Enhanced Carbonyl Reactivity and Conformational Effects in *peri*-Dioxocycloalka[*de*]naphthalenes

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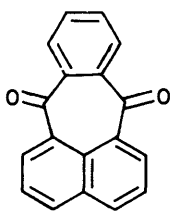
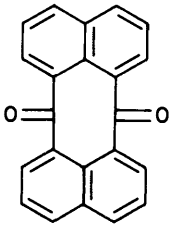
Cycloalka[*de*]naphthalenes with two *peri* carbonyl groups in ten-, seven-, and nine-membered rings add water or methanol in the presence of acetic acid with relative rates ten > seven- > nine-membered, but hydrations stop at 17, 30, and 90% respectively. Methanol gives with the ten- and nine-membered diketones respectively, a bridged acetal and a bridged hemiacetal. Force field calculations give minimum energy conformations for the diketones that are confirmed by study of their temperature dependent ^{1}H n.m.r. spectra.

Enhanced carbonyl reactivity as shown by additions of water, methanol, or sodium hydroxide, has been described for some strained or conformationally restricted medium ring diketones (**1**),[1] (**2**),[2] (**3**),[3] (**4**),[4] and (**5**).[5]



(**1**)



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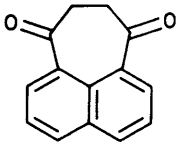
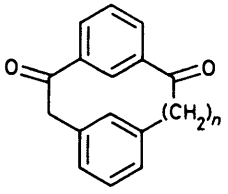


(**3**)



(**4**; *n* = 1)
(**5**; *n* = 2)

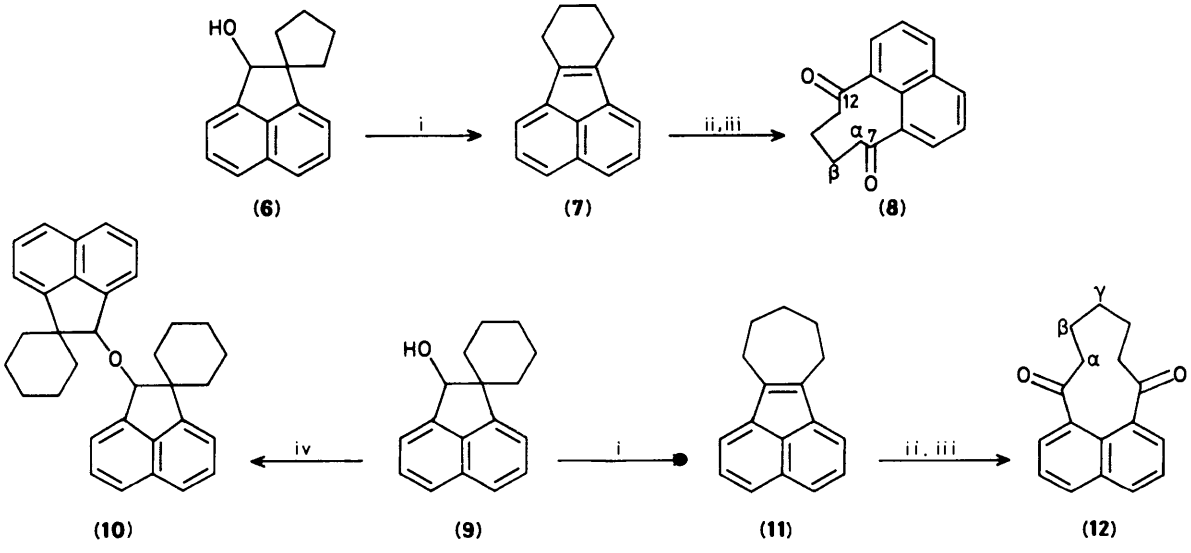
To extend this picture, two further diketones (**8**) and (**12**) have been synthesized.

Results and Discussion

The diketones (**8**) and (**12**) were synthesized making use of the reactivity of acenaphthylenes (**7**) and (**11**) with ozone, as in Scheme 1. The symmetrical ether (**10**) has the melting point that was erroneously attributed to the alcohol (**9**).[6]

As with the diketone (**3**), diketones (**8**) and (**12**) were found to form hydrates in water, as revealed by partial replacement of their characteristic u.v. absorptions by that of the unconjugated naphthalene chromophore. This occurs with isosbestic points which implies simultaneous loss of both carbonyl groups and therefore a bridged structure (**13**) for the hydrates. The hydrations are incomplete and therefore reversible and extinction measurements reveal the extent of hydration to be 30% for the diketone (**3**), 90% for (**8**), and 17% for (**12**). The hydrations are slow, are catalysed by acetic acid and vary widely in their rates with the order (**12**) > (**3**) > (**8**). The slowest hydration is the most complete.

