Radical Anions of [2.2](2,7)Naphthalenophane, [2.2](2,7)Naphthalenophane-1,11-diene, and *trans*-12b,12c-Dihydrocoronene as Studied by Electron Spin Resonance Spectroscopy

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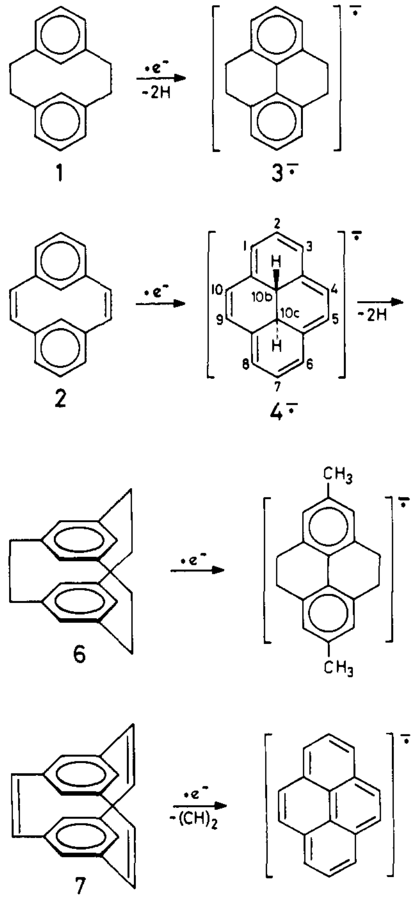
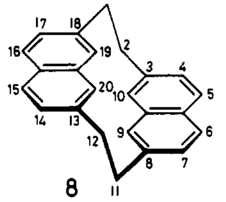
Abstract: In contrast to *anti*-[2.2]metacyclophane (**1**) and its 1,9-diene (**2**), [2.2](2,7)naphthalenophane (**8**) and its 1,11-diene (**9**) yield relatively stable radical anions when treated with potassium in 1,2-dimethoxyethane at low temperatures. A facile uptake of a second electron by **8** leads to the dianion $\mathbf{8}^{2-}$, from which two radical anions of 2,7-dimethylnaphthalene (**10**) are formed upon scission of the dimethylene chains and uptake of four hydrogen atoms. On the other hand, the final paramagnetic product in the alkali metal reduction of **9** is the radical anion of coronene (**11**). The loss of four hydrogen atoms required for the conversion of $\mathbf{9}^{\cdot-}$ to $\mathbf{11}^{\cdot-}$ occurs stepwise as shown by the observation of the radical anion of *trans*-12b,12c-dihydrocoronene (**12**), a compound which, to our knowledge, has not yet been synthesized. The primary radical anions $\mathbf{8}^{\cdot-}$ and $\mathbf{9}^{\cdot-}$, as well as the secondary species $\mathbf{12}^{\cdot-}$, have been fully characterized by their ESR spectra.

It has been observed by means of ESR spectroscopy that *anti*-[2.2]metacyclophane (**1**)[2] and *anti*-[2.2]metacyclophane-1,9-diene (**2**)[3] rapidly form tetracyclic systems when treated with an alkali metal in ethereal solvents.[4,5] A similar conversion occurs upon the corresponding reaction of [2.2.2](1,3,5)cyclophane (**6**)[6] and its 1,9,17-triene (**7**),[6] whereby one of the bridging C_2 units is cleaved or eliminated.[5] ESR spectra of the short-lived primary radical anions $\mathbf{1}^{\cdot-}$, $\mathbf{2}^{\cdot-}$, $\mathbf{6}^{\cdot-}$, and $\mathbf{7}^{\cdot-}$ could not be detected.[5] The pertinent results are summarized in Scheme I.

Scheme I



The present paper reports on an ESR study of the reaction of [2.2](2,7)naphthalenophane (**8**)[7] and [2.2](2,7)naphthalenophane-1,11-diene (**9**)[8] with potassium in 1,2-dimethoxyethane (DME). The purpose of this investigation was to test whether the compounds **8** and **9**[9] exhibit a behavior analogous to the one displayed by their benzene counterparts **1** and **2**.



