Persistent oxidation dications of dialkyl- and tetraalkyl-perylenes and dibenzo[*cd*,*lm*]perylene; charge distribution mode, substituent effects and conformational aspects

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Starting with appropriate alkylnaphthalenes, 3,10-dimethyl- 2, 3,10-diethyl- 3, 2,3,10,11-tetramethyl- 4 and 3,4,9,10-tetramethyl-perylene 5 were synthesized by a sequence of radical cation and radical anion coupling steps. Persistent oxidation dications of parent perylene 1, alkylperylenes 2–5 and dibenzo[*cd*,*lm*]perylene 6 were generated in SbF_5–SO_2ClF.

Based on 1D- and 2D-NMR experiments combined with AMl calculations the charge delocalization mode in the dications was deduced. The total deshielding ($\Sigma\Delta\delta^{13}C$), substituent effects, conformational/ geometrical changes and tropicity in the dications are examined.

Whereas alkylperylene dications represent 18π electron Hückel dictations with a diamagnetic ring current (more diatropic than their neutral precursors), the 24π (20π periphery) dication of dibenzoperylene exhibits a paramagnetic ring current which greatly shields its protons (more paratropic than neutral hydrocarbon).

Introduction

There have been extensive studies of π-conjugated dianions (two electron reduction) of fused polycyclic compounds (both carbocyclic and heterocyclic).[1–13] NMR and theoretical studies have provided much insight into their electronic structure and charge alternation modes. In comparison, the literature on persistent dications (two-electron oxidation) of alternant and non-alternant polycyclic arenes and annulenes is not as extensive.[14]

An area of substantial interest, where only limited data are available so far, is substituent control of charge delocalization, and geometrical changes that may be induced *via* such substituents. The importance of strain-induced distortions in polyaromatic hydrocarbon (PAH) radical cations has been recognized in materials chemistry, where changes can be induced in the local electronic structures in organic conducting solids.[15,16]

Although the proportionality between ^{13}C NMR chemical shift and charge (F_c) has been established and tested for numerous systems,[14] recent studies showed that a more rigorous correlation (K_c) is derived when the paramagnetic shielding contributions (X_c) are taken into account.[17,18] Thus, paratropicity in the 12π perimeter of pyrene dication leads to a large total deshielding ($K_c = 235$ ppm/e)[17] as compared to other PAHs and annulenes.

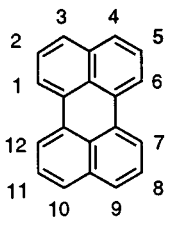
In a previous study, we generated several crowded alkyl-(cycloalkyl)pyrene dications and examined the substituent effects on $\Delta\delta^{13}C$ values and ^1H NMR chemical shifts.[19] There is a revival of interest in perylene **1** as a building block of conducting organics.[15,16] The ^1H NMR spectrum of $\mathbf{1}^{2+}$ was first reported by Brouwer[20] and its ^{13}C NMR spectrum by Forsyth and Olah.[21] As part of a broader study of ring current anisotropy effects, it was re-studied by Edlund *et al.*[17]

In the present study, in an effort to examine substituent effects and to induce distortion and geometrical changes, we have generated alkylperylene dications $\mathbf{2}^{2+}$–$\mathbf{5}^{2+}$ and dibenzoperylene dication $\mathbf{6}^{2+}$. For comparison, parent $\mathbf{1}^{2+}$ was included in our study.

Results and discussion

Scope and limitation of synthetic protocol

A recent study by Tanaka *et al.*[22] showed that NO^+ generated *in situ* from $NaNO_2$–TfOH (Tf = CF_3SO_2) is an effective oxidant for one-pot generation of binaphthyls from naphthalenes. We used this step to prepare the alkyl–binaphthyl precursors (Scheme 1). The radical anion coupling approach (cyclodehydrogenation) introduced by Michel and Moradpour[23] was used to prepare the alkylperylenes. Despite simplicity and reasonable overall yields, there are several limitations to each step which reduced the number of perylenes that could be synthesized.



