202. The Radical Anions and Trianions of 1,8-Diphenylnaphthalene and of Some of its Derivatives Containing a Cyclophane Substructure[1])

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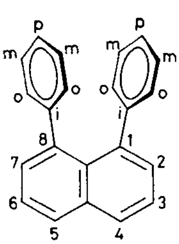
The radical anions of 1,8-diphenylnaphthalene (**1**) and its decadeuterio-(D_{10}-**1**) and dimethyl-(**2**) derivatives, as well as those of [2.0.0] (1,4)benzeno(1,8)naphthaleno(1,4)benzenophane (**3**) and its olefinic analogue (**4**) have been studied by ESR and ENDOR spectroscopy. At a variance with a previous report, the spin population in $\mathbf{1}^{\cdot-}$ and $\mathbf{2}^{\cdot-}$ is to a great extent localized in the naphthalene moiety. A similar spin distribution is found for $\mathbf{3}^{\cdot-}$ and $\mathbf{4}^{\cdot-}$. The ground conformations of $\mathbf{1}^{\cdot-}$– $\mathbf{4}^{\cdot-}$ are chiral of C_2 symmetry. For $\mathbf{1}^{\cdot-}$, an energy barrier between these conformations and the angle of twist about the bonds linking the naphthalene moiety with the phenyl substituents were estimated as *ca.* 50 kJ/mol and *ca.* 45°, respectively. The radical trianions of **1**, D_{10}-**1**, and **2** have also been characterized by their hyperfine data. In $\mathbf{1}^{3\cdot-}$ and $\mathbf{2}^{3\cdot-}$, the bulk of the spin population resides in the two benzene rings so that these radical trianions can be regarded as the radical anions of 'open-chain cyclophanes' with a fused naphthalene π-system bearing almost two negative charges. The main features of the spin distribution in both $\mathbf{1}^{\cdot-}$ and $\mathbf{1}^{3\cdot-}$ are correctly predicted by an HMO model of **1**.

Introduction. – Due to its peculiar geometry, 1,8-diphenylnaphthalene (**1**) [2] can be considered as embracing both naphthalene and cyclophane substructures. This description applies even more strictly to [2.0.0](1,4)benzeno(1,8)naphthaleno(1,4)benzenophane (**3**) and its monoene **4** [3] in which the *para*-positions of the Ph substituents of **1** are bridged by an ethano and an etheno group, respectively. In [1], we have recently reported the hyperfine data for the radical anion of **1**, as well as for those of 1,8-bis(perdeuteriophenyl)- (D_{10}-**1**) and 1,8-bis(*p*-tolyl)naphthalene (**2**). The advanced publication of these



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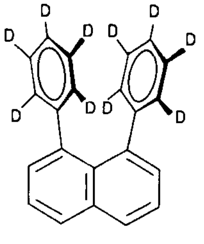
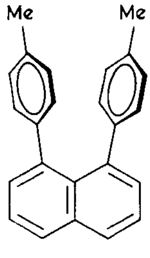


D_{10}-**1**



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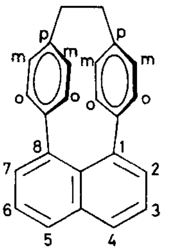

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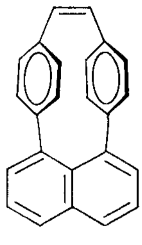
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data aimed at rectifying previous results given by other workers [4] who were led to erroneous conclusions from an incomplete analysis of the ENDOR spectra. In the present paper, we describe the ESR and ENDOR studies of $\mathbf{1}^{\cdot-}$, D_{10}-$\mathbf{1}^{\cdot-}$, and $\mathbf{2}^{\cdot-}$ in full detail, along with analogous investigations of the radical trianions $\mathbf{1}^{3\cdot-}$, D_{10}-$\mathbf{1}^{3\cdot-}$, and $\mathbf{2}^{3\cdot-}$. Also dealt with are the radical anions $\mathbf{3}^{\cdot-}$ and $\mathbf{4}^{\cdot-}$.

Experimental. – The compounds **1**, D_{10}-**1**, and **2** were prepared according to procedures reported by *Clough et al.* [5]. The synthesis of **3** and **4** was described in [3].