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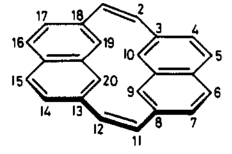

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Results and Discussion

[2.2](2,7)Naphthalenophane (8). Short contact of **8** with a potassium mirror in DME yields a radical anion which exhibits a relatively complex ESR spectrum shown in Figure 1. The analysis of this spectrum in terms of five sets of four equivalent protons was achieved with the aid of the ENDOR method,[10] and the coupling constants thus determined served for the computer simulation of the ESR derivative curve also reproduced in Figure 1. The pertinent values are listed in Table I against the hyperfine data for the radical anion of 2,7-dimethylnaphthalene (**10**).[11] Comparison of these values with the halves of the corresponding numbers for $\mathbf{10}^{\cdot-}$ leaves no doubt that the spectrum in Figure 1 arises from the primary radical anion $\mathbf{8}^{\cdot-}$, where the π-spin population is equally distributed between the two naphthalene moieties. Consequently, the assignment of the α-proton[12] coupling constants, a_{H_μ}, made in Table I for $\mathbf{8}^{\cdot-}$ has been based on the similarity between the two sets of values. This procedure suffers from some uncertainty with respect to the coupling constants 1.04 and 0.83 G. Although the latter (0.83 G) compares more favorably with the value $a_{\mathrm{H}_\mu} = (\frac{1}{2})1.76$ G = 0.88 G, expected for the four equivalent α protons at the centers μ = 4, 7, 14, 17, assignment of the former (1.04 G) to these protons cannot be excluded. Either choice implies that the alternative value must be assigned to one of the two sets of fourequivalent methylene β protons[12] in $\mathbf{8}^{\cdot-}$. It is possible to relate the coupling constants, $a_{\mathrm{H}_{\bar\mu}}(\beta)$, of such β protons to the value, 2.16 G, of the methyl β protons in $\mathbf{10}^{\cdot-}$ by means of the well-known formula[13]

Table I. Coupling Constants, a_{H_μ} in G, of the Protons in the Radical Anions $\mathbf{8}\cdot^-$ and $\mathbf{10}\cdot^-$ (Halves of the Values for $\mathbf{10}\cdot^-$ Are Given in Parentheses)

$\mathbf{8}\cdot^-$		$\mathbf{10}\cdot^-$	
Center μ	a_{H_μ}[a]	μ	a_{H_μ}[b]
4,7,14,17	0.83 or 1.04	3,6	1.76 (0.88)
5,6,15,16	2.68	4,5	5.12 (2.56)
9,10,19,20	1.94	1,8	4.32 (2.16)
3,8,13,18[c]	1.04[d] or 0.83[d] 0.43[d]	2,7[c]	2.16[e] (1.08)

[a] This work; experimental error ±1%. [b] Reference 11. [c] Alkyl-substituted centers $\bar{\mu}$. [d] Coupling constants of four methylene β protons. [e] Coupling constants of six methyl β protons.

Table II. Experimental and Calculated Coupling Constants, a_{H_μ} in G, of the Protons in the Radical Anion $\mathbf{9}\cdot^-$

	a_{H_μ}		
Center μ	Expt[a]	HMO[b]	McLachlan[b,c]
1,2,11,12	0.87	−1.12	−1.08
4,7,14,17	0.32	−0.30	−0.08
5,6,15,16	1.08	−1.21	−1.30
9,10,19,20	3.07	−2.69	−3.63

[a] Observed values; experimental error ±1%. [b] Values calculated with k = 0.64 for the bonds 18–1, 2–3, 8–11, and 12–13; Q = −24 G. [c] λ = 1.0.

$$a_{H_{\bar{\mu}}}(\beta) = B\rho_{\bar{\mu}}\,\langle\cos^2\theta\rangle \qquad (1)$$

where θ denotes the dihedral angle between the $2p_z$ axis at the alkyl-substituted carbon π center $\bar{\mu}$ and the C–H(β) bond. The product $B\rho_{\bar{\mu}}$, of the parameter B and the π-spin population $\rho_{\bar{\mu}}$ at the center $\bar{\mu}$, amounts to $2a_{H_{\bar{\mu}}}(\beta)$ for β protons of a freely rotating methyl group, since then $\langle\cos^2\theta\rangle$ equals 0.5. Thus $B\rho_{\bar{\mu}}$ is 2(2.16) G for $\mathbf{10}\cdot^-$, and half of this value should be a suitable choice for the pertinent product in the case of $\mathbf{8}\cdot^-$. Insertion of $B\rho_{\bar{\mu}}$ = 2.16 G, together with the observed β proton coupling constants, $a_{H_{\bar{\mu}}}(\beta_1)$ = 1.04 or 0.83 G and $a_{H_{\bar{\mu}}}(\beta_2)$ = 0.43 G, yields θ_1 = 46 or 52° and θ_2 = 64° as estimates of the two dihedral angles between the $2p_z$ axis at a bridged π center ($\bar{\mu}$ = 3, 8, 13, 18) and the two nonequivalent C–H(β_1) and C–H(β_2) bonds in a methylene group of the radical anion $\mathbf{8}\cdot^-$. These estimates are judged reasonable from inspection of a molecular model[9] which mimics the geometry of *anti*-[2.2]metacyclophane (**1**) as established by x-ray structure determination.[14]