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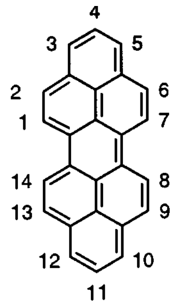

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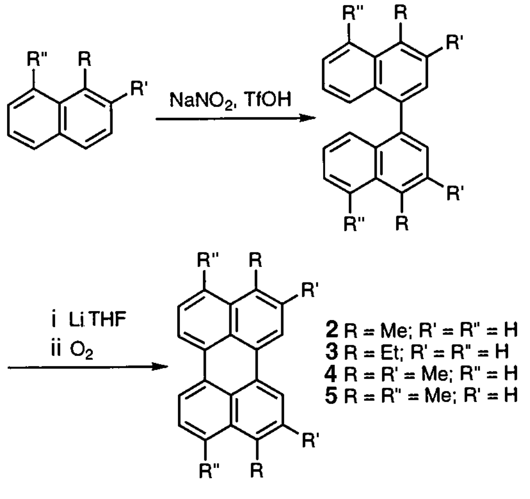


Scheme 1

(1) An inherent limitation in the radical cation coupling process was the failure to synthesize fluorinated binaphthyls: thus oxidative-coupling of 1-fluoronaphthalene to 4,4′-difluoro-1,1′-binaphthyl could not be achieved (fluoronaphthalene was recovered unchanged).

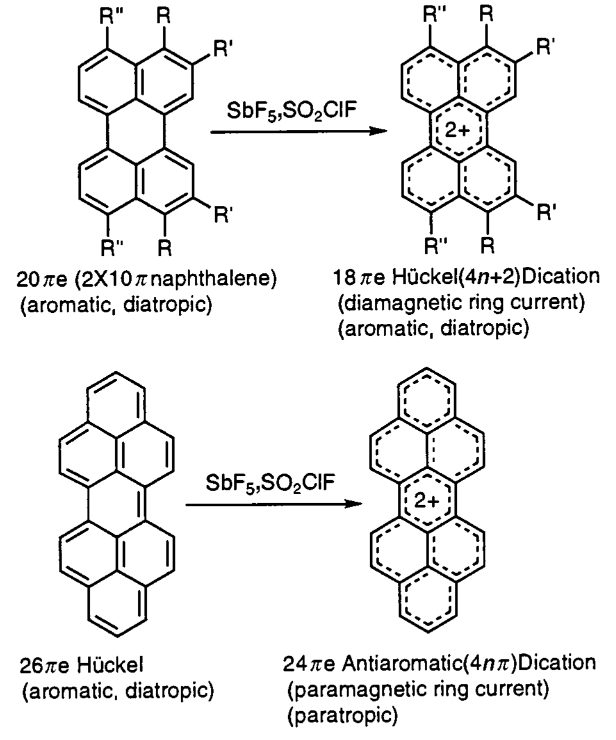
(2) Radical cation coupling occurs only in a symmetrical sense; attempts to oxidatively couple alkylnaphthalenes in a manner to obtain unsymmetrical binaphthyls (to be used for preparation of alkylperylenes with 'crossed' substituents) were unsuccessful.

(3) Presence of alkyl groups at the 2,2′- or 7,7′-positions of binaphthyls leads to failure to produce any perylenes.

(4) Attempted radical anion coupling of 2,2′- and 4,4′-dimethoxy-1,1′-binaphthyl was unsuccessful; instead, elimination of methoxy occurred with formation of perylene in low yield.

Dication generation

The perylenes were cleanly oxidized to persistent dications by reaction with SbF_5–SO_2ClF system at dry-ice–acetone temperature (Scheme 2). The dication solutions obtained were all dark-red except for $\mathbf{6}^{2+}$ for which a dark-blue solution resulted. Superacid solutions of the dications were stable for several days at low temperature. Quenching of the dications in all cases returned the skeletally intact perylenes (^{1}H NMR).



