Synthesis of [2,2](2,7)Naphthalenophane-1,11-diene[1]

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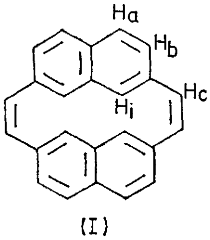
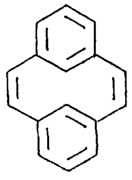
Summary [2,2](2,7)Naphthalenophane-1,11-diene (I) and its dideuteriated analogue (IV) have been synthesized by elimination reactions of the bis(dimethylsulphonium)-naphthalenophane salt (III); the diene (I) photocyclizes to coronene in high yield under oxidative conditions.

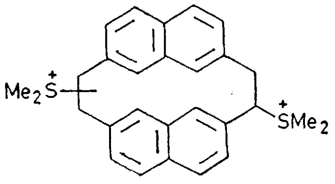
WE report the synthesis of [2,2](2,7)naphthalenophane-1,11-diene (I) a metacyclophane based on the naphthalene nucleus and incorporating bridging ethylenic groups. As in the case of the previously reported[2] [2,2]metacyclophane-1,9-diene (II) molecular models indicate over-crowding in the structure and consequently, the loss of formal conjugation between the ethylenic groups and the aromatic rings. Previous attempts to synthesize the diene (I) have been recorded,[3,4] and others have commented on the unlikely existence of the compound.[5]



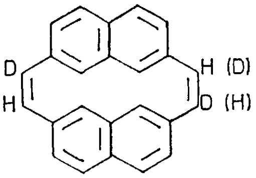
(I)



(II)



(III)



(IV)

The diene (I) was synthesized in 25% yield by a base-induced elimination reaction of the bis(dimethylsulphonium) naphthalenophane tetrafluoroborate salt (III)[4] with potassium hydroxide in ethanol under reflux, and the product was obtained as bright yellow plates, m.p. 239—242°. The n.m.r. spectrum (CD_2Cl_2) of the diene (I) showed resonance peaks at δ 6·57 (4H, s), 7·08 (4H, apparent s) superimposed on a peak at 7·12 (4H, 2d, J 8·5 and 1·5 Hz, H_b), and 7·68 (4H, d, J 8·5 Hz, H_a). Its mass spectrum (70 eV) showed a parent molecular ion at m/e 304 (71%) and fragmentation ions at 303 (37%), 302 (36%), 301 (54%), and 300 (71%) indicating that a successive loss of hydrogen atoms to give a coronene radical cation is highly favourable. At 10 eV, the mass spectrum of the diene showed $M^+ + 1$ at 305 (25%), M^+ at 304 (100%) and $M^+ - 1$ at 303 (8%). No other ions above 300 mass units were observed.

The superimposition of two of the major peaks in the n.m.r. spectrum of the diene (I) did not allow for the complete unambiguous assignment of the internal protons H_i and the vinylic protons H_c. In order to differentiate between the internal and the vinylic protons, the elimination reaction of the bis-sulphonium salt (III) was repeated using KOD in EtOD. The product obtained was shown to be 1,11- (or 1,12-)dideuterio[2,2](2,7)naphthalenophane-1,11-diene (IV). Its n.m.r. spectrum showed a decrease in intensity of the peak at δ 6·57 (2H) by 47 ± 3%. In all other respects, the n.m.r. spectrum was identical to that of the parent diene (I). On the basis of this deuterium labelling experiment, the n.m.r. assignments for the vinylic protons, H_c δ 6·57, and for the internal protons, H_i δ 7·08, have been made. This represents a small relative upfield shift of the internal protons by comparison with the internal protons of [2,2]metacyclophane-1,9-diene (δ 7·90).[2]

The photochemistry of the diene is of intrinsic interest in that the molecule incorporates two stilbene units each of which may undergo a reaction analogous to the well documented photocyclization dehydrogenation reaction of stilbene to phenanthrene.[6] A solution of the diene (I) λ_{max} (EtOH) 239 (log ϵ 4·99), 282·5 (4·31), 324 (3·33), 363sh nm (3·20)] dissolved in light petroleum in the presence of iodine to act as an oxidant was irradiated with a 254 nm medium pressure mercury lamp. Coronene was obtained from the reaction mixture in high yield.

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