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Synthesis and ^{1}H NMR Spectral Behavior of a Methano[20]annulenedione Derivative

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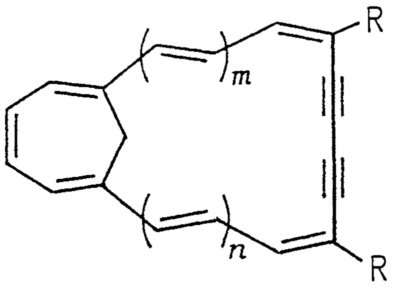
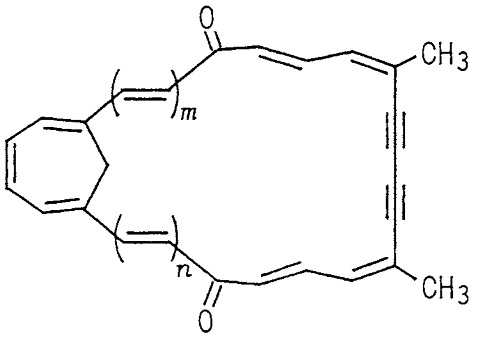
A potential 18π-electron system, 11,16-dimethyl-12,14-bisdehydro-1,6-methano[20]annulene-7,20-dione was synthesized and its ^{1}H NMR spectral behavior in $CDCl_3$, CF_3CO_2D, and D_2SO_4 was studied. The energy barrier to the methylene flipping was highly dependent on the medium.

We previously reported the synthesis of a series of bisdehydromethanoannulenes **1** in which the (4n+2)-membered-ring derivatives showed diatropism and the 4n-membered-ring ones paratropism.$^{1)}$ We have extended our work to the study of bisdehydromethanoannulenediones **2** formally related to **1**, since this type of compounds are expected to show an enhanced tropicity upon protonation of the carbonyl groups and only a few members of annulenediones are so far known.$^{2)}$ We have prepared the 20-, 24-, 26-, 28-, 30-, and 32-membered-ring derivatives of **2**.$^{3)}$ In this article we report the synthesis and interesting ^{1}H NMR spectral behavior of the lowest member of **2**, *i.e.* 11,16-dimethyl-12,14-bisdehydro-1,6-methano[20]annulene-7,20-dione (**3**).

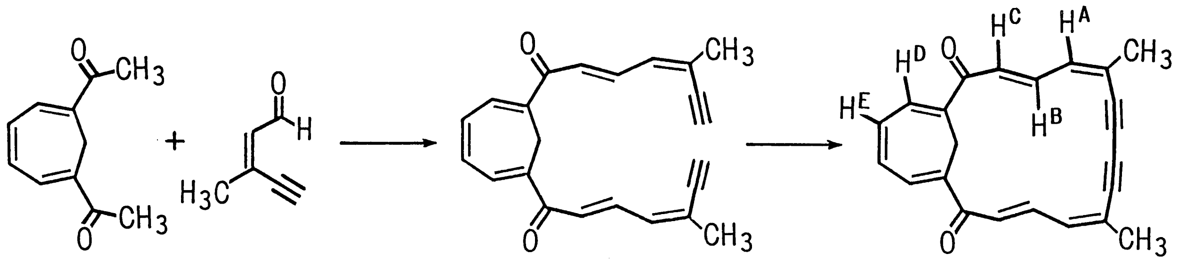


1: R=CH_3, $C(CH_3)_3$
m,n=1-5



2: m,n=0-3

Aldol condensation of 1,6-diacetylcyclohepta-1,3,5-triene (**4**)$^{4)}$ with 3-methylpent-2-en-4-ynal (**5**)$^{5)}$ in the presence of ethanolic sodium ethoxide



4 5 6 3

in benzene afforded 1,6-bis(5-methylhepta-2,4-dien-6-ynoyl)cyclohepta-1,3,5-triene (6)[6] in 44% yield as pale yellow needles, mp 103-104 ℃(dec). Intramolecular oxidative coupling of 6 with anhydrous copper (II) acetate in pyridine-diethyl ether afforded 3[6] in 58% yield as pale yellow needles, mp 195 ℃(dec).

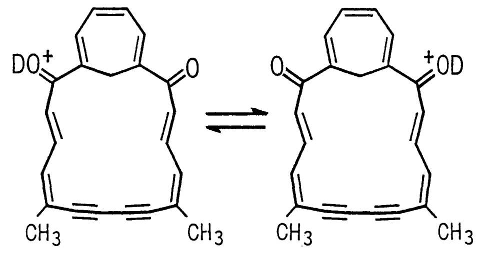
The ^1H NMR spectral data of 3 in $CDCl_3$ are given in Table 1, which clearly suggest that 3 adopts the geometry shown and the compound is of atropic and polyolefinic character in this medium. If both of the carbonyl groups are protonated to form a dicationic species, it can be a potential 18π-electron system and is expected to show diatropicity. Thus, ^1H NMR spectra of 3 in acidic media were studied and the data are also given in Table 1. In CF_3CO_2D, all the olefinic protons show downfield shift by 0.16—0.42 ppm, which indicates that 3 exists probably as a rapidly equilibrating, monodeuterated species ($7A \rightleftharpoons 7B$) and contribution of a dication is very low, if any. Upon changing the medium from CF_3CO_2D to D_2SO_4, H^A and H^C move further downfield by *ca.* 0.35 ppm but H^B shifts