Additions of methanol to the diketones (**3**), (**8**), and (**12**) are similarly revealed. The initial products are thought to be bridged hemiacetals, *e.g.* (**14**) and extinction measurements reveal the extent of addition to be: 56% for the diketone (**3**), 87% for (**8**), 85% for (**12**), and 93% for 1,8-diacetylnaphthalene. These

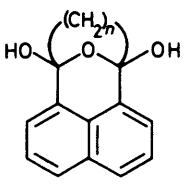


(**6**) (**7**) (**8**) (**10**) (**9**) (**11**) (**12**)

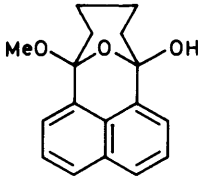
Scheme 1. *Reagents:* i, toluene-*p*-sulphonic acid–boiling propionic acid; ii, ozone–acetic acid; iii, dimethyl sulphide–acetic acid; iv, potassium hydrogen sulphate, 130 °C

figures are not strictly comparable since, as described below, the reaction with methanol goes further than hemiacetal formation in the last two cases. The methanol additions are slow, are catalysed by acetic acid, and vary widely in their rates with the order 1,8-diacetylnaphthalene > (**12**) > (**3**) > (**8**). Inclusion of 1,8-diacetylnaphthalene implicates proximity of the carbonyl groups rather than ring strain as the cause of enhanced reactivity. Curiously, 1,8-diacetylnaphthalene in water exhibits no detectable hydrate formation.

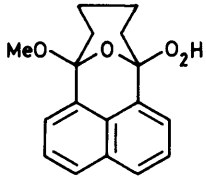
No addition compound was isolated from the diketone (**3**). In the cases of (**8**) the equilibrium solution in methanol containing acetic acid, gave a stable crystalline hemiacetal (**14**) when evaporated; this was also obtained by deoxygenating with dimethyl sulphide the crystalline ozonide formed by ozonation



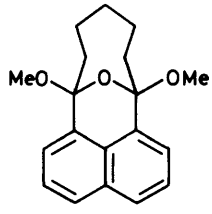
(**13**)



(**14**)



(**15**)



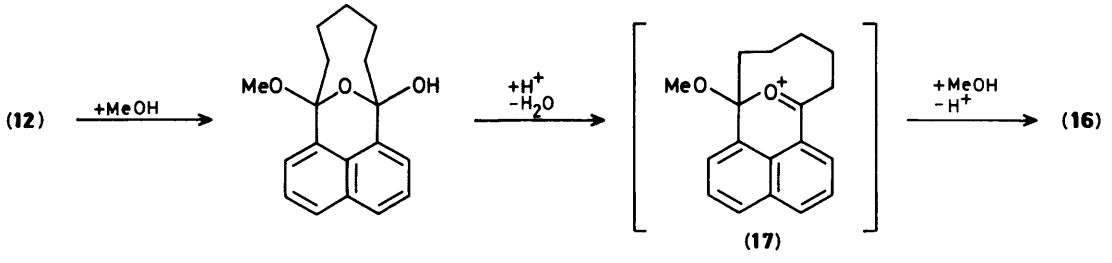
(**16**)

of the hydrocarbon (**7**) in methanol. Chemical shifts of the exchangeable protons, δ 3.4 in the hemiacetal (**14**) and δ 8.7 in the ozonide, argue the hydroperoxide structure (**15**) for the latter. Ozonation of the hydrocarbon (**11**) in methanol gave a product that was unstable but which exhibited an exchangeable proton at δ 8.2. The equilibrium solution of the diketone (**12**) in methanol containing acetic acid, gave the crystalline acetal (**16**) when evaporated. This is consistent with an observation that 1,8-diacetylnaphthalene yields an epimeric pair of bridged acetals in methanol containing acetic acid.[7]

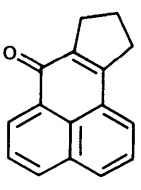
Hydrate and hemiacetal formation by carbonyl compounds is catalysed by molecular weak acids without ionization, but acetal formation calls for ionization (Scheme 2) and if exceptionally it is induced by an acid as weak as acetic acid then the intermediate cation, *e.g.* (**17**), is presumably very favoured. Prolonged contact with methanol containing acetic acid fails to produce an acetal from the hemiacetal (**14**); here, and also in the case of the hemiacetal in equilibrium with the diketone (**3**), overlap implicit in the C=O double bond of the cation is prevented by the smaller bicyclic systems. Thus acetalisation of the diketone (**3**) with methanol required sulphuric acid, and the bridged acetal was not the first product but appeared only slowly.[3] Adduct formation with sodium hydroxide such as has been described for the diketones (**1**)[1] and (**3**),[3] is precluded for (**8**) and (**12**) by intramolecular aldol condensations leading to phenalenones. The phenalenones (**18**) and (**19**) were obtained by warming pyridine solutions of the diketones (**8**) and (**12**) respectively, with piperidine as a catalyst. Even contact with silica induces the diketones (**8**) and (**12**) to enolise, so that if their solutions are allowed to dry on silica subsequent chromatography reveals the presence of both β-hydroxy ketones and phenalenones.

