A ^1H and ^{13}C N.M.R. Study of the Pyrene Dianion and Proposed Tetra-anion

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Sodium or potassium metal reduction of pyrene in tetrahydrofuran is shown to yield the paratropic, D_{2h} symmetric dianion and minor amounts of the 1-hydropyrenyl monoanion; the latter compound affords n.m.r. data that earlier had been incorrectly assigned to an unsymmetrical dianion or tetra-anion.

The alkali metal reduction products of pyrene are very valuable synthons for the preparation of a variety of polycyclic systems.[1] Several structural studies of reduced pyrene have been undertaken mostly to investigate various forms of cyclic conjugation, or more specifically, to see if perimeter-type structures contribute to the ground state.[2,3]

Using Na or K metal in [$^2H_8$]tetrahydrofuran (THF), it was recently reported that the reduction products revealed more complex ^1H and ^{13}C n.m.r. spectra than expected for a single D_{2h} symmetric species.[2a] In addition, the ^1H n.m.r. signals were considerably downfield from the resonances reported earlier for the symmetric pyrene dianion (P^{2-}) (Li, [$^2H_8$]THF).[3] The existence of two diatropic tetra-anions was claimed to account for these experimental observations, where the induced asymmetry is caused by different locations of the cations relative to the anion system. The formation of a symmetric dianion during the reduction process was assumed in the study, but not actually observed.

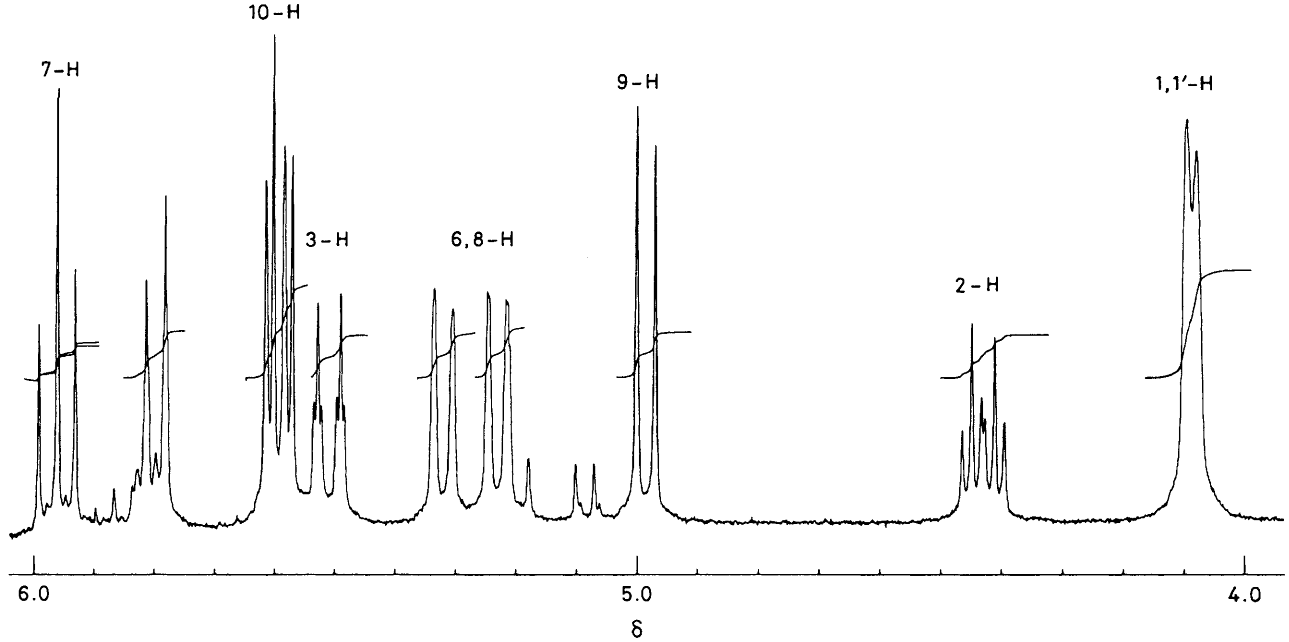


Figure 1. 250.13 MHz ^{1}H N.m.r. spectrum of the potassium 1-hydropyrenyl anion (PH^-) in [$^2H_8$]THF.