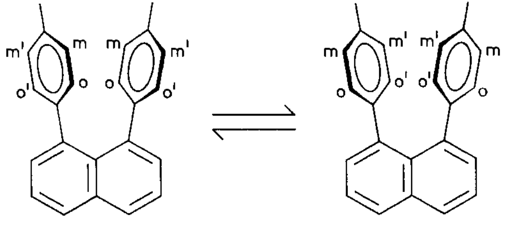
The radical anions $\mathbf{1}^{\cdot-}$, D_{10}-$\mathbf{1}^{\cdot-}$, $\mathbf{2}^{\cdot-}$, $\mathbf{3}^{\cdot-}$, and $\mathbf{4}^{\cdot-}$ were generated from the corresponding neutral compounds by reaction with K in 1,2-dimethoxyethane (DME). They were persistent at temp. up to 293 K, except for $\mathbf{4}^{\cdot-}$ which gradually converted into $\mathbf{3}^{\cdot-}$. Such a conversion is brought about by a formal uptake of two protons and two electrons and must be attributed to traces of protic impurities in the solns. It is fully analogous to formation of the radical anion of [2.2]paracyclophane from that of its 1-monoene or 1,9-diene [6].

Prolonged contact of the solns. with the metal mirror yielded the dianions, $\mathbf{1}^{2-}$, D_{10}-$\mathbf{1}^{2-}$, $\mathbf{2}^{2-}$, $\mathbf{3}^{2-}$, and $\mathbf{4}^{2-}$, as indicated by disappearance of the ESR spectra of the radical anions. In the case of $\mathbf{1}^{2-}$, D_{10}-$\mathbf{1}^{2-}$, and $\mathbf{2}^{2-}$, further reaction of the dianions with K led to the corresponding, fairly persistent radical trianions, $\mathbf{1}^{3\cdot-}$, D_{10}-$\mathbf{1}^{3\cdot-}$, and $\mathbf{2}^{3\cdot-}$; these were identified by their ESR and ENDOR spectra, as well as by their behaviour in electron transfer reactions (see *Results*). On the other hand, new paramagnetic species could not be detected by ESR spectroscopy upon exhaustive reduction of $\mathbf{3}^{2-}$ and $\mathbf{4}^{2-}$.

The ESR studies of the radical anions and the radical trianions were conducted in the range of 183 to 293 K, while the ENDOR technique could be successfully applied only at temp. below 213 K. The instrument employed was a *Varian-ESR-E9* spectrometer coupled to a *Varian-ENDOR-1700* system. The photolytic apparatus used in the irradiation experiments on the radical trianions consisted of a high-pressure Hg-lamp *(Philips 1000 W)* of which the short wave emission (λ < 330 nm) was cut off by the *Pyrex* glass of the sample tubes [7].

Results. – *Radical Anions. Fig. 1* shows the ESR and proton-ENDOR spectra of $\mathbf{1}^{\cdot-}$, D_{10}-$\mathbf{1}^{\cdot-}$, and $\mathbf{2}^{\cdot-}$ at 193 K; those of $\mathbf{3}^{\cdot-}$ and $\mathbf{4}^{\cdot-}$, taken under the same conditions, are displayed in *Fig. 2*. *Table 1* gives the proton coupling constants obtained by a computer-assisted analysis of the spectra. Assignments of these values to pairs of equivalent protons in $\mathbf{1}^{\cdot-}$ and $\mathbf{2}^{\cdot-}$ either follow from the effects of the D and Me substitution or are based on the MO model presented in the *Discussion*. For $\mathbf{3}^{\cdot-}$ and $\mathbf{4}^{\cdot-}$, such assignments rely largely on analogy with the hyperfine data of $\mathbf{1}^{\cdot-}$ and $\mathbf{2}^{\cdot-}$; they are supported by the dependence of the individual coupling constants on temperature (see below).

The finding that the protons in the four *ortho*-(*o*) and the four *meta*-(*m*) positions of $\mathbf{1}^{\cdot-}$ and $\mathbf{2}^{\cdot-}$ are only pairwise equivalent indicates that the interconversion between the two chiral conformations of C_2 symmetry is slow on the hyperfine time-scale at 193 K.



An analogous statement holds for the protons in corresponding positions of $\mathbf{3}^{\cdot-}$ and $\mathbf{4}^{\cdot-}$, also denoted as *ortho* and *meta*. It likewise applies to the four CH_2 protons in the ethano bridge of $\mathbf{3}^{\cdot-}$, these protons being only pairwise equivalent in the chiral conformation.

