CHEMISTRY LETTERS, pp. 1233-1236, 1977. Published by the Chemical Society of Japan

CATA-CONDENSED DIBENZOPENTALENYL DIANIONS

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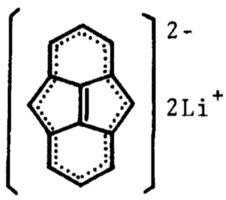
Nuclear magnetic resonance spectrum (^1H) of dilithium indeno[1,2-a]indenide (2) and that of the [2,1-a]-isomer (4) indicate unique charge delocalization, which reflects that those dianions consist of two charge delocalized indenides.

Peri-condensed dibenzopentalenyl dianion 1 is a typical peripheral charge delocalized dianion and a perturbed [12]annulene dianion.[1] During investigation of indeno[1,2-a]indenes, for one of which has been predicted lower symmetry (C_s) in the ground state,[2] dilithium indeno[1,2-a]indenide (2) was obtained easily from 9,10-dihydroindeno[1,2-a]indene (3).[3] In this letter, we wish to report charge distribution of the cata-condensed dianion 2 and the isomeric dianion (4)[4] on the basis of ^1H-nmr.

Treatment of compound 3 (20mg) in tetrahydrofuran-d_8 (0.3ml) with a solution of n-butyllithium in hexane at -76° followed by warming to room temperature affords a deep violet solution of the dianion 2, whose nmr is shown in Figure 1. The spectrum was analyzed using the computer program,[5] as a five-spin system, and the results are given in Table 1. The assignment of the chemical shifts to the appropriate protons was readily made on the basis of multiplicities and intensities. The fact that we can explain the spectrum as the ABCDE-system suggests that compound 2 has a structure with C_{2v}-symmetry. Treatment of the



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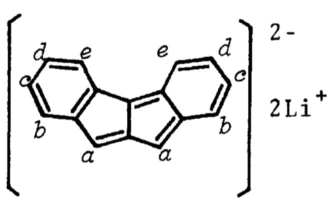

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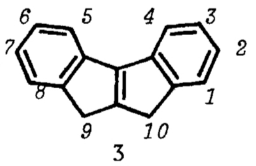

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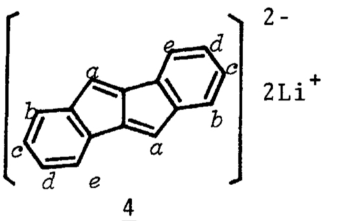

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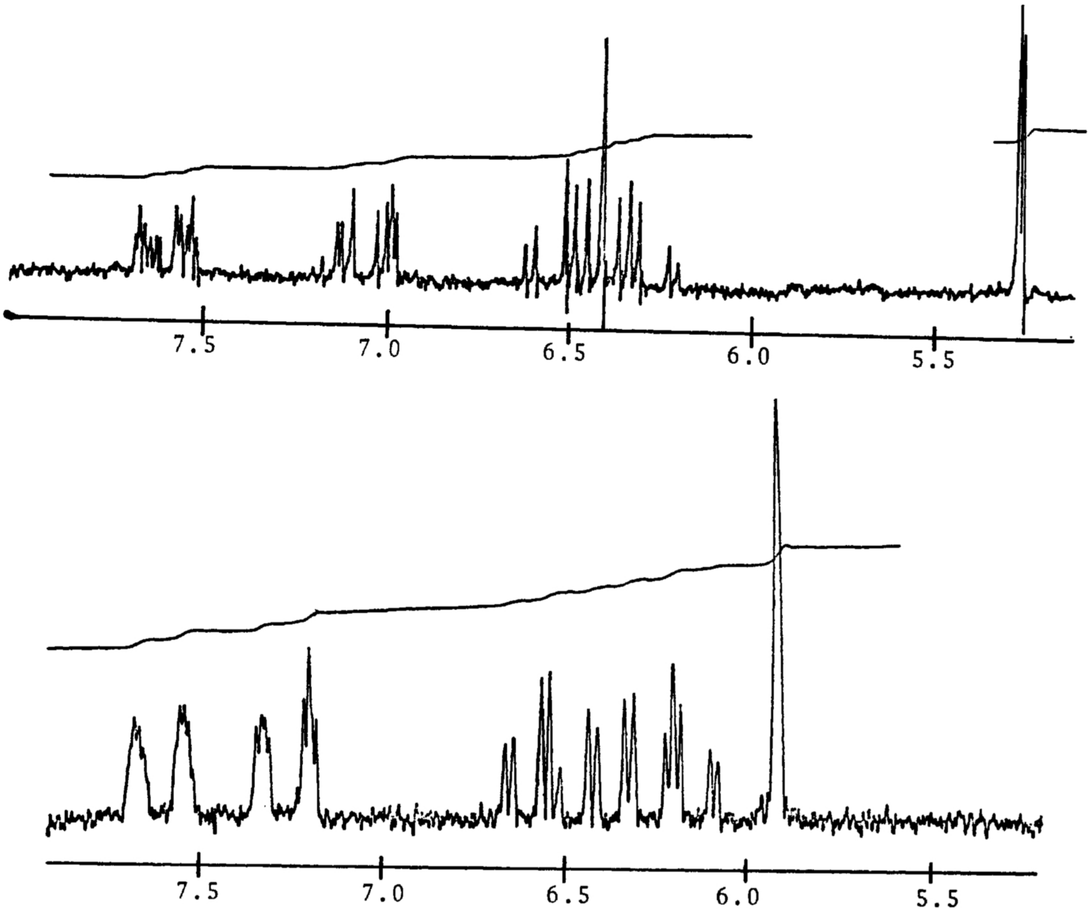