Table 1. ^{1}H and ^{13}C N.m.r. chemical shifts of the 1-hydropyrenyl anion (PH^-) and pyrene dianion (P^{2-}).[a]

δ_H (*J* in Hz)	PH^-	(K^+, [$^2H_8$]THF, 25 °C)[b]	1-H: 4.08 (d, *J* 3.9),[e] 2-H: 4.43 (dt, *J* 9.6, 4.0), 3-H: 5.51 (dt, *J* 9.6, 1.6), 4,5-H: 5.80 (d, *J* 7.8), 5.58 (d, *J* 7.8), 6,8-H: 5.32 (d, *J* 7.6), 5.23 (d, *J* 7.5), 7-H: 5.97 (t, *J* 7.6), 9-H: 4.98 (d, *J* 7.7), 10-H: 5.60 (d, *J* 7.6).
	P^{2-}	(Na^+, [$^2H_8$]THF, −60 °C)[c]	1-H: −0.72, 2-H: 1.72, 4-H: 0.26.
		(K^+, [$^2H_8$]THF, −68 °C)[c]	1-H: −0.60, 2-H: 1.70, 4-H: 0.28.
δ_C (p.p.m.)	PH^-	(Na^+, THF, 25 °C)[d]	C-1: 35.2, C-2: 109.7, C-3—10: 130.5, 128.2, 128.0, 127.6, 109.5, 106.0, 105.1, 101.6, C-3a, -5a, -8a, -10a—c: 144.2, 141.9, 139.2, 137.4, 110.7, 108.2.
	P^{2-}	(Na^+, THF, −80 °C)[d]	C-1: 93.3, C-2: 141.8, C-4: 108.9, C-3a: 149.2, C-10b: 163.4.

[a] The n.m.r. spectra were obtained on a Bruker WM-250 spectrometer. [b] Reference: internal cyclohexane, with δ 1.43 on the Me_4Si scale. [c] Reference: [$^2H_7$]THF signals, with δ 1.77 and 3.61. [d] Reference: internal cyclohexane, with δ 27.0 on the Me_4Si scale. [e] Assignments are based on ^{1}H homodecoupling, $^{13}C[^1H]$ selective decoupling, and HMO charge pattern of the vinyl phenalenyl system.

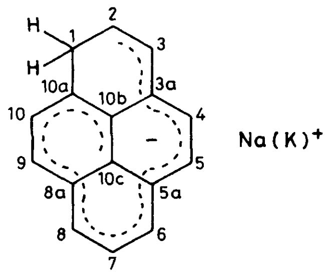
The proposed tetra-anion structure must assume a slow cation exchange on the n.m.r. time scale, and to our knowledge, this is the only reported polycyclic carbanion that shows this type of behaviour. An interesting observation also is that the Na and K salts are stable at room temperature. Most of the perimeter-type tetra-anions reported in the literature have been lithium salts observed at low temperature.[4] Sodium and potassium tetra-anions are rarely described and then only as large perimeter anions ($\geqslant$22 π-electrons).[4b] Evidently, as has also been proposed, the stability of tetra-anions decreases with increasing cation size. It is quite likely that electron repulsive effects are counterbalanced by the electro-stabilizing effects of the cations, *e.g.* this effect is most efficient for lithium species.[4b]

Very recently, a ^{13}C n.m.r. study of the Li and Na reductions of pyrene in diethyl ether or Et_2O–NH_3 (1 : 1), presented an alternative structure of the anion product.[2c] Although the ^{13}C n.m.r. spectrum obtained was identical to that of the claimed tetra-anion, a fully asymmetric pyrene dianion was suggested. The ^{13}C n.m.r. spectrum contained only fifteen separate signals in the sp^2 carbon region and the remaining peak was assumed to be overlapped at δ *ca.* 125 p.p.m.

