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OXYGEN-BRIDGED THIA[15]ANNULENES: DEMONSTRATION OF A STRONG PARAMAGNETIC RING CURRENT IN A 4nπ-THIA-ANNULENE (n = 4)

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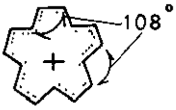
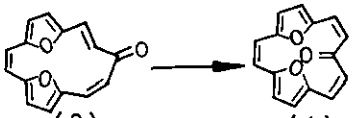
Abstract - The synthesis of 4,7:10,13-diepoxy-2-*trans*-8,14-di-*cis*-thia[15]annulene (9) and 4,7:10,13-diepoxy-2,8,14-tri-*cis*-thia[15]annulene (10) is described. The ^{1}H-nmr spectrum of (9) revealed the existence of a paramagnetic ring current, showing that (9) has a planar and diminished bond alternate rigid frame, as expected for an anti-aromatic 16π system. Conversely, the ^{1}H-nmr spectrum of (10) revealed that (10) is atropic and consequently non-planar.

A hypothetical [15]annulenyl ion system (1) whose geometry is constructed formally with regular pentadecagon seems to offer an angle-strain-free annulene frame, since all the inside and outside angles of (1) are confined to the inside angle of cyclopentadienide anion, viz. 108°. However, replacement of some of the inside hydrogen atoms with divalent atoms is necessary to realize a planar 15-membered molecular framework, because the non-bridged 15-membered ring does not possess a sufficient large cavity as to accommodate all the inner hydrogens without causing serious H-H interactions. This is the reason why that chemistry of pentadecagons made up of sp^2 carbon skeleton and of its heteroatom incorporated variants has been scarcely studies until oxygen-bridged oxa[15]annulene (2)[1] and [15]annulenones (3 and 4)[2] were prepared as real members. Available findings so far obtained revealed that the oxygen bridges keep the perimeters relatively

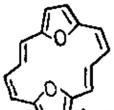


(1)

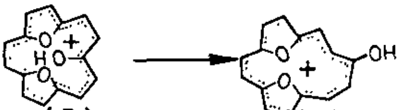
(2)



(3) (4)



(11)



(5) (6)

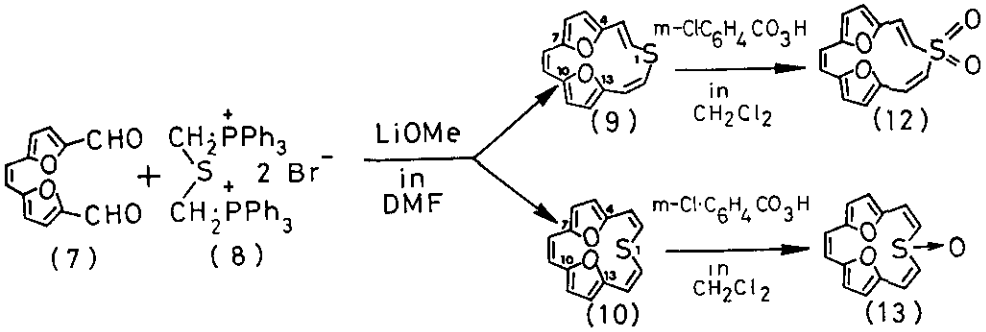
flexible as to allow the uni-directional thermal isomerizations both in the [15]annulenone (3 → 4) and the corresponding [15]annulenyl ion (5 → 6), respectively,[3] whereas oxa[15]annulene (2) adopts exclusively all cis configuration as a thermally rigid frame.

We now report the synthesis of thia[15]annulenes (9 and 10), potential 16π anti-aromatic species, whose preparations were previously unsuccessful by us.[4] In terms of the successful sulphur incorporation, although it be still in lower yields, we became intrigued with following two points:

(1) Should the thia-annulenes be more paratropic than oxa[15]annulene (2), based on the increasing availability of the sulphur lone pair?

(2) What arranged geometry should have the thia-annulene, if the accession of the increased paratropicity does hold for the molecule?

The double Wittig reaction of the dialdehyde (7)[5] with the phosphonium salt (8)[6] in DMF, at 60°C, LiOMe as a base under an enforced high-dilution condition[7] followed by a subsequent low temperature work-up, and chromatographic separation on SiO_2 (n-hexane) gave mono-*trans* thia[15]-annulene (9) and all-*cis* counterpart (10) [for physical data , see Table I].



The ^1H-nmr spectrum of (9) indicated that the proton within the perimeter is deshielded, whereas those outside are shielded, i.e., a doublet at δ 14.59 ppm for the inner proton on the *trans* double bond and a doublet at δ 5.02 ppm for the outer proton on the *trans* double bond, together with other outer protons at δ 4.65 - 5.50 ppm (9H) [in $CDCl_3$ at 25°C, Fig. 1]. Thus it became clear that (9) is strongly paratropic. In contrast, the ^1H-nmr spectrum of (10) consisted only of three signals appearing at the ordinary olefinic region [δ 6.26, s, 2H (*cis* double bond), 6.54, s, 4H (furanoid H), and 6.57, AB system with $J/\nu_0\delta > 5$[8a] (*cis* double bonds adjacent to the S-atom)], indicating that (10) is atropic and consequently non-planar.

