

THE CHEMISTRY OF PHENALENIUM SYSTEMS XXXIII.¹⁾
THE DIBENZO[de;hi]NAPHTHACENYL DICATION AND THE DIANION

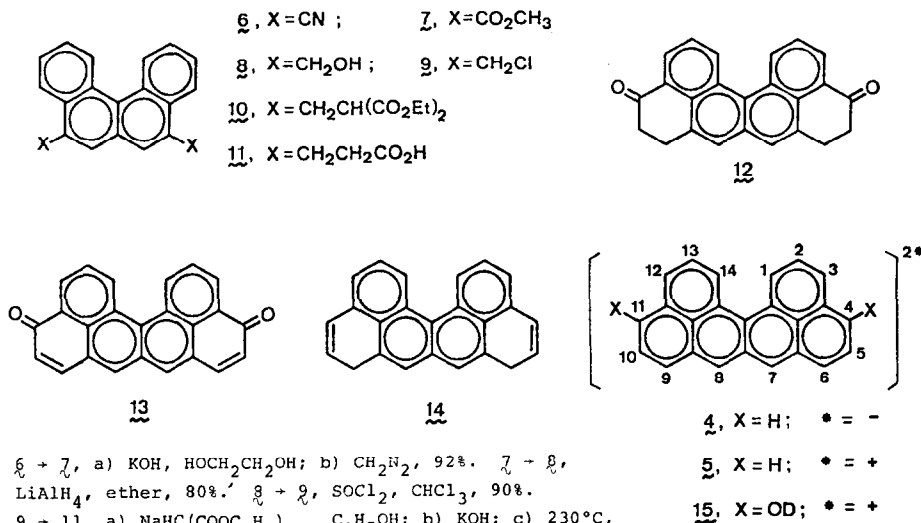
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Summary: The dibenzo[de;hi]naphthacenyl dication (\mathcal{A}) and dianion (\mathcal{B}) have been generated from a mixture of the corresponding precursor hydrocarbons. The pmr spectra of \mathcal{A} and \mathcal{B} indicated that the positive and the negative charges were found to be fully delocalized over the molecules, respectively, consistent with the C_{2v} -symmetry structures. The pmr chemical shifts of \mathcal{A} correlate well with the Hückel charge densities.

The successful generation of the dibenzo[de;jk]pentacenyl dication (\mathcal{C}) and the dianion (\mathcal{D}),²⁾ and the triangulenyl dianion (\mathcal{E})³⁾ as parts of our studies on even-alternant non-Kekulé systems led us to examine the generation of the dibenzo[de;hi]naphthacenyl dication (\mathcal{A}) and the dianion (\mathcal{B}) which are parent systems of \mathcal{C} and \mathcal{D} , respectively. Although elaboration of the full conjugated neutral species, which may exist⁴⁾ as diradical predicted from the theoretical considerations, has been fruitless, the previous findings on \mathcal{C} , \mathcal{D} , and \mathcal{E} predict that \mathcal{A} and \mathcal{B} might be accessible from the appropriate precursor hydrocarbon. We now wish to describe the characterization of \mathcal{A} and \mathcal{B} .

The precursor of these species was prepared starting from the readily available known benzo[c]phenanthrene-5,8-dicarbonitrile (\mathcal{F})⁵⁾ according to the Scheme shown. Hydrolysis of \mathcal{F} with potassium hydroxide in ethylene glycol followed by treatment with diazomethane to give the diester \mathcal{G} , which was converted to the dichloride \mathcal{H} via the diol \mathcal{I} in good yield in the standard manner. The extension of the requisite two-carbon chains to form the diketone \mathcal{J} was carried out by the conventional method using diethylmalonate. The dicarboxylic acid \mathcal{K} , obtained after hydrolysis and subsequent decarboxylation of the ester \mathcal{L} , was subjected to the cyclization in anhydrous hydrogen fluoride, giving rise to the diketone \mathcal{M} ⁶⁾ in high yield. It should be noted that the attempted cyclization reaction of \mathcal{K} by polyphosphoric acid and sodium *m*-nitrobenzene sulfonate, or that of the acid chloride derived from \mathcal{K} with anhydrous stannic chloride suffered from low yield with a fairly concomitant formation of the full conjugated diketone \mathcal{N} ,⁷⁾ which was also obtained by treatment of \mathcal{J} with *o*-chloranil in moderate yield. Although the reductive conversion of \mathcal{M} to the precursor hydrocarbon for the generation of the ionic species was unsuccessful, the crucial

