Cyclopenta[*a*]phenalen-9(8*H*)-one: an extended phenalenone system

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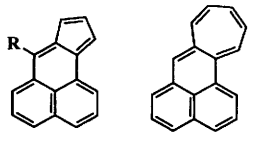
Cyclopenta[*a*]phenalen-9(8*H*)-one, a keto form of cyclopenta[*a*]phenalen-9-ol, has been found to be exclusively in an extended phenalenone form.

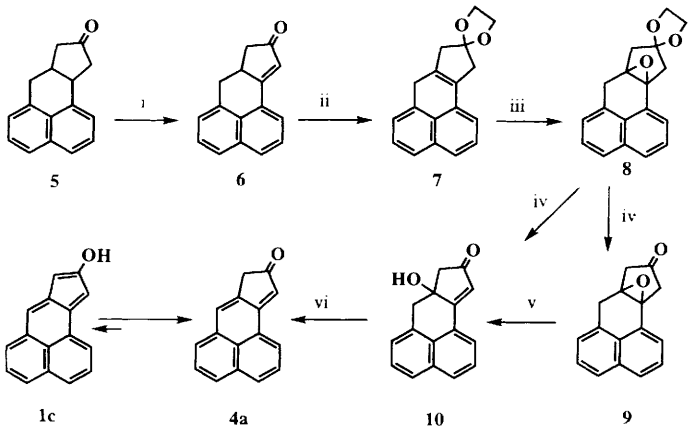
Molecular orbital calculations show moderate and comparable aromatic resonance energies for cyclopenta[*a*]phenalene **1a** and cyclohepta[*a*]phenalene **2**, compounds which are of theoretical interest.[1] Whilst our successful synthesis of **2**[2] has shown it to have a polar and highly electron-donating aromatic structure, the parent molecule of **1a** has yet to be synthesized although the downfield shifts of the skeletal protons for a simple derivative **1b** were consonant with the calculated resonance energy.[3] Cyclopenta[*a*]phenalen-7(8*H*)-one **3**, a keto form of cyclopenta[*a*]phenalen-7-ol, however, showed no propensity for enolization under the neutral conditions,[3] behaviour which



1a: R = H **1b**: R = OMe **2**

resembles keto-enol equilibration for azulenols[4] rather than phenols. In attempting to identify the structural features which affect keto–enol equilibration for a cyclopenta[*a*]-phenalenol, we examined cyclopenta[*a*]phenalen-9(8*H*)-one **4a** and discovered a number of novel properties associated with its keto–enol equilibration.

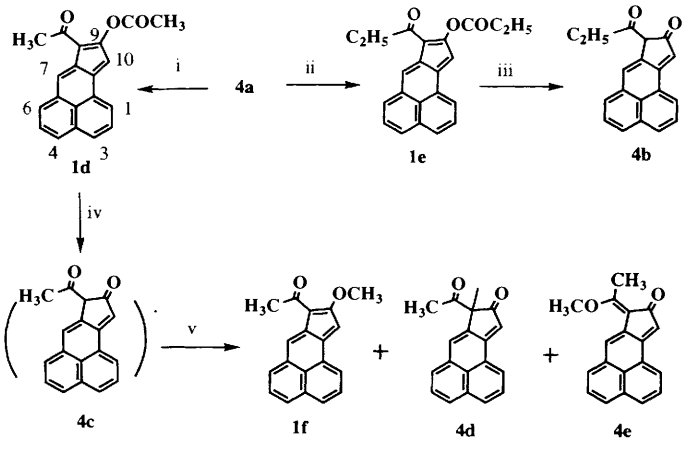
Introduction of α,β-unsaturation into **5** was effected by enolization followed by oxidation,[5] to give **6**. Acetalization of **6** accompanied with a double-bond shift gave **7**, which was epoxidized with MCPBA to yield **8**. Deacetalization of **8** with 2 mol dm^{-3} aqueous hydrochloric acid gave **9** together with **10**. The former was smoothly converted into the latter with $KOBu^t$. Treatment of **10** with toluene-*p*-sulfonic acid in benzene yielded **4a** as a stable crystalline compound.