Further contact of the solution with potassium at −80 °C rapidly leads to disappearance of the ESR spectrum of $\mathbf{8}\cdot^-$, as expected for a ready uptake of a second electron by **8** and a facile formation of the dianion $\mathbf{8}^{2-}$ When at this stage the sample is left overnight, a new multiline spectrum appears which is identical with that of the radical anion of 2,7-dimethylnaphthalene (**10**).

[2.2](2,7)Naphthalenophane-1,11-diene (9). Reaction of **9** with potassium in DME immediately produces a radical anion which displays an intense well-resolved spectrum shown in Figure 2. This spectrum is readily analyzed in terms of four sets of four equivalent protons, as borne out by the computer-simulated derivative curve also reproduced in Figure 2. The coupling constants, a_{H_μ}, which have been confirmed by ENDOR studies,[10] are given in Table II, along with the values obtained by means of the McConnell equation[15]

$$a_{H_\mu} = Q\rho_\mu \qquad (2)$$

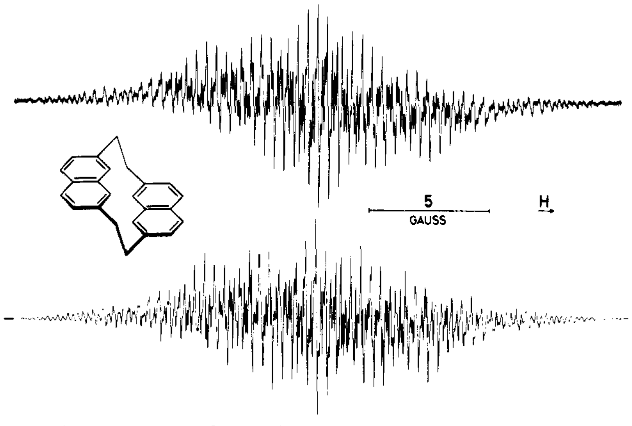


Figure 1. ESR spectra of the radical anion $\mathbf{8}\cdot^-$. Top: experimental spectrum; solvent, DME; counterion, K$^+$; temperature, −80 °C. Bottom: spectrum simulated by means of the proton coupling constants listed in Table I; line shape, Lorentzian; line width, 0.07 G.

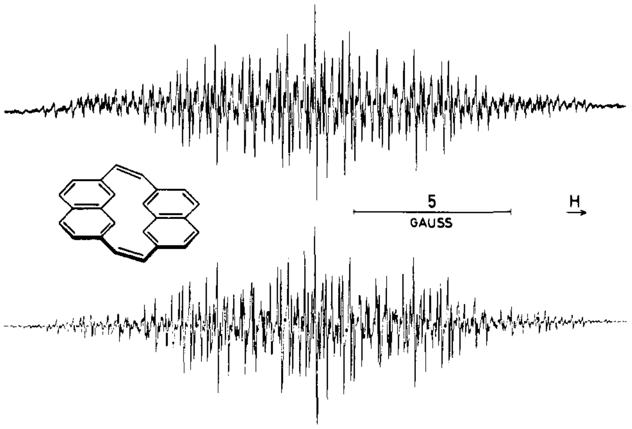


Figure 2. ESR spectra of the radical anion $\mathbf{9}\cdot^-$. Top: experimental spectrum; solvent, DME; counterion, K$^+$; temperature, −80 °C. Bottom: spectrum simulated by means of the proton coupling constants listed in Table II; line shape, Lorentzian; line width, 0.05 G.