Scheme



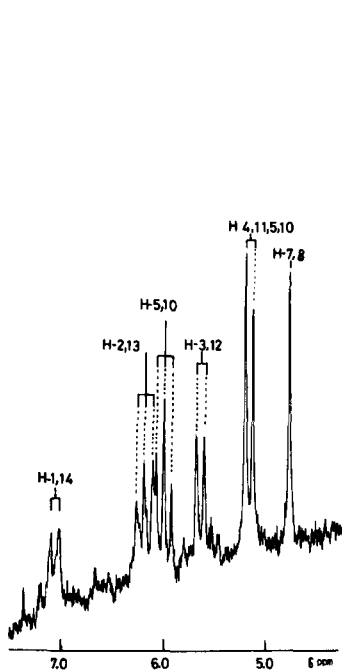
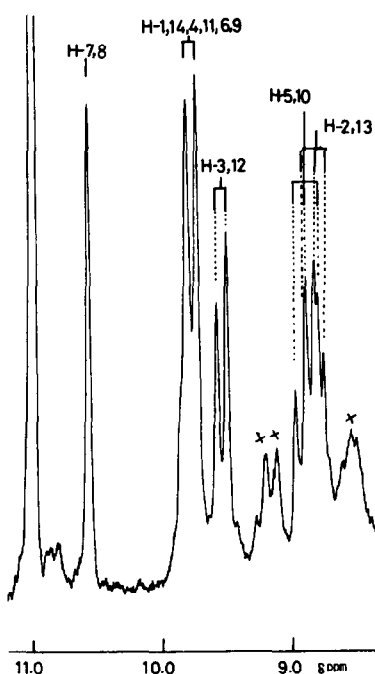
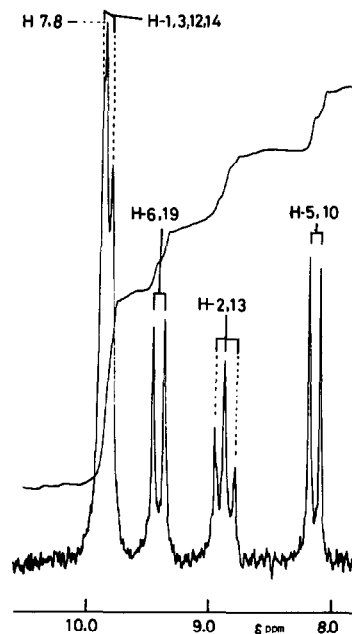
$\underline{6}$ + $\underline{7}$, a) KOH, HOCH₂CH₂OH; b) CH₂N₂, 92%. $\underline{7}$ + $\underline{8}$, LiAlH₄, ether, 80%. $\underline{8}$ + $\underline{9}$, SOCl₂, CHCl₃, 90%.
 $\underline{9}$ + $\underline{11}$, a) NaHC(COOC₂H₅)₂, C₂H₅OH; b) KOH; c) 230°C, 30 min., 42%. $\underline{11}$ + $\underline{12}$, HF, room temperature, 95%.
 $\underline{12}$ + $\underline{13}$, o-chloranil, xylene, reflux, 57%. $\underline{12}$ + $\underline{14}$, a) LiAlH₄, THF, 77%; b) p-TsOH, PhH, 77%.

dehydration of the slightly soluble diol, derived from $\underline{12}$ with lithium aluminum hydride, was accomplished by treatment with a catalytic amount of *p*-toluenesulfonic acid in a large quantity of boiling benzene for a short time in excellent yield. Pmr analysis of the product disclosed that it to be a mixture of $\underline{14}$ and its isomeric hydrocarbons of C₁₄H₁₆ which was further confirmed by elemental analysis and mass spectrum of the mixture.

