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THE CHEMISTRY OF PHENALENIUM SYSTEMS. XXV[1] THE TRIANGULENYL DIANION

Osamu Hara, Katsuaki Tanaka, Kagetoshi Yamamoto, Tomoo Nakazawa, and Ichiro Murata*

Department of Chemistry, Faculty of Science, Osaka University,

Toyonaka, Osaka 560, Japan

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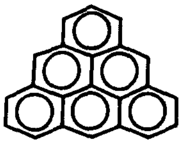
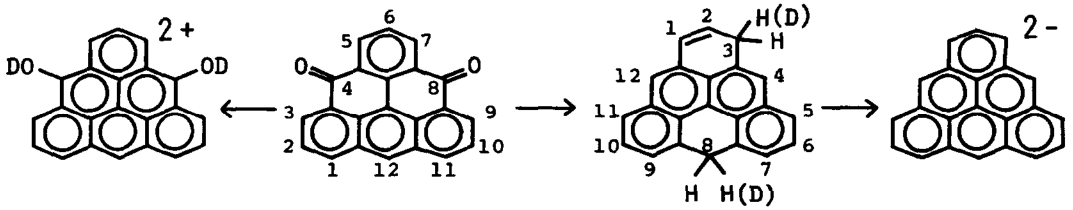
In 1953, Clar[2] suggested that so-called Clar's hydrocarbon, triangulene (*1*), would be impossible to prepare because no Kekulé structure can be written for *1*. Dehydrogenation of hexahydro- and dodecahydrotriangulene led in fact only to polymeric products. In terms of the valence bond theory *1* has twenty-two carbon atoms in the molecule and has no resonance structures with more than ten double bonds suggesting that *1* should have 22-20=2 nonbonding molecular orbitals.[3] This prediction was also proved theoretically by Longuet-Higgins[4] using MO theory. Therefore, *1* might exist as diradical and divalent ions (dication and dianion) in the neutral and ionic forms, respectively. We now wish to report the formation and characterization of the hitherto unknown triangulenyl dianion (*1a*) showing it to be the fully delocalized species with D_{3h}-symmetry.



(*1*)

Reduction of triangulene-4,8-quinone (*2*)[5] with $LiAlH_4$-$AlCl_3$ complex in ether at room temperature afforded 3H,8H-triangulene (*3*) as yellow needles, mp 178-181°C, MS *m/e* 278 (M^+,100%). The structure assignment to *3* is easily borne out by its NMR spectrum which shows signals at δ 4.14 (bs, H-3,3'), 4.89 (s, H-8,8'), 6.14 (dt, H-2, $J_{1,2}$=10.0, $J_{2,3}$=4.0 Hz), 6.71 (dt, H-1, $J_{1,2}$ =10.0, $J_{1,3}$=2.0 Hz) along with multiplet at 7.24-7.64 (8H). Irradiation at δ 4.14 converted the two doublets of triplet at δ 6.14 and 6.71 into a clean AB-quartet with J=10.0 Hz. Treatment of a solution of *3* in THF with *n*-BuLi at -78°C under nitrogen resulted in the formation of the desired triangulenyl dianion (*1a*). The formation of *1a* was established by the following reaction and NMR spectral evidence. When the above reaction mixture was quenched with D_2O the labeled hydrocarbon (*3*-d_2) was obtained by careful work-up. Incorporation of two deuterium atoms in *3*-d_2 was confirmed by its MS which shows parent ion peak at *m/e* 280. A solution of *1a* for NMR measurement was prepared by treatment of a degassed solution of *3* in freshly distilled (over $LiAlH_4$) d_8-THF with *n*-BuLi in hexane at -78°C *in vacuo*. The NMR spectrum recorded at



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

-50°C displays a simple pattern as shown in Fig. 1. The first order analysis of the spectrum was in complete accord with the expected delocalized structure with D_{3h}-symmetry. This analysis makes it possible to examine the relationship between the chemical shift (after ring current correction, see Table 1) and Hückel charge density (qi). As can be seen from Fig. 2, the plot for *1a* do not fall on the same line which hold for the dibenzo[de;jk]pentacenyl dianion[1], however, almost parallel linear relationship was observed.

Although the synthesis of the parent dication is not met with success so far, the dihydroxy dication (*4*) could be prepared by treatment of *2* with 97% D_2SO_4. NMR spectrum of the resulting dark red solution (Fig. 3) is compatible with the delocalized 4,8-dihydroxytriangulenyl dication.

Table 1. NMR spectral data of *1a*.

i	Obs. Chem. Shift[a)]	Ring Current Correct.[b)]	Correct. Chem. Shift	$\lvert q_i \rvert$	J
1,3,5,7,9,11	4.72	-1.45	3.27	0.1818	
2,6,10	5.70	-0.85	4.85	0.0000	7.5 Hz
4,8,12	4.82	-1.96	2.86	0.2424	

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

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

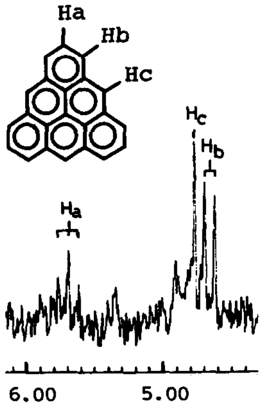


Fig. 1. Nmr spectrum of (*1a*).

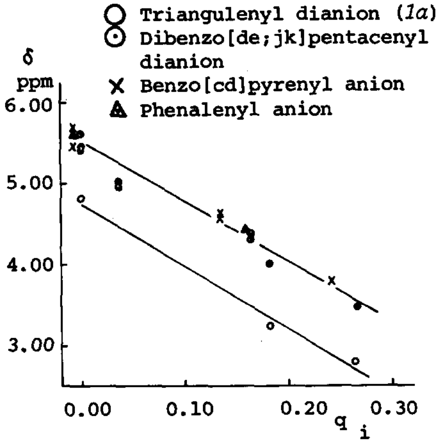


Fig. 2. Plots of chemical shift *vs.* charge density.

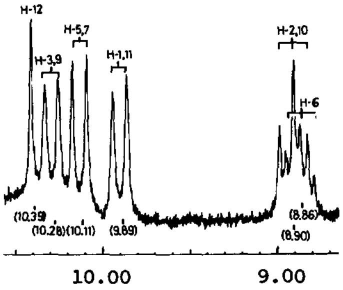


Fig. 3. Nmr spectrum of (*4*).

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1) For part XXIV of this series, see preceding paper of this issue.

2) E. Clar and D. G. Stewart, J. Am. Chem. Soc., 75, 2667 (1953); J. Chem. Soc., 1951, 3215.

3) K. Higashi and H. Baba, "Quantum Organic Chemistry", Asakura Publ. Co., Tokyo, 1965.

4) H. C. Longuet-Higgins, J. Chem. Phys., 18, 265 (1950).

5) ^{1}H-NMR spectrum of *2* in $AsCl_3$: δ 7.84 (t, J=8.0 Hz, H-6), 7.93 (dd, J=8.3 and 7.3 Hz, H-2, 10), 8.56 (dd, J=8.3 and 1.5 Hz, H-1,11), 8.78 (d, J=8.0 Hz, H-5, 7), 8.88 (s, H-12), and 8.90 (dd, J=7.3 and 1.5 Hz, H-3, 9).