where the parameter Q was taken as −24 G, and the π-spin populations ρ_μ at the carbon centers μ were calculated according to the HMO model of $\mathbf{9}\cdot^-$ and the McLachlan procedure[16] (λ = 1.0). The nonplanarity of the π system was taken into account b modifying the standard HMO integral β of the four bonds which link the naphthalene and ethylene π systems. The adopted value $k\beta$ with k = 0.64 corresponds to a twisting angle ϕ of 50° between the $2p_z$ axes at the two carbon π centers in question (18–1, 2–3, 8–11, 12–13)[9] if the relation[17a] k = cos ϕ is applied. It should, however, be noted that the computed π-spin populations ρ_μ are only moderately sensitive to variations of the parameter k in the range 0.8 to 0.5, and thus the crudeness of the model does not warrant any preference for a particular value of ϕ between 40 and 60°.

The good correlation between the observed and calculated α-proton coupling constants, a_{H_μ}, ascertains that the ESR spectrum in Figure 2 stems from the primary radical anion $\mathbf{9}\cdot^-$. As is evident from Table II, use has been made of this correlation to assign the experimental data to the four sets of four equivalent α protons. Whereas the assignment of the largest (3.07 G) and the smallest (0.32 G) coupling constants to the protons at the centers μ = 9, 10, 19, 20, and 4, 7, 14, 17, respectively, is well secured, there is some ambiguity with respect to the two remaining medium-size values of similar magnitude (1.08 and 0.87 G). This ambiguity is removed by a study of the radical anion produced from 1,11-dideuterio[2.2](2,7)-naphthalenophane-1,11-diene (**9**-d_2), which has been pre-

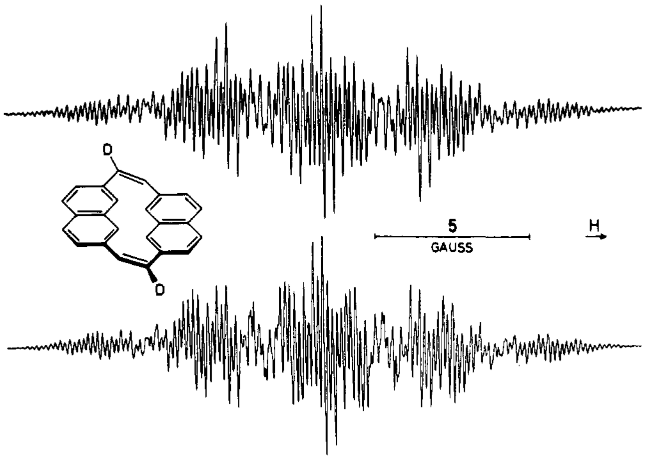


Figure 3. ESR spectra of the radical anion $\mathbf{9}$-$d_2^{\cdot-}$. Top: experimental spectrum; solvent, DME; counterion, K$^+$; temperature, −80 °C. Bottom: spectrum simulated by means of the coupling constants listed in Table II, with the exception of the value $a_{H_\mu} = 0.87$ G for two protons, which was replaced by $a_{D_\mu} = 0.135$ G for two deuterons; line shape, Lorentzian; line width, 0.07 G.

viously synthesized along with the parent compound **9**.[8b,18] Comparison of the ENDOR spectra of $\mathbf{9}^{\cdot-}$ and $\mathbf{9}$-$d_2^{\cdot-}$ proves unequivocally that the coupling constant of 0.87 G must be assigned to the protons at the centers 1, 2, 11, 12, leaving the value of 1.08 G to the protons at μ = 5, 6, 15, 16. Figure 3 shows the ESR spectrum of $\mathbf{9}$-$d_2^{\cdot-}$, as well as its computer simulation which made use of the coupling constant a_{D_μ} = 0.135 G for two deuterons instead of the value a_{H_μ} = 0.87 G for two protons.