Scheme 1 *Reagents and conditions:* i, lithium diisopropylamide, Me_3SiCl (1.7 equiv.), tetrahydrofuran, room temp. 30 min, then 2,3-dichloro-5,6-dicyanobenzoquinone (1.8 equiv.), 2,4,6-trimethylpyridine, benzene, room temp., 4 h, 35%; ii, ethylene glycol, toluene-*p*-sulfonic acid, benzene, reflux, 4 h, 61%; iii, *m*-chloroperbenzoic acid (1.3 equiv.), sodium hydrogen phosphate, dichloromethane, 0 °C, 45 min ⟶ room temp., 4 h, 72%; iv, 2 mol dm^{-3} hydrochloric acid, 71 and 11% for **9** and **10**, respectively; v, $KOBu^t$ (1.1 equiv.), Et_2O, −78 °C, 1 h, 76%; vi, toluene-*p*-sulfonic acid, benzene, reflux, 2 h, 62%

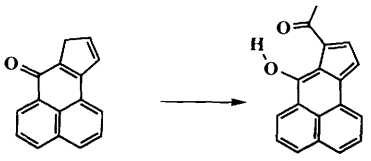
The ^1H NMR spectra of **4a** in various aprotic solvents [$CDCl_3$, CD_2Cl_2, $(CD_3)_2CO$] show a signal due to two aliphatic protons at δ_H 3.15. The maximum of the longest wavelength absorption band in cyclohexane appears at 414 nm (log ε 4.26), which is quite different both in shape and intensity from that of **1b**.[3] These findings indicate that the equilibrium between **4a** and **1c** is exclusively in favour of the former.

As for **1b**, the ^1H NMR spectrum of **4a** in deuteriotrifluoroacetic acid displays a pattern characteristic of a phenalenyl cation moiety.



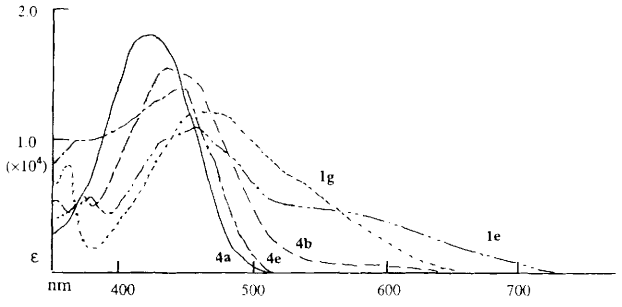
Scheme 2 *Reagents and conditions:* i, lithium diisopropylamide (3.0 equiv.), tetrahydrofuran, −78 °C, 1 h then MeCOCl (3.0 equiv.), −78 °C ⟶ room temp. for 2 h, 46%; ii, lithium diisopropylamide (3 equiv.), tetrahydrofuran, −78 °C, 1 h, then EtCOCl (10.0 equiv.), −78 °C ⟶ room temp. for 1 h, 61%; iii, 5% aq. KOH, EtOH, room temp., 10 min, 53%; iv, 5% aq. KOH, EtOH, room temp., 5 min; v, CH_2N_2, ether, room temp., 31, 16 and 32% for **1f**, **4d** and **4e** respectively

Although attempted *O*-alkylation of **4a** with methyl fluorosulfonate[3] to yield a fully conjugated product was a failure, acylation successfully gave the diacylated products **1d** and **1e**. Since use of less than one equivalent of the acylation reagent with **4a** yielded the *C*-acylated product **4b**, it is likely that the diacylated products were produced by initial *C*-acylation followed by *O*-acylation. Treatment of compound **4c** with diazomethane gave a *C*-methylation product **4d** together with two *O*-methylation products **1f** and **4e**. Acetylation of compound **3** under conditions similar to those described above afforded



3 1g

Scheme 3 *Reagents and conditions:* lithium diisopropylamide (4 equiv.), tetrahydrofuran, −78 °C, 40 min, then CH_3COCl (15.3 equiv.), −78 °C ⟶ room temp. for 30 min, 50%



Visible absorption spectra of **4a**, **4e**, **4b**, **1g**, and **1e**.

1g. These results of enol fixation show that the aromatic stabilization energy of the cyclopenta[*a*]phenalene system is small.

