J. Am. Chem. Soc. **1981**, *103*, 4586–4587

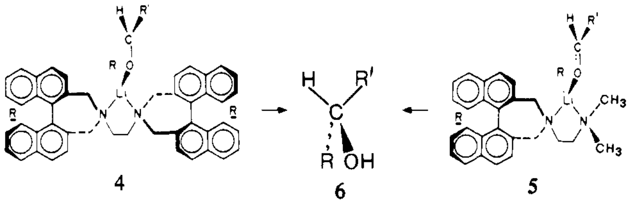
Table I. Chiral Catalysis in Additions of Alkyl- or Aryllithiums to Aldehydes in 150 mL of Et_2O at −120 °C

	diamine		RLi		R'CHO		$C_6H_5CH(OH)R$				
							% optical yield (ee)				
run no	struct	mmol	R	mmol	R'	mmol	$[\alpha]_D^{25}$ [a]	NMR[b]	yield, %	config	$\Delta(\Delta G^{\ddagger})$,[c] kcal mol^{-1}
1	(*R*,*R*)-1	5	$CH_3(CH_2)_3$	4.4	C_6H_5	1.2	95	89	73	*R*	1.0
2	(*R*,*R*)-1	3.8	C_6H_5	3.1	$CH_3(CH_2)_3$	1.2	43	55	47	*S*	0.3
3	(*R*,*R*)-1	3.6	$CH_3(CH_2)_2$	3.4	C_6H_5	1.2	59	63	63	*R*	0.4
4	(*R*,*R*)-1	3.4	CH_3CH_2	3.3	C_6H_5	1.2	66	67	75	*R*	0.5
5	(*R*,*R*)-1	3.9	CH_3	3.1	C_6H_5	1.2	36	35	35	*R*	0.2
6[d]	(*R*)-2	3.3	$CH_3(CH_2)_3$	3.0	C_6H_5	1.0	58	55	71	*R*	0.4
7	(*R*)-2	3.4	$CH_3(CH_2)_2$	3.0	C_6H_5	1.2	53	54	75	*R*	0.4
8	(*R*)-2	3.3	CH_3CH_2	2.2	C_6H_5	1.2	30	30	73	*R*	0.2
9	(*R*)-2	3.6	CH_3	3.0	C_6H_5	1.2	23	22	65	*R*	0.1

[a] Reference 8 lists maximum rotations used. [b] From ^1H NMR of (+)-α-methoxy-α-[(trifluoromethyl)phenyl]acetic esters. [c] $\Delta(\Delta G^{\ddagger}) = RT \ln$ [dominant enantiomer/subordinate enantiomer]. Values of ee determined by the two methods were averaged. [d] Volume of Et_2O was 20 mL.

than pentanal as the aldehyde component.

Without exception, the configurational bias is correlated by the formulations of generalized transition states **4** and **5** to give **6**.

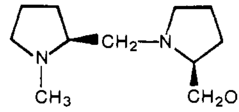


4 **6** **5**

Although we examined only 14 out of many possible combinations of solvents, temperatures, reagents, catalysts, and orders of attaching groups to the asymmetric centers, the fact that all 14 reactions fit this correlation suggests that a single mechanistic feature dominates the chiral tilt. Examination of CPK molecular models of **4** with R = $CH_3(CH_2)_3$ and R' = C_6H_5 in advance of experiment provided the correct prediction of the configuration of the dominant product. Because of the rigid polyspirane structures of the presumed transition states, the only degree of freedom is the placement of the H and R' groups. In **4** and **5**, that diastereomer is formulated in which the H is directed toward the face of the upper left naphthalene and, in **4**, R is directed alongside the face of the lower right naphthalene. Models of **4** and **5** appear less sterically constrained than those of their diastereomers in which the positions of the H and R' groups are interchanged. Since N: rapidly inverts, catalyst (*R*,*R*)-**1**, in effect, contains three C_2 axes, and **4** can be generated four different ways from (*R*,*R*)-**1**, R'CHO, and RLi. Since catalyst (*R*)-**2** in effect contains one C_2 axis, **5** can be generated two different ways from (*R*)-**2**, R'CHO, and RLi. This degeneracy reduces the number of transition states that compete with one another, the averaging of compensating effects, and probably is at least partly responsible for the high chiral recognition of the catalysts.

This correlation shows the following similarities to the rule of steric control of asymmetric induction for additions to carbonyl groups adjacent to chiral centers.[12] In both correlations, the differences in free energies between the diastereomeric transition states cover about the same range and depend on steric effects. An inversion in the order of attachment of groups to the forming asymmetric center inverts the configuration of that center.

