104. Radical Ions of Conjugated Polycyclic Hydrocarbons Containing Two Phenalenyl π-Systems

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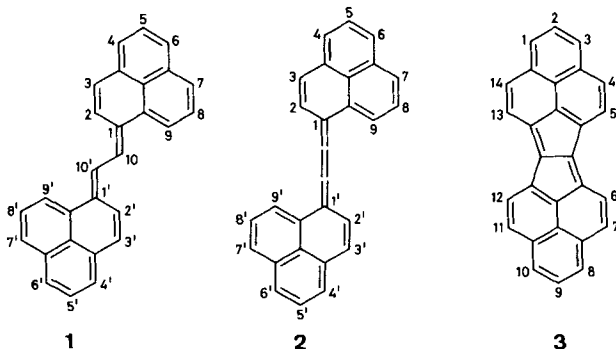
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Summary

The radical cations and the radical anions of 1,2-bis(phenalen-1-ylidene)ethane (1), 1,2-bis(phenalen-1-ylidene)ethene (2) and pentaleno[1,2,3-*cd*:4,5,6-*c'd'*]diphenalene (3) have been characterized by ESR and ENDOR spectroscopy. The ease of formation of these radical ions and their π-spin distributions are interpreted in terms of a simple model which correlates the frontier orbitals of 1, 2 and 3 with the nonbonding MO's of two phenalenyl π-systems.

Introduction. – Recently, three conjugated polycyclic hydrocarbons, each containing two phenalenyl moieties, have been synthesized: 1,2-bis(phenalen-1-ylidene)ethane (BPLA; 1) [1a], 1,2-bis(phenalen-1-ylidene)ethene (BPLE; 2) [1b] and pentaleno[1,2,3-*cd*:4,5,6-*c'd'*]diphenalene (PDPL; 3) [1c].

The presence of two phenalenyl π-systems bestows multi-stage redox properties on the compounds 1, 2 and 3. As demonstrated by their voltammetric oxidation and reduction potentials *(Table 1)* [1] [2], the three hydrocarbons readily donate and accept two electrons. The first of these potentials, E_1^{ox} and E_1^{red}, correspond to the formation of

1　　　　　　　　2　　　　　　　　3

Table 1. *Redox Potentials of 1,2-Bis(phenalen-1-ylidene)ethane* (**1**), *1,2-Bis(phenalen-1-ylidene)ethene* (**2**) *and Pentaleno[1,2,3-cd:4,5,6-c′d′]diphenalene* (**3**). *Values in V vs. SCE.*[a])

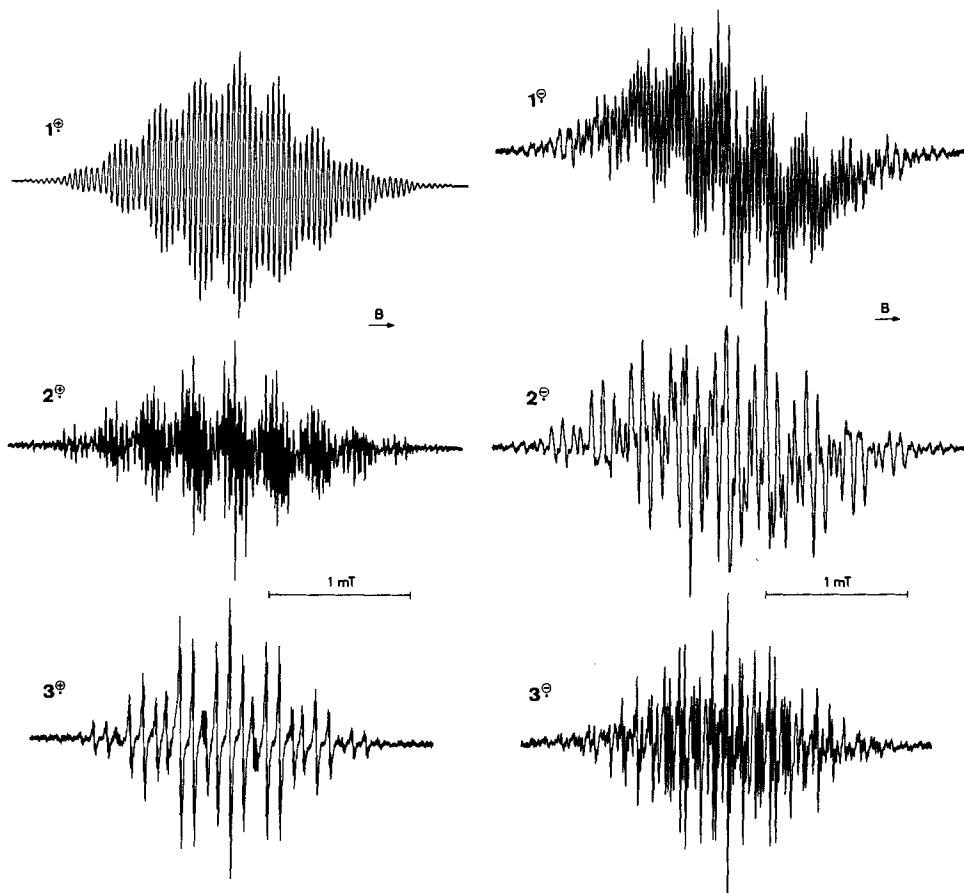|	**1**	**2**	**3**		**1**	**2**	**3**
E_1^{ox}	+ 0.39	+ 0.51	+ 0.56	E_1^{red}	– 1.12	– 0.83	– 0.43
E_2^{ox}	+ 0.83	+ 0.78	+ 1.02	E_2^{red}	– 1.35	– 1.21	– 1.17