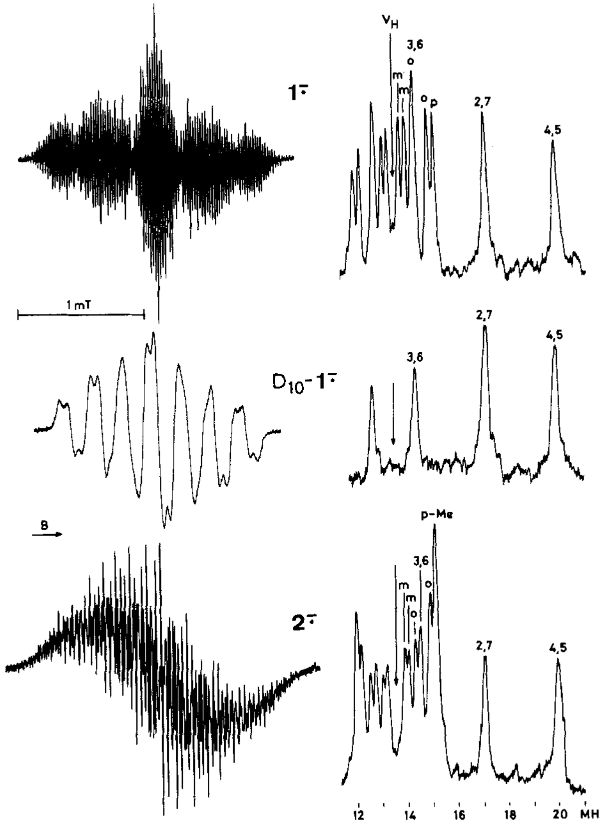


Fig. 1. *ESR and proton-ENDOR spectra of* $\mathbf{1}^{\cdot-}$, D_{10}-$\mathbf{1}^{\cdot-}$, *and* $\mathbf{2}^{\cdot-}$. Solvent: DME; counterion: K^+; temp.: 193 K.

Table 1. *Proton Coupling Constants* [mT] *and g Values for the Radical Anions* $\mathbf{1}^{\cdot-}$, $\mathbf{2}^{\cdot-}$, $\mathbf{3}^{\cdot-}$, *and* $\mathbf{4}^{\cdot-}$[a])

Position	$\mathbf{1}^{\cdot-}$	$\mathbf{2}^{\cdot-}$	$\mathbf{3}^{\cdot-}$	$\mathbf{4}^{\cdot-}$
2,7	0.261(2H)	0.250(2H)	0.243(2H)	0.273(2H)
3,6	0.060(2H)	0.070(2H)	0.065(2H)[c])	0.058(2H)
4,5	0.459(2H)	0.456(2H)	0.464(2H)	0.451(2H)
o	0.096(2H)[b]) 0.057(2H)[b])	0.098(2H) 0.057(2H)	0.081(2H)[c]) 0.065(2H)[c])	0.058(2H)[c]) 0.038(2H)[c])
m	0.035(2H)[b]) 0.019(2H)[b])	0.034(2H) 0.025(2H)	0.045(2H)[c]) 0.019(2H)[c])	0.038(2H)[c]) 0.019(2H)[c])
p	0.114(2H)[b])	0.113(6H)[d])	0.081(2H)[c])[e]) 0.065(2H)[c])[e])	0.196(2H)[f])
g value	2.0027	2.0026	2.0026	2.0026

[a]) Experimental errors: ±1% in coupling constants, ±0.0001 in g values. [b]) Replaced by deuterons in D_{10}-$\mathbf{1}^{\cdot-}$. [c]) Assignment uncertain. [d]) CH_3 protons. [e]) CH_2 protons. [f]) Olefinic protons.