The series of structures represented by diketone (**3**), the unknown compound (**20**), and the diketones (**8**) and (**12**), pose interesting conformational questions. Structures of this homologous series of diketones have been examined by empirical force field methods, and the minimum energy conformation of each with its associated steric energy obtained using the MM2 force field,[8] is displayed in the Figure. As might be expected with compounds containing medium rings, all are strained showing close non-bonded interactions and angular distortions. In all cases the carbonyl groups are in anti- or near anti-parallel alignment, twisted slightly from the plane of the naphthalene ring. Twisting of the diketone rings renders non-equivalent the hydrogens within each bridging methylene group. The calculated conformations of (**8**) and (**3**) show true C_2 symmetry with the rotation axis passing along the C(4a)–C(8a) bond of the naphthalene nucleus. The conformations of (**20**) and (**12**) lack this symmetry and therefore non-equivalence extends to the central methylene group of their bridges. As described later, the ^{1}H n.m.r. spectroscopic properties of (**8**) and (**12**) are fully consistent with these calculated structures.

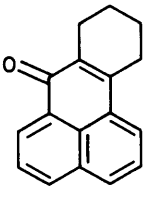
Inclination of the carbonyl groups out of the naphthalene plane is suggested by some of the spectroscopic parameters in Table 1. The downward trend in the first three columns of Table



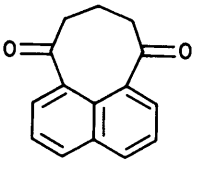
Scheme 2.



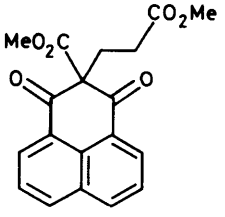
(**18**)



(**19**)



(**20**)



(**21**)

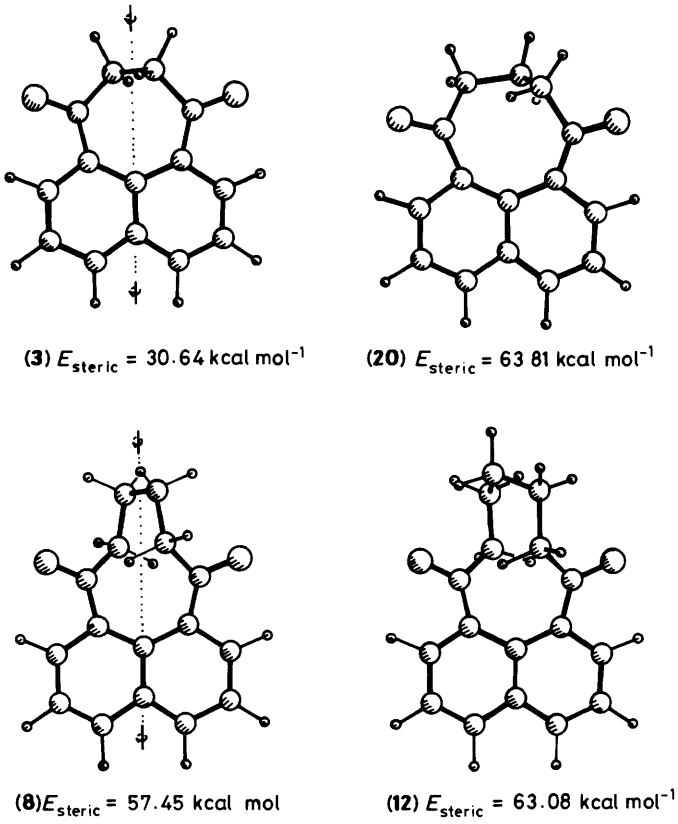


Figure. Minimum energy conformations for some *peri*-dioxocycloalka[*de*]naphthalenes obtained by empirical force field calculations

1 suggests decreasing conjugation of the carbonyl groups with the aromatic nuclei. In line with this, the dipole moment of 1,8-diacetylnaphthalene was found to agree with *transoid* carbonyl groups orthogonal to the aromatic rings.[9]

The ^{1}H n.m.r. spectra of the diketones (**8**) and (**12**) are temperature dependent, with magnetic non-equivalence in all the geminal pairs of protons (Table 2). This non-equivalence is attributable mainly to varying proximity with a transannular carbonyl oxygen; a ketone carbonyl group, though deshielding protons near the *xy* plane, shields protons that lie near the *z* axis through oxygen.[10]

If the diketone (**12**) had adopted a conformation with C_2 symmetry the protons of its γ methylene group would have been magnetically equivalent, however, this pair of protons shows the greatest degree of non-equivalence in Table 2, confirming the situation predicted by the force field calculations.