[a]) Taken from [1].

Fig. 1. *ESR spectra of the radical cations of 1,2-bis(phenalen-1-ylidene)ethane* (**1**), *1,2-bis(phenalen-1-ylidene)ethene* (**2**) *and pentaleno[1,2,3-cd:4,5,6-c′d′]diphenalene* (**3**). *For* **1**⊕ *and* **2**⊕: *solvent:* $CH_2Cl_2/CF_3COOH/(CF_3CO)_2O$ (10:1:1); *temp.:* 273 K. *For* **3**⊕: *solvent:* CH_2Cl_2; *temp.:* 298 K.

Fig. 2. *ESR spectra of the radical anions of 1,2-bis(phenalen-1-ylidene)ethane* (**1**), *1,2-bis(phenalen-1-ylidene)ethene* (**2**) *and pentaleno[1,2,3-cd:4,5,6-c′d′]diphenalene* (**3**). *For* **1**⊖ *and* **2**⊖: *solvent:* DME; *counter-ion:* $K^⊕$; *temp.:* 233 K. *For* **3**⊖: *solvent:* DMF; *counter-ion:* $Et_4N^⊕$; *temp.:* 213 K.

the radical cations and the radical anions, respectively, which have been studied in the present work.

Results. – The radical cations **1**⊕ and **2**⊕ were prepared by oxidation of the corresponding neutral compounds, **1** and **2**, in a 10:1:1 mixture of CH_2Cl_2, CF_3COOH and $(CF_3CO)_2O$, while the conversion of **3** into **3**⊕ was carried out with $AlCl_3$ in CH_2Cl_2.

The radical anions $1^\ominus$, $2^\ominus$ and $3^\ominus$ were generated from **1**, **2** and **3**, respectively, both by reaction with K-metal in 1,2-dimethoxyethane (DME) and by electrolytic reduction at a helical cathode of amalgamated gold [3] in N,N-dimethylformamide (DMF) with 0.1M $Et_4N^\oplus ClO_4^\ominus$ as the supporting salt. Under these conditions the radical cations were more persistent than the radical anions, so that the former could be studied at higher temperatures (up to 298 K) than the latter (below 233 K). *Fig. 1* shows the ESR spectra of $1^\oplus$, $2^\oplus$ and $3^\oplus$; those of $1^\ominus$, $2^\ominus$ and $3^\ominus$ are reproduced in *Fig. 2*. The analysis was carried out with the assistance of the ENDOR technique and it was confirmed by computer simulation of the ESR derivative curves [2]. The hyperfine data thus determined are listed in *Table 2* for $1^\oplus$, $2^\oplus$, $1^\ominus$ and $2^\ominus$, and in *Table 3* for $3^\oplus$ and $3^\ominus$. Assignments of the coupling constants to sets of equivalent protons are justified by arguments put forward in the *Discussion*.

