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Exceptional Dimerisation of 7,9-Dimethylcyclopent[*a*]acenaphthylen-8-one; *X*-Ray Crystal Structure of the Diol–Diacetate of one of the Dimeric Products

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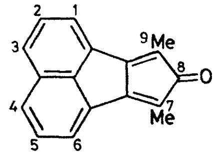
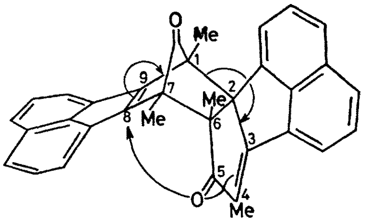
Summary In solution at 20 °C the cyclopentadienone (**1**) is in equilibrium with the normal *endo*-Diels–Alder dimer (**2**) and the formal $[_{\pi}2 + _{\pi}2]$-dimer (**3**) the structure of the diol–diacetate of which has been determined by *X*-ray crystallography; on heating at 80 °C this mixture affords the *exo*-Diels–Alder dimer (**4**).

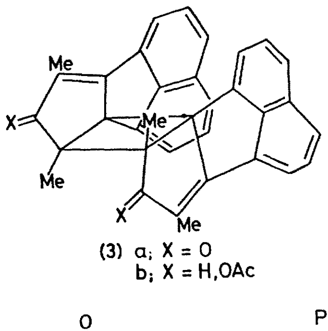
CERTAIN cyclopentadienones with 3,4-aryl substituents constrained to be coplanar with the cyclopentadienone ring form Diels–Alder dimers in which Cope rearrangement is rapid on the n.m.r. time scale.[1] Since 7,9-dimethylcyclopent[*a*]acenaphthylen-8-one (**1**) is of this type and was reported[2] to form a Diels–Alder dimer we repeated the preparation of the dimer of (**1**) with a view to detecting the Cope rearrangement (**2**; arrows). The product (from CH_2Cl_2–EtOH) had m.p. 158—160 °C rather than 200 °C as originally reported[2a] but in agreement with a later observation.[2b] Surprisingly this dimer lacked the high frequency carbonyl absorption characteristic of structures of type (**2**) showing ν_{max} (Nujol) at 1 698 and 1 648 cm^{-1}. However on standing in the spectrometer, or on warming, the mull developed a strong additional peak at 1 774 cm^{-1}, and the original sample in chloroform solution showed ν_{max} 1 646, 1 695, and a weaker band at 1 768 cm^{-1}. If this dimer was either crystallised from benzene–petroleum or stirred with acetic acid a new crystalline product with m.p. 163—167 °C was obtained which showed ν_{max} (Nujol) at 1 774, 1 696, and 1 644 cm^{-1} without prior warming of the mull; this spectrum was identical to that obtained by warming the mull of the first crystalline compound. In



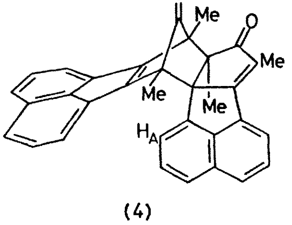
(1)



(2)



(3) a; X = O
b; X = H,OAc



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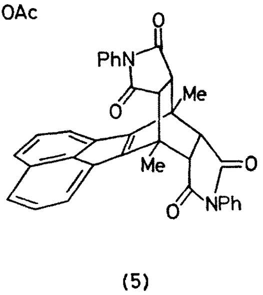

(5)

deuteriopyridine both crystalline products gave an identical n.m.r. spectrum, which indicated the presence of two dimers in a ratio of *ca.* 2 : 1. The methyl groups of the minor component appear as two broadened singlets at δ 1·20 and 1·76 at 35 °C which at −30 °C are replaced by three peaks at 2·17 (3H), 1·38 (6H), and 1·08 (3H). This behaviour is consistent with structure (**2**) for the minor component of the mixture; at 35 °C Cope rearrangement (**2**; arrows) interchanging the environments of both the C-1 and C-4, and the C-7 and C-6 methyl groups is presumably rapid. The methyl resonances (δ 1·54 and 2·33) due to the major component of the mixture are temperature-invariant and are consistent with the $[_{\pi}2 + {}_{\pi}2]$ structure (**3a**). This structure was confirmed as follows. The crystalline dimer (from CH_2Cl_2–EtOH) was added to a large excess of lithium aluminium hydride in ether at 0—5 °C to give a diol of m.p. 166—168 °C in good yield. On acetylation (Ac_2O–C_5H_5N, 20 °C) this gave a diacetate with m.p. 174—176 °C (from benzene). Deshielding of one methyl pair in the diacetate (δ 1·99) compared with the diketone (δ 1·45) is most consistent with an *anti*-head-to-head structure (**3a**) for the cyclopentadienone dimer. The structure of the diol–diacetate (**3b**) was established by a single-crystal *X*-ray analysis of the benzene solvate, $C_{38}H_{32}O_4 \cdot \frac{1}{2}C_6H_6$.