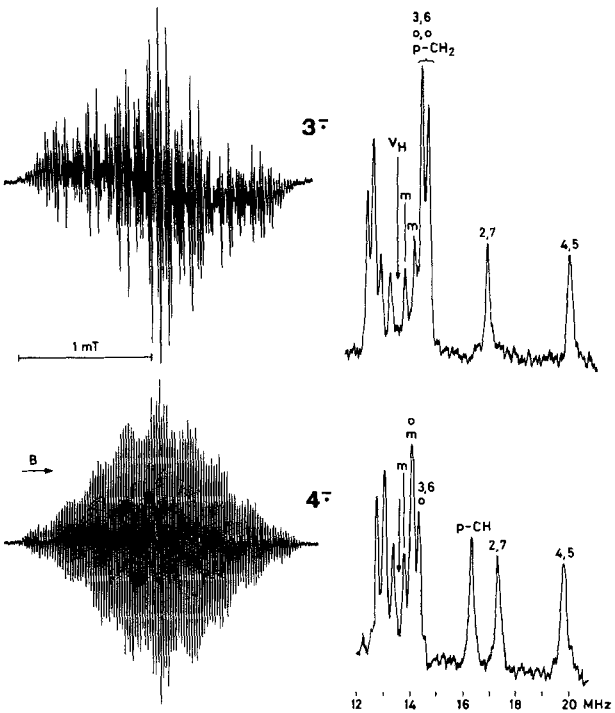


Fig. 2. *ESR and proton-ENDOR spectra of* $\mathbf{3}^{\cdot-}$ *and* $\mathbf{4}^{\cdot-}$. Solvent: DME; counterion: K^+; temp.: 193 K.

An increase in the rate of conformational interconversion is manifested by changes in the ESR spectra on raising the temperature from 193 to 293 K. Analysis of these changes in terms of a two-jump model [8] implies an exchange of the pertinent positions, *i.e.*, *ortho* $(o) \rightleftharpoons$ *ortho'* (o') and *meta* $(m) \rightleftharpoons$ *meta'* (m') for $\mathbf{1}^{\cdot-}$–$\mathbf{4}^{\cdot-}$, as well as *pseudo-axial* $\rightleftharpoons$ *pseudo-equatorial* for $\mathbf{3}^{\cdot-}$. The coupling constants involved in the exchange are those assigned to protons in these positions *(Table 1)*, a finding which provides an experimental support for the assignments in question. Precise evaluation of the thermodynamical parameters for the interconversion process [9] proved rather tedious. An *Arrhenius* plot was set up in the case of $\mathbf{1}^{\cdot-}$ and $\mathbf{3}^{\cdot-}$; it yielded the activation energies of 54 ± 6 and 33 ± 10 kJ/mol, respectively.

Radical Trianions. As stated in *Experimental,* exhaustive reduction of **1**, D_{10}-**1**, and **2** afforded the corresponding radical trianions $\mathbf{1}^{3\cdot-}$, D_{10}-$\mathbf{1}^{3\cdot-}$, and $\mathbf{2}^{3\cdot-}$. The reaction can be formulated as

$$\mathbf{1} \xrightarrow{+e^-} \mathbf{1}^{\cdot-} \xrightarrow{+e^-} \mathbf{1}^{2-} \xrightarrow{+e^-} \mathbf{1}^{3\cdot-}$$

for the parent compound **1** and analogously for its derivatives D_{10}-**1** and **2**. The identity of these radical trianions has been ascertained by their ESR and proton-ENDOR spectra taken at 193 K and shown in *Fig. 3*. The pertinent hyperfine data are listed for $\mathbf{1}^{3\cdot-}$ and $\mathbf{2}^{3\cdot-}$ in *Table 2*. They have been determined from the positions of the ENDOR signals and confirmed by the overall agreement between the poorly resolved ESR derivative curves and their computer simulations. Assignments of the coupling constants to pairs of

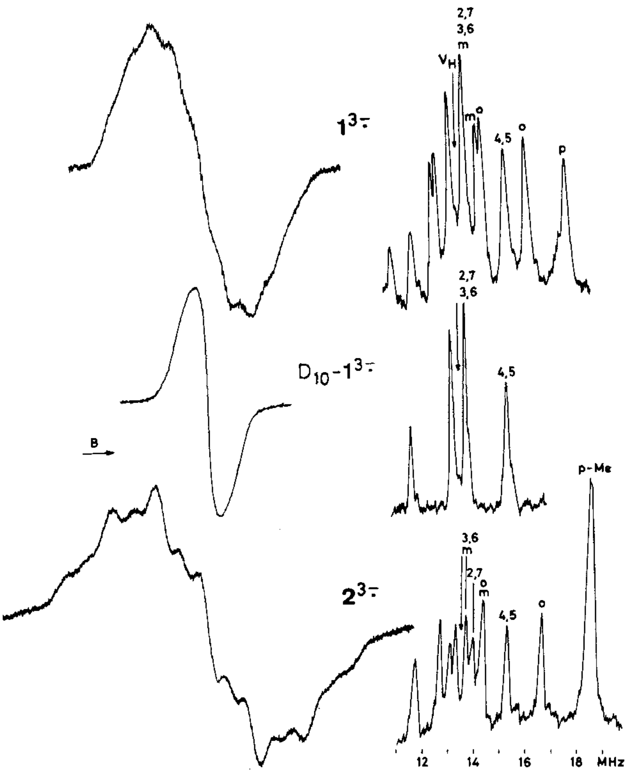


Fig. 3. *ESR and proton-ENDOR spectra of* $\mathbf{1}^{3\overline{\cdot}}$, D_{10}-$\mathbf{1}^{3\overline{\cdot}}$, and $\mathbf{2}^{3\overline{\cdot}}$. Solvent: DME; counterions: K^+; temp.: 193 K.

