The Chemistry of Phenalenium Systems. XXIII.[1] Syntheses and Properties of Cyclohepta[*cd*]phenalen-6-one and the Cyclohepta[*cd*]phenalenium Ion[2]

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The syntheses of cyclohepta[*cd*]phenalen-6-one (**8**) and the cyclohepta[*cd*]phenalenium tetrafluoroborate (**1**) are reported. As expected, it is apparent that in the transition from 10,11-dihydrocyclohepta[*cd*]phenalen-6-one to the fully conjugated ketone **8**, all the vinyl protons move downfield by 0.22 to 0.53 ppm. The plausible explanation suggests that these shifts arise from deshielding due to the existence of a diamagnetic ring current induced in the 14π periphery of **8**. In accord with theoretical prediction, the cation **1** is extremely stable. The substantial thermodynamic stability of **1** is reflected to its pK_R^+ of 8.4. The ion **1** can be regarded as a perturbed [15]annulenium ion weakly coupled with a localized central vinyl crosslink.

Although there has been considerable interest in the neutral nonalternant isomers of pyrene such as cyclohept[*fg*]acenaphthylene (acepleiadiene),[3] cyclohepta[*def*]fluorene,[4] cyclohept[*bc*]acenaphthylene,[5] cyclohepta[*klm*]benz[*e*]indene,[6] dicyclopenta[*ef,kl*]heptalene (azupyrene),[7] pentaleno[6,6a,1,2-*def*]heptalene,[8] and dicyclohepta[*cd,gh*]pentalene,[9] the ionic 14π perimeter species which are isoelectronic with pyrene have received little attention. The ionic 14π perimeter species so far known have been confined to the anions, *e.g.* cyclopenta[*cd*]phenalenide ion,[10] pyracylene dianion,[11] dibenzo[*cd,gh*]pentalenyl dianion,[12] and cyclopenta[*def*]phenanthrenide ion,[13] no cationic species have been reported to date. According to theoretical (HMO) prediction by Zahradnik *et al.*[14] the cyclohepta[*cd*]phenalenium ion (**1**) ought to be quite stable and might be reasonably accessible.

On the other hand, cyclohepta[*cd*]phenalen-6-one (**8**), a key intermediate for the synthesis of **1**, is of interest in connection with current studies on the peripheral conjugation in peri-condensed polyarenes. We have recently reported the synthesis and properties of cyclopenta[*cd*]phenalen-4-one,[15] cyclopenta[*cd*]phenalen-5-one,[16] cyclohepta[*cd*]phenalen-1-one,[17] and cyclohepta[*cd*]phenalen-4-one,[18] wherein the structural phenalenone moiety is incorporated into the molecule. In these cases, we have proposed that these compounds can be regarded as [13]- and [15]annulenone perturbed by internal vinyl crosslink. Here we describe the synthesis of **1** as the first example of a 14π perimeter cationic system along with **8** as an adequate model compound for perturbed [15]annulenone.