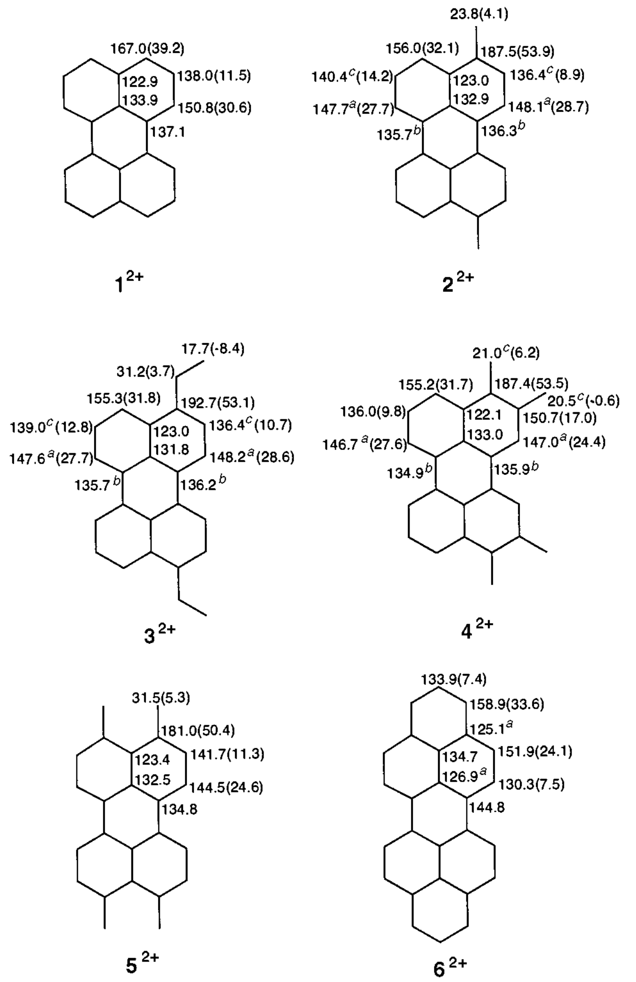
Scheme 2

NMR of the dications

^{13}C NMR assignments were based on the chemical shifts, C–H coupled spectra, and C–H HETCOR relationships (in the case of $\mathbf{6}^{2+}$). Assignments of the protons were based on H–H COSY relationships coupled to multiplicities, coupling constants, chemical shifts and C–H HETCOR relationships (in the case of $\mathbf{6}^{2+}$). For $\mathbf{4}^{2+}$, NOED spectra corroborated the assignment of the methyls. AMl calculated carbon charges were used as a guiding tool in fine-tuning the carbon assignments.

Charge delocalization mode and substituent effects

The ^{13}C NMR chemical shifts and $\Delta\delta^{13}$C values are summarized in Fig. 1. For $\mathbf{1}^{2+}$, our data are in very close agreement with those of Edlund *et al.*[17] (after adjusting for the correction they applied for solvent bulk effects). The positive charge resides predominantly at the 3/4/9/10 and 1/6/7/12 positions. Introduction of methyl and ethyl groups into the 3/10 positions (**2** and **3**) has a significant cation stabilizing effect, whereas methyl substitution at C-2/C-11 is less effective.



a,b,c pairs of resonances whose assignment may be interchangeable

Fig. 1 ^{13}C NMR chemical shifts and $\Delta\delta^{13}$C values for perylene and dibenzoperylene dications

The overall charge distribution pattern based on AMl calculated changes in carbon charges [$\Delta q_c = q_c(\text{ion}) - q_c(\text{neutral})$] and the relative energies ($\Delta\Delta H_f^\circ$) of the dications are gathered in Fig. 2.

AMl predicts that among alkylperylene dications the symmetrical $\mathbf{5}^{2+}$ is the most stable. Methyl substitution at C-2 has little stabilization effect.