The coalescences of the signals listed in Table 2 are attributable to the temperature effect on conformational inversions, and lead to energy barriers for these processes of 10.8 and 15.4 kcal mol^{-1} in (**8**) and (**12**) respectively. According to force field calculations, structure (**12**) with the larger diketone ring starts with more steric strain (Figure), therefore it is perhaps surprising that its activation energy for conformational inversion is also higher. However the course of conformational inversion in the diketones (**8**) and (**12**) could differ depending upon whether the carbonyl groups rotate together or successively.

Experimental

1,2-*Dihydroacenaphthylene*-1-*spirocyclopentan*-2-*ol* (**6**).—2-Cyclopentanespiroacenaphthylen-1-one[11] (3.2 g) in propan-2-ol (35 ml) was added to a freshly made slurry of sodium tetrahydridoborate (3.9 g) in water (21 ml). The mixture was left overnight then diluted with water and extracted with ether. Concentration of the extract afforded an orange product that was recrystallised from acetone–light petroleum (b.p. 60—80 °C) to give cream prisms (3.11 g, 96%), m.p. 120—123 °C (lit.,[6] 123 °C).

Table 1. U.v. absorption maxima and some ^{1}H n.m.r. chemical shifts of *peri*-diketones

Compound	$\lambda_{max.}$(MeOH)/nm		δ_H ($CDCl_3$; 300 MHz)		
			*o-H	*m-H	*p-H
(**21**)	234	335†	8.4	7.7	8.2
(**3**)	230	315	8.2	7.6	8.1
(**8**)	226	304	8.0	7.6	7.6
(**12**)	225	301	8.0	7.6	7.7
1,8-Diacetylnaphthalene	223	296	7.8	7.5	7.9

* Relative to carbonyl. † Centre of plateau.

Table 2. ^{1}H N.m.r. parameters for the methylene groups in the diketones (**8**) and (**12**)

Positions relative to carbonyl	$\Delta\delta_H$(*gem.*)	Coalescence temperatures observed at 300 MHz (°C)
(**8**) α	0.52	−39
β	0.26	−45
(**12**) α	0.44	+51
β	0.23	+46
γ	0.69	+58

1,2-*Dihydroacenaphthylene*-1-*spirocyclohexan*-2-*ol* (**9**).—This was prepared in the same way from cyclohexane-2-spiroacenaphthylen-1-one[11] (2.85 g) as cream prisms from ether–light petroleum (b.p. 60—80 °C) (2.08 g, 73%), m.p. 70—72 °C (lit.,[6] 201 °C) (Found: C, 85.9; H, 7.4. Calc. for $C_{17}H_{18}O$: C, 85.7; H, 7.6%); $\lambda_{max.}$(EtOH) 243, 279, 289, 300, 316, and 321 nm (log ε 2.99, 3.78, 3.86, 3.67, 2.82, and 2.61); $\nu_{max.}$($CHCl_3$) 3 580 cm^{-1} (OH); δ_H (60 MHz: $CDCl_3$) 1.5—2.0 (11 H, m), 5.2 (1 H, d, *J* 8 Hz), and 7.1—7.9 (6 H, m).

meso- *or* (±)-*Bis*(1,2-*dihydroacenaphthylene*-1-*spirocyclohexan*-2-*yl*) *Ether* (**10**).—The alcohol (**9**) (4.64 g) and potassium hydrogen sulphate (9.24 g) were heated under nitrogen; the organic component melted, but at 130 °C resolidified. After having being cooled the mixture was extracted with water and ether leaving undissolved solid (0.92 g). Further solid (1.05 g) was obtained by concentrating the organic layer and more still (0.57 g) by chromatography of the final filtrate on silica. Recrystallisation of the combined solids from chloroform and ether gave the *ether* (**10**) as colourless needles (1.77 g), m.p. 204—206 °C (Found: C, 88.6; H, 7.4. $C_{34}H_{34}O$ requires C, 89.0; H, 7.5%); $\lambda_{max.}$(cyclohexane) 268, 279, 290, 300, 304, 315, and 319 nm (log ε 3.93, 4.15, 4.24, 4.08, 3.94, 3.33, and 2.99); $\nu_{max.}$($CHCl_3$) 2 930, 2 860, and 1 055 cm^{-1}; δ_H (60 MHz; $CDCl_3$) 1.0—2.1 (20 H, m), 5.5 (2 H, s), and 7.0—7.9 (12 H, m); *m/z* 458 (M^+, 4%), 237 (48), and 219 (100).

