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5H-CYCLOPENTA[cd]PHENALEN-5-ONE. A MODEL COMPOUND OF PERTURBED [13]ANNULENONE.

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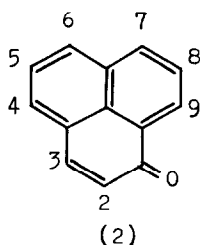
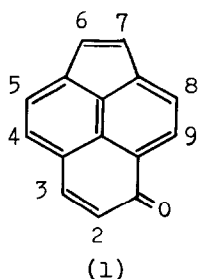
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The series of full conjugated planar monocyclic ketones, named annulenones by Sondheimer<sup>1)</sup>, are interesting class of compound and predicted to be aromatic or nonaromatic if they contain  $(4n+3)$ -membered ring or  $(4n+1)$ -membered ring, respectively. This prediction has recently been verified by the experimental evidences of [3],<sup>2)</sup>[5],<sup>3)</sup>[7],<sup>4)</sup>[9],<sup>5)</sup>[11],<sup>6)</sup>[13],<sup>1)</sup>[15]<sup>7)</sup> and [17]annulenones.<sup>8)</sup> On the other hand, considerable evidence has been accumulated indicating the peripheral conjugation of unsaturated polycyclic compounds, in which slight perturbation arises by insertion of an internal ethylenic double bond into a  $(4n+2)$  and/or a  $(4n)$  monocyclic periphery.<sup>9)</sup>

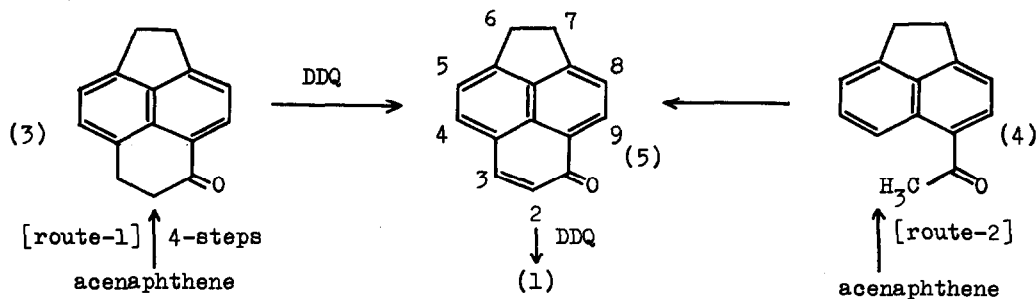
In order to gain some insight into the possibility of peripheral conjugation in the polycyclic ketones we examined the 5H-cyclopenta[cd]phenalen-5-one (1) [in order to compare the NMR data the convenient numbering corresponding to the phenalene (2) are used for compounds (1), (5) and (6) in the figures and the tables],



where the molecule has a phenalene unit (2). We now wish to report our studies on the synthesis of (1) and provide evidence for the peripheral electronic model describing (1) as a perturbed [13]-annulenone (7).

The synthesis of (1) was achieved by two alternative routes depicted in the following scheme. 1,2,6,7-Tetrahydro-5H-cyclopenta[cd]phenalen-5-one (3), a potential precursor of the required ketone (1), was prepared from acenaphthene

according to the known procedure of Fieser et. al.<sup>10)</sup> with slight modification [route-1]. The dihydroketone (5) was also synthesized starting from acenaphthene [route-2]. 5-Acetyladenaphthene (4),<sup>11)</sup> obtained through the Friedel-Crafts acetylation of acenaphthene, was subjected to condensation with ethylformate in the presence of sodium metal. The resulting keto-aldehyde cyclized upon stirring with 80 % sulfuric acid to give (5) in 17 % yield.



Although dehydrogenation of the tetrahydroketone(3) with two moles equivalent of DDQ in benzene fails to oxidize (3) to the fully unsaturated ketone (1), successful oxidation was performed by stepwise manner via the dihydroketone (5) using a mole of the quinone at each stage. Thus, a solution of 250 mg [1.2 mmole] of (3) and 295 mg [1.3 mmole] of DDQ in 50 ml of dry benzene was gently refluxed 2 hrs under nitrogen. Examination of the tlc spots indicate the nearly quantitative conversion to (5) was achieved at this stage of reaction. The solution was treated further 1.2 mmole of the quinone for 12 hrs under the same condition. After filtration of the resulted hydroquinone, the benzene solution was evaporated in vacuo. The residue was chromatographed on 5 g of alumina with benzene as the eluting solvent to produce 60 mg [21 % yield based on (3)] of (1) as crystalline solid which on recrystallization from pet. ether afforded bright dark red needles, mp. 154 - 156°C. Anal. Found, C, 87.98; H, 3.89. Calcd. for  $C_{15}H_8O$ , C, 88.22; H, 3.95 %.