The g-factors of the radical ions of **1**, **2** and **3** are all 2.0027 ± 0.0001.

Table 2. *Proton Coupling Constants* (in mT) *for the Radical Ions of 1,2-Bis(phenalen-1-ylidene)ethane* (**1**) *and 1,2-Bis(phenalen-1-ylidene)ethene* (**2**)[a]

Position μ	$1^\oplus$	$2^\oplus$	$1^\ominus$	$2^\ominus$	Position μ	$1^\oplus$	$2^\oplus$	$1^\ominus$	$2^\ominus$
2,2′	0.041	0.046	0.059	0.070	7,7′	0.282	0.294	0.292	0.288
3,3′	0.245	0.264	0.257	0.272	8,8′	0.079	0.076	0.079	0.080
4,4′	0.278	0.294	0.264	0.281	9,9′	0.271	0.279	0.257	0.281
5,5′	0.079	0.076	0.079	0.091	10,10′	0.070	–	0.069	–
6,6′	0.291	0.294	0.309	0.313					

[a]   Experimental error: $\pm 2\%$.

Table 3. *Proton Coupling Constants* (in mT) *for the Radical Ions of Pentaleno[1,2,3-cd:4,5,6-c′d′]diphenalene* (**3**)[a]

Position μ	$3^\oplus$	$3^\ominus$	Position μ	$3^\oplus$	$3^\ominus$
1,3,8,10	0.353	0.338	5,6,12,13	0.010	0.106
4,7,11,14	0.261	0.297	2,9	0.092	0.086

[a]   Experimental error: $\pm 1\%$.

Discussion. – The frontier orbitals of **1**, **2** and **3**, *i.e.*, the highest occupied (HOMO's) and the lowest unoccupied MO's (LUMO's), can be regarded as combinations of two nonbonding MO's (NBMO's) of phenalenyl, perturbed by the interaction with an MO of the intervening two-centre π-system. It is evident from *Fig. 3*, which depicts the pertinent correlation diagrams for **1** and **3**, that the HOMO of the alternant hydrocarbon **1** (point group C_{2h}) is obtained as the B_g-combination of the two NBMO's with a small 'admixture' of the antibonding π-MO of ethene. Correspondingly, the LUMO of **1** results from slightly 'admixing' the bonding π-MO of ethene into the A_u-combination of these NBMO's.

The correlation diagram for **1** is, on the whole, also representative for **2**. The mere replacement of two sp^2- by sp-hybridized centres, on going from **1** to **2**, should somewhat lower the energy levels of both the HOMO and the LUMO without greatly affecting their pairing properties.

On the other hand, since the frontier orbitals of the nonalternant hydrocarbon **3** do not exhibit the pairing properties, and since **3** has higher symmetry (point group D_{2h})
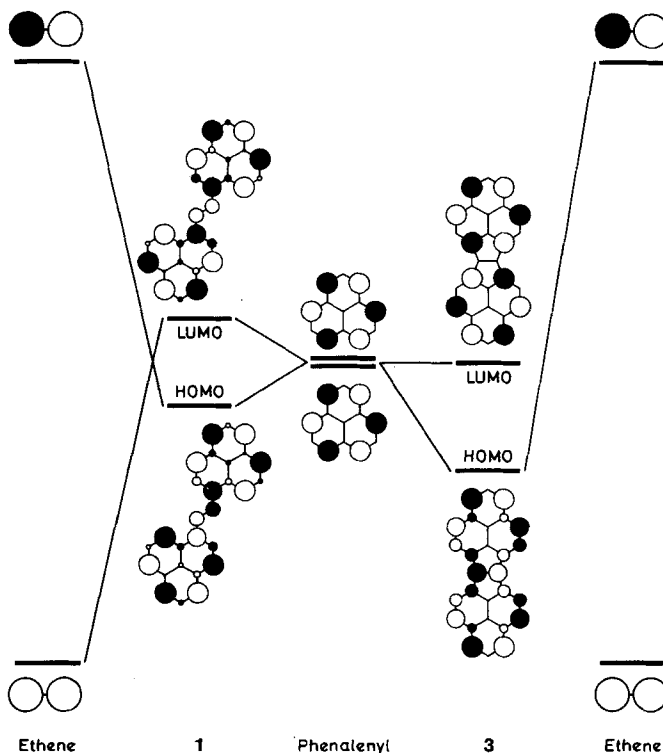
Fig. 3. *Diagram correlating the frontier orbitals of 1,2-bis(phenalen-1-ylidene)ethane* (**1**) *and pentaleno[1,2,3-cd:4,5,6-c'd']diphenalene* (**3**) *with NBMO's of phenalenyl and the π-MO's of ethene.* The areas of the circles are proportional to the squares of the LCAO coefficients. Filled and blank circles symbolize different signs of these coefficients.