The AMl-deduced overall charge delocalization mode points to extensive charge alternation throughout the 'rim' which is enhanced by alkyl substitution (Fig. 2). These are more effective at the 3-position than at the 2-position. Influence of alkyl groups in the 'bay-region' and distortions thereof cannot be judged due to synthetic limitations to accessing these substrates.†

Based on ^{13}C NMR, the methyl and ethyl substituent effects at C-3 are 20.5 and 25.7 ppm respectively ($\mathbf{2}^{2+}$ and $\mathbf{3}^{2+}$), whereas methyl at C-2 causes only 12.7 ppm deshielding (Fig. 3). An interesting feature in the dications is the upfield shift of C-4 upon *peri* alkylation at C-3. This shielding effect increases with increasing size of the alkyl group and is clearly due to steric interaction. A similar effect has been observed in the phenalenyl anion where methyl introduction at C-1 causes shielding at

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† AMl predicts same changes in bond lengths upon oxidation, with the order being opposite for $\mathbf{6}^{2+}$ as compared to perylene dications (see Fig. 4).

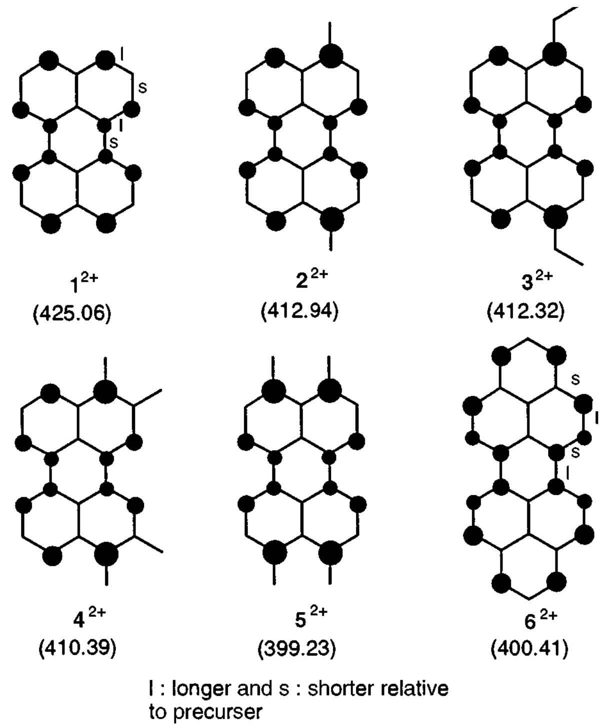

Fig. 2 Δq profiles and $\Delta\Delta H^{\circ}_{f}$(kcal mol^{-1}) (1 cal = 4.184 J) for alkyl- and dibenzo-perylene dications

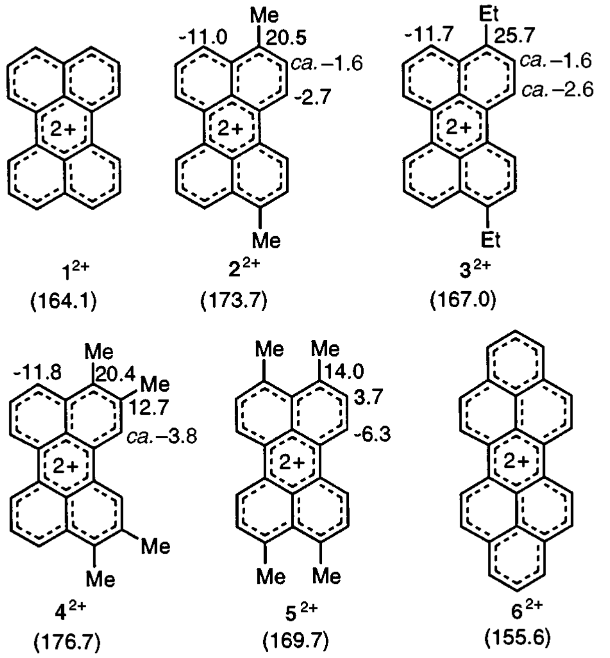

Fig. 3 Substituent effect (compared to parent perylene dication), and total deshielding ($\Sigma\Delta$ ^{13}C ppm/e) in perylene and dibenzoperylene dications

C-9.[13] Carbon shielding is also observed at C-1 and is maximized in **5**$^{2+}$. Slight shielding at C-2 is observed in the case of **2**$^{2+}$ and **3**$^{2+}$ which changes to a deshielding trend upon *peri*-alkylation (**5**$^{2+}$).