The electronic spectrum of (1) is found to be no solvent dependent:  $\lambda_{max}$  (methanol); 222 nm (log  $\epsilon$ , 4.48), 234 (sh, 4.46), 365 (sh, 4.08), 380 (4.13), 415 (3.73).  $\lambda_{max}$  (cyclohexane): 222 (4.20), 232 (4.20), 361 (sh, 3.70), 376 (3.80) 394 (sh, 3.55), 415 (3.43). The ir spectrum of (1) displays a strong band at  $1638\text{cm}^{-1}$  in chloroform solution. The nmr spectra<sup>12)</sup> of (1) in deuteriochloroform and in trifluoroacetic acid indicate not only the proposed structure but also interesting

electronic feature of (1). The chemical shifts of (1) are moved upfield only to an extent of 0.2 - 0.5 ppm compared with those of (5) and phenalenone (2)<sup>13)</sup> as shown in Table-1.

Table-1. Nmr Data of (1), (5) and (2) in CDCl<sub>3</sub> ( $\delta$ -values)

	H-2	H-3	H-4	H-5	H-6	H-7	H-8	H-9	J <sub>23</sub>	J <sub>45</sub>	J <sub>67</sub>	J <sub>89</sub>
(1)	6.17	7.17	7.14	7.10	6.65	6.60	7.32	7.94	10.0	7.0	5.5	7.5
(5)	6.63	7.63	7.43	7.29	3.36	3.36	7.61	8.42	9.8	7.8		8.0
(2)	6.66	7.63	7.63	7.48	7.91	8.08	7.67	8.52	9.6	7.5		7.2
$\Delta[(5)-(1)]$	0.46	0.47	0.29	0.19			0.29	0.48	(Hz)			

When the spectrum of (1) is recorded in trifluoroacetic acid striking differences from the cases of (5) and (2)<sup>13)</sup> are observed. Table-2 provides a comparison of these chemical shifts in trifluoroacetic acid. The most noticeable effect on the

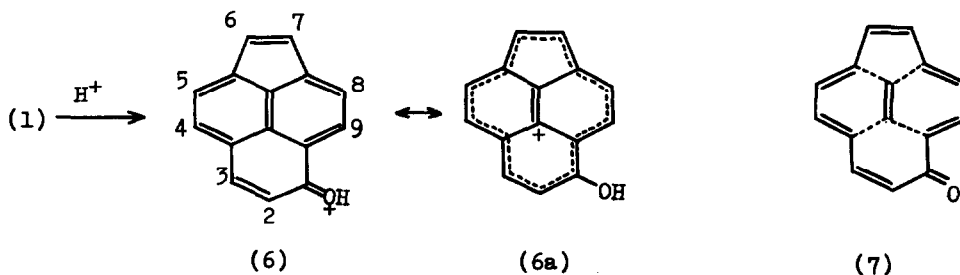
Table-2. Nmr Data of (1), (5) and (2) in CF<sub>3</sub>COOH ( $\delta$ -values)

	H-2	H-3	H-4	H-5	H-6	H-7	H-8	H-9	J <sub>23</sub>	J <sub>45</sub>	J <sub>67</sub>	J <sub>89</sub>
(1)	6.42	7.46	7.27	6.99	6.41	6.33	7.15	8.05	9.2	7.0	5.2	7.8
(5)	7.73	8.82	8.84	8.14	3.94	3.94	8.25	9.43	9.0	8.0		8.5
(2)	7.76	8.88	8.78	8.20	8.86	9.01	8.30	9.46	9.0	7.6		7.7
$\Delta[(5)-(1)]$	1.31	1.36	1.57	1.15			1.10	1.38	(Hz)			

 $\delta_{CF_3COOH} - \delta_{CDCl_3}$ 

(1)	0.25	0.29	0.13	-0.13	-0.24	-0.27	-0.17	0.11
(5)	1.10	1.19	1.41	0.85			0.64	1.01

spectra caused by the protonation of (5) and (2)<sup>13)</sup> are the large downfield shift of all protons due to the formation of the aromatic phenalenium ions, whereas the present ketone (1) exhibits both the slight up and downfield shifts on protonation [see 5th and 6th rows of Table-2]. It is apparent that the major changes occur



at H-2, H-3, H-4, H-5, H-8 and H-9 (all upfield shift) on formation of the 6,7-double bond in (5) as shown in the 4th row of Table-2. The large upfield shifts could perhaps be attributed to the effect of a magnetically induced paramagnetic

ring current<sup>14)</sup> in the peripheral 12- $\pi$  electron framework such as (6a). These observations suggest that (1) be regarded as a [13]annulenone unit weakly coupled with a strongly localized central vinyl crosslink represented such as (7). The slight difference in the chemical shift of the protonated ketone (6) relative to unprotonated ketone (1) may due to the deshielding effect of the positive charge which would compensate the net shielding due to the paramagnetic ring current.

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