Table 2. *Proton Coupling Constants* [mT] *and g Values for the Radical Trianions* $\mathbf{1}^{3\overline{\cdot}}$ *and* $\mathbf{2}^{3\overline{\cdot}}$[a])

Position	$\mathbf{1}^{3\overline{\cdot}}$	$\mathbf{2}^{3\overline{\cdot}}$
2,7	0.021(2H)	0.034(2H)[d])
3,6	0.021(2H)	0.013(2H)[d])
4,5	0.130(2H)	0.129(2H)
o	0.189(2H)[b])	0.222(2H)
	0.070(2H)[b])	0.059(2H)
m	0.059(2H)[b])	0.059(2H)
	0.021(2H)[b])	0.013(2H)[d])
p	0.301(2H)[b])	0.355(6H)[c])
g value	2.0028	2.0028

[a]) Experimental errors: ±2% in coupling constants, ±0.0001 in g values. [b]) Replaced by deuterons in D_{10}-$\mathbf{1}^{3\overline{\cdot}}$. [c]) CH_3 protons. [d]) Assignment uncertain.

equivalent protons in $\mathbf{1}^{3\overline{\cdot}}$ and $\mathbf{2}^{3\overline{\cdot}}$ are based on arguments similar to the ones advanced in the case of $\mathbf{1}^{\overline{\cdot}}$ and $\mathbf{2}^{\overline{\cdot}}$.

In addition to the evidence provided by their hyperfine data, which are fully consistent with those predicted in terms of a simple MO model (see *Discussion*), the identity of $\mathbf{1}^{3\overline{\cdot}}$,

D_{10}-$\mathbf{1}^{3\cdot-}$, and $\mathbf{2}^{3\cdot-}$ has been corroborated by their reconversion into the corresponding radical anions. This reaction could be performed by both comproportionation and photooxidation, as represented for $\mathbf{1}^{3\cdot-}$ by

$$\mathbf{1}^{3\cdot-} + 2 \times \mathbf{1} \longrightarrow \mathbf{1}^{2-} + \mathbf{1}^{\cdot-} + \mathbf{1} \longrightarrow 3 \times \mathbf{1}^{\cdot-}$$

and

$$\mathbf{1}^{3\cdot-} \xrightarrow{h\nu;\,-\,e^-} \mathbf{1}^{2-} \xrightarrow{h\nu;\,-\,e^-} \mathbf{1}^{\cdot-},$$

respectively. Either process is readily monitored by ESR spectroscopy. *Fig. 4* displays the spectra observed upon irradiating a solution of D_{10}-$\mathbf{1}^{3\cdot-}$ in DME at 193 K (see *Experimental*). The gradual reconversion of D_{10}-$\mathbf{1}^{3\cdot-}$ into D_{10}-$\mathbf{1}^{\cdot-}$ is easily followed for these deuterated species, owing to the apparent simplicity of their hyperfine patterns. The photooxidative decay of D_{10}-$\mathbf{1}^{3\cdot-}$ seems to obey the first-order kinetics (half-life time of *ca.* 2.5 min).

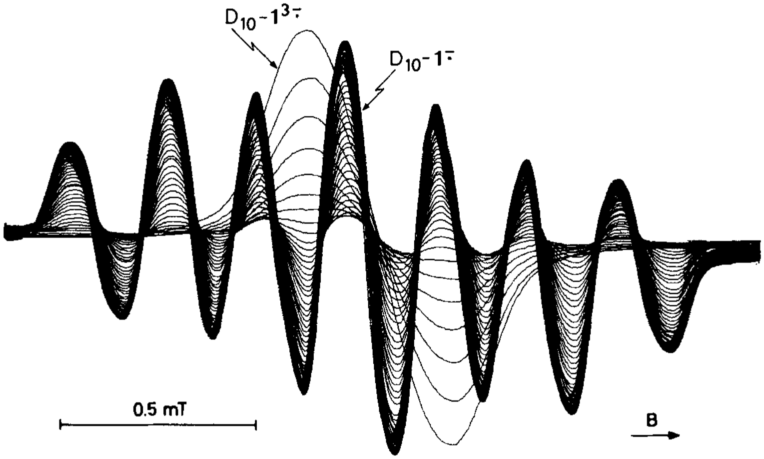


Fig. 4. *ESR spectra observed upon photooxidation of the radical trianion* D_{10}-$\mathbf{1}^{3\cdot-}$ *in DME at 193 K* (counterions: K^+). The consecutive derivative curves are recorded in time intervals of *ca.* 1 min.

