Tetrahedron Letters No. 23, pp 2047 - 2048, 1974. Pergamon Press. Printed in Great Britain.

THE CHEMISTRY OF PHENALENIUM SYSTEM XVII.[1] BENZO[cd]PYRENYL ANION

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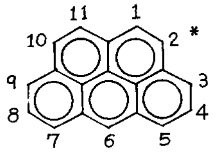
(Received in Japan 20 April 1974; received in UK for publication 6 May 1974)

In our continuing studies on the chemistry of phenalenyl system (2) we have extended our attention to the higher benzolog of 2, benzo[cd]pyrenyl system (1). The benzo[cd]pyrenyl systems, cation (1a), radical (1b) and anion (1c), are odd-alternant hydrocarbons possessing a NBMO which contains zero, one, and two electrons respectively[2] as in the case of 2.[3] The cation (1a) has already been synthesized and examined the detailed chemical reactivity by Reid and Bonthrone.[2] Recently, the radical (1b) is also prepared and characterized by epr spectroscopy by Reddoch and Paskovich.[4] Although the generation of the anion (1c) from 6H-benzo[cd]pyrene (3: X=H) with sodium ethoxide was described in the literature by Jutz,[5] none of the spectroscopic properties of 1c have been reported to date. This paper presents evidence for the formation of 1c and its visible and nmr spectra.

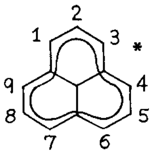


(1)

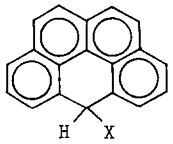
a : * = +

b : * = •

c : * = -



(2)



(3)

The parent hydrocarbon (3: X=H) was prepared from 6H-benzo[cd]pyrene-6-one[6] by LiAlH$_4$-AlCl$_3$ reduction[2,7] as pale yellow plates of mp 121-128°C [Lit. 134°[8], 123-124°[9], and 124-130°[2]]. Treatment of (3: X=H) in THF-d$_8$ [distilled over LiAlH$_4$] with n-BuLi in n-hexane and ether at -78°C in vacuo gave a dark brown solution of 1c in high yield. The solution can be quenched into D$_2$O to produce exclusively (3: X=D), m/e 241, δ 4.89 (bs, 1H), 7.4-7.8 (m, 10H). The visible spectrum of 1c shows maxima at 460 nm (ε, 44,900), 490(13,000), 527(13,000), 574(3,320), 623 (3,770) and 679(5,250). The ε-values were estimated assuming quantitative conversion of 3 into 1c.

The 100 MHz nmr spectrum for 1c recorded at 0°C is summarized in Table 1 together with that of the cation (1a)[10], prepared from (3: X=H) with o-chloranil and 70% HClO$_4$ in CH$_3$CN[2]. The first-order analysis of the signals is in full accord with the delocalized structure (1c) with C_{2v}-symmetry. For 1c and 1a the assignment of H-1 and H-2 was made according to the calculated pi-electron density at their respective carbon atoms. The substantial up- and down-field shift of H-6 in 1c and 1a is attributable to the largest negative (-0.2424 for 1c) and positive charge density (+0.2424 for 1a) at C-6.

A plot of the nmr chemical shift (after correction for the ring current effects of the

Table 1. Proton Nmr Data of 1a and 1c

Position	Cation 1a[a]		Anion 1c				
	Obs. Chem. Shift[b]	Coupl. Const.	Obs. Chem. Shift[c]	Ring Current Correct.[d]	Correct. Chem. Shift	Charge Density	Coupl. Const.
1, 11	7.65	$J_{1,2}$=	6.47	1.05	5.42	0	$J_{1,2}$=
2, 10	7.91	9.0 Hz	6.24	1.01	5.23	-0.0606	8.2 Hz
3, 9	8.37	$J_{3,4}$=	5.53	0.94	4.59	-0.1364	$J_{3,4}$=
4, 8	7.56	$J_{4,5}$=	6.20	0.51	5.69	0	$J_{4,5}$=
5, 7	8.39	7.8 Hz	5.63	1.02	4.61	-0.1364	7.5 Hz
6	9.27		5.31	1.51	3.80	-0.2424	

a) Perchlorate. b) δ-Values were determined in CF_3COOH, relative to the CF_3COOH signal assumed to lie at δ 10.44 from TMS. c) δ-Values were determined in THF-d_8, relative to the low-field THF signal assumed to lie at δ 3.63 from TMS. d) The sum of ring current corrections for adjacent benzene rings by the simple point dipole approximation calculated by using the well-known formula[11], $(e^2a^2/2mc^2)\Sigma R_i^{-3}$.

adjacent rings[12], see Table 1) of the protons of 1c versus the Hückel charge density of the corresponding carbon atom provides a good straight line and the points for lithium phenalenide (2c)[13] (after correction for the ring current effects : 0.75 ppm for H-1,3,4,6,7,9 and 0.36 ppm for H-2,5,8) also fall almost exactly on this line. The excellent correlation between the ^1H nmr chemical shift and the Hückel charge density provides evidence that the negative charge resides on the alternate carbon atoms of the molecule 1c.

1) For part XVI, see I. Murata, K. Nakasuji, and H. Kume, *Tetrahedron Lett.*, 3405 (1973).
2) D. H. Reid and W. Bonthrone, *J. Chem. Soc.*, **1965**, 5920.
3) Cf. D. H. Reid, *Quart. Revs.*, **19**, 274 (1965).
4) A. H. Reddoch and D. H. Paskovich, *Chem. Phys. Lett.*, **3**, 351 (1969).
5) C. Jutz, R. Kirchlechner, and H-J. Seidel, *Chem. Ber.*, **102**, 2301 (1969).
6) H. Vollmann, H. Becker. M. Correll, and H. Streeck, *Justus Liebigs Ann. Chem.*, **531**, 1 (1937); R. Scholl and K. Meyer, *Ber.*, **69**, 152 (1936).
7) B. R. Brown and A. M. S. White, *J. Chem. Soc.*, **1957**, 3775.
8) E. Clar, "Polycyclic Hydrocarbon," Academic Press, London, 1964, p. 416.
9) A. W. Johnson, *J. Org. Chem.*, **24**, 833 (1959).
10) Reid and Bonthrone have been reported the nmr spectral data of benzo[cd]pyrenyl perchlorate as two groups of signals centered at δ 8.62 and 9.25. See ref. 2).
11) J. A. Pople, W. G. Schneider, and H. J. Bernstein, High Resolution Nuclear Magnetic Resonance, McGraw-Hill, Inc. New York (1959), p. 180.
12) Cf. T. J. Katz, M. Yoshida, and L. C. Siew, *J. Amer. Chem.Soc.*, **87**, 4516 (1965); T. J. Katz, V. Balogh, and J. Schulman, *ibid.*, **90**, 734 (1968).
13) H. Prinzbach, V. Freudenberger, and U. Scheidegger, *Helv. Chim. Acta*, **59**, 1087 (1967).