7,8,9,10-*Tetrahydrofluoranthene* (**7**).—The alcohol (**6**) (4.8 g), propionic acid (30 ml) and toluene-*p*-sulphonic acid (100 mg) were boiled for 1 h under partial reflux allowing only a few drops of distillate to escape, was then cooled, neutralised with an excess of aqueous sodium carbonate, and extracted with ether. Concentration of the extract and distillation of the residue

gave an orange liquid (3.9 g, 88%), b.p. 132—133 °C/0.1 mmHg (lit.,[6] 165 °C/2 mmHg) (Found: C, 93.1; H, 6.9. Calc. for $C_{16}H_{14}$: C, 93.2; H, 6.8%); $\lambda_{max.}$(cyclohexane) 231, 272, 282, 309, 323, 331, 337, 405, and 485 nm (log ε 4.72, 3.57, 3.63, 3.94, 4.02, 3.71, 3.64, 2.64, and 1.78); δ_H (60 MHz; $CDCl_3$) 1.8 (4 H, m), 2.6 (4 H, m), and 7.1—7.6 (6 H, m); *m/z* 206 (M^+, 100%). A higher boiling fraction (0.11 g) was chromatographed on silica in 1,1,1-trichloroethane to give further hydrocarbon (**7**) (0.01 g), and then an orange glass (0.04 g), *m/z* 412 (12%), 358 (71), and 205 (100) that appeared to be a dimer $C_{32}H_{28}$.

8,9,10,11-*Tetrahydrocyclonona*[de]*naphthalene*-7,12-*dione* (**8**).—The hydrocarbon (**7**), freshly chromatographed and resublimed (204 mg) in acetic acid (3 ml) was cooled in an ice bath without freezing the solvent, and treated with ozonised oxygen until the orange colour disappeared (10 min), then with dimethyl sulphide (0.25 ml), and after 0.5 h, was diluted with water and aerated to expel dimethyl sulphide and crystallise the product. This was collected, supplemented by an ethyl acetate extract of the filtrate, then recrystallised from chloroform and 1,1,1-trichloroethane as pale cream *plates* (180 mg, 76%), m.p. 153—155 °C (Found: C, 80.4; H, 6.0. $C_{16}H_{14}O_2$ requires C, 80.6; H, 5.9%); $\nu_{max.}$(CS_2) 1 705s and 1 685m cm^{-1}; *m/z* 238 (M^+, 51%), 210 (47%), and 209 (100%).

The Ozonide (**15**).—The hydrocarbon (**7**), freshly chromatographed and resublimed (202 mg), in methanol (5 ml) cooled in a mixture of methanol and solid carbon dioxide, was treated with a stream of ozonised oxygen until the orange colour disappeared (10 min). The mixture was then concentrated under reduced pressure at room temperature to a colourless gum that crystallised. Recrystallisation of the residue from chloroform–1,1,1-trichloroethane gave colourless *prisms* (227 mg, 81%), m.p. 145—146 °C (Found: C, 71.2; H, 6.4. $C_{17}H_{18}O_4$ requires C, 71.3; H, 6.3%); $\lambda_{max.}$(ether) 278, 288, 299, and 315 nm (log ε 3.72, 3.80, 3.66, and 2.84); $\nu_{max.}$(CS_2) 3 520 and 3 400 cm^{-1}; δ_H (60 MHz; $CDCl_3$) 0.9—2.5 (8 H, m), 3.1 (3 H, s), 7.2—7.8 (6 H, m), and 8.7 (1 H, br exch.).

The Hemiacetal (**14**).—(*a*) The ozonide (**15**) (158 mg) in warm methanol (5 ml) and dimethyl sulphide (0.5 ml) was kept for 1 h, then diluted with water and extracted with ether to give a colourless oil that solidified (148 mg), m.p. 106—108 °C; recrystallisation from ether and pentane gave colourless *prisms*, m.p. 109—110 °C.

(*b*) The diketone (**8**) (31 mg) was suspended in methanol (5 ml) containing acetic acid (10 drops), and stirred until dissolution occurred, and was then kept for 18 h. Concentration of the mixture under reduced pressure at room temperature left a colourless oil that crystallised when seeded with the previous product, and crystallised from ether–pentane as colourless *prisms*, m.p. 109—110 °C (Found: C, 75.4; H, 6.8. $C_{17}H_{18}O_3$ requires C, 75.5; H, 6.7%); $\lambda_{max.}$(MeOH) 278, 287, 298, and 316 nm (log ε 3.79, 3.87, 3.72, and 2.74); $\nu_{max.}$(CS_2) 3 580 and 3 440 cm^{-1}; δ_H (60 MHz; $CDCl_3$) 0.8—2.6 (8 H, m), 3.0 (3 H, s), 3.4 (1 H, br. exch), and 7.2—7.8 (6 H, m).