The pairwise equivalence of the protons in the *o*- and *m*-positions of $\mathbf{1}^{3\cdot-}$ and $\mathbf{2}^{3\cdot-}$ points again to the chiral conformation of C_2 symmetry being frozen out on the hyperfine time-scale at 193 K. As in the case of the corresponding radical anions, the ESR spectra are temperature dependent, thus suggesting a change in the rate of conformational interconversion. A detailed analysis of these changes was not attempted, in view of the poorly resolved ESR spectra and the difficulty of performing ENDOR studies at higher temperatures.

Discussion. – *π-Spin Distribution in* $\mathbf{1}^{\cdot-}$ *and* $\mathbf{1}^{3\cdot-}$. *Fig. 5* depicts the lowest-unoccupied (LUMO) and the next lowest-unoccupied orbital (NLUMO) of 1,8-diphenylnaphthalene (**1**) in the HMO approximation. Use was made of standard parameters α and β, except for the bonds linking the naphthalene with the benzene π-systems; a reduced value of 0.7β for

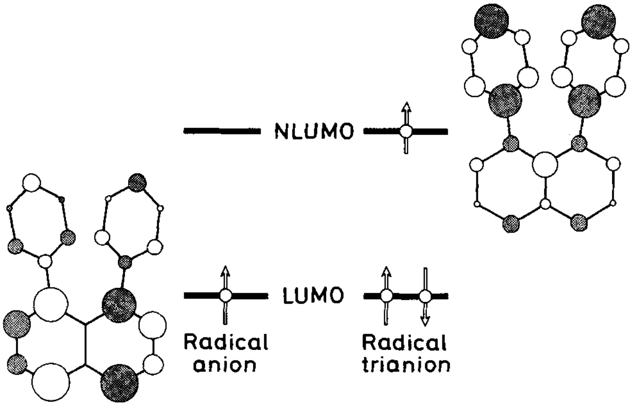


Fig. 5. *Diagrams of LUMO and NLUMO of 1,8-diphenylnaphthalene* (**1**) *and their occupancy in* $\mathbf{1}^{\cdot-}$ *and* $\mathbf{1}^{3\cdot-}$

Table 3. *Calculated and Experimental π-Spin Populations* ρ_μ *in* $\mathbf{1}^{\cdot-}$ *and* $\mathbf{1}^{3\cdot-}$

μ[a])	$\mathbf{1}^{\cdot-}$		$\mathbf{1}^{3\cdot-}$	
	Calc.	Exp.	Calc.	Exp.
1,8	+0.138	–	+0.012	–
2,7	+0.081	0.104	+0.018	0.011
3,6	+0.014	0.024	−0.014	0.011
4,5	+0.194	0.184	+0.027	0.065
4a	−0.032	–	+0.002	–
8a	−0.023	–	+0.085	–
i	+0.013	–	+0.147	–
o	+0.030	0.031[b])	+0.045	0.065[b])
m	−0.008	0.011[b])	+0.007	0.020[b])
p	+0.043	0.046	+0.163	0.151

[a]) Centre μ; *i* = *ipso* (see formula). [b]) Average value.

these bonds should account for the twist about them. The LUMO, which is singly occupied in $\mathbf{1}^{\cdot-}$, closely resembles the corresponding MO of naphthalene, aside from partial electron delocalization into the two Ph substituents. On the other hand, the NLUMO, representing the singly occupied orbital in $\mathbf{1}^{3\cdot-}$, can be regarded as a combination of two 'symmetric' benzene-LUMO's with some 'admixture' of the third lowest antibonding naphthalene MO [10].

