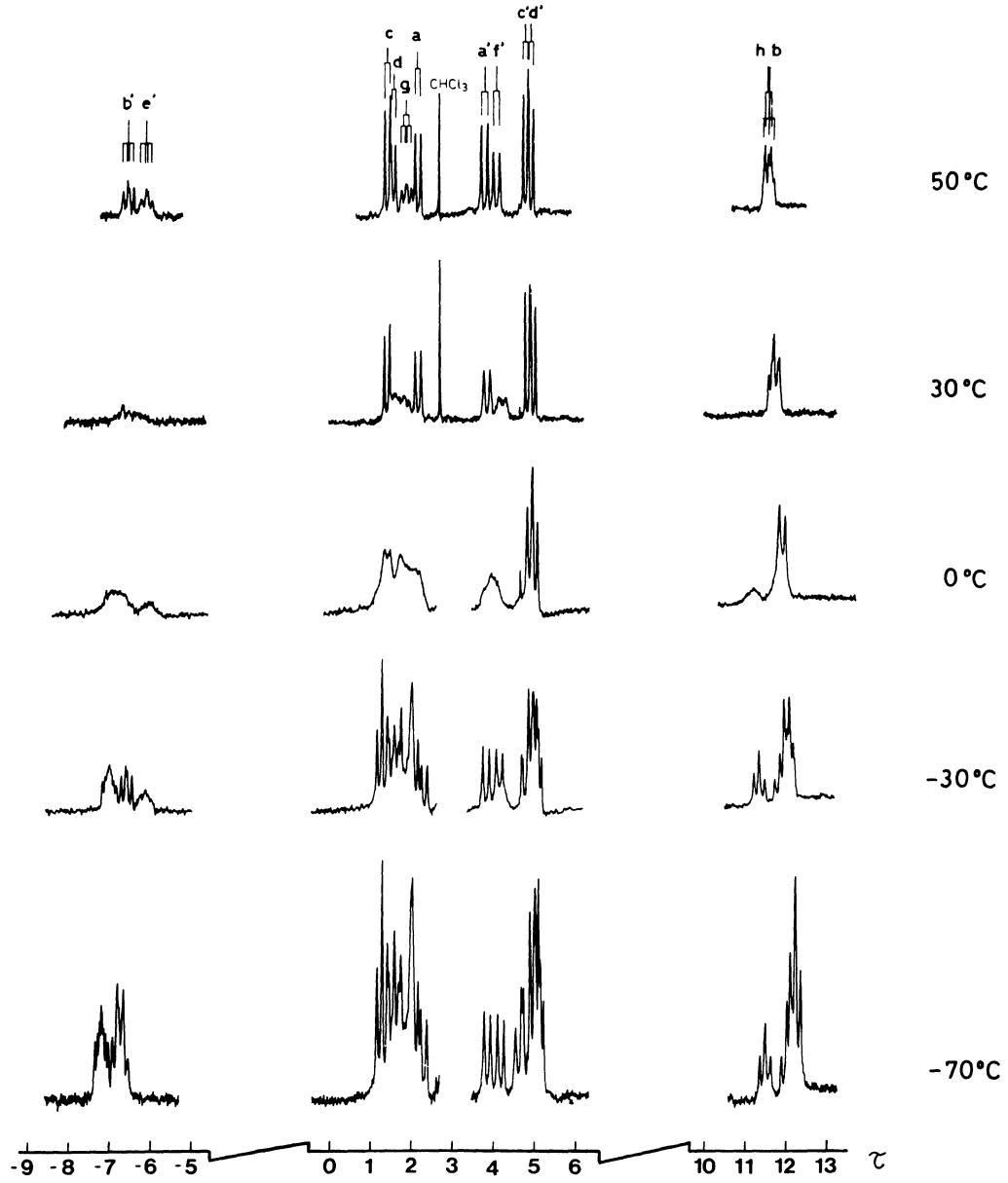


Figure. ^{1}H NMR Spectra of 3 in $CDCl_3$ at Different Temperatures.

Table 1. ^{1}H NMR Parameters of 3 ($CDCl_3$, τ-values at 50°C).

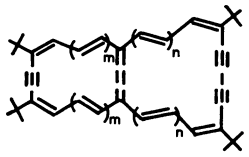
18-membered ring	H_a	2.22 d, J=13	H_b	11.73 t, J=13
	H_c	1.44 d, J=13	H_h	11.74 d, J=13
	H_d	1.51 d, J=13	*t*-Bu	8.30 s, 8.32 s
	H_g	1.92 dd, J=11, 13		
16-membered ring	$H_{a'}/H_{f'}$	3.68 d, J=15	$H_{b'}/H_{e'}$	-5.98 dd, J=12, 15
		3.89 d, J=15		-6.45 dd, J=12, 15
	$H_{c'}/H_{d'}$	4.87 d, J=12	*t*-Bu	9.19 s, 9.21 s
		5.00 d, J=12		

mentioned temperature dependent ^{1}H NMR spectral behavior. It is noteworthy that the position of conformationally labile *trans*-double bond in 3 is different from that in 2. The cause of this difference is not clear yet, but annelation of conformationally stable 16-membered ring seems to exert some effect on the conformational behavior of the 18-membered ring.

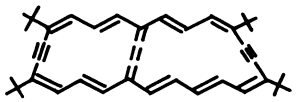
As summarized in Table 1, ^{1}H NMR parameters of 3 at 50°C show the induction of strong paramagnetic and diamagnetic ring currents in 16- and 18-membered rings, respectively. During the course of our studies on tetrakisdehydro[4n]annuleno[4n'+2]annulenes (8a ∿ 8d)[5] and trisdehydro-[14]annuleno[16]annulene (9)[3], a general trend has been observed that the antiaromatic moiety is apt to preserve its inherent paratropicity suppressing diatropicity of the aromatic moiety. It should be noted that the diatropicity of 18π-electron moiety in 3 as judged by the $\Delta\tau = \tau_i - \tau_o$ value was found remarkably larger than that of 8c, although both of them are fused with the same trisdehydro[16]annulene ring (Table 2). It is difficult to give a definite account of the interesting difference observed between 3 and 8c. However, the decrease of diatropicity of the 18π-electron system in 8c seems to reflect an enhanced contribution of peripheral 28π-electron system as compared with that of 3.

Table 2. The difference in the chemical shifts between inner protons (τ_i) and outer protons (τ_o) (3 and 8c).

		$\Delta\tau$ ($\tau_i - \tau_o$) [16]	$\Delta\tau$ ($\tau_i - \tau_o$) [18]
3	(50°C)	-9.66 ∿ -11.45	9.15 ∿ 11.09
8c	(35°C)	-10.38 ∿ -10.81	7.93 ∿ 8.92



8a, m=n=1
8b, m=1, n=2
8c, m=2, n=1
8d, m=n=2



9

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