Tetrahedron Letters Vol. 21, pp 3299 - 3302
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0040-4039/80/0815-3299$02.00/0

STRUCTURE AND CONFORMATIONAL ISOMERISM OF THE MAJOR DIMER OF 2,3-NAPHTHOQUINODIMETHANE[1]

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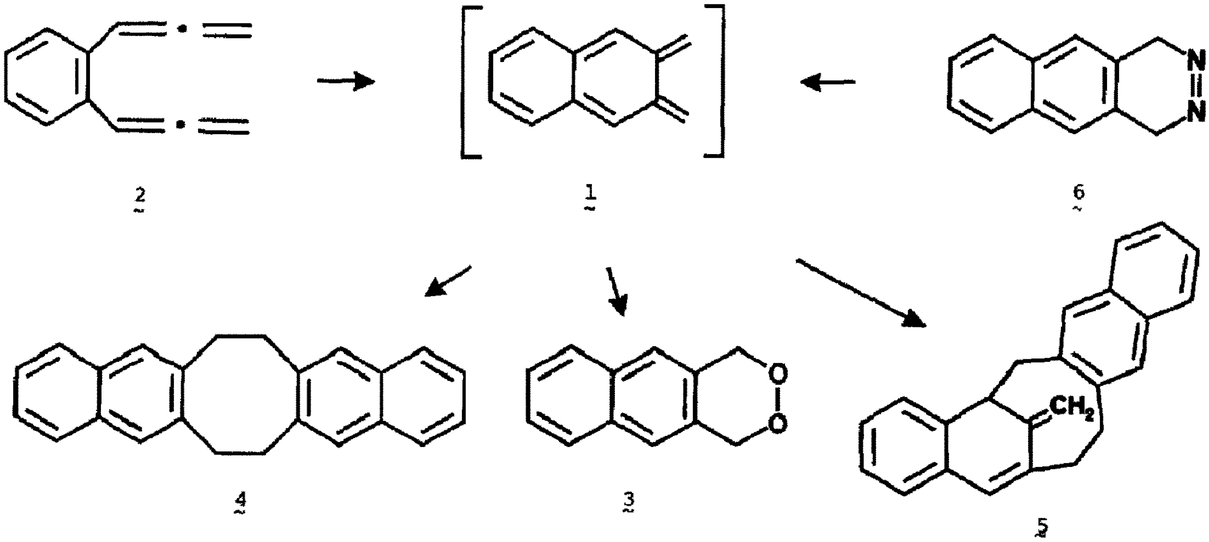
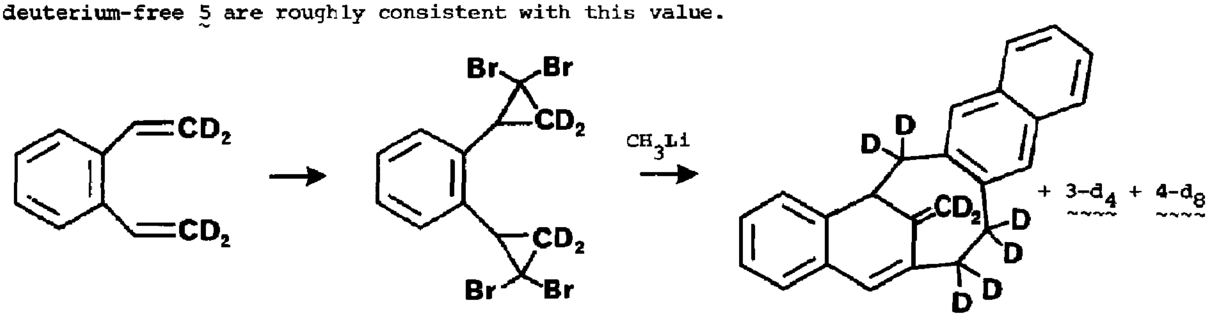
Abstract: The major product from 2,3-naphthoquinodimethane formed by cyclisation of o-dipropadienylbenzene was found to be the dimer 5 containing an eight-membered ring, for which the inversion barrier was determined by dynamic ^{1}H NMR spectrometry, $\Delta G^‡ = 18$ kcal/mole.

The 1,2-quinodimethanes are of considerable interest as synthetic intermediates[2] and as the objects of theoretical[3,4], mechanistic[5-8] and spectroscopic[4,9] investigations. The products of cycloaddition reactions of unsubstituted 1,2-quinomethanes are important as indicators of the biradicaloid[4a] character of their ground states. Previously[6b], we postulated the formation of 2,3-naphthoquinodimethane (1) by rapid cyclisation of o-dipropadienylbenzene (2). In the absence of trapping agents other than oxygen, 1 was rapidly transformed[6b] to the peroxide 3[10] (25%), the symmetrical dimer 4 (8%) and what appeared to be an isomeric mixture of naphthalenic dimers (5, 47%). More recently, the matrix isolation and observation of 1, generated by photolysis of 6, and conversion to 3 in the presence of air, were reported[4b].