Crystal data: crystals are triclinic, space group $P\bar{1}$, with $a = 8{\cdot}799(3)$, $b = 23{\cdot}868(9)$, $c = 8{\cdot}440(4)$ Å, $\alpha = 93{\cdot}40(3)$, $\beta = 113{\cdot}49(3)$, $\gamma = 98{\cdot}49(3)^\circ$ and $Z = 2$. The structure is based on 3305 independent F_0 having $I > 3\sigma(I)$, and least-squares refinement of non-hydrogen atoms with anisotropic temperature factors gave a final *R* of 0·093.

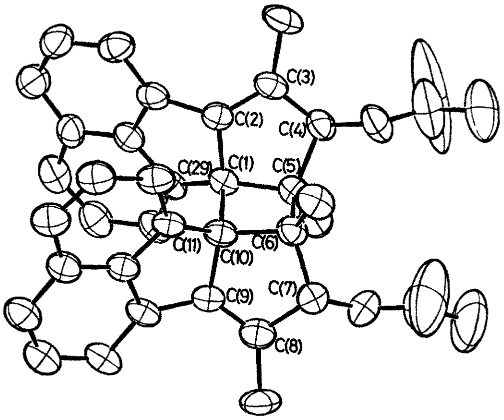

FIGURE. ORTEP drawing of the molecular structure of the diol–diacetate (**3b**). Some bond lengths and angles associated with the strained 4-membered ring: C(1)–C(10) 1·585(7), C(5)–C(6) 1·608(7), C(1)–C(5) 1·553(6), C(6)–C(10) 1·569(7) Å, C(5)–C(1)–C(29) 133·3(3), C(6)–C(10)–C(11) 133·8(4)°.

The molecule, shown in the Figure, has non-crystallographic C_2 symmetry, while the benzene molecule occupies a centre of symmetry.‡

Although the structure of this product indicates structure (**3a**) for the dimer a mobile equilibrium involving the monomer (**1**) and the dimers (**2**) and (**3a**) prevails at 20 °C in solution; reaction with *N*-phenylmaleimide gives the expected *endo*-adduct of (**1**), and reduction with sodium borohydride gives two stereoisomeric hydroxyketones formed by attack on the strained bridging carbonyl group of (**2**).

Formation of the dimer (**3a**) could involve a symmetry-forbidden $[_{\pi}2_s + {}_{\pi}2_s]$ dimerisation of (**1**), a forbidden suprafacial 1,3-shift in (**2**), or appropriate two-step equivalents of these processes. The C-1 to C-2 bond in (**2**) would be expected to be weakened by steric and strain effects as well as by the stability of the resulting biradical. Accordingly dimerisation and/or 1,3-rearrangement *via* a biradical is an attractive possibility, although a concerted-forbidden 1,3-shift is also possible. The substituents at positions 7- and 9- in (**1**) exert a marked influence on the mode of dimerisation for the dimers of the cyclopentadienones (**1**; Et replacing Me) and (**1**; Pr^n replacing Me) exist almost exclusively as cyclobutanes like (**3a**) (solution i.r. and n.m.r. spectra). Formation of these formal $[_{\pi}2 + {}_{\pi}2]$-dimers is remarkable for, with the exception of 1,3-diphenylinden-2-one which forms a formal $[_{\pi}4 + {}_{\pi}4]$-dimer,[3] cyclopentadienones dimerise by $[_{\pi}4 + {}_{\pi}2]$-addition.[4]

Whilst the difference in thermodynamic stability between (**2**) and (**3a**) is small and solvent-dependent (1 : 1 ratio in benzene) both are converted into a third thermodynamically preferred isomer, m.p. 206—210 °C, in boiling benzene (2 h). This is formulated as the *exo*-$[_{\pi}4 + {}_{\pi}2]$-dimer (**4**) since it shows four distinct methyl resonances [δ ($CDCl_3$) 1·02, 1·21, 1·92, and 2·1] and a strongly shielded aromatic proton {δ 6·18, [d, *J* 8 Hz; H_A in (**4**)]}, as well as the expected i.r. bands at 1 648, 1 698, and 1 778 cm^{-1}. With *N*-phenylmaleimide in boiling benzene (**4**) gives the adduct (**5**) (75%). Dimerisation of cyclopentadienones in the *exo*-mode has not been observed previously although the photochemical caging of 2,5-dimethyl-3,4-diphenylcyclopentadienone requires the presence of the *exo*-isomer under photochemical conditions.[5]

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‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by a full literature citation for this communication.

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