Upon standing of the DME solution over potassium mirror at −80 °C, the spectrum of $\mathbf{9}^{\cdot-}$ (Figure 2) gradually decreases in intensity, presumably due to formation of the dianion $\mathbf{9}^{2-}$. When, however, the contact with alkali metal is interrupted, new ESR signals develop, and the spectrum shown in Figure 4A can be observed. This spectrum arises from three paramagnetic species which differ distinctly in their g values. One of them ($g = 2.00273 \pm 0.00002$) is presumably the primary radical anion $\mathbf{9}^{\cdot-}$ present in low concentration. Its contribution to the spectrum of Figure 4A is revealed only in the regions where the absorption by the two remaining species is weak. The pertinent features (marked by dots) resemble those observed for $\mathbf{9}^{\cdot-}$ under a resolution which is less good than the one achieved in the spectrum of Figure 2. The second species ($g = 2.00305 \pm 0.00003$) exhibits broad hyperfine components spaced by 1.47 G. It is readily identified as the radical anion of coronene (**11**) by comparison with the spectrum obtained directly from **11** upon reduction with K in DME.[19] The radical anion $\mathbf{11}^{\cdot-}$ is mainly responsible for the central part of the spectrum where its absorption overlaps with the hyperfine lines of $\mathbf{9}^{\cdot-}$ and those of the third species ($g = 2.00265 \pm 0.00002$). This species, which will be characterized in the next section as the radical anion of *trans*-12b,12c-dihydrocoronene (**12**), has a half-life of only 20 min at −80 °C and converts completely into $\mathbf{11}^{\cdot-}$. The final spectrum, which stems exclusively from the latter radical anion ($\mathbf{11}^{\cdot-}$), is shown in Figure 4C, whereas Figure 4B reproduces the computer-simulated derivative curve for $\mathbf{12}^{\cdot-}$.

***trans*-12b,12c-Dihydrocoronene (12).** In contrast to the radical anion of coronene (**11**), its transient attendant in the spectrum of Figure 4A displays a complex multiline hyperfine pattern extending over a range of 50 G. The most striking feature of this pattern, due to seven pairs of equivalent protons (Figure 4B), is a very large 1:2:1 splitting of 17.25 ± 0.05 G. A splitting of such magnitude, as well as the next largest coupling constant, 5.79 ± 0.04 G, is reminiscent of the values 19.10 and 5.48 G found for two pairs of equivalent β and α protons,[12] respectively, in the radical anion of *trans*-10b,10c-dihydropyrene (**4**) (cf. Scheme I).[5] This similarity justifies the identification of the transient species under consideration as the radical anion of *trans*-12b,12c-dihydrocoronene (**12**), a compound which, to our knowledge, has not yet been synthesized. Figure 5 illustrates the close correspondence of the two major coupling constants for $\mathbf{12}^{\cdot-}$ and $\mathbf{4}^{\cdot-}$, and substantiates the respective assignments of 17.25 and 5.79 G to the pertinent pairs of β and α protons in $\mathbf{12}^{\cdot-}$. The a_{H_μ} values for the remaining α protons in $\mathbf{12}^{\cdot-}$ are all of considerably smaller