9,10-*Dihydrocyclopenta*[b]*phenalen*-7(8H)-*one* (**18**).—The diketone (**8**) (54 mg) in pyridine (1 ml) was warmed on steam and remained almost colourless until piperidine (1 drop) was added. After 15 min on steam, the orange solution was diluted with chloroform, washed with dilute hydrochloric acid, dried (Na_2SO_4), and concentrated to a solid residue. Recrystallisation from 1,1,1-trichloroethane–light petroleum (b.p. 60—80 °C) gave orange *needles* (38 mg), m.p. 150—151 °C (Found: C, 87.1; H, 5.6. $C_{16}H_{12}O$ requires C, 87.2; H, 5.5%); $\lambda_{max.}$(MeOH) 229, 251, 258, 330, 359, and 395 nm (log ε 4.35, 4.37, 4.33, 3.96, 4.06, and 3.88); $\nu_{max.}$($CHCl_3$) 1 710m, 1 630s, 1 610s, 1 580s, and 1 560s cm^{-1}; δ_H (300 MHz; $CDCl_3$) 2.2 (2 H, quintet, *J* 8 Hz), 3.0 (2 H, t, *J* 8 Hz), 3.2 (2 H, t, *J* 8 Hz), 7.6 (1 H, t, *J* 8 Hz), 7.8 (1 H, t, *J* 7.5 Hz and 1 H, d, *J* 7 Hz), 8.0 (1 H, d, *J* 8 Hz), 8.2 (1 H, d, *J* 8 Hz), and 8.7 (1 H, d, *J* 7 Hz); *m/z* 220 (M^+, 86%) and 219 (100).

8,9,10,11-*Tetrahydro*-7H-*cyclohept*[a]*acenaphthylene* (**11**).—The alcohol (**9**) (3.9 g), propionic acid (40 ml), and toluene-*p*-sulphonic acid (109 mg) were boiled for 3 h under partial reflux allowing only part of the solvent (15 ml) to distil. The mixture was then cooled, neutralised with an excess of aqueous sodium carbonate and extracted with ether. Concentration of the extract gave an orange gum (3.9 g) that was chromatographed on t.l.c. grade silica using a dry column technique.[12] Light petroleum (b.p. 60—80 °C) eluted first an orange solid (1.07 g). This was sublimed at 110—120 °C/0.5 mmHg and recrystallised from acetone as thick orange *needles*, m.p. 104—106 °C (lit.,[6] orange liquid, b.p. 175 °C/3 mmHg) (Found: C, 92.5; H, 7.4. Calc. for $C_{17}H_{16}$ C, 92.7; H, 7.3%); $\lambda_{max.}$(cyclohexane) 229, 277sh, 286, 312, 325, 333sh, 340, 411, and 500sh nm (log ε 4.81, 3.71, 3.76, 3.99, 4.07, 3.72, 3.64, 2.68, and 1.60); δ_H (60 MHz; $CDCl_3$) 1.4—2.1 (6 H, m), 2.5—3.0 (4 H, m), and 7.1—7.7 (6 H, m); *m/z* 220 (M^+, 100%). Next eluted was an orange glass (1.04 g) nearly homogeneous on analytical t.l.c., *m/z* 440 (100%) and 220 (35), that appeared to be a dimer $C_{34}H_{32}$. Finally eluted was an orange glass (0.02 g) also nearly homogeneous on analytical t.l.c., *m/z* (438 (38%), 220 (27), and 219 (100).

9,10,11,12-*Tetrahydrocyclodeca*[de]*naphthalene*-7,13(8H)-*dione* (**12**).—The hydrocarbon (**11**) (91 mg) in acetic acid (25 ml) was cooled in an ice bath without freezing the solvent and treated with ozonised oxygen until the orange colour disappeared (10 min), then with dimethyl sulphide (0.25 ml), and after 0.5 h the mixture was diluted with water and extracted with ethyl acetate. Concentration of the extract left colourless crystals (115 mg), m.p. 160—167 °C. Recrystallisation from chloroform and 1,1,1-trichloroethane gave thick colourless *needles* (71 mg, 68%), m.p. 167—171 °C (Found: C, 81.1; H, 6.3. $C_{17}H_{16}O_2$ requires C, 80.9; H, 6.4%); $\nu_{max.}$($CHCl_3$) 1 685 cm^{-1}; *m/z* 252 (M^+, 71%), 235 (20), 223 (44), and 210 (100).