Results and Discussion

Synthesis and Properties of Cyclohepta[cd]*phenalen-6-one (8).* Reduction of the hydroxy ester, which was obtained by the Reformatsky reaction of 2,3-dihydrophenalenone (**2**)[19] with methyl 4-bromocrotonate, over palladium hydroxide on charcoal proceeds accompanying with hydrogenolysis of the benzylic hydroxyl group. The butylate thus obtained was hydrolyzed with potassium hydroxide in ethanol to give the carboxylic acid (**3**) in 48% yield. Cyclization of **3** with polyphosphoric acid at 90 °C for 1 h afforded the tetracyclic ketone (**4**) in 75% yield. The ketone (**4**) was converted into the α,α-dibromo ketone (**5**) in quantitative yield by treatment with bromine in dry carbon tetrachloride. Dehydrobromination of **5** to give 10,11-dihydrocyclohepta[*cd*]phenalen-6-one (**6**) was accomplished by heating in hexamethylphosphoric triamide with lithium chloride for 1 h at 95—100 °C. The structure of **6** was confirmed on the basis of its spectroscopic properties. The mass spectrum of **6** showed intense peaks at m/e 232 (M$^+$, 64%), 204 (M$^+$$-$CO, 100%), 203 (93%) and 202 (pyrene ion, 82%). The IR spectrum exhibited characteristic absorption of tropone skeleton at 1625, 1590, and 1580 cm^{-1}.[20] The absorption bands of the UV spectrum of **6**, 243 nm (log ε, 4.38), 287 (4.33), and 344 (3.91), are in good agreement with those of cyclohepta[*a*]naphthalen-7-one (**7**).[21] The conversion of **6** into the desired fully conjugated ketone (**8**) was effected by treatment with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone in benzene in a sealed tube at 120 °C for 20 h in 21% yield. However, it was found that the compound (**8**) could be more readily obtained in a higher yield (33%) on treatment of **6** with triphenylmethyl tetrafluoroborate in refluxing acetic acid under nitrogen

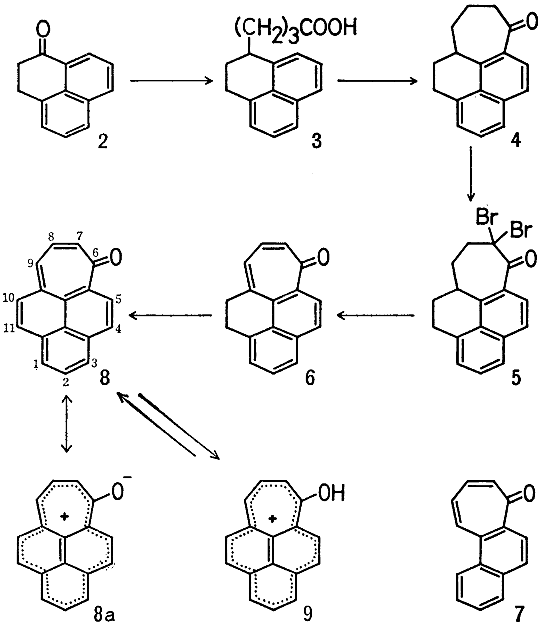


Table 1. Comparison of NMR data for **6** and **8**[a)]

	in $CDCl_3$			in CF_3COOH			**6**	**8**
	6	**8**	$\Delta\delta$(**8**—**6**)	**6**	**8**	$\Delta\delta$(**8**—**6**)	$\delta_{CF_3COOH}-\delta_{CDCl_3}$	$\delta_{CF_3COOH}-\delta_{CDCl_3}$
H-1, 2, 3	7.30—7.78	7.68—8.02	0.38—0.24	7.82—8.21	8.63—9.16	0.81—0.95	0.52—0.43	0.95—1.14
H-7, 8, 9	6.73—7.10	7.20—7.56	0.41—0.46	8.24—8.62		0.39—0.54	1.90—2.06	1.43—1.60
H-10, 11	2.88—3.35			3.43—3.82			0.55—0.47	
H-4	7.96	8.18	0.22	8.62	9.23	0.61	0.66	1.05
H-5	8.24	8.77	0.53	9.05	9.74	0.69	0.81	0.97
$J_{4,5}$	9.0	9.0		9.2	9.2			

a) Chemical shifts are given in δ-values with respect to TMS as an internal standard and coupling constants are given in Hz.

atmosphere for 2 h. The identity of **8** was established in the following manner. Mass spectrometry gave a parent peak at *m/e* 230. As would be expected for a compound containing tropone moiety, the base peak in the mass spectrum was found to be M^+-CO (*m/e* 202).[22)] The UV spectrum of **8** showed maxima at 249 nm (log ε, 4.48), 311 (4.07), 321 (4.08), 430 (4.23) indicating an extend conjugation. Further evidence was also provided by ^{1}H-NMR spectrum.

