

## Unusual Formation of a Methano-bridged Didehydro[20]annulenedione. A Highly Diatropic, Dicationic 18 $\pi$ -Electron Species in D<sub>2</sub>SO<sub>4</sub>

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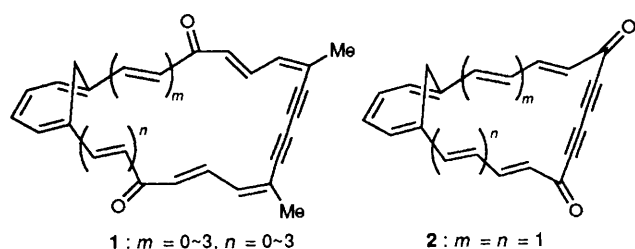
An intramolecular coupling of 1,6-bis(5-oxohepta-1,3-dien-6-ynyl)cyclohepta-1,3,5-triene under Glaser conditions affords 12,15-dichloro-13,14-didehydro-1,6-methano[20]annulene-11,16-dione, which exhibits strong diatropicity in D<sub>2</sub>SO<sub>4</sub>, suggesting the formation of the highly delocalized dicationic species.

Although several annulenediones are known, there are few that possess a 20–30-membered ring.<sup>1</sup> Recently, we reported successful syntheses of a series of methano-bridged tetrahydroannulenediones **1** and showed that the [24]annulenedione (**1**:  $m = n = 1$ ) exhibits diatropicity in D<sub>2</sub>SO<sub>4</sub>, suggesting the formation of the corresponding dicationic species.<sup>2</sup> During our attempts to prepare another series of annulenediones **2**, we encountered the unexpected formation of a [20]annulenedione **3** containing a butatriene moiety and two chlorine atoms, and of a strongly diatropic dicationic species **7** therefrom in D<sub>2</sub>SO<sub>4</sub>.

Bisethynylation of 1,6-bis(4-formylbuta-1,3-dienyl)-cyclohepta-1,3,5-triene **4**<sup>3</sup> with a large excess of ethynylmagnesium bromide in tetrahydrofuran afforded an isomeric mixture of the diol **5**, from which an isomer with the olefin configuration shown by the formula was isolated in 40% yield. Oxidation of **5** with BaMnO<sub>4</sub><sup>4</sup> in dichloromethane afforded the corresponding diketone **6** in 85% yield. An intramolecular oxidative coupling of **6** was carried out using the Glaser conditions<sup>5</sup> by

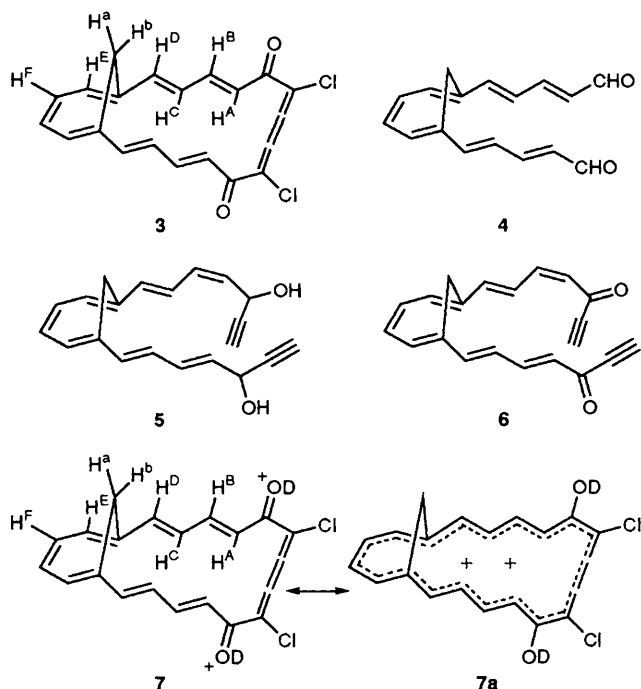
bubbling oxygen through a mixture of the diacetylene **6**, copper(I) chloride and ammonium chloride in aqueous ethanol–benzene with conc. hydrochloric acid at 60 °C. Chromatography of the product on silica gel afforded dark-purple needles, m.p. 156–161 °C, in 10% yield.

