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THE CHEMISTRY OF PHENALENIUM SYSTEMS. XXIV.1)

THE DIBENZO[*de,jk*]PENTACENYL DICATION AND THE DIANION

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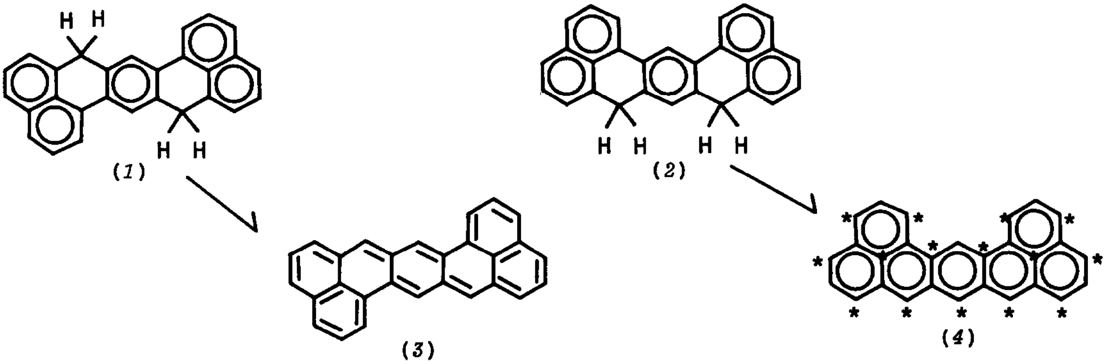
Our interest in non-Kekulé hydrocarbons containing phenalenyl system led us to explore the chemistry of dibenzopentacenyl system. It was presumed that dehydrogenation of dihydroheptazethrene (*1*) and 7*H*,9*H*-dibenzo[*de,jk*]pentacene (*2*) produces the fully conjugated hydrocarbons (*3*) and (*4*), respectively. The compound *3*, acutually exists as heptazethrene, can be obtained in this manner by Clar and his co-workers.2) However, dehydrogenation of *2* leads only to a polymeric product.2) This is probably attributed to the fact that any Kekulé structure cannot be written for *4*.

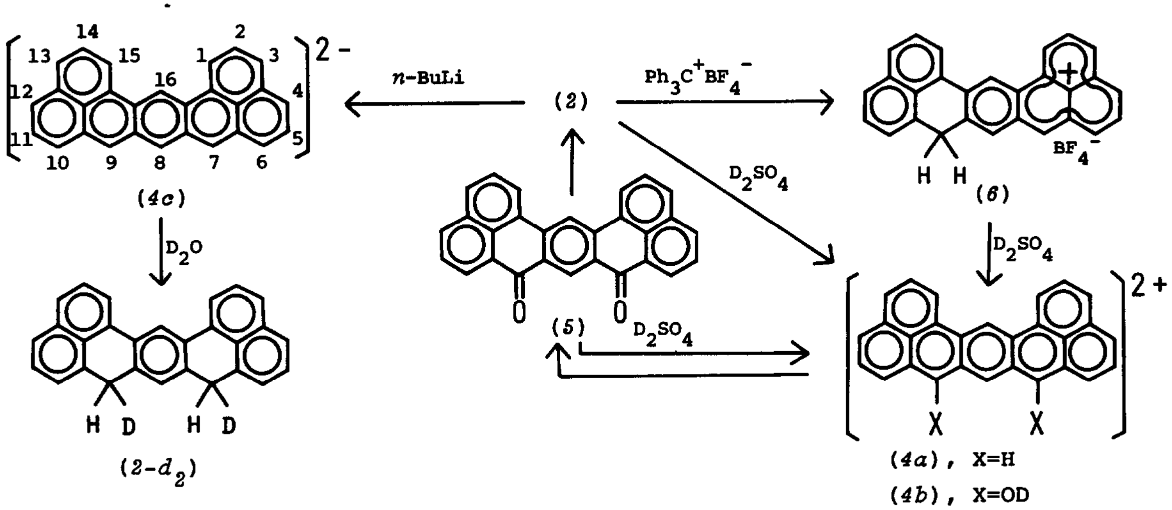


(*1*) (*2*) (*3*) (*4*)

The dibenzo[*de,jk*]pentacenyl system (*4*) is a non-Kekulé even alternant hydrocarbon consisting of twenty-eight carbon atoms which are divided into fifteen starred and thirteen unstarred carbon atoms. Therefore simple Hückel MO theory predicts that *4* should possess thirteen bonding and two nonbonding molecular orbitals. According to the above prediction, two divalent ionic species with closed shell electronic configuration, dication (*4a*) and dianion (*4c*), might be reasonably accessible. We wish to describe the characterization of *4a* and *4c*.