The NMR chemical shifts and coupling constants of **8** compared with those of the reference compound **6** are summarized in Table 1. Although complete assignments of the proton chemical shifts could not be made except H-4 and H-5 due to their complex spectral pattern, it is apparent that (i) in the transition from the dihydro ketone (**6**) to the fully conjugated ketone (**8**), all the vinyl protons move downfield by 0.2—0.5 ppm (ii) the downfield shift is enhanced (0.4—0.95 ppm) when **8** is protonated in trifluoroacetic acid (iii) in the case of **6**, only protons of seven-membered ring (H-7, 8, and 9) move downfield in trifluoroacetic acid compared with those of the neutral form whereas the full conjugated ketone (**8**) exhibited marked downfield shifts of all the vinyl protons. These findings suggest the existence of a diamagnetic ring current induced in the 14π periphery (**8a**) of **8**. The diatropic effect is enhanced in trifluoroacetic acid owing to the formation of the 6-hydroxycyclohepta[*cd*]phenalenium ion (**9**). Furthermore, supportive evidence for the formation of **9** in an acidic media was provided by the UV-visible spectrum of **8** in concentrated sulfuric acid which was closely similar to that of the parent cation (**1**) [*vide infra*] in acetonitrile both in absorption maxima and in band shape [see Fig. 1].

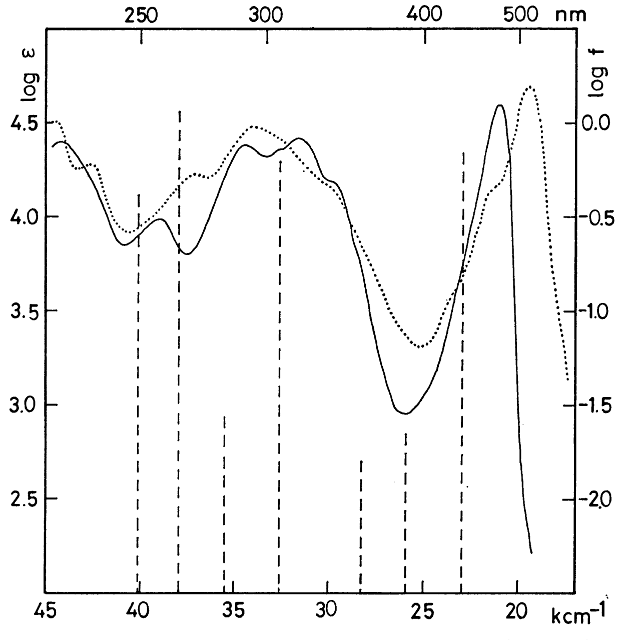
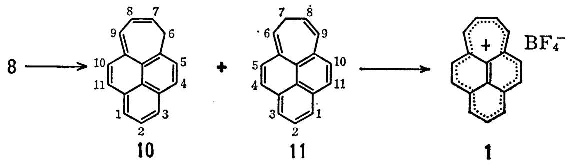


Fig. 1. Electronic spectra of the cyclohepta[*cd*]phenalenium tetrafluoroborate (**1**) in CH_3CN and cyclohepta-[*cd*]phenalen-6-one (**8**) in concd H_2SO_4.
——: (**1**), ……: (**8**).
Vertical dashed lines denote calculated transitions for (**1**).