The maxima of the longest wavelength in the absorption bands for **4a**, **4d** and **4e** are centred at *ca.* 410–450 nm, a sharp drop being shown to the longer wavelength side of each band. In contrast, absorption bands in the visible region of **1d**, **1e** and **1f** are shifted to the longer wavelengths with long tailing up to > 700 nm. The positions and shapes for **4b** and **4c** are interestingly intermediate, namely at *ca.* 450 nm with tailing up to 650 nm. This spectroscopic evidence indicates that **4b** and **4c** are partly enolized with conjugation as in **1**. The longest wavelength absorption for **1g** appears at 470 nm with tailing up to 650 nm, the band shape of which resembles that for **1d**, **1e**, **1f** and **1b**.

The significant dependence upon structure of keto–enol equilibration indicates that the π electron delocalization energies for the keto and enol forms of cyclopenta[*a*]-phenalenones are comparable, the naphthalene skeleton being mainly responsible for the total stabilization energy of each form. The resultant marked UV spectral changes are explained by characteristic non-alternant conjugation[3] in the cyclopenta[*a*]phenalene and alternant conjugation in extended phenalenone systems.

Experimental

Structures for all the compounds were established by spectroscopic methods and combustion analyses.

Cyclopenta[*a*]phenalen-9(8*H*)-one 4a

A solution of 7,7a-dihydro-7a-hydroxycyclopenta[*a*]phenalen-9(8*H*)-one **10** (120.3 mg, 0.509 mmol) and a catalytic amount of toluene-*p*-sulfonic acid (10 mg, 0.05 mmol) in benzene (50 cm^3) was refluxed for 2 h. After cooling, the solution was washed with 10% aq. $NaHCO_3$ and worked up. Column chromatography of the product over deactivated silica gel (3% H_2O) gave **4a** as light brown needles (68.7 mg, 62%), mp 164–167 °C: ν_{max} cm^{-1} ($CHCl_3$) 1660 and 1550; δ($CDCl_3$) 3.15 (d, *J* 1.5, 2 H), 6.54 (d, *J* 1.7, 1 H), 6.79 (dd, *J* 1.7 and 1.5, 1 H), 7.26–7.72 (m, 4 H), 7.88 (dd, *J* 8.0 and 1.3, 1 H) and 8.04 (dd, *J* 7.1 and 1.3, 1 H); δ(CF_3CO_2D) 3.92 (br s, 1.2 H), 7.25 (br s, 0.5 H), 7.88 (t, *J* 7.4, 1 H), 7.91 (s, 1 H), 7.99 (t, *J* 6.9, 1 H), 8.26 (d, *J* 7.4, 1 H), 8.35 (d, *J* 7.4, 1 H), 8.59 (d, *J* 6.9, 1 H) and 8.80 (d, *J* 6.9, 1 H).

8-Propionyl-9-propionyoxycyclopenta[*a*]phenalene 1e

Lithium diisopropylamide was prepared from diisopropylamine (0.51 cm^3, 2.84 mmol) in anhydrous THF (3.0 cm^3) and butyllithium in hexane (2.84 mmol, 1.81 cm^3) in the customary manner. Cyclopenta[*a*]phenalen-9(8*H*)-one **4a** (206.8 mg, 0.947 mmol) in anhydrous THF (18 cm^3) was added over a period of 30 min, the mixture held at −78 °C which was then stirred at this temperature for 1 h. Freshly distilled propionyl chloride (0.82 cm^3, 9.47 mmol) was added dropwise to the mixture which was then allowed to rise to room temperature over 1 h. The reaction was quenched with water and extracted with ether. Column chromatography of the product over deactivated silica gel (10% water) with benzene gave **1e** as dark brown needles (191.9 mg, 61%), mp 114–116 °C: ν_{max}/cm^{-1} ($CHCl_3$) 1765 and 1615; δ($CDCl_3$) 1.22 (t, *J* 7.5, 3H), 1.34 (t, *J* 7.5, 3 H), 2.69 (q, *J* 7.5, 2 H), 2.85 (q, *J* 7.5, 2 H), 7.02 (br s, 1 H), 7.40–7.66 (m, 2 H), 7.68–7.92 (m, 3 H), 8.16 (dd, *J* 7.3 and 1.1, 1 H) and 8.65 (br s, 1 H).