Table 3 gives the π-spin populations ρ_μ calculated by the *McLachlan* procedure ($\lambda = 1.0$) [11] for the centres μ in $\mathbf{1}^{\cdot-}$ and $\mathbf{1}^{3\cdot-}$ with the single occupancy of the LUMO and NLUMO, respectively. The theoretical $|\rho_\mu|$ values for the proton-bearing centres compare favourably with their experimental counterparts (*Table 3*). These were obtained with use of the *McConnell* relationship, $a_{H_\mu} = Q\rho_\mu$ [12], in which a_{H_μ} are the observed coupling constants (*Table 1* and *2*) of the protons at the centres μ; the charge dependent parameter |Q| was taken as 2.5 mT for $\mathbf{1}^{\cdot-}$ and 2.0 mT for $\mathbf{1}^{3\cdot-}$.

According to both theory and experiment, nearly 80% of the spin population resides in the naphthalene moiety of $\mathbf{1}^{\cdot-}$. The corresponding value for $\mathbf{1}^{3\cdot-}$ is merely *ca.* 25%. Whereas $\mathbf{1}^{\cdot-}$ represents a naphthalene radical anion only slightly modified by a diphenyl substitution (at a variance with the conclusion drawn in [4]), $\mathbf{1}^{3-}$ can be regarded as an 'open-chain cyclophane' with a fused naphthalene-π-system bearing almost two negative charges. This interpretation is consistent with the first half-wave reduction potential of **1** (−2.3 V *vs.* SCE) which is close to that of naphthalene (−2.5 V), but which is less negative by 0.7 V than that of [2.2]paracyclophane (−3.0 V [13]).

Geometry of $\mathbf{1}^{\bar{\cdot}}$. In addition to mapping the spin distribution, the hyperfine data for $\mathbf{1}^{\bar{\cdot}}$ provide some information concerning the twist angle θ about the bonds which link the naphthalene moiety with each of the two approximately parallel Ph rings. According to an X-ray analysis, this angle should be about 70° in crystalline **1** [14]. It has been deduced from experimental findings for Ph-substituted π-radicals [15] that for twist angles of this size the coupling constants of the Ph protons in the *p*-, *o*-, and *m*-positions no longer exhibit the usual relationship, $|a_{H(p)}| \geqslant |a_{H(o)}| \gg |a_{H(m)}|$. As a consequence of the twisting, π–σ delocalization counteracts π–π conjugation, thus leading to a decrease in $|a_{H(o)}|$ and, particularly, in $|a_{H(p)}|$; the resulting relationship is then $|a_{H(p)}| < |a_{H(o)}| \approx |a_{H(m)}|$. It is obvious that this relationship, characteristic of large twist angles θ, does not hold for $\mathbf{1}^{\bar{\cdot}}$, since $|a_{H(p)}|$ is markedly larger than $|a_{H(o)}|$ and $|a_{H(m)}|$ *(Table 1)*. One must, therefore, conclude that for $\mathbf{1}^{\bar{\cdot}}$ in solution θ is considerably smaller than 70°. The good agreement between the experimental and theoretical π-spin populations $|\rho_\mu|$ in $\mathbf{1}^{\bar{\cdot}}$ *(Table 3)*, when 0.7β is used for the bonds linking the naphthalene moiety with the Ph substituents, suggests that θ might be about 40–50° ($\approx$ arc cos 0.7). A substantial conjugation across these bonds is also in line with the relatively high activation energy for the conformational interconversion in $\mathbf{1}^{\bar{\cdot}}$ (see *Results*). The transition state between the two equivalent chiral conformations should have C_{2v} symmetry with the benzene rings perpendicular to the plane of the naphthalene moiety. Thus, the activation barrier of *ca.* 50 kJ/mol is related to the decrease in the π-electron energy by inhibition of conjugation between the naphthalene and benzene π-systems. The HMO estimate of such a decrease is the difference in π-electron energies of $\mathbf{1}^{\bar{\cdot}}$ ($\theta \approx 45°$) and that of the radical anion of naphthalene plus two non-interacting benzene rings ($\theta = 90°$). This difference amounts to *ca.* 0.5β which is of the same order of magnitude as the observed activation barrier (a value $|\beta| \approx 70$ kJ/mol has been estimated from delocalization energies of aromatic systems [16]).