We have repeated the ^{1}H and ^{13}C n.m.r. studies of the reduction of pyrene using Na(K) in THF or [$^2H_8$]THF. The reactions were performed in sealed n.m.r. tubes. The samples (0.05—0.1 M) were degassed with repeated freeze-pump-thaw cycles before sealing. The metal was kept in the upper part of the n.m.r. tube, either as a metal mirror or as pieces above a constriction in the tube. The tube was turned and the reaction was allowed to proceed overnight or for a few hours in an ultrasonic bath. Longer reaction time or lower temperature (−15 °C) did not induce any spectral changes. The samples could be kept at room temperature for several weeks without any decomposition.

The ^{1}H n.m.r. spectrum obtained at room temperature shows a striking similarity to the spectra claimed to characterize the pyrene tetra-anion except for a signal (dt) at δ 4.43 (Figure 1, Table 1). The coupling pattern and the integrated area of the peak at δ 4.08, strongly indicate a proton adduct. The resonances of the vinylic protons 2-H and 3-H (dt) and that of the 1,1′-H protons support a 1-hydropyrenyl structure. Homodecoupling of the 1,1′-H signal affords a clean AB pattern of 2-H, 3-H and selective decoupling of this signal identifies a ^{13}C n.m.r. signal at δ 35.2 p.p.m. A value of δ 4.08 for 1,1′-H is quite reasonable, considering that the corresponding signal of 1,9-dihydropyrene appears at δ 3.65.[5]

In our experiments, the amount of PH^- constitutes less than



PH$^-$

5% of the total pyrene concentration. This was estimated by a comparison of the PH$^-$: $[^2H_7]$THF peak area ratio with the initial pyrene : $[^2H_7]$THF ratio. A plausible explanation is then that the signals of other pyrene species were broadened into the baseline due to fast electron exchange with pyrene radical anions. This assumption is supported by the spectra of the potassium salts obtained at low temperature. A new set of three high-field signals appear at δ −0.60 (br. d), 0.28 (br. s), and 1.70 (partly overlapped by the $[^2H_7]$THF peak). The sodium reduction products reveal a similar spectrum, although they are less resolved. The chemical shifts and the integrated peak areas are in agreement with the earlier reported spectrum of the paratropic, D_{2h} symmetric dianion (P^{2-}).[3] Compared with the lithium salt of the dianion, the Na and K salts give rise to signals that are shifted slightly upfield (*ca.* 0.6 p.p.m.). A cation influence on paratropicity is consistent with tight ion pair structures, where larger cations give systems with reduced HOMO–LUMO gaps.[6]

The ^{13}C n.m.r. spectrum of PH^-–$Na^+(K^+)$ in THF or $[^2H_8]$THF is similar to that earlier reported,[2] except that the high-field portion shows the C-1 methylene peak at δ 35.2 p.p.m. According to the empirical relationship between ^{13}C n.m.r. chemical shifts and π-charge, an anion charge may be calculated, using the equation $\delta_{av} = 289.5 - 156.3\rho_{av}$.[7] Using a value $\delta_{av} = 121.9$ obtained from the fifteen sp^2 carbon atoms of PH$^-$, the total charge of the sp^2 system is estimated to be 1.1 electrons. This strongly excludes the possibility of multiply charged anions being responsible for the obtained spectra. In addition, since the proposed structure reacts with only one equivalent of an electrophile (see below), the monoanionic structure PH$^-$ seems unequivocal. In accordance with the ^1H n.m.r. experiments above, a temperature decrease yields a ^{13}C n.m.r. spectrum that shows five additional signals belonging to the P^{2-} dianion. Prolonged metal contact did not further reduce the system under the specified conditions.

Oxidation of the reduction products using dry air or quenching experiments using water or alcohol afford pyrene as the sole product. These findings are in accordance with earlier reports where it was noted that hydrogenated pyrenes, *e.g.* 1,9-dihydropyrene, are very unstable and easily form pyrene.[5,8]

The formation of 1,9-dihydropyrene-9-acetate (which rearranges to 4,5-dihydropyrene-4-acetic acid during work-up) by an addition of sodium iodoacetate to a pyrene–Na, Et_2O–NH_3 solution, has been taken as additional support for the existence of P^{2-} in this medium.[1a,2c] In a similar fashion, 9-methyl-1,9-dihydropyrene was claimed to be formed by consecutive addition of MeI and NH_4Cl to P^{2-}−2 Na^+ in Et_2O–NH_3.[1a] Based on these reactions it was stated that P^{2-} undergoes electrophilic attack initially at the 9(4) positions. A second electrophile would then react at the 1(6) position.

