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DIINDENO[cd:lm]PERYLENE DIANION.
LOCAL vs. PERIPHERAL CONTRIBUTIONS TO THE AROMATIC CHARACTER

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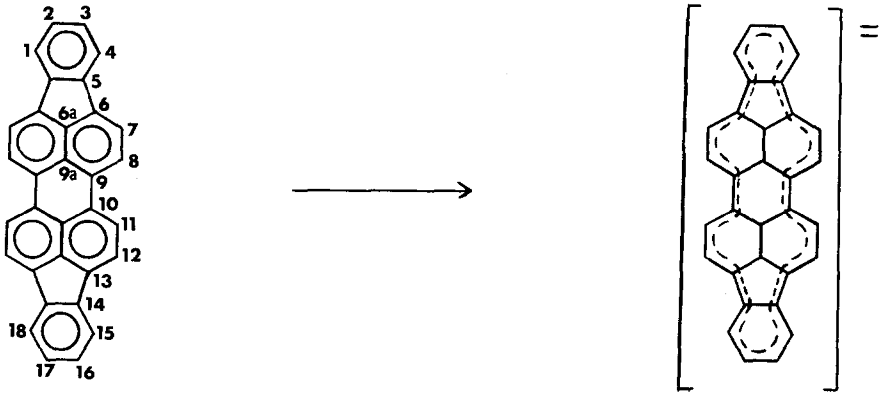
Abstract: *Diindeno[cd;lm]perylene (1) is shown to undergo a two electron reduction process to its dianion 2. Both neutral and doubly charged systems exhibit an enhanced diamagnetic character which is believed to be acquired via two different mechanisms.*

In fused polycyclic systems both the local contributions of the various components and the peripheral π-delocalisation influence the net nature of the species.[1] The possibility of predicting whether one of those two kinds of contributions will prevail in a given species is of interest. The diindeno[cd:lm]perylene (periflanthene) system (1), and its dianion derivative 2 should offer suitable examples when probing this question.

The neutral system 1 is composed of fully aromatic components - i.e. a perylene fused to two benzene moieties, yet having a 28 "antiaromatic" number of peripheral π electrons. On the other hand, the doubly charged species 2 has in principle an "aromatic" periphery of 28c-30 π electrons while the different charged components can no longer be described as aromatic moieties. We wish therefore to report the reduction of 1 to its hitherto unknown dianion 2 and to describe the ^{1}H and ^{13}C NMR spectra of 1 and 2. While ^{1}H NMR characteristics are a useful probe of the various kinds of ring current which prevail in the system[2], the ^{13}C chemical shifts shed light on distribution of charge densities[3].

The ^{1}H NMR spectrum[4] of 1 (Table 1) consists of an AA'BB' pattern, centered at 7.65 ppm, attributed to the protons of the benzene rings and of an AB pattern at 8.32 ppm, which belongs to the perylene moiety (see Table 1 for detailed assignment). Being a planar, fully conjugated system of an antiaromatic periphery, the low field ^{1}H NMR spectrum of 1 - centered at 8.00 ppm - points towards the existence of diamagnetic ring currents which are "localised" in the different components (perylene and benzene rings) of the molecule. Consequently, we have to conclude that those components are coupled to only a weak extent,



1 2

Upon treatment of 1 with sodium in THF, the two-electron reduction product 2 is obtained. The ^{1}H NMR spectrum[4] (Table 1) of the deep blue solution consists of an AA'BB' pattern, centered at 7.75 ppm, assigned to the protons of the benzene moieties, along with an AB spectrum which belongs to the perylene moiety centered at 8.04 ppm.

Table 1. ^{1}H NMR Parameters[4] of 1 and 2[a]

	H_1,H_4,H_{15},H_{18}	H_2,H_3,H_{16},H_{17}	H_7,H_{12},H_{21},H_{26}	H_8,H_{11},H_{22},H_{25}
1	7.98 (dd,[b], J_1=6.3 Hz J_2=5.0 Hz)	7.41 (dd[b], J_1=6.3 Hz J_2=5.0 Hz)	8.53 (d[c],J=7.5 Hz)	8.15 (d[c],J=7.5 Hz)
2	8.34 (dd[b],J_1=6.4 Hz J_2=5.9 Hz)	7.20 (dd[b], J_1=6.4 Hz J_2=5.9 Hz)	8.19 (d[c],J=8.6 Hz)	7.89 (d[c],J=8.6 Hz)

[a] Chemical shifts (ppm) are recorded with respect to the solvent signals and then referred to TMS The assignment is based on ring current effects and on charge densities considerations as obtained from theoretical calculations.[6] [b] Part of an AA'BB' pattern. [c] Part of an AB pattern.

It has been shown in a series of charged conjugated molecules that the ^{1}H chemical shifts correlate linearly with the electron density[5] (taking the correlation coefficient as 10.7 ppm per unit charge). On this basis the total proton NMR upfield shift - caused by the two negative charges shielding - is expected to be of 0.67 ppm - shifting the center of gravity of the spectrum revealed by 2 to 7.33 ppm. This result is obtained when including the four central

Table 2. ^{13}C Chemical Shifts[4] and Charge Densities of 2[a,b]

	C_1	C_2	C_5	C_6	C_7	C_8	C_9	C_{6a}	C_{9a}
δ	127.6	115.6	117.9	107.7	120.0	110.1	118.2	125.6	134.1
ρ^c	-0.0301	-0.0457	-0.0786	-0.1273	-0.0396	-0.0740	-0.0614	-0.0660	-0.0202

[a] Chemical shifts (ppm) are recorded with respect to the solvent signals (THF) and referred to TMS. The assignment is based on nondecoupled spectrum and on charge densities. [b] We were unable to obtain the ^{13}C spectrum of the neutral species 1 because of its very low solubility.

[c] Deduced from ωβ calculations.[6]

carbon atoms in the computation. As shown by ^{13}C NMR spectrum (Table 2) and by ωβ calculations[6], performed on 2, those atoms bear only a minor portion of negative charge densities, so that the expected value of upfield shift should be even higher. However, the observed proton chemical shift's center of gravity upon reduction of 1 to 2 shifts upfield by only 0.08 ppm. This result clearly indicates the existence of a substantial diamagnetic ring current in the dianion 2, a ring current which efficiently cancels the upfield shift due to the negative charges. The low field NMR spectrum of 2, along with theoretical calculations which show that the doubly charged species have a HOMO orbital exhibiting a nodal plane through the central carbon atoms, point out that 2 should be considered as an aromatic perturbed [28c-30π]annulene. The aromatic diamagnetic character of the dianion is emphasized by the relatively large framework of the system, taking into consideration the gradual decay of aromatic character when enlarging the number of the periphery carbon atoms.

In view of these results we suggest that two different mechanisms operate in the neutral and charged systems for the purpose of acquiring aromatic character. While the neutral species 1 is best visualized as being composed of aromatic moieties weakly coupled with "localised" ring currents, the dianion should be regarded as a peripheral 4n+2 system (see figure). Theoretical calculations[6] lend strength to this assumption. The length of bonds which link the perylene moiety and the benzene rings in 1 are substantially longer than the other bonds in the system (1.45 Å vs. 1.39 to 1.41 Å). The alternation of bond length in the doubly charged species is much smaller (1.39 to 1.42 Å).

References and Notes

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