Table 1. ^1H NMR spectral data of 3 at 26℃ [a)]

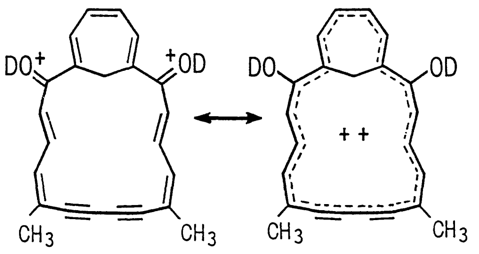
Solvent	Proton						
	CH_3	CH_2	H^A	H^B	H^C	H^D	H^E
$CDCl_3$	1.934 s	b)	6.594 d (11.0)	7.138 dd (16.0,11.0)	6.209 d (16.0)	6.89 m	7.00 m
CF_3CO_2D	2.031 s	2.22 br[c)] 4.18 br	6.756 d (11.0)	7.560 dd (15.6,11.0)	6.446 d (15.6)	7.13 m	7.30 m
D_2SO_4	2.116 s	2.380 d 3.889 d (14.0)	7.120 d (10.9)	6.940 dd (13.9,10.9)	6.683 d (13.9)	7.14 br	7.28 br

a) Chemical shifts are given in δ. Internal tetramethylsilane (TMS) was used as the reference for $CDCl_3$ and CF_3CO_2D solutions and external TMS was used for D_2SO_4 solutions. In parentheses are coupling constants in Hz.

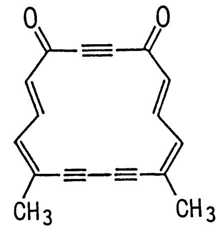
b) Too broad to be detected. Observed as an AB quartet at -36 ℃: δ 1.931 and 4.179 (J=13.6 Hz). c) Observed as an AB quartet at -26 ℃: δ 2.277 and 4.192 (J=14.0 Hz).



7A 7B



8 8A



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upfield by 0.62 ppm, which might be explainable in terms of the ring-current effect.[7)] This therefore suggests that **3** exists in this medium mainly as a dicationic species **8** where the delocalized 18π-electron structure **8A** contributes to some extent, although the magnitude is very low compared, for example, with that in the case of the [16]annulenedione **9** reported by Lombardo and Sondheimer,[2b)] because of the low planarity of the present system as suggested by molecular model considerations.

The methylene proton signal showed a diverse appearance depending on the medium. In $CDCl_3$ at 26 ℃, the methylene signal was hardly detectable because it was extremely broad and buried under the baseline. At -36 ℃ it appeared as an AB quartet at δ 1.931 and 4.179 with $J = 13.6$ Hz and at 60 ℃ a broad singlet was observed at δ 3.08. This suggests that the molecule adopts a conformation in which the methylene group is located out of the average plane of the macrocycle and the methylene protons are diastereotopic, although the precise geometry of the conformer is not known, and the interconversion between this and its mirror-image conformer by flipping of the methylene bridge through the average macrocyclic plane is taking place on the NMR time scale. Total lineshape analysis of the signal in the temperature range of 0—60 ℃ using the DNMR3 program[8)] afforded the kinetic parameters for the methylene flipping as shown in Table 2. In CF_3CO_2D the flipping was somewhat slower and the methylene protons gave two broad signals at 26 ℃. The kinetic parameters were again obtained by

Table 2. Kinetic parameters for the methylene flipping in **3**

Solvent	$\Delta H^{\ddagger}$ / kcal mol^{-1}	$\Delta S^{\ddagger}$ / cal mol^{-1} K^{-1}	$k_{26℃}$ / s^{-1}	$\Delta G^{\ddagger}_{26℃}$ / kcal mol^{-1}	Method[a)]
$CDCl_3$	14.6 ± 0.3	4.7 ± 1.0	1400	13.2	TLA
CF_3CO_2D	15.4 ± 0.7	3.2 ± 2.3	170	14.5	TLA
D_2SO_4			3.3	16.8	ST

a) TLA: total lineshape analysis; ST: saturation transfer.

total lineshape analysis at 26–70 ℃ as given in Table 2. In D_2SO_4 the methylene signal appeared as a definite AB quartet at 26 ℃ but irradiation of either one of the doublets caused a decrease in the intensity of the other together with decoupling, indicating the occurrence of slow mutual exchange. Quantitative saturation transfer experiments[9] were carried out to give the rate constant for the flipping of 3.3 s^{-1} at 26 ℃ (Table 2).

The energy barrier to the methylene flipping significantly increases by changing the solvent from $CDCl_3$ to CF_3CO_2D to D_2SO_4, suggesting that the rigidity of the macrocyclic ring increases in this order owing presumably to the decrease in the bond alternation. This result also supports the aforementioned inference that the charges are considerably delocalized to form an 18π-electron system in D_2SO_4.

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