than **1**, the correlation diagram for **3** differs significantly from that of **1** *(Fig. 3)*. In the HOMO of **3**, the B_{2g}-combination of the two phenalenyl NBMO's 'mixes' more strongly with the antibonding π-MO of ethene than the corresponding B_g-combination in **1**. By contrast, the LUMO of **3** is a 'pure' A_u-combination of the two NBMO's, since its interaction with the π-MO's of ethene is not allowed by symmetry. As a consequence, the HOMO of **3** is markedly lower in energy than that of **1**, and the same holds for the (nonbonding) LUMO of **3** relative to the analogous orbital of **1**.

The predicted energy sequence for both HOMO's and LUMO's is thus **1** > **2** > **3**, in qualitative agreement with the observed first oxidation and reduction potentials, E_1^{ox} and E_1^{red} *(Table 1)*. Moreover, representation of these orbitals as combinations of two phenalenyl NBMO's accounts for the most prominent hyperfine features of the radical ions of **1**, **2** and **3**. Not only is the unpaired electron accomodated mainly in the two phenalenyl π-systems, but also the spin distribution in each of the two moieties resembles the pattern characteristic of the phenalenyl radical (**4·**) [4]. A prominent feature of this distribution pattern in **4·** is the large (positive) π-spin population ρ_μ at the 'active' positions $\mu = 1,3,4,6,7,9$. The pertaining six equivalent protons give rise to the coupling constant of 0.629 mT, while the second coupling constant of 0.181 mT is due to the

three equivalent protons in the positions $\mu = 2,5,8$, exhibiting smaller (negative) π-spin population p_μ [4a]. The proton-bearing carbon atoms which correspond to the 'active' positions in $4\cdot$ are $\mu = 3,3'$; $4,4'$; $6,6'$; $7,7'$ and $9,9'$ in 1 and 2, and $\mu = 1,3,8,10$ and $4,7,11,14$ in 3. One therefore expects that five pairs of equivalent protons in the radical ions of 1 and 2, and two sets of four equivalent protons in the radical ions of 3 will have coupling constants approximately half as large as 0.629 mT. This expectation is fully borne out by experiment, as the pertinent values range from 0.245 to 0.353 mT (*Tables 2* and *3*). The coupling constants of the remaining protons in the radical ions of 1, 2 and 3 are throughout smaller than 0.11 mT; most of them cluster about 0.07 to 0.09 mT which is close to half the corresponding value, 0.181 mT, for $4\cdot$. The best agreement with the halved coupling constants for $4\cdot$ is shown by their counterparts in the hyperfine data for $3^{\ominus}$ *(Table 3)*. This finding is in accordance with the represent-ation of the LUMO of 3 as a 'pure' combination of two phenalenyl NBMO's (see *above*).

The separation of the coupling constants by their size into two distinct groups enables one to differentiate between the two types of positions μ to which the protons are attached in the radical ions of 1, 2 and 3. Assignments of these values within each group to protons in individual positions are less straightforward. Those made in *Tables 2* and *3* have largely been based on correlation with π-spin populations p_μ calculated by the *McLachlan* procedure [5]; they are subject to some uncertainty.

Conclusion. – The spectroscopic studies reported in this paper provide further con-vincing evidence of the leading role played by the phenalenyl moieties in determining the remarkable redox properties of the hydrocarbons 1, 2 and 3.

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