Figure 1. Nmr signals of 2 (above) and 4 (below) at 60MHz and 25° in THF-d_8.

Table 1. Spectral analysis results for dianions.[a]

	δ_a	δ_b	δ_c	δ_d	δ_e	J_{ab}	J_{ac}	J_{ad}	J_{ae}	J_{bc}	J_{bd}	J_{be}	J_{cd}	J_{ce}	J_{de}
2	5.347	7.047	6.475	6.354	7.599	-0.08	0.02	0.05	0.60	7.33	0.94	0.28	6.80	0.63	7.48
4	5.912	7.247	6.526	6.206	7.590	0.24	0.23	0.05	0.40	7.29	1.31	1.12	6.17	1.35	7.77

a) All chemical shifts are in parts per million from TMS and all coupling constants are in hertz. The final analyses gave the sum of squares of energy level errors less than 0.08.

Table 2. Proton chemical shifts, derived electron densities and calculated electron densities.

2						4					
position	δ^a_{obs}	δ'	δ_{corr}	ρ^b_{exp}	ρ^c_{calc}	position	δ^a_{obs}	δ'	δ_{corr}	ρ^b_{exp}	ρ^c_{calc}
a	1.92	0.94	2.86	1.27	1.289	a	1.36	1.06	2.42	1.23	1.264
b	0.22	0.66	0.88	1.08	1.111	b	0.02	0.65	0.67	1.06	1.103
c	0.79	0.28	1.07	1.10	1.117	c	0.74	0.27	1.01	1.09	1.114
d	0.92	0.32	1.24	1.12	1.176	d	1.06	0.29	1.25	1.12	1.193
e	-0.33	0.84	0.51	1.05	1.056	e	-0.32	0.72	0.40	1.04	1.043

a) Chemical shifts in ppm from benzene. *b)* $\rho_{exp}=1+\Delta\rho$; reference 7.

c) Variable bond-length SCF MO ; reference 8.

dianion containing solution with D_2O formed 9,10-dihydroindeno[1,2-a]indene-d_2 as the major product.[6] Dilithium indeno[2,1-a]indenide 4, whose nmr spectrum and analysis are shown in Figure 1 and Table 1, respectively, was afforded from 5,10-dihydroindeno[2,1-a]indene and n-BuLi.[4]

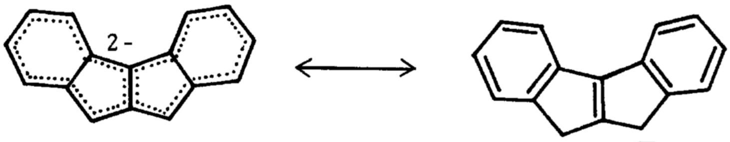
It has been reported that a plot of the nmr chemical shift of the protons of dianion 1 *vs*. the Hückel charge density of the corresponding carbon atom, in which the excess charge density is restricted to the periphery of the molecule, produces a reasonably straight line even without correcting for differential ring current effects.[1] However, the relation between those of cata-condensed dianions 2 and 4 did not show good linearity.