Referring to our observations above, we therefore suggest that P^{2-} is not observed in the diethyl ether–NH_3 medium. The main product is PH$^-$, *i.e.* where initial proton attack occurs at position 1 in accordance with HMO charge densities,[9] or a Birch-type reaction where the anion radical is protonated and reduced.[10] An independent study by other workers will consider these possibilities in more detail.[11] In diethyl ether media (Et_2O, THF) the proton donor is most likely to be residual water. These assumptions are supported by carboxylation reactions, where it was found that pyrene–Na in Et_2O–NH_3 yields exclusively monocarboxylic acids after work-up.[12] In pure Et_2O, both mono- and di-carboxylic acids were formed.[12,13]

In conclusion, the alkali metal reduction of pyrene in diethyl ether solution yields the D_{2h} symmetric, paratropic dianion P^{2-} as the final product. Without rigorously excluding proton sources, the 1-hydropyrenyl anion is formed as a by-product. Our results show that ^1H and ^{13}C n.m.r. spectra previously claimed to be those of an unsymmetrical dianion or tetra-anion of pyrene are in fact spectra of the 1-hydropyrenyl anion.

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References

1 (a) C. Tintel, J. Cornelisse, and J. Lugtenburg, *Recl. Trav. Chim. Pays-Bas,* 1983, **102**, 14; (b) C. Tintel, J. Lugtenburg, G. A. J. van Amsterdam, C. Erkelens, and J. Cornelisse, *ibid.*, p. 228; (c) P. E. Hansen, O. Blaabjerg, and A. Berg, *Acta Chem. Scand.*, 1978, **32**, 720.

2 (a) A. Minsky, A. Y. Meyer, and M. Rabinovitz, *J. Am. Chem. Soc.*, 1982, **104**, 2475; (b) M. Rabinovitz, I. Willner, and A. Minsky, *Acc. Chem. Res.*, 1983, **16**, 298; (c) C. Tintel, J. Cornelisse, and J. Lugtenburg, *Recl. Trav. Chim. Pays-Bas*, 1983, **102**, 231.

3 K. Müllen, *Helv. Chim. Acta,* 1978, **61**, 2307.

4 K. Müllen, J. F. M. Oth, H.-W. Engels, and E. Vogel, *Angew. Chem., Int. Ed. Engl.*, 1979, **91**, 251; (b) K. Müllen, W. Huber, T. Meul, M. Nakagawa, and M. Iyoda, *J. Am. Chem. Soc.*, 1982, **104**, 5403; (c) B. C. Becker, W. Huber, C. Schnieders, and K. Müllen, *Chem. Ber.*, 1983, **116**, 1573.

5 R. G. Harvey and P. W. Rabideau, *Tetrahedron Lett.*, 1970, **42**, 3695.

6 H. V. Carter, B. J. McClelland, and E. Warhurst, *Trans. Faraday Soc.*, 1960, **56**, 455; J. A. Pople and K. G. Untch, *J. Am. Chem. Soc.*, 1966, **88**, 4811; F. Baer, H. Kuhn, and W. Regel, *Z. Naturforsch., Teil A*, 1967, **22**, 103.

7 D. H. O'Brien, A. J. Hart, and C. R. Russell, *J. Am. Chem. Soc.*, 1975, **97**, 4410.

8 O. Neunhoeffer and H. Woggon, *Liebigs Ann. Chem.*, 1958, **612**, 98.

9 A. Streitwieser, Jr., and S. Suzuki, *Tetrahedron,* 1961, **16**, 153.

10 P. W. Rabideau and E. G. Burkholder, *J. Org. Chem.*, 1978, **43**, 4283.

11 C. Schneiders, K. Müllen, and W. Huber, *Tetrahedron,* to be submitted.

12 O. Neunhoeffer and H. Woggon, *Liebigs Ann. Chem.*, 1956, **600**, 34.

13 E. Bergmann and E. Bograchov, *J. Am. Chem. Soc.*, 1940, **62**, 3016.