The total deshielding values ($\Sigma\Delta\delta^{13}$Cppm/e) for alkylperylene dications (Fig. 3) are *ca.* 177–164 ppm/e.

For dibenzoperylene dication **6**$^{2+}$, the observed total deshielding is 155.6 ppm/e, to which the paramagnetic term should make a positive contribution (see the ^{1}H NMR features below), leading to an increase in the total deshielding (K_c scale).[17]

^{1}H NMR spectral features and tropicity

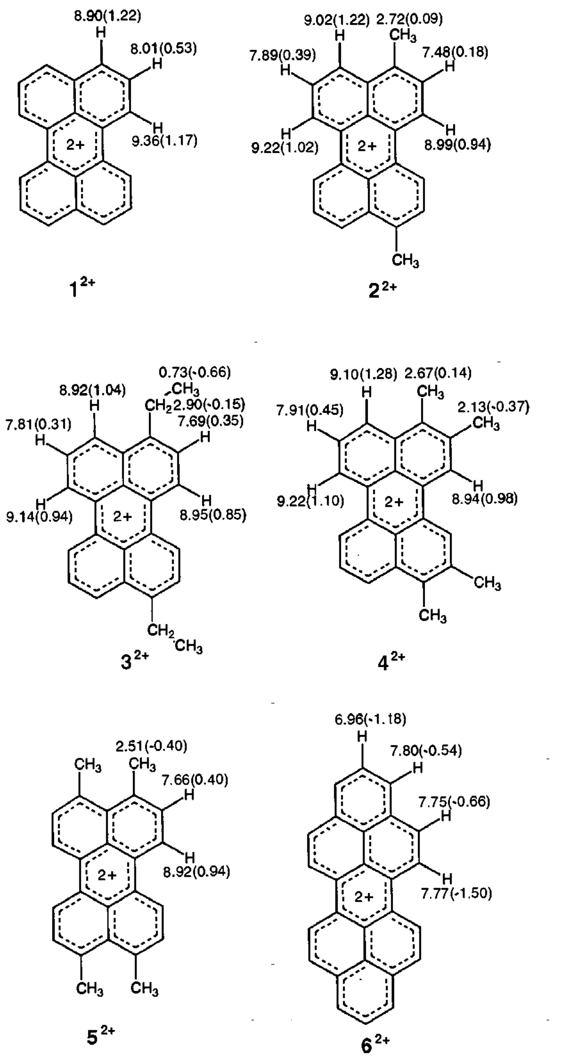

Fig. 4 ^{1}H NMR chemical shifts and substituent induced ^{1}H NMR values (in parentheses) for perylene dications

The proton resonances in the alkylperylene dications are significantly deshielded relative to the neutral precursors, with the deshielding order H-3 > H-1 > H-2. The data are summarized in Fig. 4.

Introduction of methyl groups at C-3/C-10 (**2**$^{2+}$) reduces proton deshielding at H-2/H-11, presumably due to buttressing. In **3**$^{2+}$, anisotropic shielding of the ethyl groups is clearly seen. To our knowledge, this is the first example of anisotropic shielding of a substituent by conformational change in a PAH oxidation dication. The previous examples of alkyl-buttressing leading to anisotropic shielding by the ring current were for *ipso*-protonated alkylanthracenium, alkylpyrenium as well as *ipso*-protonated (alkylated) polyalkylbenzenium cations.[14,24]

In **4**$^{2+}$, the 3/10 methyls are deshielded whereas the 2/11 methyls are highly shielded. In **5**$^{2+}$, the methyl groups are shielded by 0.4 ppm relative to the neutral precursor. This indicates that *peri*-strain is more severe in the dication than in the neutral perylene.

The presence of a paramagnetic ring current in the $4n\pi$ dication **6**$^{2+}$ leads to a strong shielding of the protons (shielding order: H-4 > H-2 > H-1 > H-3), suggesting an 'antiaromatic' dication, more paratropic than the aromatic neutral hydrocarbon.

Another noteworthy feature in the proton spectra of the dications is the increase in H–H vicinal coupling constants. For example for **2**$^{2+}$, $J_{H_1-H_2}$/Hz increases from 7.61 to > 9 and for **5**$^{2+}$ from *ca.* 7.7 to *ca.* 8.9.