In order to estimate the electron densities (ρ_{exp}) from the nmr data, the correction for a particular proton due to the ring current in the neighbor ring, (δ'), was performed using the equation: $\delta'=12.0\ a^2/R^3$; a and R are respectively the radius (Å) of the neighbor ring and the distance of the proton from the center of the neighbor ring.[7] The local "excess" charge ($\Delta\rho$) was derived from the linear correlation: $k\Delta\rho=\delta_{obs}+\delta'$; $k=10.7$.[7]

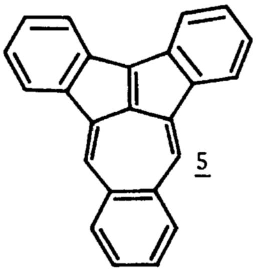
As shown in Table 2, there is a good correspondence between the electron densities derived from the nmr data and those calculated by the variable bond-length SCF MO method,[8] for each compound. Charge distribution on the benzene ring carbons of 2 and that of 4 are identical with that of indenyl anion whose electron densities (ρ_{exp}) are 1.17 (C_1 and C_3), 1.09 (C_2), 1.03 (C_4 and C_7) and 1.09 (C_5 and C_6).[7] Therefore, the cata-condensed dianions have not strong peripheral charge delocalized structures. Dianions 2 and 4 may consist of two charge delocalized indenyl anions and may be imaged as 2a and 4a, respectively. However, charge localized structures 2b and 4b should contribute largely because the electron densities at the 9 and 10 positions of 2 and those at 5 and 10 positions of 4 are larger than those at corresponding positions of indenyl anion.

It prompted us to use the dianion 2 for a synthesis of polycyclic condensed novel aromatic hydrocarbons that the electron densities at the 9 and 10 positions of 2 are relatively large. Treatment of the dianion with phthalaldehyde gave dibenzo[a,g]indeno[1,3-c,d]azulene, 5, mp 250°, deep red needles, in 24% yield.[9] The ultraviolet and visible spectrum of the compound indicates bathochromic shifts in comparison with that of compound 6;[10] (5), λ_{max}^{THF} 230nm (logε=4.34), 276 (4.75), 299 (4.75), 321 (4.49), 447 (3.58) and 504 (3.51)-sh.

When the dianions 2 and 4 were treated with acetone, compound 3 and 5,10-dihydroindeno[2,1-a]indene were recovered, respectively. We thus estimate the pK-values of 3 and the isomer to be at least larger than 20, like that of indene.



2a 2b



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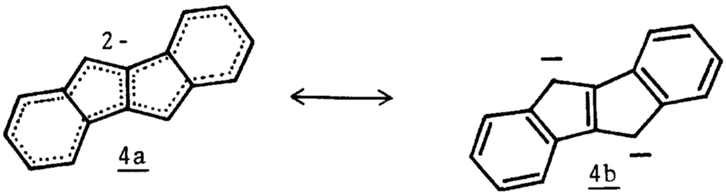
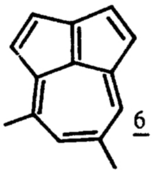


4a 4b



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References and Notes

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2) T. Nakajima, A. Toyota, and S. Fujii, Bull. Chem. Soc. Jpn., 45, 1022 (1972).
3) T. Haga, Japan Patent 00509 (1968); Chem. Abs., 70, P11411f (1968).
4) A. J. Silvestri, Tetrahedron, 19, 855 (1963).
5) Iterative calculations were performed using FACOM 230-38 system at Computer Center Tohoku University.
6) Exact percentage of d_2 incorporation was not derived from the mass spectrum, because the mass spectrum of 3 shows strong M-1 and M-2 peaks.
7) T. Schaffer and W. G. Schneider, Can. J. Chem., 41, 966 (1963).
8) We are indebted to Dr. Azumao Toyota, Yamagata University, for providing us the results of the calculation; reference 2.
9) Satisfactory elemental analysis was obtained for the compound.
10) K. Hafner and J. Schneider, Ann., 624, 37 (1959).

(Received July 4, 1977)