

Formation of a Paratropic, Dicationic 24π -Electron System in D_2SO_4

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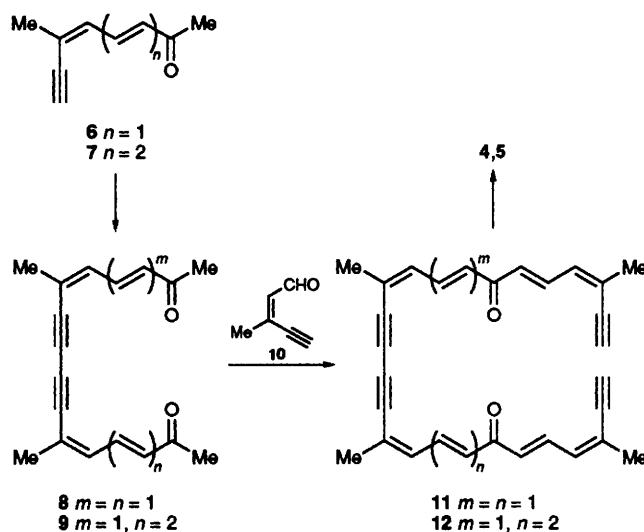
Tetramethyloctadecahydro-[26] and -[28]annulenediones have been synthesized; the corresponding dicationic species in D_2SO_4 showed paratropicity and diatropicity, respectively, affording the first confirmation of tropicity alternation in monocyclic annulenediones.

We have reported the alternation of para- and dia-tropicity between $(4n + 2)\pi$ - and $4n\pi$ -electron systems in di- or trimethyltetradecahydroannulenediones **1** with 13- to 25-membered rings.^{1,2} Judging from the fact that the annulenediones **1** showed a smaller degree of para- and dia-tropicity than the corresponding carbocyclic annulenes,³ annulenediones with an additional carbonyl group were expected to show even smaller tropicity than annulenes. However, a dimethylhexadecahydro[16]annulenedione prepared by Lombardo and Sondheimer⁴ proved to be diatropic. Also, we have recently reported the preparation of methano-bridged didehydro-[20] **2**^{5a} and -[24]annulenedione **3**,^{5b} both of which showed extremely strong diatropicity in D_2SO_4 due to the formation of the highly delocalized dicationic species, but we could not obtain paratropic species in this series of compounds because of synthetic difficulties. Thus, although several annulenediones have been prepared,⁶ those which show paratropicity have not so far been observed probably due to lower thermal stability of paratropic $4n\pi$ systems than diatropic $(4n + 2)\pi$ ones.⁷

In this paper, we report the synthesis of tetramethyloctadecahydro-[26] **4** and -[28]annulenedione **5**, and their tropic nature as revealed by 1H NMR spectroscopy in $CDCl_3$ and D_2SO_4 .

The annulenediones **4** and **5** were synthesized as illustrated in Scheme 1. The intermolecular oxidative coupling of the dimethyl ketone **6**^{1a} or the cross-coupling of **6** and **7**^{1b} afforded the tetramethyl diketone **8** or **9** in ca. 30% yield.⁹ Condensation of **8** and **9** with (*Z*)-3-methyl-2-penten-4-ynal **10**⁸ in the presence of ethanolic sodium ethoxide in benzene afforded the acyclic diketones **11** (73%) and **12** (60%), respectively. The intramolecular oxidative coupling of **11** was carried out with copper(II) acetate monohydrate in pyridine-methanol under high dilution conditions with diethyl ether as an entraining solvent to give the [26]annulenedione **4** in 45% yield.¹⁰ Compound **12** afforded the [28]annulenedione **5** in 14% yield under similar conditions.¹⁰

The 1H NMR spectral data of **4** and **5** in $CDCl_3$ (Table 1) are consistent with the structures shown. It is concluded from



Scheme 1

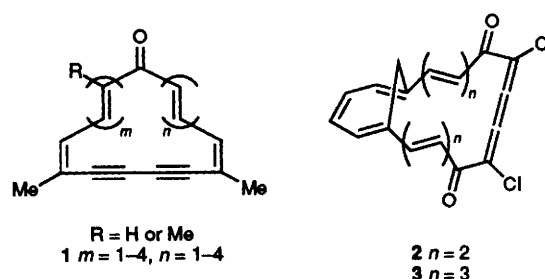
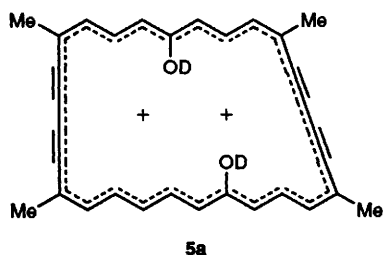
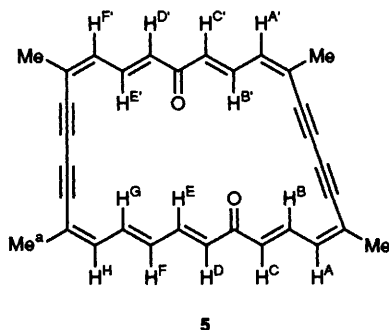
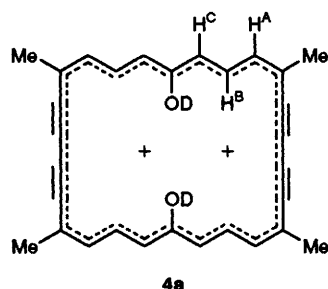
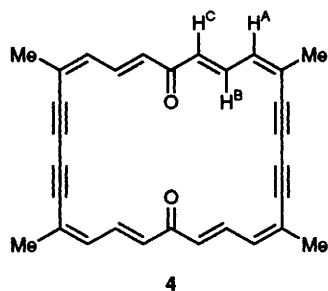