Seebach et al. have used optically active amino ethers derived from tartaric acid to get 56–15% ee in stoichiometric catalysis of additions of organometallics to aldehydes.[13] However, Mukaiyama et al. reported the highest observed stoichiometric catalysis of additions of alkylorganometallics to aldehydes to provide alcohols.[14] When RLi complexed by (*S*,*S*)-**7** was added to C_6H_5CHO, the optical yields varied from 83[15] to 21% ee, and the



(*SS*)-**7**

dominant isomer produced depended on the R of RLi and the solvent. The highest optical yield (92% ee) involved Et_2Mg reacting with C_6H_5CHO.

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(15) These authors based their optical yields on a maximum rotation for $C_6H_5CH(OH)(CH_2)_3CH_3$ of $[\alpha]_D$ 31.3° (*c* 3, C_6H_6). We have corrected their ee values to a maximum of $[\alpha]^{25}_D$ 35.7° (*c* 3, C_6H_6) so that their results and ours can be compared (see ref 9).

Aromatic Polycyclic Benzenoid Tetraanions: Pyrene and Perylene Anions Revisited

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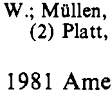
Recently, it has been reported that four-electron reduction of conjugated hydrocarbons is feasible.[1] Conjugated systems of $(4n + 2)\pi$ electrons in their periphery are of particular interest, being predicted to acquire aromatic character as a consequence of a four-electron reduction process.[2]

No information exists on quadruply charged ions which originate from $4n + 2$ peripheries of the "ultimate aromatics", i.e., benzenoid systems. We wish to report a reduction of two polycyclic benzenoid $(4n + 2)\pi$ systems which occupy a cardinal position in the understanding of aromaticity, i.e., pyrene (**1**) and perylene (**2**) leading to the formation of the respective tetraanions. These



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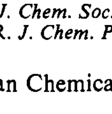

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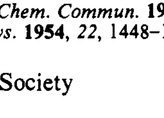

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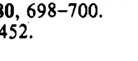

4

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Table I. ^{1}H NMR Chemical Shifts of Pyrene (1), Perylene (2), and Tetraanions 3 and 4[7]

	pyrene (1)	pyrene[a] dianion	pyrene tetraanion (3)	perylene (2)	perylene tetraanion (4)	isopyrene[a]	isopyrene dianion[a]
center of gravity of ^{1}H NMR bands	8.15	0.97	5.3	7.89	5.35	8.05	6.72
$\Delta\langle\delta\rangle$ from the neutral compd		7.18	2.85		2.54		1.33[b]

[a] Data taken from ref 3. [b] The isopyrene has a LUMO with a nodal plane which does not bisect the central carbon atoms: so this orbital is not a pure peripheral one, a fact which explains the reduced paratropicity revealed in isopyrene dianion.[3]

two systems have already been subjected in the past to reduction by metals. A doubly charged paratropic species was detected as a dilithium salt[3] of **1** to yield $\mathbf{1}^{2-}$ and a disodium salt salt was reported to be formed by metal reduction of **2**.[4] Comparison of the reported ^{1}H NMR spectra of these two charged systems shows a striking difference between them. Upon reduction of **1** to $\mathbf{1}^{2-}$ the proton chemical shift's center of gravity $\Delta\langle\delta\rangle$ shifts upfield by 7.18 ppm, while the total change in reduction of **2** is only 2.54 ppm. This difference cannot be ascribed to the nonsimilarity of the π periphery of these hydrocarbons as they accomodate 14- and 18π electrons and **1** and **2**, respectively.[5] Simple HMO of **1** and **2** show that each one of them has a LUMO orbital exhibiting a nodal plane through the central carbon atoms.[6] This leads to an important conclusion: in $\mathbf{1}^{2-}$ and $\mathbf{2}^{2-}$ the molecular orbitals which are occupied by the two additional electrons represent those of a pure peripheral annulene.