Reaction of 8-acetylcyclopenta[*a*]phenalen-9(8*H*)-one 4c with diazomethane

A few drops of 5% aq. KOH were added to a solution of 8-acetyl-9-acetoxycyclopenta[*a*]phenalene **1d** (148.4 mg, 0.491 mmol) in ethanol (20 cm^3) at room temperature. After evaporation of the mixture to one third of its volume under reduced pressure it was acidified with 2 mol dm^{-3} aq. HCl and extracted with ether (× 3). Column chromatography of the product over deactivated silica gel (10% water) with benzene gave **4c** (68 mg, 53%), which was used without further purification.

To a solution of compound **4c** (114.3 mg, 0.439 mmol) in ether (300 cm^3) cooled in an ice-bath was added diazomethane in ether [from *N*-methyl-*N*-nitrosourea (5g)] and then MeOH (20 cm^3). After being stirred for 2 h the mixture was evaporated under reduced pressure and the residue column chromatographed over deactivated silica gel (3% water) with benzene–ether (1 : 1, v/v) to give **1f** as dark brown needles (37.3 mg, 31%), **4d** as yellowish brown crystals (37.5 mg, 32%) and **4e** as a brown solid (18.7 mg, 16%). Compound **1f**: mp 200–205 °C (decomp.): ν_{max}/cm^{-1} ($CHCl_3$) 1595; δ($CDCl_3$) 2.52 (s, 3 H), 4.16 (s, 3 H), 6.98 (d, *J* 1.0, 1 H), 7.61 (t like, *J* 7.5, 1 H), 7.69 (t like, *J* 8.2 and 7.5, 1 H), 7.90–7.99 (m, 3 H), 8.37 (dd, *J* 7.5 and 1.1, 1 H) and 8.70 (d, *J* 1.0, 1 H). Compound **4d**: mp 139–141 °C: ν_{max} cm^{-1} ($CHCl_3$) 1710, 1665 and 1545; δ($CDCl_3$) 1.54 (s, 3 H), 2.06 (s, 3 H), 6.76 (d, *J* 1.6, 1 H), 6.90 (d, *J* 1.5, 1 H), 7.48–7.92 (m, 4 H), 8.08 (dd, *J* 8.3 and 1.1, 1 H) and 8.33 (dd, *J* 7.3 and 1.0, 1 H). Compound **4e**: mp 139–141 °C: ν_{max} cm^{-1} ($CHCl_3$) 1655 and 1602; δ($CDCl_3$) 2.75 (s, 3 H), 4.01 (s, 3 H), 6.68 (d, *J* 1.6, 1 H), 7.45–7.80 (m, 4 H), 7.67 (d, *J* 1.6, 1 H), 7.94 (dd like, *J* 8.0, 1 H) and 8.20 (dd, *J* 7.3 and 1.2, 1 H).

8-Propionylcyclopenta[*a*]phenalen-9(8*H*)-one 4b

Compound **4b**, prepared as reddish brown needles in a way similar to that of **4c**, had mp 138–139 °C: ν_{max} cm^{-1} ($CHCl_3$) 1600 and 1575; δ($CDCl_3$) 1.35 (t, *J* 7.4, 3 H), 2.82 (q, *J* 7.4, 2 H), 6.77 (d, *J* 1.5, 1 H), 7.26 (d, *J* 1.5, 1 H), 7.52–7.90 (m, 5 H), 8.00 (br d, *J* 7.5, 1 H) and 8.29 (dd, *J* 7.7 and 1.0, 1 H).

8-Acetylcyclopenta[*a*]phenalen-7-ol 1g

Lithium diisopropylamide was prepared from diisopropylamine (0.20 cm^3, 1.42 mmol) in anhydrous THF (5.0 cm^3) and butyllithium in hexane (1.4 mmol, 0.95 cm^3) in the customary manner. Acetyl chloride (4.9 mmol, 0.35 cm^3) was added dropwise to the solution of **3** and lithium diisopropylamide, and the mixture was gradually warmed from −78 °C to room temperature. After 20 min the mixture was diluted with ether and extracted with ether. Column chromatography of the

product over deactivated silica gel (20% water) gave **1g** as dark red needles (39 mg, 50%), mp 168.5–169.6 °C; ν_{max}/cm^{-1} ($CHCl_3$) 1600 and 1575; $\delta(CDCl_3)$ 2.60 (s, 3 H), 6.95 (d, *J* 4.0, 1 H), 7.40 (d, *J* 4.0, 1 H), 7.55–8.70 (m, 6 H) and 17.9 (s, 1 H).

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