Synthesis and Properties of Cyclohepta[cd]*phenalenium Tetrafluoroborate (1).* Reduction of **8** with lithium aluminum hydride–aluminum chloride complex in ether at −50 °C for 2 h led to a mixture of isomeric hydrocarbons, 6*H*-cyclohepta[*cd*]phenalene (**10**) and 7*H*-cyclohepta[*cd*]phenalene (**11**) in a ratio of about 9: 13. The mixture was isolated in 56% yield after chromatography on alumina deactivated with 10% water. Owing to their highly unstable nature, compounds **10** and **11** have to be handled under nitrogen atmosphere throughout reaction and isolation. Although **10** and **11** could not be separated due to their pronounced sensitivity toward air and heat, their structural assignments were readily borne out by 100 MHz ^{1}H-NMR and NMDR experiments. The mixture of **10** and **11** showed signals assignable to **10** at δ 2.71 (H-6,6′, d, $J_{6,7}=6.7$ Hz), 5.51 (H-7, dt, $J_{7,6}=6.7$, $J_{7,8}=9.2$ Hz), 6.33 (H-8, dd, $J_{8,7}=9.2$, $J_{8,9}=6.5$ Hz), 6.84 (H-9, d, $J_{9,8}=6.5$ Hz), and **11** at 1.66 (H-7,7′, dd, $J_{7,6}=7.3$, $J_{7,8}=6.5$ Hz), 4.82 (H-8, dtd, $J_{8,7}=6.5$, $J_{8,9}=8.5$, $J_{8,6}=2.4$ Hz), 5.27 (H-6, td, $J_{6,7}=7.3$, $J_{6,8}=2.4$ Hz), and 6.66 (H-9, d, $J_{9,8}=8.5$ Hz) along with multiplet of the aromatic protons at 7.02—8.07. Irradiation at δ 2.71 (H-6,6′ of **10**) converted the doublets of triplet at δ 5.51 attributed to H-7 of **10** into a clean doublet with $J=9.2$ Hz. Another irradiation at δ 1.66 assigned to H-7,7′ of **11** changed the triplets of doublet at δ 5.27 and the doublets of triplets of doublet at δ 4.82 into a broad singlet and a broad doublet, respectively. Additional evidence in favor



10   **11**   **1**

of the assigned structures is the mass spectrum of the mixture which showed peaks at *m/e* 216 (M^+, 100%), 215 (M^+—H, 73%), and 202 (pyrene ion, 21%).

Hydride abstraction from the freshly prepared mixture of **10** and **11** with triphenylmethyl tetrafluoroborate in chloroform at room temperature immediately gave the desired cation (**1**).

In conformity with the theoretical prediction by Zahradnik *et al.*[14] the cyclohepta[*cd*]phenalenium tetrafluoroborate (**1**) is extremely stable reddish brown crystals which sinter at 199—201 °C and show no definite melting point. **1** can be stored without any change under atmospheric condition. The electronic spectrum of **1** is reproduced in Fig. 1. At least three major bands can be discerned. In either acetonitrile or water **1** shows essentially the same spectrum. The analysis of the electronic spectrum was kindly carried out by Zahradnik and Slanina[23] and was summarized in Table 2 and displayed in Fig. 1. The 100 MHz ^{1}H-NMR spectrum of **1** in deuteriotrifluoroacetic acid (see Fig. 2) consists of superimposed signals of AA'XX',[24] 2×AB, and A_2B spin systems at δ 9.08 (H-7, 8 or H-6, 9), 9.66 (H-6, 9 or H-7, 8), 9.16 (H-5, 10),[25] 9.50 (H-4, 11),[25] 9.40 (H-1, 3), and 9.00 (H-2) with coupling constants of $J_{6,7}=J_{8,9}=10.9$, $J_{7,8}=9.0$, $J_{6,8}=J_{7,9}=1.4$, $J_{6,9}=0$, $J_{4,5}=J_{10,11}=8.9$, and $J_{1,2}=J_{2,3}=7.7$ Hz. The observed vicinal coupling constants in the six-membered ring are in good agreement with those predicted by the empirical correlation against SCF bond orders.[26] Thus using SCF bond orders,[23] we obtain 8.5 Hz for $J_{4,5}$ and $J_{10,11}$ and 7.6 Hz for $J_{1,2}$ and $J_{2,3}$. The comparative uniformity of the coupling constants indicates no appreciable bond fixation exists in the periphery of **1**. Both the substantial downfield chemical shifts with rather narrow range (δ 9.00—9.66 ppm) and the symmetrical pattern of the signals show the cation **1** to have fully delocalized structure with C_{2v}-symmetry.