In summary, introduction of alkyl groups into perylene dication induces interesting substituent effects which not only cause changes in charge delocalization but also in geometry. We hope to provide additional examples with other classes of PAH dications especially with fluorine substituents as a probe.

Experimental

Alkylnaphthalenes were the highest quality commercial samples (Aldrich) which were used without further purification.

SbF_5 (Fluorochem or Aldrich) was distilled twice under a dry argon atmosphere in an all-glass distillation unit and stored in Nalgene bottles under argon.

SO_2ClF was synthesized from SO_2Cl_2 by halogen exchange using NH_4F and TFA according to a modified procedure of Prakash *et al.*[25]

Dibenzo[*cd*,*lm*]perylene was synthesized according to Fetzer and Biggs,[26] and purified by HPLC.

AMl calculations (Dewar-based) and energy minimizations were performed with the HYPERCHEM Package (Hypercube, 1994).

NMR spectra were recorded on a wide-bore GE-GN300 MHz instrument using a 5 mm C/H switchable probe.

Synthesis of the alkylperylenes

Alkylbinaphthyls were synthesized according to ref. 22.

The radical anion coupling of the binaphthyls were accomplished using lithium powder in tetrahydrofuran (THF) according to ref. 23. The isolated yields of the alkylperylenes were **2** (35%), **3** (38%) and **4** (41%) respectively.

^1H and ^{13}C NMR in $CDCl_3$ and melting points for alkylperylenes.

2: δ_H 2.63 (s, 6H, CH_3), 7.30 (d, 2H, Ph protons), 7.50 (t, 2H, Ph protons), 7.80 (d, 2H, Ph protons), 8.05 (d, 2H, Ph protons), 8.20 (d, 2H, Ph protons); δ_C 19.7 (CH_3), 119.4, 120.0, 123.9, 126.2, 127.5, 128.4, 129.6, 131.7, 133.6 (Ph carbons); mp *ca.* 202–203 °C.

3: δ_H 1.39 (t, 6H, CH_3), 3.05 (q, 4H, CH_2), 7.34 (d, 2H, Ph protons), 7.50 (t, 2H, Ph protons), 7.88 (d, 2H, Ph protons), 8.10 (d, 2H, Ph protons), 8.20 (d, 2H, Ph protons); δ_C 26.1 (CH_3), 27.5 (CH_2), 119.6, 119.9, 123.5, 125.7, 126.2, 129.6, 132.0, 132.8, 139.6 (Ph carbons); mp *ca.* 187–189 °C.

4: δ_H 2.50 (s, 6H, CH_3), 2.53 (s, 6H, CH_3), 7.46 (t, 2H, Ph protons), 7.82 (d, 2H, Ph protons), 7.96 (s, 2H, Ph protons), 8.12 (d, 2H, Ph protons); δ_C 14.8, 21.1 (CH_3), 119.1, 122.1, 122.6, 123.5, 126.2, 128.7, 130.8, 131.6, 133.7, 133.9 (Ph carbons); mp *ca.* 238–240 °C.

Compound **6** has very low solubility in normal solvents; detection of the quaternary carbons was achieved by using CS_2–$CDCl_3$ as solvent and after collecting > 20 000 scans.

General procedure for dication generation

SbF_5 (1 ml) was charged into a 10 mm NMR tube under argon. SO_2ClF (2 ml) was condensed into a 5 mm NMR tube using a high-vacuum line and was subsequently poured directly into SbF_5 in the 10 mm tube at dry-ice–acetone temperature. Upon vigorous mixing (vortex) and slight periodic warming, a clear homogeneous solution resulted. A slurry of the perylene (30 mg) in SO_2ClF (0.3 ml) was prepared in another 5 mm NMR tube at dry-ice–acetone temperature to which the solution of SbF_5–SO_2ClF was subsequently added under argon with vigorous mixing (vortex), whereupon dark-red (dark-blue in the case of **6**), homogeneous, solutions of the dications resulted.

Acknowledgements

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