Acetal (**16**).—The diketone (**12**) (28 mg) in methanol (5 ml) containing acetic acid (5 drops) was stirred until it dissolved (10 min) and was then kept for 18 h. Colourless prisms (9 mg) were deposited, m.p. 157—158 °C. The mother liquor was concentrated and recrystallised from chloroform and methanol to give a further quantity (12 mg), m.p. 154—157 °C (Found: C, 76.5; H, 7.4. $C_{19}H_{22}O_3$ requires C, 76.5; H, 7.4%); $\lambda_{max.}$(MeOH) 225, 276, 286, 298, and 316 nm (log ε 4.27, 3.82, 3.92, 3.76, and 2.70); δ_H (60 MHz; $CDCl_3$) 0.9—2.5 (10 H, m), 3.2 (6 H, s), and 7.2—7.8 (6 H, m); *m/z* (c.i.; NH_3) 229 (M^+ + 1, 1%), 298 (M^+, 2%), and 267 (100).

8,9,10,11-*Tetrahydrobenz*[de]*anthracen*-7-*one* (**19**).—The diketone (**12**) (33 mg) in pyridine (1 ml) and piperidine (1 drop) was heated on steam for 15 min. The orange product was taken up in chloroform, washed with dilute hydrochloric acid, dried (Na_2SO_4), and concentrated to a gum that was sublimed at 145—155 °C/0.01 mmHg. Recrystallisation from 1,1,1-trichloroethane and light petroleum (b.p. 60—80 °C) gave orange *prisms* (13 mg), m.p. 111—112 °C (Found: C, 87.0; H, 6.1. $C_{17}H_{14}O$ requires C, 87.1; H, 6.0%); $\lambda_{max.}$(MeOH) 228, 250, 257, 327, 360, and 389 nm (log ε 4.29, 4.37, 4.33, 3.90, 4.00, and 3.88); $\nu_{max.}$($CHCl_3$) 1 625s, 1 610s, 1 580s, and 1 565s cm^{-1}; δ_H (300 MHz; $CDCl_3$) 1.9 (4 H, m), 2.7 (2 H, t, *J* 6 Hz), 3.0 (2 H, t, *J* 6 Hz), 7.6 (1 H, t, *J* 8 Hz), 7.7 (1 H, t, *J* 8 Hz), 8.0 (1 H, d, *J* 8 Hz and 1 H, d, *J* 8 Hz), 8.2 (1 H, d, *J* 8 Hz), and 8.7 (1 H, d, *J* 8 Hz); *m/z* 234 (M^+, 100%).

Hydrations and Methanol Additions. The acetal (**16**) in methanol provided the following ratios used below in calculating the extent of the reversible additions: E_{313}/E_{288}, 0.05; E_{313}/E_{292}, 0.07.

Hydration of the Diketone (**3**).—Crystals of the diketone (**3**) were crushed under water at 60 °C then cooled to room temperature and filtered. The filtrate had $E_{max.}$ (1 cm) 2.57 at 318 nm with no evidence of hydrate formation. An aliquot (3 ml) was treated with acetic acid (10% in water; 3 drops) and its u.v. spectrum was recorded at intervals of 2 min; the changes showed isosbestic points at 258 and 288 nm and were half completed in 5 min. At completion the ratio E_{313}/E_{288} had decreased from 1.62 to 1.15, therefore 30% of the diketone had been hydrated.

Hydration of the Diketone (**8**).—Prepared in the same way, a saturated aqueous solution of (**8**) had $E_{max.}$ (1 cm) 1.59 at 309 nm with no evidence of hydrate formation. An aliquot (3 ml) was treated with undiluted acetic acid (3 drops) and its u.v. spectrum was recorded at intervals of 10 min; the changes showed isosbestic points at 270 and 292 nm and were half completed in 90 min. At completion the ratio E_{313}/E_{292} had decreased from 1.31 to 0.20, therefore 90% of the diketone had been hydrated.

Hydration of the Diketone (**12**).—Prepared in the same way, a saturated aqueous solution of (**12**) had $E_{max.}$ (1 cm) 0.57 at 306 nm with no evidence of hydrate formation. An aliquot (3 ml) was treated with acetic acid (1% in water; 1 drop) and its u.v. spectrum was recorded at intervals of 2 min; the changes showed isobestic points at 266 and 288 nm and were half completed in 4 min. At completion the ratio E_{313}/E_{288} had decreased from 1.23 to 1.03, therefore 17% of the diketone had been hydrated.

Non-hydration of 1,8-*Diacetylnaphthalene.*—Prepared in the same way, a saturated aqueous solution, mixed with an equal volume of water, had $E_{max.}$ (1 cm) 1.97 at 296 nm. An aliquot (3 ml) treated with undiluted acetic acid (0.1 ml) showed no changes in its u.v. spectrum.