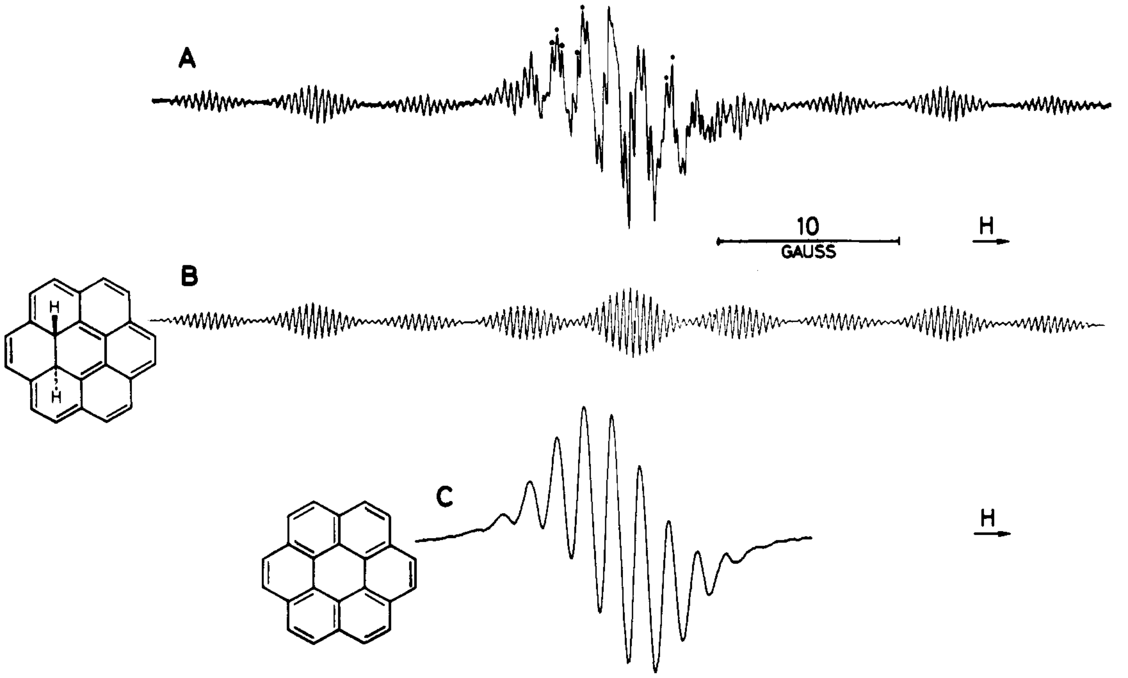


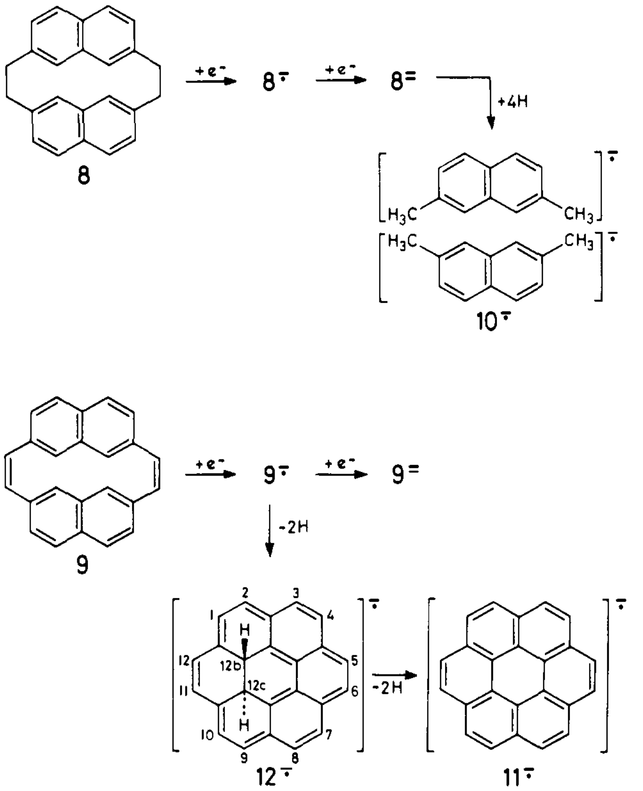
Figure 4. ESR spectra of the radical anions $\mathbf{11}^{\cdot-}$ and $\mathbf{12}^{\cdot-}$. (A) Experimental spectrum of a mixture containing $\mathbf{9}^{\cdot-}$ (hyperfine lines marked by dots), $\mathbf{11}^{\cdot-}$, and $\mathbf{12}^{\cdot-}$; solvent, DME; counterion, K$^+$; temperature, −80 °C. (B) Spectrum of $\mathbf{12}^{\cdot-}$ simulated by means of the coupling constants given in Figure 5; line shape, Lorentzian; line width, 0.10 G. (C) Experimental spectrum of $\mathbf{11}^{\cdot-}$ taken under the same conditions as A.

magnitude ($\leq$1 G) and their assignment in Figure 5 is less secure. It has been based on correlation with the proton coupling constants calculated for a model radical anion **13**$^{\bullet-}$ by means of the McLachlan procedure (λ = 1.0) and the McConnell equation (eq 2, $Q = -24$ G). The general agreement between the a_{H_μ} values observed for **12**$^{\bullet-}$ and those predicted for **13**$^{\bullet-}$ (Figure 5) supports the description of **12** as a bridged [14]annulene (represented by the dihydropyrene **4**) which is fused to a phenanthrene π system.

Concluding Remarks

Scheme II rationalizes the results obtained by means of ESR spectroscopy for the reactions of [2.2](2,7)naphthalenophane (**8**) and its 1,11-diene (**9**) with potassium in DME. Comparison of these results with those reported previously for the corresponding reactions of *anti*-[2.2]metacyclophane (**1**) and its 1,9-diene (**2**), respectively (Scheme I), points to substantial differences in the two series.