A comparison of the chemical shifts of the fifteen membered ring protons in the related system is shown in Table II. Crucial role of the sulphur atom for the demonstration of paratropic character became evident in (9). A confirmative evidence was given, which implies that forcible participation of the sulphur lone pair occurred only in the mono-trans geometry, not in the all-cis geometry. Model examination shows that an extensive twisting of the cis double bonds of (10) hinders the effective overlap of the sulphur lone pair. The difference of chemical shifts of the inner and outer proton resonances on the trans double bond of (9) [$\Delta\delta = \delta_i - \delta_{o_{av}} = 9.6$ ppm] gave the largest value yet recorded in nutral hetero[15]annulenes so far prepared, and the value is close to the corresponding value obtained from di-oxygen-bridged [16]-annulene dioxide (11)[9] [$\Delta\delta = 12.8$ ppm], an iso-electronic 16π annulene frame possessing same number of oxygen-bridge [see Table II].

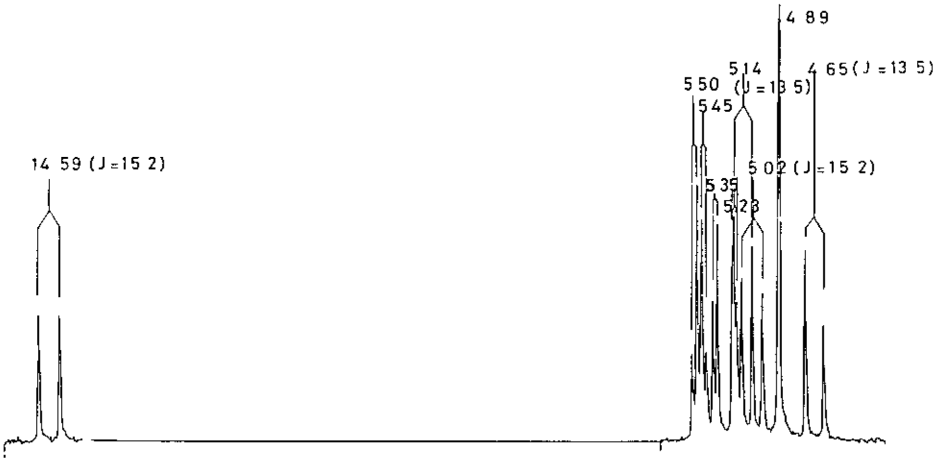


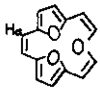
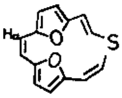
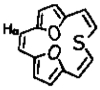
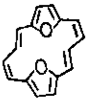
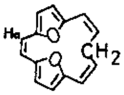
Fig. 1. ^{1}H-Nmr Spectrum of (9) in $CDCl_3$ at 25°C

In agreement with the large paratropic shift of (9), electronic spectrum of (9) in n-hexane showed a very close resembrance in shape with that of (11)[9] [Fig. 2]. Indeed, the position of the longest wavelength bands of (9) and (10), which appeared at 503 nm ($\log\varepsilon = 2.57$) and at 530 nm ($\log\varepsilon = 2.43$), respectively, indicate clearly the participation of lone pair electrons of sulphur atom. The ^{1}H-nmr and electronic spectral properties of (9) reveal that the molecule should be planar with delocalized 16π-electron system. In contrast, the electronic spectrum of (10) remains markedly different from those of (9) and (11).

It was found that no thermal isomerization occurred in both thia-annulenes, since the ^{1}H-nmr spectra did not show significant changes in DMF-d_7, up to 150°C. In contrast, a facile isomerization $(9) \rightarrow (10)$ occurred in the presence of H^+ (CF_3COOH) at room temperature (uv and ^{1}H-nmr spectroscopy).