Despite the fact that an unit positive charge resides over the fifteen peripheral carbon atoms, the ^{1}H-NMR signals of **1** are comparable to those of the tropylium ion (δ 9.20 in acetonitrile)[27] and the phenalenium ion (δ 9.30 and 8.48 in arsenic trichloride).[28] This provides evidence of the existence of a strong induced diamagnetic ring current associated with the 14π perimeter of **1**. These evidences support the idea that the cation **1** is best thought of as a perturbed [15]annulenium ion weakly coupled with a localized central vinyl cross-link.[29]

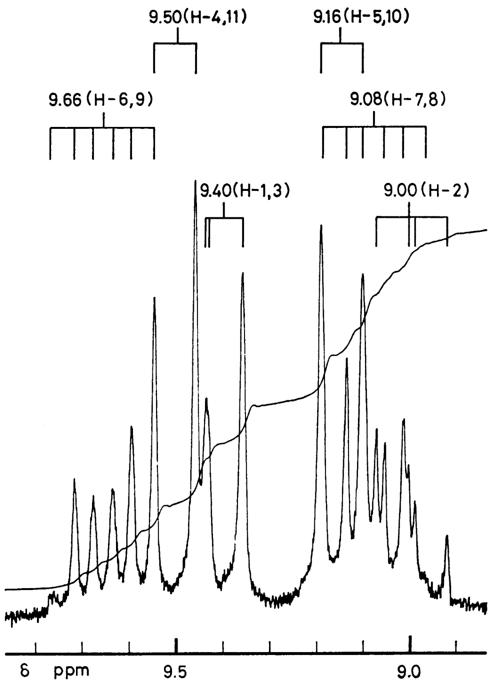


Fig. 2. 100 MHz ^{1}H-NMR spectrum of the cyclohepta[*cd*]phenalenium tetrafluoroborate (**1**) in CF_3COOD.

TABLE 2. ELECTRONIC SPECTRA OF **1**

No.	Calcd[a)]						Obsd[b)]	
	E (eV)	10^{-3} ν(cm^{-1})	λ (nm)	Polarization[c)]	log *f*	Configuration	λ	log ε
1	2.86	23.1	433	y	−0.17	8—9	475	4.49
2	3.21	25.9	386	x	−1.64	8—10 7—9	344	4.18 s
3	3.49	28.2	355	x	−1.79	6—9	316	4.40
4	4.05	32.7	306	x	−0.21	7—9	307	4.37 s
5	4.42	35.6	281	y	−0.56	6—10	291	4.37
6	4.70	37.9	264	y	0.03	7—10	257	3.99
7	4.98	40.2	249	x	−0.51	8—12	224	4.40
8	4.99	40.2	249	y	−0.38	5—9		

a) The calculations are based upon the LCI-SCF (PPP-type) method. Parameters used are: I_c= 11.42 eV, A_c=0.58 eV, β_{cc}^{core}=−2.318 eV. Singly excited configurations were formed by promotions of electrons between the four highest occupied and the four lowest unoccupied MO's. b) The values are obtained in acetonitrile solution. c) x and y denote polarization along short and long axes of **1**, respectively.

The thermodynamic stability of **1** is clearly reflected in its pK_R^+ value. Standard spectrophotometric method was used for the pK_R^+ determination in 20% aqueous acetonitrile solution. The pK_R^+ value of 8.4 thus obtained is the lower limit, since the intensity of absorbancy decreases with elapse of time in the pH range near pK_R^+. Thus the measurement at 180 s after preparation of the solution yields a somewhat small value of 8.1. In any way, pK_R^+ value of **1** is about 1 p*K* unit larger than that of the 8-cycloheptatrienylheptafulvenyl cation (pK_R^+=7.1,[30] 7.49[31]). To our knowledge, **1** is the most stable hydrocarbon cation so far reported.