Addition of Methanol to the Diketone (**3**).—The diketone (**3**) in methanol (38 mg dm^{-3}; 3 ml) had $E_{max.}$ (1 cm) 1.62 at 315 nm, with no evidence of adduct formation and after the addition of undiluted acetic acid (1 drop) the u.v. spectrum was recorded at intervals of 5 min; the changes showed isosbestic points at 258 and 288 nm and were half completed in 35 min. At completion the ratio E_{313}/E_{288} had decreased from 1.40 to 0.65, therefore 56% of the diketone had been converted.

Addition of Methanol to the Diketone (**8**).—The diketone (**8**) in methanol (37 mg dm^{-3}; 3 ml) had $E_{max.}$ (1 cm) 1.30 at 304 nm, with no evidence of adduct formation, and after the addition of undiluted acetic acid (1 drop) the u.v. spectrum was recorded at intervals of 20 min; the changes showed isosbestic points at 268 and 292 nm and were half completed in 360 min. At completion, the ratio E_{313}/E_{292} had decreased from 1.09 to 0.20, therefore 87% of the diketone had been converted.

Addition of Methanol to the Diketone (**12**).—The diketone (**12**) in methanol (36 mg dm^{-3}; 3 ml) had $E_{max.}$ (1 cm) 1.13 at 301 nm, with no evidence of adduct formation, and after the addition of acetic acid (1% in methanol; 1 drop) the u.v. spectrum was recorded at intervals of 20 min. The changes showed isosbestic points at 267 and 288 nm and were half completed in 220 min. At completion, the ratio E_{313}/E_{288} had decreased from 0.99 to 0.19 therefore 85% of the diketone had been converted.

Addition of Methanol to 1,8-*Diacetylnaphthalene.*—1,8-Diacetylnaphthalene in methanol (24 mg dm^{-3}; 3 ml) had $E_{max.}$ (1 cm) 0.96 and 296 nm, with no evidence of adduct formation, and after addition of acetic acid (1% in methanol; 1 drop) the u.v. spectrum was scanned at intervals of 2 min. The changes showed isosbestic points at 272 and 288 nm and were half completed in 7 min. At completion, the ratio E_{313}/E_{288} had decreased from 0.60 to 0.09 therefore 93% of the diketone had been converted.

Temperature Dependent Proton Magnetic Resonance Spectra of Methylene Groups.—(*a*) *In the diketone* (**8**). δ_H (CD_2Cl_2; 300 MHz; 216 K) 1.85 (2 H)* 2.10 (2 H),* 2.52 (2 H),† and 3.05 (2 H);† δ_H (CD_2Cl_2; 300 MHz; 295 K) 2.0 (4 H)* and 2.8 (4 H).†

(*b*) *In the diketone* (**12**). δ_H ($CDCl_3$; 300 MHz; 273 K) 1.3 (1 H, m),‡ 1.9 (2 H, m),§ 2.0 (1 H, m),‡ 2.2 (2 H, m),§ 2.8 (2 H, m),¶ and 3.2 (2 H, m);¶ δ_H ($CDCl_3$; 300 MHz; 331 K) 1.6—1.8 (2 H, coalescing),‡ 2.1 (4 H),§ and 3.0 (4 H);¶ δ_H (C_2Cl_4; $C_6D_5CD_3$; 300 MHz; 298 K) 1.3 (1 H), 1.9 (3 H), 2.2 (2 H), 2.6 (2 H), and 3.0 (2 H); δ_H (C_2Cl_4; $C_6D_5CD_3$; 300 MHz; 374 K) 1.7 (2 H), 2.0 (4 H), and 2.8 (4 H).

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* Coalescence occurs at 228 K; Δν 78 Hz, therefore K_C 191.6 s^{-1} and $\Delta G^{\ddagger}$ 10.8 kcal mol^{-1}.

† Coalescence occurs at 234 K; Δν 156 Hz, therefore K_C 356.0 s^{-1} and $\Delta G^{\ddagger}$ 10.8 kcal mol^{-1}.

‡ Coalescence occurs at 331 K, Δν 209 Hz, therefore K_C 471.4 s^{-1} and $\Delta G^{\ddagger}$ 15.3 kcal mol^{-1}.

§ Coalescence occurs at 319 K, Δν 70 Hz, therefore K_C 175.6 s^{-1} and $\Delta G^{\ddagger}$ 15.4 kcal mol^{-1}.

¶ Coalescence occurs at 324 K, Δν 131 Hz, therefore K_C 302.2 s^{-1} and $\Delta G^{\ddagger}$ 15.4 kcal mol^{-1}. In calculating K_C, the rate of conformation inversion, each geminal coupling constant is assumed to be 15 Hz so that $K_C = \pi/\sqrt{2} \times \sqrt{\Delta\nu^2 + 1\,350}$ s^{-1}.

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