The reasons for the apparent discrepancy in the twist angle θ between the X-ray data for the crystalline 1,8-diphenylnaphthalene and the present finding for its radical anion in solution are not quite evident. The increase of *ca.* 0.05 in the order of the bonds linking the naphthalene moiety with the Ph substituents on passing from **1** to $\mathbf{1}^{\bar{\cdot}}$ (bond parameter 0.7β) is not sufficiently large to account for a substantial enhancement of π–π conjugation. In this context, it is noteworthy that a significant π–π delocalization between the naphthalene and benzene systems has been deduced from the electronic spectra of neutral **1** in solution [17]. Such a delocalization also plays an important role in the spectroscopic behaviour of 1,4,5,8-tetraphenylnaphthalene [18]. An X-ray analysis of this compound [18] suggests a value of 58° for the twist angle θ about the bonds linking the naphthalene moiety with each of the four benzene rings. Such a value lies between that indicated for $\mathbf{1}^{\bar{\cdot}}$ in solution (40–50°) and the one derived from an X-ray analysis of **1** (*ca.* 70°). One is thus left with two possible explanations for the large angle θ reported in [14]. An increase in θ relative to the value in solution could be brought about by the lattice forces in the crystal. Also, the angle θ might have been overestimated in the X-ray analysis.

Effect of Bridging. Introduction of Me groups in the *p*-positions of the Ph substituents of **1**, to yield **2**, is expected not to markedly influence the geometry and electronic structure. This expectation is borne out by the close similarity of the hyperfine data for $\mathbf{1}^{\cdot-}$ and $\mathbf{2}^{\cdot-}$ *(Table 1)* and also by the conformity of the analogous values for $\mathbf{1}^{3\cdot-}$ and $\mathbf{2}^{3\cdot-}$ *(Table 2)*. On the other hand, as has been shown by the X-ray analysis of crystalline **3** [19], bridging of the *p*-positions in **1**, to yield **3**, leads to substantial changes in geometry. In particular, the distance between the *p*-C-atoms is greatly reduced [19]. Although an X-ray analysis of **4** has not yet been performed, a similarity of the C-framework in **4** to that in **3** can be anticipated, by analogy to [2.2]paracyclophane [20] and its 1,9-diene [21]. Changes in geometry on passing from **1** and **2** to **3** and **4** should, thus, have an appreciable effect on the electronic structure of the two benzene rings in these compounds, but they are unlikely to cause a major spin redistribution in the radical anions, as the bulk of the spin population in $\mathbf{1}^{\cdot-}$ is localized in the naphthalene moiety. In fact, the two largest coupling constants assigned to protons in the naphthalene moiety of $\mathbf{3}^{\cdot-}$ (0.464 and 0.243 mT) and $\mathbf{4}^{\cdot-}$ (0.451 and 0.273 mT) are very similar to the analogous values for $\mathbf{1}^{\cdot-}$ (0.459 and 0.261 mT) and $\mathbf{2}^{\cdot-}$ (0.456 and 0.250 mT). The additional coupling constant of a substantial magnitude observed for $\mathbf{4}^{\cdot-}$ (0.196 mT) must arise from the two olefinic protons in the etheno bridge (a value of 0.422 mT was found for the corresponding protons in the radical anion of [2.2]paracyclophane-1,9-diene [6]). A more pronounced effect of bridging the *p*-C-atoms in **1** is expected for $\mathbf{3}^{3\cdot-}$ and $\mathbf{4}^{3\cdot-}$, since the spin population in $\mathbf{1}^{3\cdot-}$ resides to a large extent in the benzene rings. Unfortunately, because of the failure to observe the ESR spectra of $\mathbf{3}^{3\cdot-}$ and $\mathbf{4}^{3\cdot-}$, this effect could not be tested by experiment.

Conclusion. – The behaviour of 1,8-diphenylnaphthalene and its derivatives as electron acceptors complies fully with their molecular structure. On passing to the radical anion, the unpaired electron is taken up mainly by the naphthalene moiety, *i.e.*, that part of the molecule exhibiting the larger electron affinity. The same moiety also accomodates the second additional (paired) electron in the diamagnetic dianions. As a consequence of this charge distribution, formation of the radical trianions comes about by locating the third (unpaired) electron essentially in the two cyclophane-like benzene rings.

Note Added in Proof. – ^{1}H-NMR measurements on a derivative of **1** by H. O. House, W. J. Campbell, M. Gall, *J. Org. Chem.* **1970**, *35*, 1815 have yielded an activation energy (ΔG^{+}) of 67 kJ/mol for the *rotation* of a substituted Ph group. In the case of conformational interconversion of $\mathbf{1}^{\cdot-}$, the rotation cannot be separated from the *flipping* of the Ph groups. It is reasonable to expect that the flipping, which has been solely considered in the present paper, should require less energy than the rotation.

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