Interestingly, neither the sulphone (12) nor sulphoxide (13) [obtainable by the oxidation of (9) and (10) with m-chloroperbenzoic acid in CH_2Cl_2 at - 20°C for 2 h, respectively] showed any tendency to exhibit diatropicity (14π), in agreement with the theoretical prediction, which implies that ring current intensity is substantially more higher for delocalized 4nπ compounds than (4n+2)π compounds with same size, if pronounced bond alternation does not occur in the 4nπ system.[8b, 8c]

Table II. ^{1}H-Nmr Parameters of the Oxygen-bridged 16π- and related Compounds in $CDCl_3$ (δ values in ppm, J values in Hz, at 25°C)

Compound		H_a	H_{trans}	H_{cis}	H_{furan}
	(2)	5.20, s		4.78 d, J=6.4 5.56 d, J=6.4	5.62 d, J=3.4 5.73 d, J=3.4
	(9)	5.00, s	5.20 d, J=15.2 14.55 d, J=15.2	4.65 d, J=13.5 5.14 d, J=13.5	5.23 d, J=3.4 5.35 d, J=3.4 5.45 d, J=3.4 5.50 d, J=3.4
	(10)	6.26, s		6.57 AB system ($J/\nu_0\delta > 5$)	6.54, s
	(11)		4.43 d, J=15.0 17.18 d, J=15.0	4.41 d, J=10.0 4.60 d, J=10.0	4.86 d, J=3.5 4.93 d, J=3.5
	(14)	6.40, s		5.97 d, J=12.5 6.50 d, J=12.5	6.54 d, J=3.5 6.65 d, J=3.5

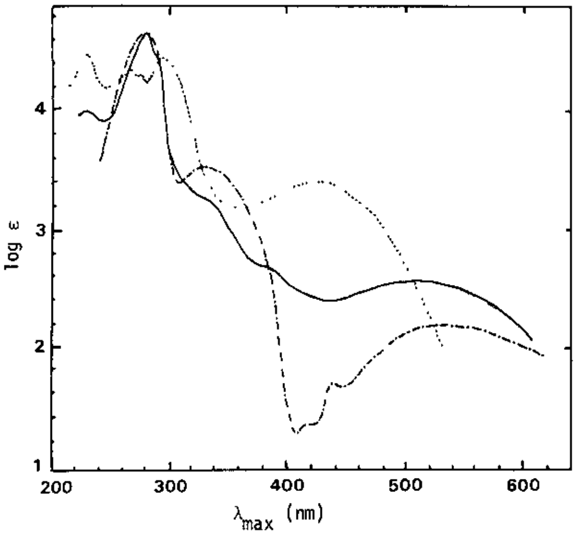


Fig. 2. Electronic Spectra of (9) ———, (10) ··········, and (11) —·—·— in n-hexane

Table I. Physical Data of Compounds

Thia[15]annulene dioxide (9): mp 98 - 100°C (n-hexane); yield 1.6 %; MS: m/e 242 (M^+); electronic spectrum λ_{max} (n-hexane): 227 (10700), 280.5 (49100), 336 sh (1700), 350 sh (1000), 380 sh (480), 503 (370); ^{1}H-nmr ($CDCl_3$) see Text; ^{13}C-nmr ($CDCl_3$) 106.5 (d), 110.9 (d), 114.4 (d), 114.5 (d), 115.8 (d), 116.2 (d), 116.5 (d), 117.2 (d), 120.4 (d), 129.8 (d); signals due to the four singlet carbons on the furan rings were obscured in the ^{13}C-nmr spectrum; ir (KBr) 1600, 1038, 1020, 933 cm^{-1}.

Thia[15]annulene dioxide (10): mp 92 - 93°C (n-hexane); yield 5.5 %; MS: m/e 242 (M^+); electronic spectrum λ_{max} (n-hexane): 228 (31400), 265 (23450), 271 (22500), 296 (31700), 425 (2750); ^{1}H-nmr ($CDCl_3$) see Text; ^{13}C-nmr ($CDCl_3$) 151.4 (s), 149.9 (s), 120.8 (d), 114.4 (d), 113.5 (d), 111.4 (d); ir (KBr) 1330, 1182, 1030 cm^{-1}.

The sulphone (12): mp 130°C (decomp) (EtOH); yield 75 %; MS: m/e 274 (M^+); ^{1}H-nmr ($CDCl_3$) 6.12 (d, J = 15 Hz, 1H), 6.17 (d, J = 13.5 Hz, 1H), 6.66 (s, 2H), 6.76 (d, J = 3.2 Hz, 1H), 6.78 (d, J = 13.5 Hz, 1H), 6.83 (d, J = 3.2 Hz, 1H), 6.93 (d, J= 3.2 Hz, 1H), 7.04 (d, J = 3.2 Hz, 1H), 7.57 (d, J = 15 Hz, 1H).

The sulphoxide (13): mp 188 - 190°C (EtOH); yield 90 %; MS: m/e 258 (M^+); ^{1}H-nmr ($CDCl_3$) 7.08 (s, 2H), 7.09 (d, J = 11 Hz, 2H), 7.26 (d, J = 3.5 Hz, 2H), 7.33 (d, J = 3.5 Hz, 2H), 7.46 (d, J = 11 Hz, 2H).

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7. To a solution of (7) (1.62 g, 7.5 mM) and (8) (5.58 g, 7.5 mM) in dry DMF (240 ml) was added a solution of LiOMe (208 mg of lithium in 30 ml of absolute MeOH) dropwisely at 60°C over 7 h under nitrogen.
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