Generation of the dianion $\underline{4}$ from the mixture of hydrocarbons in THF at -78°C with 2 equiv. of *n*-butyllithium under a nitrogen atmosphere was ascertained by quantitative recovery of $\underline{14}$ and other isomers in which two deuterium atoms were incorporated after quenching with deuterium oxide.

Treatment of the hydrocarbons in THF-d₈ with 2 equiv. of *n*-butyllithium in hexane *in vacuo* in a nmr tube at -78°C yields also a deep red solution of the dianion $\underline{4}$, whose pmr spectrum at -40°C is depicted in Figure 1. The spectrum shows anticipated absorption pattern and is in full accord with the delocalized structure of C_{2v} symmetry as shown in the Scheme. Chemical shifts and coupling constants are summarized in Table 1. The plot of the chemical shifts (after ring current corrections of the adjacent benzene rings) of $\underline{4}$ versus the Hückel charge densities on the corresponding carbon atoms provides a good straight line [see Figure 4], similar to the case of the dibenzo[*de;jk*]pentacenyl dianion.¹⁾

The dication $\underline{5}$ was obtained from the mixture of $\underline{14}$ and its isomers as a deep red solution in 97% dideuteriosulfuric acid by the oxidative hydride abstraction reaction as described previously.²⁾ The pmr spectrum of $\underline{5}$ also shows a simple pattern [see Figure 2 and Table 1] with the delocalized structure of C_{2v} symmetry.

Fig. 1. Nmr spectrum of 4 .Fig. 2. Nmr spectrum of 5 .Fig. 3. Nmr spectrum of 15 .

This cation 5 was also obtained when the monocation 16 ⁸⁾ prepared from 14 with trityl fluoroborate was dissolved in 97% diduteriosulfuric acid like in the case of the (1) .²⁾ A striking feature of the chemical shifts of the cation 5 is that the signals of hydrogens at fjord region,⁹⁾ H_1 and H_{14} , are found in higher field than those expected from the ring current effects of the adjacent benzene rings. Similar feature is also observed in the pmr spectrum of the hydroxy cation 15

generated from the diketone 13 in 97% diduteriosulfuric acid (chemical shifts and coupling constants of 13 are summarized in Table 1). Since the anomalous behavior of these chemical shifts remains yet to be explained definitely, we are planning to synthesize the appropriate molecules for gaining further insight into the disputed point.

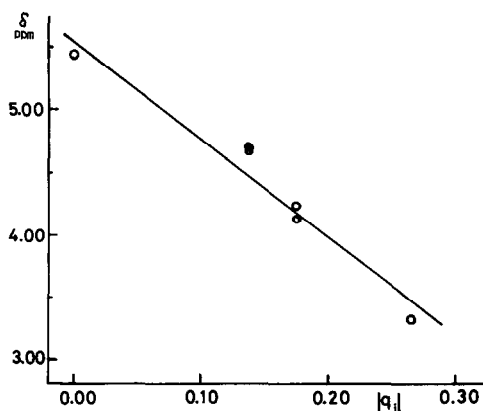


Fig. 4. Plots of chemical shift vs. charge density.