A precursor for formation of *4a* and *4c* seems to be 7*H*,9*H*-dibenzo[*de,jk*]pentacene-7,9-quinone

(*5*)[3] which was obtained by the method described in the literature.[2] The quinone *5* was converted to 7*H*,9*H*-dibenzo[*de*,*jk*]pentacene (*2*) by lithium aluminum hydride-aluminum chloride complex reduction in 40-50% yield. The structure of *2* was unambiguously confirmed on the basis of its elemental analysis and spectral properties.[4,5]



When the hydrocarbon *2* is dissolved in 97% dideuteriosulfuric acid a dark green solution results, the species of which has been shown by NMR spectrum to be the desired dication *4a*, which indicates that *2* may undergo oxidative hydrides abstraction reaction similar to that reported by Pagni et al.[6] As shown in Fig. 1, all signals appear as symmetrical pattern and the 1st-order analysis (Table 1) of the spectrum is in full accord with the delocalized structure of C_{2v}-symmetry. On the other hand, treatment of *2* with two molar equivalents of trityl tetrafluoroborate in a mixture of chloroform and acetonitrile resulted in the formation of black solids, mp >300°C; IR 1020-1140 cm^{-1} (broad, BF_4^-); NMR (in $AsCl_3$) δ 9.68-7.60 (m, 15H), 4.90 (s, 2H), which is believed to be the monocation (*6*) because a solution of *6* in 97% dideuteriosulfuric acid shows an exactly identical NMR spectrum with that of *4a*. The quinone *5* could be dissolved reversibly in sulfuric acid. Thus, treatment of *5* with 97% dideuteriosulfuric acid led to the formation of a dark red solution whose NMR spectrum was displayed in Fig. 2. Inspection of the spectrum reveals that *5* exists as the dihydroxy dication (*4b*).[7]

Reaction of *2* in freshly distilled tetrahydrofuran with butyllithium under nitrogen at -60°C followed by quenching with deuterium oxide to give the labeled hydrocarbon (*2*-d_2). Incorporation of two deuterium atoms in *2*-d_2 is borne out by its mass spectrum which showed parent ion peak at m/e 356 indicating the formation of the dianion *4c*. The sites of the deuterium incorporation

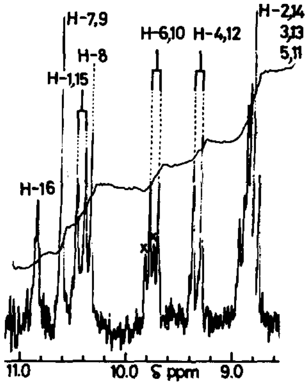


Fig. 1. Nmr spectrum of *4a*.

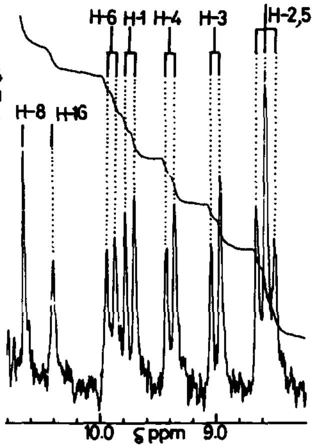


Fig. 2. Nmr spectrum of *4b*.

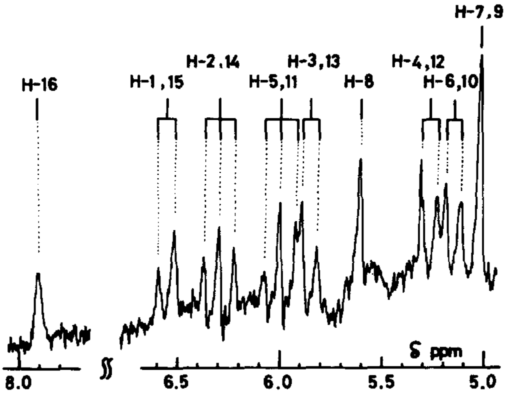


Fig. 3. Nmr spectrum of *4c*.

are unequivocally proved to be C-7 and C-9 positions because *2*-d_2 exhibits a broad 2H singlet at δ 4.50 along with signals of the aromatic protons identical with those of *2*. Exclusive deuteriation at C-7 and C-9 is well accord with the maximum charge density found on these carbon atoms. The NMR spectral measurement of *4c* was performed in a degassed solution of d_8-tetrahydrofuran at -40°C by using CAT technique (see Fig. 3). Chemical shifts and coupling constants are readily obtained from the spectrum and are summarized in Table 1. The upfield shift of signals H-7,9; 6,10; 4,12; and 8 are ascribed to the relatively large negative charge densities on the respective carbon atoms. As shown in Fig. 4, plot of the chemical shifts (after ring current correc-

Table 1. Chemical Shifts and Charge Densities for *4a*, *4b*, and *4c*.

i	Obs. Chem. Shift			Ring Current Correct.$^{c)}$	Correct. Chem. Shift for *4c*	$\lvert q_i \rvert$
	4a$^{a)}$	*4b*$^{a)}$	*4c*$^{b)}$			
1, 15	10.44	9.74	6.62	1.67	4.95	0.1037
2, 14	8.94 ∼ 8.74	8.58	6.36	0.71	5.65	0.0000
3, 13		8.98	5.93	0.97	4.96	0.1037
5, 11		8.58	5.33	0.93	4.40	0.1650
4, 12	9.34	9.36	6.07	0.58	5.49	0.0000
6, 10	9.75	9.92	5.22	1.02	4.20	0.1650
7, 9	10.61		5.08	1.60	3.48	0.2670
8	10.34	10.67	5.67	1.67	4.00	0.1839
16	10.86	10.40	7.89	2.46	5.43	0.0000

a) δ-values from external TMS.