Experimental

All melting points are uncorrected. The IR spectra were obtained on a Hitachi EPI G21 spectrometer. The electronic spectra were taken with a Hitachi 124 double beam spectrophotometer and were recorded in nm and the log ε values were given in parentheses. The mass spectra were obtained on a Hitachi RM-50 spectrometer at 70 eV. The ^{1}H-NMR spectra measured on a Varian T-60 and a Varian XL-100-15 spectrometers were given in δ-values with respect to tetramethylsilane as an internal standard, and the coupling constants (*J*) are given in Hz.

γ-(2,3-Dihydrophenalenyl)butyric Acid (3). A soln of 2,3-dihydrophenalenone (**2**) (9.1 g, 50 mmol) in a 1 : 1 mixture of anhyd benzene and ether (100 ml), zinc amalgam (10 g), and a small amount of iodine were placed in a three-necked flask. To this mixture methyl 4-bromocrotonate (2.2 g, 20 mmol) was added. The mixture was heated to 60 °C to start the reaction. After exothermic reaction occur additional methyl 4-bromocrotonate (8.8 g, 40 mmol) was added dropwise. After refluxing for 24 h the mixture was cooled and treated with dil hydrochloric acid. The organic layer was separated and washed successively with water, saturated sodium hydrogencarbonate soln, and water, dried (Na_2SO_4) and the solvent was removed to give methyl γ-(2,3-dihydro-1-hydroxyphenalenyl)crotonate as a viscous oil. IR (neat): 3450 (OH), 1700 cm^{-1} (C=O); NMR ($CDCl_3$): 1.8—2.1 (m, 2H), 2.4 (d, J=7, 2H), 2.8—3.1 (m, 2H), 2.9 (s, 1H), 3.6 (s, 3H), 5.6 (d, J=15, 1H), and 6.7—7.6 (m, 7H).

The crude ester thus obtained, palladium hydroxide charcoal (2 g), and 100 ml of ethanol were placed in a flask. The mixture was stirred under hydrogen atmosphere in an usual manner. After filtration of the catalyst, resulting soln was concd and the residue was dist under reduced pressure to give methyl γ-(2,3-dihydrophenalenyl)butylate as yellow oil, bp 170—174 °C/2 Torr, 8.4 g; IR (neat): 1730 cm^{-1} (C=O); NMR (CCl_4): 1.5—2.4 (m, 8H), 2.9—3.3 (m, 3H), 3.6 (s, 3H), and 7.0—7.7 (m, 6H).

Found: C, 80.34; H, 7.52%. Calcd for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51%.

A mixture of the ester (8.4 g), 50% aq potassium hydroxide (10 ml), and ethanol (50 ml) was stirred for overnight at room temp. Most of the ethanol was removed and replaced by water. The aq layer was then washed with ether and acidified with 3M hydrochloric acid. The mixture was extracted with ether and the extract was washed with water and dried (Na_2SO_4). Evaporation of the solvent gave crude **3**. Recrystallization of the crude **3** from benzene–hexane yielded pure **3** as colorless plates, mp 90.0—90.5 °C; 6.11 g (48% yield based on **2**). IR(KBr): 3500—2500 (OH), 1700 cm^{-1} (C=O); NMR($CDCl_3$): 1.6—2.5(m, 8H), 2.9—3.3(m, 3H), 7.0—7.7(m, 6H), 10.7(bs, 1H).

Found: C, 80.42; H, 7.13%. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13%.

*6*H*-7,8,9,9a,10,11-Hexahydrocyclohepta*[cd]*phenalen-6-one (4).* To polyphosphoric acid prepared from 130 ml of phosphoric acid and 260 g of phosphorus pentaoxide was added 6.11 g of **3** at 90 °C by portion with care. The resultant soln was stirred at this temp for 1 h, then poured onto ice. Extraction with ether and the extract was washed successively with water, saturated aq soln of sodium hydrogencarbonate, and water, and dried (Na_2SO_4). Evaporation of the solvent gave crude **4** which on recrystallization from benzene–hexane afforded **4** as colorless plates, mp 97.5—98 °C; 4.7 g (75%); IR(KBr): 1665 cm^{-1} (C=O); NMR(CCl_4): 1.6—2.2(m, 6H), 2.5—2.7(m, 2H), 2.9—3.5(m, 3H), 7.0—7.7(m, 5H); MS: *m/e* 236(M^+, 100%), 208(M^+−CO, 27%).