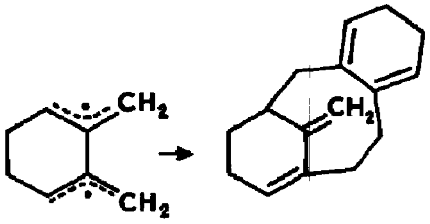
We have now determined that the major product from 2,3-naphthoquinodimethane generated by our method is the unsymmetrical dimer 5 [m.p. 142-145°C, from EtOH; λ_{max} (EtOH) 227 (ε 74,000), 264 (11,000), 275 (12,600), 284 (13,500), 293 (sh) (12,000), 323 (sh) (1,400) nm], which exists in solution as a mixture of conformers. The 100 MHz ^{1}H NMR spectrum of 5 at 27°C proved very complex in the olefinic region (Figure 1), though at 150°C the spectrum was simplified to that expected for structure 5 on the basis of NMR model compounds[11,12]. Computer simulation of the line shapes at intermediate temperatures was complicated by overlapping peaks, so the deuterated derivative 5-d_8 was synthesised from 7 via 8.[1] The dynamic ^{1}H NMR spectra of 5-d_8 (Figure 2) accurately matched the calculated line shapes in the benzyl proton (H_b) region, and the average free energy of activation was estimated, ΔG‡ = 18.1 ± 0.2 kcal/mole. The variable temperature spectra of deuterium-free **5** are roughly consistent with this value.



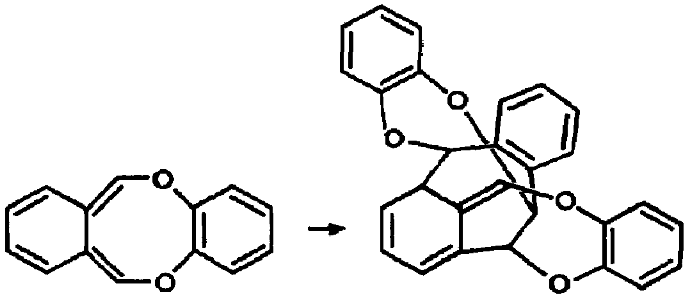
7 **8** **5-d$_8$**

According to molecular models, there are two possible conformations of **5**, designated *exo* ar *endo* (*vide infra*), which are consistent with the ^{1}H NMR spectroscopic data (Table 1). The two ex cyclic methylene protons (H_m) of *exo*-**5** are shielded by the naphthalene ring by 0.6 ppm, relative to reference compounds[11,12]. In the *endo* conformation the α-styryl (H_S) proton is shielded inste (1.3 ppm). The *exo*/*endo* ratio was found to be 2:1 in $CDCl_3$ at 27°C, corresponding to a free ener difference of 420 cal/mole. Interestingly, crystalline **5** consists of pure *exo*-**5**, since only the ^{1}H NMR signals assigned to *exo*-**5** were observed when crystalline **5** was dissolved in THF-d_8 at -40 The geometries of the central rings of *exo* and *endo*-**5** closely resemble those of the two conforme of (1E,5Z)-cyclooctadiene which were postulated by Cope[13] and later observed by low temperature ^{13}C NMR spectrometry[14]. Though the latter ring inversion barrier has been estimated as only abou 8 kcal/mole[14], the fusion of aromatic rings to cyclooctenes generally increases such barriers[15]. Preliminary results[16] suggest that the barrier to ring inversion for (3E)-1,2,5,6-tetrahydrocycl octa[1,2-*b*]naphthalene is similar to that for **5**.

Structures analogous to the dimer **5** have been reported previously, although they have not been found to exhibit conformational isomerism. Thus, the dimer **10** has been isolated by Roth and Erker[17] from a reaction involving the diradical 2,3-dimethylene-1,4-cyclohexadienyl **9** as an inte mediate. Defoin *et al*[18] have shown that the dimer **12** is one of the products obtained from the substituted 1,2-quinodimethane **11**, a reaction which was postulated to involve a concerted Woodwa Hoffmann allowed[19] [$_\pi 8_s + _\pi 6_s$][20] cycloaddition. The isolation of the dimers **4** and **5** from 2,3-