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

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

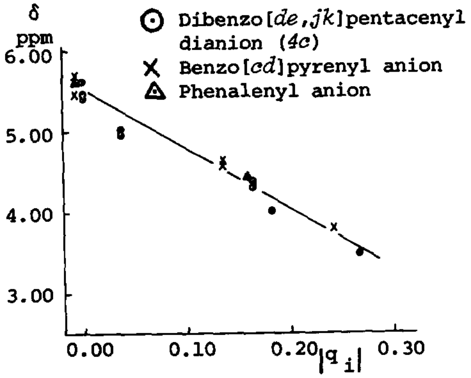


Fig. 4. Plots of chemical shift *vs*. charge density.

tions of adjacent benzene rings) of *4c* versus the Hückel charge densities on the corresponding carbon atoms provides a good straight line. The points for phenalenide ion[9] and benzo[*cd*]pyrenide ion[9] also fall almost on the same line. The excellent linear relation suggests that the excess negative charge resides on the alternate starred carbon atoms of *4c* as predicted by simple Hückel MO theory.

1) For part XXIII of this series, see K. Yamamoto, Y. Kayane, and I. Murata, *Bull. Chem. Soc. Jpn.*, in the press.

2) E. Clar, W. Kemp, and D. G. Stewart, *Tetrahedron*, **3**, 325 (1958); E. Clar and I. A. Macpherson, *ibid.*, **18**, 1411 (1962).

3) *5* : mp >350°C (lit.[2] 435°C); IR(KBr) 1647, 1702 cm^{-1}; UV λ_{max}(CH_3CN) 428 nm (log ε 4.36) 405(4.27), 330(4.31), 301.5(4.35), 290(4.27), 277(4.24), 228(4.67); MS m/e 382(M^+, 100%), 354(M^+-CO, 20%), 326(M^+-2CO, 35%); NMR(in $AsCl_3$) δ 7.82(dd, 4H, H-2,5,11,14, $J_{1,2}=J_{14,15}=$ 7.5 Hz, $J_{2,3}=J_{13,14}=8.0$ Hz, $J_{4,5}=J_{11,12}=8.0$ Hz, $J_{5,6}=J_{10,11}=7.5$ Hz), 8.12(d, 2H, H-3,13), 8.27(d, 2H, H-4,12), 8.74(d, 4H, H-1,15,6,10), 9.25(s, 1H, H-16), 9.41(s, 1H, H-8).

4) *2* : pale yellow needles, mp 213-214°C, UV λ_{max}(cyclohexane) 362 nm (log ε 4.14), 347(sh, 4.29), 332(4.44), 316(4.37), 264(4.32), 246(4.76) 217(4.78); MS m/e 354(M^+, 100%), 353(M^+-H, 97%), 352(M^+-2H, 42%); NMR($CDCl_3$) 4.53(s, 4H, H-7,7',9,9'), 7.17(s, 1H, H-8), 7.36-7.76 (m, 10H, H-2～6, 10～14), 8.13(d, 2H, H-1,15, $J_{1,2}=J_{14,15}=7.0$ Hz), 8.67(s, 1H, H-16).

5) Although reduction product of *5* with Zn/HOAc/pyridine was shown to be *2* by Clar, the reported melting point (345°C) and the electronic spectrum of this compound are quite distinct from those of *2*. The UV spectrum of *2*, unlike Clar's hydrocarbon, is closely similar to that of the model compound, 7H-benzanthrene, both in absorption maxima and in intensities. Therefore, Clar's hydrocarbon should be assigned to one of the possible isomers having the methylene group(s) at different position(s).

6) J. W. Larsen and R. M. Pagni, *J. Am. Chem. Soc.*, **96**, 2284 (1974); R. M. Pagni, P. A. Bouis, and P. Easley, *Tetrahedron Lett.*, 2671 (1975).

7) While the substantial blue shift was observed in the UV spectrum of *5* in 97% sulfuric acid, λ_{max} 550 nm (log ε 4.58), 381(4.71), 273(sh, 4.44), 265(4.49), and 253(4.52). Compared to that of *4a* in 97% sulfuric acid, λ_{max} 606 nm (log ε 4.51), 434(4.66), 342(sh, 4.02), 320(4.14), 270(4.53), 262(4.52),[8] there is a strong resemblance in band shape between the spectra of *4b* and *4a*.

8) The ε-values were estimated assuming quantitative conversion of *2* to *4a*.

9) I. Murata, K. Yamamoto, and O. Hara, *Tetrahedron Lett.*, 2047 (1974).