Scheme II



First of all, the strikingly different stability of the primary radical anions should be noted. In contrast to **1**$^{\bullet-}$ and **2**$^{\bullet-}$, the lifetime of which is too short for an ESR study, **8**$^{\bullet-}$ and **9**$^{\bullet-}$ are sufficiently long-lived for a full characterization. The higher stability of the latter pair as compared to the former is readily explained in terms of both thermodynamic and kinetic arguments. Not only are the electron affinities of **8** and **9** greatly superior to those of **1** and **2**, respectively, but also conversion of **8**$^{\bullet-}$ and **9**$^{\bullet-}$ into heptacyclic radical anions is less favored than the corresponding cyclization of **1**$^{\bullet-}$ and **2**$^{\bullet-}$ (Scheme I). Whereas such reactions imply the formation of two C-C bonds between the aromatic moieties of the naphthalenophanes, only one C-C bond has to be formed between the benzene rings of the metacyclophanes.

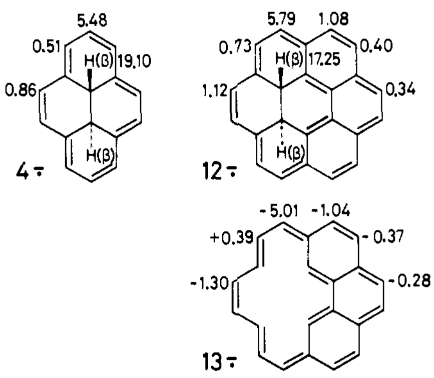
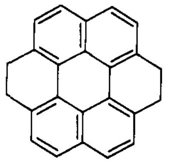


Figure 5. Proton coupling constants, in G, observed for the radical anions **4**$^{\bullet-}$ and **12**$^{\bullet-}$, and calculated for the model species **13**$^{\bullet-}$ with the aid of the McLachlan procedure (λ = 1.0; $Q = -24$ G). The assignment of the minor values ($\leq$ 1 G) for **12**$^{\bullet-}$ is uncertain.

Interestingly, no heptacyclic species such as the radical anion of 5,6,11,12-tetrahydrocoronene (**14**) could be detected when the decay of **8**$^{\bullet-}$ was followed by ESR spectroscopy,[20] although the formation of this radical anion might have been expected in analogy to the conversion of **1**$^{\bullet-}$ into the radical anion of 4,5,9,10-tetrahydropyrene (**3**). The facile uptake of a second electron by **8**$^{\bullet-}$ to form the dianion **8**$^{2-}$ is certainly due to the presence of two nonconjugated naphthalene moieties so that each of the two additional electrons can be essentially localized in one π system. The electrostatic repulsion of the two negative charges should be one of the driving forces for the scission of **8**$^{2-}$ into two negatively charged 2,7-dimethylenenaphthalene fragments (**15**$^{\bullet-}$), which subsequently take up four hydrogen atoms to yield two radical anions **10**$^{\bullet-}$.[21] Moreover, simple π-electron models indicate that formation of the two fragments **15**$^{\bullet-}$ from **8**$^{2-}$ is favored relative to the analogous conversion of the neutral compound **8** into two biradicals **15**$^{\bullet\bullet}$, since the orbitals occupied by the additional electrons are *anti*bonding in **8**, but *non*bonding in **15**$^{\bullet\bullet}$.



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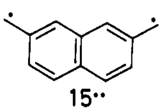

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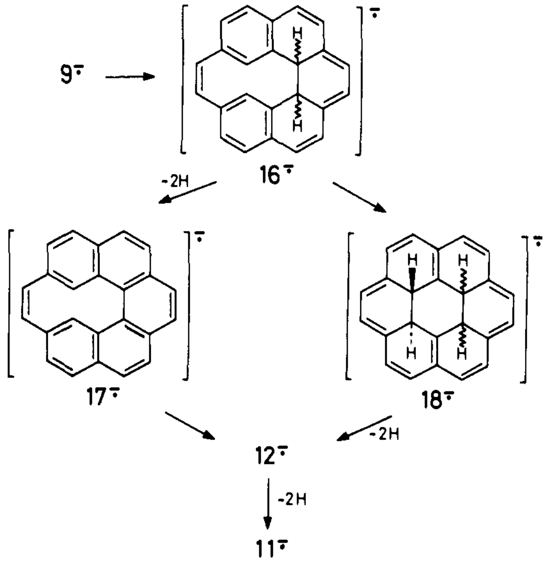
In contrast to **8**, its 1,11-diene **9** does yield heptacyclic radical anions as secondary products. The radical anions of *trans*-12b,12c-dihydrocoronene (**12**) and coronene (**11**), which have been identified by their ESR spectra, can be considered as the counterparts of the radical anions of *trans*-10b,10c-dihydropyrene (**4**) and pyrene (**5**), respectively, observed upon reaction of **2** with potassium in DME. As formulated in Scheme III, the conversion of **9**$^{\bullet-}$ to **12**$^{\bullet-}$ should proceed via