This discrepancy tempted us to study the metal reduction of **1** and **2**. Reduction of **1** with sodium metal at room temperature (THF-d_8, sealed degassed tube) was monitored by ^{1}H NMR spectroscopy.[7] After 4 days the deep purple solution exhibited a well-resolved AB_2M spectrum; the AB_2 part is centered at 5.68 ppm, the M part at 4.40 ppm, and the center of gravity of the entire spectrum at 5.30 ppm (Table I). This spectrum remains unchanged for weeks. During the first 4 days no proton bands were detected, presumably due to the formation of radical species and fast bimolecular electron-transfer processes. This ^{1}H NMR spectrum is entirely different from the spectrum of the paratropic species $\mathbf{1}^{2-}$ reported previously which was obtained with lithium metal at −80 °C.[8] An experiment conducted in dimethoxyethane showed the same spectrum. Oxidation of the anion solutions with O_2 afforded **1** as a sole product. These experiments indicate that the ^{1}H NMR bands could not originate from a reaction product of the anion itself or the anion and solvent. Quenching with D_2O afforded tetradeuteriotetrahydropyrene (m/e 210, P + 1 = 211) as shown by electron capture and chemical ionization mass spectrometry,[9] accompanied by a mixture of partially dehydrogenated products (m/e 202–209). We followed the formation of the various species in the reaction of pyrene and sodium by repeated sampling experiments. Samples were taken from the reaction mixture, quenched with water, and titrated potentiometrically to follow the formation of base. The amount of sodium was followed by atomic absorption. The amount of base and sodium increased with time, and after 4 days 3.3–4.0 equiv of base and 3.2–4.0 atoms of sodium were detected per molecule of **1**. No further increase of base and sodium could be detected even after 14 days. These results clearly indicate the formation of a quadruply charged anion **3**, i.e., $\mathbf{1}^{4-}$.[10]

Similar experiments were conducted with the perylene system (**2**). The ^{1}H NMR spectrum[7] of the purple solution formed by contact between **2** and sodium after 1 week afforded an identical ^{1}H NMR spectrum to that reported by Lawler et al.[4] (Table I) and assigned to the formation of a dianion. Quenching with D_2O as mentioned before[9] showed clearly the formation of a tetradeuteriotetrahydroperylene species (m/e 260) which oxidizes in air to give tetradeuterioperylene along with other dehydrogenated products. We believe that these spectroscopic and chemical results demonstrate that the reaction of perylene (**2**) with sodium does in fact form a tetraanion.

The ^{1}H NMR bands summarized in Table I emphasize the highly aromatic diatropic character of the neutral systems; even more so, our findings point out the aromatic character of the two quadruply charged species as manifested by their diatropicity.[11,12]

Additional studies including ^{13}C and ^{23}Na NMR spectroscopies of these systems are under way for the purpose of gaining a deeper insight into these multiply charged species.

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(5) The dianion of tetracene (18π electrons) shows ^{1}H NMR bands at high field.[4]

(6) "Dictionary of Hückel Molecular Orbitals (HMO) Heilbronner and Straub"; Springer Verlag: Berlin, 1966; Section 8, 16, 20.

(7) In THF-d_8, recorded with the aid of Bruker WH-300 pulsed FT spectrometer operating at 300.133 MHz, deuterium lock, Aspect 2000 computer, 32K memory.

(8) The reduction of **1** to $\mathbf{1}^{2-}$ was conducted by Müllen with lithium at −80 °C.[3]

(9) Du Pont 21-490 B single focusing instrument equipped with a commercial dual CI/EI source. Reagent gas was isobutane, source temperature 160 °C. The spectra were run by Dr. Shmuel Zitrin, Mass Spectrometry Unit, Criminal Identification Division, Police Headquarters, Jerusalem.

(10) The respective triply charged species being a radical anion could not be detected by ^{1}H NMR spectroscopy.

(11) The well-accepted correlation of Schaeffer and Schneider[12] predicts that the centers of gravity of the ^{1}H NMR absorptions for **3** and **4** should appear at ca. 4.2 ppm. The data shown (Table I) emphasize the enhanced diatropicity of these tetraanions.

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Synthesis and Structure of Bis(2,4,6-tri-*tert*-butylphenyl)diphosphene: Isolation of a True "Phosphobenzene"

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In 1877 Köhler and Michaelis[1] reported the isolation of a compound which was thought to be the phosphorus analogue of azobenzene, "$C_6H_5P{=}PC_6H_5$". The phosphobenzene structure for the compound, however, was proved to be incorrect. In the early 1960's the compound was shown to have an oligomeric structure by means of molecular weight determination[2] and subsequently by X-ray crystallographic analysis.[3]

A number of reports on cyclopolyphosphine $(RP)_n$ (n = 3–6) have appeared in the literature since the structure of the phenyl derivative was elucidated.[4] Up to date the smallest cyclophosphine is $(C_2F_5P)_3$.[5] The presence of the monomeric and dimeric species

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