The product was identified as compound **3** rather than the expected structure **2** ( $m = n = 1$ ) from the following spectral data and the elemental analysis. The molecular ion peak in the mass spectrum appeared at  $m/z$  368 with the expected isotope peaks for two chlorine atoms. The IR spectrum (KBr disc) showed a strong carbonyl absorption at 1655 cm<sup>-1</sup> and a weak absorption ascribable to the butatriene moiety at 2040 cm<sup>-1</sup>. In the <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, 125 MHz), the quaternary carbon signals ascribable to the terminal and central carbons of the butatriene moiety appeared at  $\delta_C$  121.1 and 158.8,



**Table 1** 500 MHz <sup>1</sup>H NMR spectral data of compound **3** at 26 °C

Proton	$\delta_H$ values (J/Hz) in solvent	
	CDCl <sub>3</sub>	D <sub>2</sub> SO <sub>4</sub>
CH <sub>2</sub> a	1.27 d (13.4)	{ -3.17 d (14.2)
b	3.06 d (13.4)	
H <sup>A</sup>	6.15 d (14.5)	-4.39 d (13.2)
H <sup>B</sup>	7.68 dd (14.5, 11.5)	11.00 t (12.7)
H <sup>C</sup>	6.27 dd (15.4, 11.5)	-2.74 t (13.3)
H <sup>D</sup>	7.06 d (15.4)	10.99 d (14.0)
H <sup>E</sup>	6.72 m	{ 9.52br m
H <sup>F</sup>	6.98 m	



respectively. The  $^1\text{H}$  NMR spectrum in  $\text{CDCl}_3$  was unambiguously analysed as shown in Table 1. The coupling pattern of the olefinic protons clearly pointed to the geometry shown by the formula **3**.

It is noted that all the olefin configurations in **5** were retained during the oxidation to give **6** but the *Z*- $\text{CH}=\text{CH}$  moiety isomerized to *E* during the Glaser coupling to form **3**. The reason for this as well as the detailed mechanism of the formation of **3** is still uncertain; an inclination to formation of a less-strained ring upon cyclization may be partly responsible.

The  $^1\text{H}$  chemical shift data of **3** (Table 1) indicate that the signals assigned to the inner olefinic protons  $\text{H}^{\text{A}}$  and  $\text{H}^{\text{C}}$  appear at a high field of  $\delta_{\text{H}}$  6.1–6.3, while the outer protons  $\text{H}^{\text{B}}$ ,  $\text{H}^{\text{D}}$ ,  $\text{H}^{\text{E}}$  and  $\text{H}^{\text{F}}$  resonate at a low field of  $\delta_{\text{H}}$  6.7–7.7, suggesting that a diamagnetic ring current, though small, is induced.

In  $\text{D}_2\text{SO}_4$ ,  $\text{H}^{\text{A}}$ ,  $\text{H}^{\text{C}}$  and the methylene protons, which are located inside the macrocycle, appear at an extremely high field of  $\delta_{\text{H}}$   $-2.6$  to  $-4.4$ , while the olefinic protons outside the macrocycle afford their signals at a very low field of  $\delta_{\text{H}}$  9.5–11.0 (Table 1). This indicates the occurrence of a large diamagnetic ring current due to the formation of the dideuteriated dicationic species **7** to which the delocalized  $18\pi$ -electron structure **7a** contributes to a great extent. The magnitude of diatropicity exhibited by **7** is even greater than that shown by the dication derived from 8,13-dimethyl-2,3,9,10,11,12-hexadehydro[16]annulene-1,4-dione.<sup>6</sup>

To our knowledge, compound **3** is the largest-membered annulenedione to show the ring current effect so far obtained and the species **7** is the most highly diatropic, dicationic species arising from the annulenedione.

This work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan.

Received, 22nd January 1993; Com. 3/00403A

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