Found: C, 86.65; H, 6.85%. Calcd for $C_{17}H_{16}O$: C, 86.40; H, 6.83%.

*7,7-Dibromo-6*H*-7,8,9,9a,10,11-hexahydrocyclohepta*[cd]*phenalen-6-one (5).* To a soln of **4** (1.0 g, 4.2 mmol) in carbon tetrachloride (30 ml) was added a soln of bromine (1.5 g, 9 mmol) in carbon tetrachloride (8 ml). The resultant soln was stirred for overnight at room temp and then washed with saturated aq soln of sodium hydrogensulfate and water, and dried (Na_2SO_4). Evaporation of the solvent under reduced pressure at 0 °C gave crude dibromide **5** as viscous oil in quantitative yield. IR(neat): 1695 cm^{-1} (C=O); NMR(CCl_4): 1.5—2.7(m, 6H), 2.8—3.3(m, 3H), 7.0—7.7(m, 5H). The crude **5** was used for subsequent reaction without further purification.

*6*H*-10,11-Dihydrocyclohepta*[cd]*phenalen-6-one (6).* Anhyd lithium chloride (0.55 g, 13 mmol) was added at once to a soln of **5**, prepared from 10 g of **4** described as above, in hexamethylphosphoric triamide (40 ml). The stirred mixture was heated at 95—100 °C for 1 h under nitrogen. After cooling the mixture was poured into 300 ml of water and the product, which was isolated by ether extraction, was chromatographed on 10 g of alumina eluted with benzene to give the tetracyclic ketone **6** (650 mg, 66.7%). Further elution with ether gave the full conjugated ketone **8** (110 mg, 10%). **6**: pale yellow plates, mp 90.0—90.5 °C, MS: *m/e* 232(M^+, 64%), 204(M^+−CO, 100%), 202(82%); IR (KBr): 1625, 1590, 1580 cm^{-1}; UV(ethanol): 243(4.38), 287 (4.33), 344(3.91); (cyclohexane): 240(4.39), 283(4.31), 337 (3.98); (concd H_2SO_4): 249(4.51), 299(4.57), 418(3.90); NMR: see text.

Found: C, 87.73; H, 5.28%. Calcd for $C_{17}H_{12}O$: C, 87.90; H, 5.21%.

Cyclohepta[cd]*phenalen-6-one (8).* (i) To a dry Pyrex tube were added 100 mg of **6** (0.43 mmol), 120 mg of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (0.53 mmol) and anhyd benzene (20 ml). The tube was evacuated and sealed and placed in a 120 °C oil bath for 20 h. Upon cooling, a small amount of ppt's was removed by filtration and the solvent was evaporated. Chromatography on alumina with benzene gave 41 mg of the starting material. Successive elution with ether afforded **5** (13 mg, 22%).

(ii) To a soln containing **6** (1.2 g, 5.2 mmol) in 30 ml of glacial acetic acid was added 1.8 g of triphenylmethyl tetrafluoroborate (5.5 mmol). The soln was refluxed under a nitrogen atmosphere for 1.5 h. After cooling, the mixture was poured into 200 ml of water and extracted with ether. The ethereal extracts were washed successively with a saturated soln of sodium hydrogencarbonate and water, dried (Na_2SO_4) and concentrated. The residue was purified by column chromatography on alumina with ether gave 500 mg of **5** (42%): orange scales, mp 144—146 °C, MS: *m/e* 230 (M^+, 27%), 202(M^+−CO, 100%); IR(KBr): 1600, 1590, 1560 cm^{-1}; UV(ethanol): 249(4.48), 311(4.07), 321(4.08), 430 (4.23); cyclohexane): 246(4.47), 311(4.10), 430(4.19); (concd H_2SO_4): 235(4.29), 269(4.27, sh), 294(4.45), 469(4.16, sh), 494 (4.58); NMR: see text.