Table 1 1H NMR spectral data of **4** and **5** at 26 °C^a

Compd.	Solvent	δ (J/Hz)		
		Outer olefin protons	Inner olefin protons	Methyl protons
4	$CDCl_3$	6.29 (d, 15.0, H ^C) 6.51 (d, 11.8, H ^A)	8.19 (dd, 15.0, 11.8, H ^B)	1.98 (s)
	D_2SO_4	5.20 (d, 15.0, H ^C) 5.87 (d, 11.8, H ^A)	11.93 (dd, 15.0, 11.8, H ^B)	1.62 (s)
5	$CDCl_3$	6.45 (d, 15.0, H ^D)	7.07 (dd, 14.8, 11.6, H ^G)	2.01 (s, Me ^a)
		6.45 (d, 15.0) } H ^C	7.43 (dd, 15.0, 11.5, H ^E)	2.04 (s)
		6.46 (d, 15.0) } H ^{C'}	7.60 (dd, 15.0, 11.7) } H ^{E'}	2.07 (s)
		6.47 (d, 15.0) } H ^{D'}	7.62 (dd, 15.0, 11.6) } H ^{B'}	2.08 (s)
		6.51 (dd, 14.8, 11.5, H ^F)	7.68 (dd, 15.0, 11.6) } H ^B	
		6.60 (d, 11.6) } H ^A		
		6.60 (d, 11.7) } H ^{A'}		
		6.65 (d, 11.6) } H ^{F'}		
	6.64 (d, 11.6, H ^H)			
	D_2SO_4	7.82–8.05 (m, 9H)	4.47 (br, 1H), 4.99 (br, 1H) 5.08 (br, 1H), 5.17 (br, 1H) 5.31 (br, 1H)	2.55 (s), 2.60 (s) 2.69 (s), 2.72 (s)

^a Internal and external tetramethylsilane was used as the reference in $CDCl_3$ and D_2SO_4 , respectively.



these NMR data that neither of these compounds show detectable tropicity in CDCl_3 .

When the [26]annulenedione **4** was dissolved in D_2SO_4 , a deeply coloured solution was obtained indicating the formation of the protonated dicationic species, although this species was unstable and rapidly decomposed. In the ^1H NMR spectrum (Table 1), the inner olefinic protons were shifted downfield by *ca.* 3.7 ppm relative to the corresponding signal in CDCl_3 , while the outer olefinic protons and the methyl protons appeared upfield by *ca.* 0.8 and 0.4 ppm, respectively.

This is clearly ascribed to the induction of paramagnetic ring current as expected for the 24π -electron species **4a**.

Dissolution of [28]annulenedione **5** in D_2SO_4 resulted in the formation of the dicationic species **5a** which again was unstable and decomposed over several hours at ambient temperature. In the ^1H NMR spectrum, complex nine-proton signals were observed in a narrow range of δ 7.82–8.05 and five broad peaks each representing one proton were observed at a high-field region of δ 4.4–5.4 together with four singlets due to the methyl groups. Although no detailed coupling information was obtained, the nine-proton signals at low field would reasonably be assigned to the outer olefinic protons and five-proton signals at high field to the inner olefinic protons. Thus, the average downfield shifts of the outer olefinic protons upon changing the solvent from CDCl_3 to D_2SO_4 amount to *ca.* 1.4 ppm and the upfield shifts of the inner protons amount to *ca.* 2.5 ppm. These shifts together with the downfield shifts of the methyl protons by *ca.* 0.6 ppm indicate that the species in D_2SO_4 is clearly diatropic as expected for a 26π -electron system.

These findings therefore confirmed that the annulenediones **4** and **5** in D_2SO_4 exist as the respective dicationic species which are significantly paratropic and diatropic, respectively. This is the first confirmation of the alternation of the tropic nature between $(4n + 2)\pi$ and $4n\pi$ electron systems in monocyclic annulenediones.¹¹

This work was supported by a Grant-in-Aid for Scientific Research No. 05453029 from the Ministry of Education, Science and Culture, Japan.

Received, 18th January 1994; Com. 4/00327F

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- All new compounds gave satisfactory elemental analysis and spectral data consistent with the assigned structures.
- Small amounts of annulenediones with the structures isomeric to **4** and **5** were obtained. These minor isomers also showed para- and dia-tropicity in D_2SO_4 similarly to **4** and **5**. Details will be described in a full paper.
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