Table 1. Chemical Shifts and Charge Densities for A , B , and A_5

position	Obs. Chem. Shift ^{d)}			Ring Current Correct. c)	Cor. Chem. Shift		Charge density $ q_i $
	A ^{a)}	B ^{b)}	A_5 ^{b)}		A	B	
1, 14	7.07(d)	9.72(d)	9.80(d)	2.34	4.73	7.38	0.1386
2, 13	6.20(t)	8.85(t)	8.83(dd)	0.77	5.43	8.08	0.0000
3, 12	5.68(d)	9.50(d)	9.80(d)	0.98	4.70	8.52	0.1386
4, 11	5.17(d)	9.72		0.93	4.24	8.79	0.1727
5, 10	6.07(t)	8.78(t)	8.11(d)	0.59	5.42	8.19	0.0000
6, 9	5.17(d)	9.72(d)	9.38(d)	1.05	4.12	8.67	0.1727
7, 8	4.78(s)	10.52(s)	9.81(s)	1.52	3.26	9.00	0.2659

a) δ -values were determined in THF- d_8 , relative to the low field THF signal assumed to lie at δ 3.63 from TMS. b) δ -values from external TMS.

c) The sum of ring current corrections for adjacent benzene ring by the simple point dipole approximation calculated by using the formula, $12.0a^2\sum R_i^{-3}$.

d) Coupling constants of A , B , and A_5 . A : $J_{1,2}=J_{2,3}=J_{5,6}=J_{9,10}=J_{12,13}=J_{13,14}=7.5$ Hz. B : $J_{1,2}=J_{2,3}=J_{5,6}=J_{9,10}=J_{12,13}=J_{13,14}=7.5$ Hz. A_5 : $J_{5,6}=J_{9,10}=9.0$ Hz, $J_{1,2}=J_{2,3}=J_{12,13}=J_{13,14}=8.0$ Hz.

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6) (A_5), Pale yellow prisms, mp. 180°C (dec.); IR(KBr), 1668 cm^{-1} , MS (F.D.), 336 (M^+); UV λ_{max} (CHCl_3) 260 nm (sh, log ϵ 4.26), 290 (sh, 4.58), 301 (4.77), 331 (sh, 4.31), 378 (sh, 3.82), 397 (3.53), NMR (CDCl_3) 2.97-3.15 (m, 4H, H-5,5',10,10'), 3.44-3.64 (m, 4H, H-6,6',9,9'), 7.75 (s, 2H, H-7,8), 7.78 (dd, 2H, H-2,13, $J_{2,3}=J_{12,13}=7.5$ Hz, $J_{1,2}=J_{13,14}=8.5$ Hz), 8.37 (dd, 2H, H-3,12, $J_{2,3}=J_{12,13}=7.5$ Hz, $J_{1,3}=J_{12,14}=1.0$ Hz), 9.16 (dd, 2H, H-1,14, $J_{1,2}=J_{13,14}=8.5$ Hz, $J_{1,3}=J_{12,14}=1.0$ Hz).

7) (A_5), Orange needles, mp. 360°C; IR(KBr), 1642 cm^{-1} ; UV λ_{max} (CHCl_3) 297 nm (log ϵ 4.51), 358 (4.63), 376 (4.91), 422 (4.05), 437 (sh, 3.83); NMR (CDCl_3) 6.86 (d, 2H, H-5,10, $J_{5,6}=J_{9,10}=10.0$ Hz), 7.88 (d, 2H, H-6,9, $J_{5,6}=J_{9,10}=10.0$ Hz), 8.02 (dd, 2H, H-2,13, $J_{1,2}=J_{13,14}=8.5$ Hz, $J_{2,3}=J_{12,13}=7.5$ Hz), 8.18 (s, 2H, H-7,8), 8.87 (dd, 2H, H-3,12, $J_{2,3}=J_{12,13}=7.5$ Hz, $J_{1,3}=J_{12,14}=1.0$ Hz), 9.16 (bd, 2H, H-1,14, $J_{1,2}=J_{13,14}=8.5$ Hz).

8) (A_5) was obtained as greenish powders, which could not be purified.

mp. 163-164°C (dec); IR(KBr) 1020-1080 cm^{-1} ; NMR(AsCl_3) 4.95-5.02 (m, 2H), 7.44-9.13 (m, 13H).

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