Found: C, 88.41; H, 4.41%. Calcd for $C_{17}H_{10}O$: C, 88.67; H, 4.38%.

*6*H*- (10) and 7*H*-Cyclohepta*[cd]*phenalene (11).* Lithium aluminum hydride–aluminum chloride complex was prepared from 1.2 g (31.6 mmol) of $LiAlH_4$, 4.2 g (31.5 mmol) of $AlCl_3$ and 100 ml of ether under reflux. The clear supernatant (40 ml) was transferred into dry flask precooled to −55 °C by syringe. To this soln was added dropwise a soln of 120 mg of **7** (0.52 mmol) in 25 ml of dry THF over a period of 1 h at −55 °C. After stirring for 2 more h at −50 °C the mixture was stand for overnight maintained at −80 °C. To this soln was added a moist THF to prevent the reaction. The resultant yellow supernatant was transferred under nitrogen into a flask containing anhyd sodium sulfate by decantation and filtered. The solvent was concd at 0 °C under reduced pressure and replaced by hexane. The hexane soluble portion was chromatographed on a column of alumina deactivated with 10% water with light pet. ether afforded a 9: 13 mixture of **10** and **11** (63 mg, 56%) as a yellow oil. MS: *m/e* 216(M^+, 100%), 215(M^+−H, 73%), 202(21%); NMR: see text. All manipulations have to be carried out under a nitrogen atmosphere to avoid decomposition.

Cyclohepta[cd]*phenalenium Tetrafluoroborate (1).* A suspension of 70 mg (0.21 mmol) of triphenylmethyl tetrafluoroborate in 2 ml of chloroform was stirred under a nitrogen atmosphere and a soln of a mixture of **10** and **11** in 2 ml of chloroform was added *via* syringe. The resultant reddish brown ppt's of **1** were filtered and washed thoroughly with chloroform followed by carbon tetrachloride. Reddish crystals, 50 mg (79%), mp sinter at 199—201 °C and show no definite melting point. IR(KBr): 1040 cm^{-1} (BF$_4^-$); UV(acetonitrile): 224(4.40), 257(3.99), 291(4.37), 307(4.37, sh), 316(4.40), 334 (4.18, sh), 475(4.49); NMR: see text.

Found: C, 67.96; H, 3.59%. Calcd for $C_{17}H_{11}BF_4$: C, 67.59; H, 3.67%.

pK Determinations. The cation **1** (1.968 mg) was dissolved in 50 ml of acetonitrile. Each 2 ml of the soln was then made up to 10 ml with the buffer soln. The region between pH 4.3 to 8.0 was covered with buffers made up from mixtures of 0.1 M citric acid and 0.2 M Na_2HPO_4. The pH's greater than 8.0 were obtained with a buffer containing 0.1 M ammonium chloride and 0.1 M ammonia water.

The standard procedure was adopted of examining the electronic spectrum of **1** in thirteen soln's of buffer spaced through a pH range of about 5.4 to 9.5. The absorbancy at a wavelength characteristic of the cation was plotted against pH and the mid-point of the resulting titration curve was taken as the p$K_R{}^+$. The wavelength used was 475 nm. The pH's were read on a Beckman model G pH meter. Because after long periods the absorbancy was irreversibly changed on the basic side (pH$>$7), all spectra were taken just after 90 s of mixing the soln of the cation with that of the buffer. The p$K_R{}^+$ value thus obtained was found to be 8.4. When the spectra were taken after 180 s of mixing, the p$K_R{}^+$ was found to be 8.1.

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