Scheme III



the intermediary radical anions **16**$^{\bullet -}$ and **17**$^{\bullet -}$ or **16**$^{\bullet -}$ and **18**$^{\bullet -}$ which are too short-lived to be detected by ESR spectroscopy.[24]

It is noteworthy that coronene (**11**) is formed upon UV irradiation of **9**.[8b] Since one expects that molecules in their excited states should undergo reactions similar to those of the corresponding radical anions, an analogous scheme, **9** → **16** → **17** → **12** → **11**, or **9** → **16** → **18** → **12** → **11**, can be envisaged. The identification of **12**$^{\bullet -}$ by ESR spectroscopy may thus be taken as an indication of the transient occurrence of **12** in the UV induced formation of **11** from **9**.

Finally it should be mentioned that polarographic data of **8** and **9**[26] are consistent with Scheme II. Thus **8** exhibits a half-wave reduction potential only at −2.53 V, i.e., in the range (−2.5 to −2.6 V) expected for dimethyl derivatives of naphthalene such as **10**.[17b] On the other hand, in the case of **9**, two half-waves are observed at a considerably less negative voltage. The first one, at −1.73 V, is due to the reduction of **9**, and presumably also of **12**, since the latter compound should have substantially higher electron affinity than the former. The second half-wave is readily identified by its value of −2.04 V as arising from the reduction of coronene (**11**).[17b]

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(9) Although the geometries of **8** and **9** are still unknown, it is reasonable to assume that the two naphthalene fragments have an anti-like arrangement in both compounds.

(10) The ENDOR studies reported in this paper were carried out at −90 °C on the same solutions as the corresponding ESR investigations. The apparatus used was VARIAN-E-1700-ENDOR system linked to a VARIAN-E-9 spectrometer.

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(12) In ESR spectroscopy, a proton directly bound to a π center is denoted α, in contrast to a β proton which is separated by one sp^3-hybridized carbon atom from such a center.

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(18) The possibility that the two deuterium atoms in **9**-d_2 are in the 1,12-, instead of 1,11-positions, cannot be completely excluded.[8b] However, in view of the equivalence of the centers 1, 2, 11, 12 in **9**$^{\bullet -}$, this uncertainty does by no means affect the conclusions drawn with respect to the assignment of the proton coupling constants for this radical anion.

(19) See also E. de Boer and S. I. Weissman, *J. Am. Chem. Soc.*, **80**, 4549 (1958); J. R. Bolton, as quoted by I. C. Lewis and L. S. Singer, *J. Chem. Phys.*, **43**, 2712 (1965).

(20) Since 14, an alkyl derivative of perylene, should have a higher electron affinity than 2,7-dimethylnaphthalene (**10**), the ESR spectrum of the radical anion **14**$^{\bullet -}$ would have been observed even at low concentration of **14**.

(21) An analogous reaction occurs upon reduction of the isomeric *anti*-[2.2]-(1,4)naphthalenophane with K in DME,[22] where two radical anions of 1,4-dimethylnaphthalene are obtained as the final paramagnetic product. The ESR spectrum of this secondary species was erroneously attributed[23] to the primary radical anion.

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(24) Since contact with an alkali metal mirror can effect dehydrogenation, the reduction of **9** was also performed by the technique of solvated electrons,[5,25] which allows one to avoid a direct exposure of the compound to the metallic surface. The results achieved by this technique were similar to those reported in the present paper and obtained by reacting **9** with potassium in a straightforward way. In particular, the radical anion **18**$^{\bullet -}$ could not be detected either.

(25) F. Gerson, G. Moshuk, and M. Schwyzer, *Helv. Chim. Acta*, **54**, 361 (1971).

(26) The polarographic reduction of **8** and **9** was performed by the use of *N,N*-dimethylformamide and tetra-*n*-butylammonium bromide as the solvent and supporting salt, respectively. All half-wave potentials refer to the saturated calomel electrode as standard.