9 **10**



11 **12**

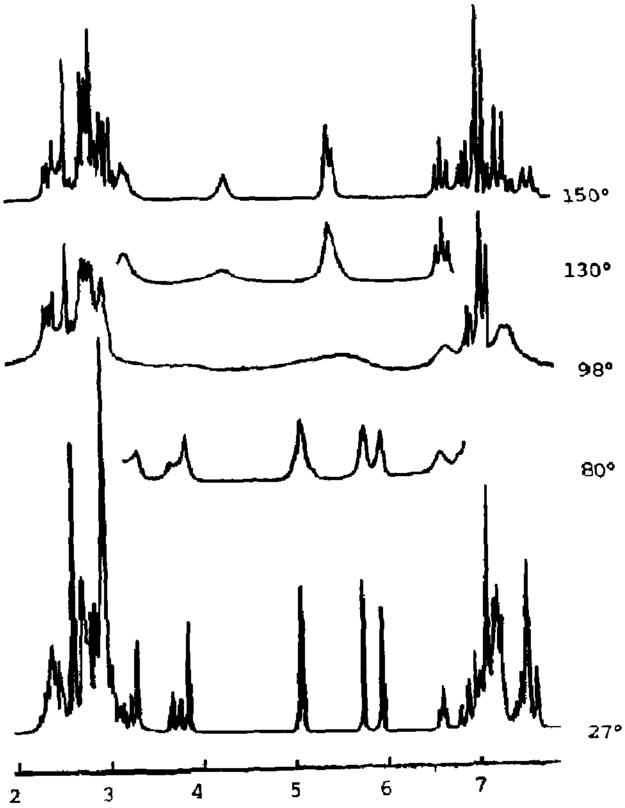


Figure 1. ^{1}H NMR Spectra of 5 in Toluene-d_8 (τ, 100 mHz, °C)

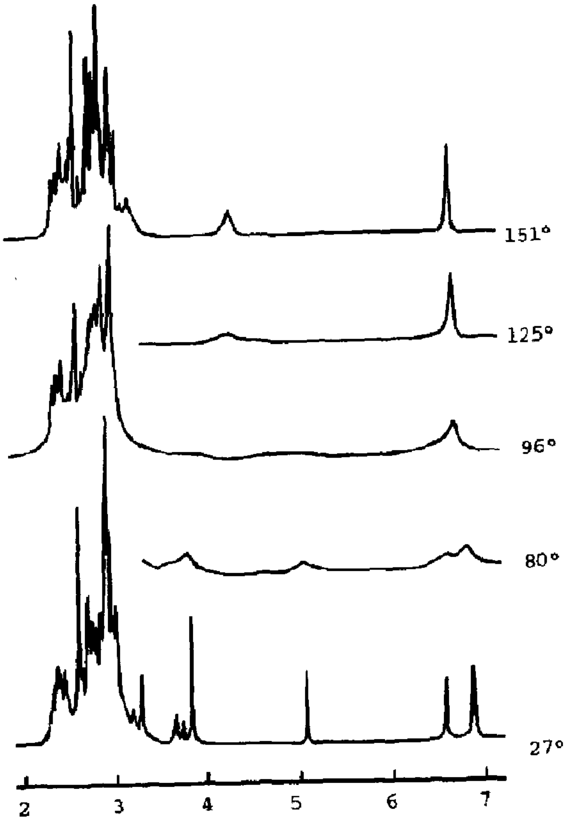
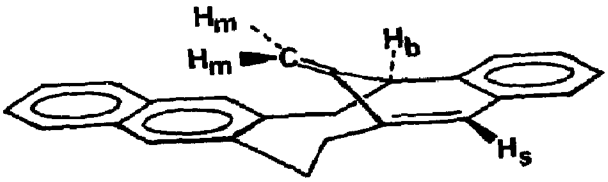
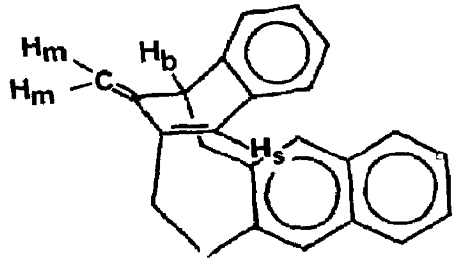


Figure 2. ^{1}H NMR Spectra of 5-d_8 in Toluene-d_8 (τ, 100 MHz, °C)



exo-5

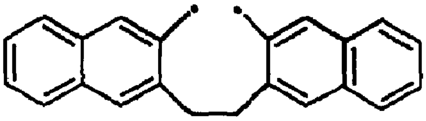


endo-5

Table 1. ^{1}H NMR Chemical Shift Assignments (τ, 100 MHz, $CDCl_3$)

Proton	exo-5	endo-5
H_b	6.73	6.34
H_s	3.61	4.94
H_m	5.60, 5.76	4.89, 4.95

naphthoquinodimethane **1** may involve initial formation of the diradical **13**, which gives rise to **4** or **5** depending on the direction of the formation of the second carbon-carbon bond. Alternatively, the dimer **5** may be produced directly from **1** by a concerted $[{}_{\pi}12_{s} + {}_{\pi}10_{s}]$[20] cycloaddition. It is of interest that the dimer **5** can be converted to **4**, presumably via the diradical **13**, but only at elevated temperatures (160°C).



13

Acknowledgements. We wish to thank Dr. D.F. Montecalvo for performing initial experiments with **2**, and Dr. J.E. Anderson for assistance with computer simulations. Financial support from the Royal Society is gratefully acknowledged.

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(Received in UK 9 June 1980)