142. Long-Range Intramolecular Electron Transfer between Two Naphthalene π-Moieties Attached to a Rigid Norbornylogous Spacer of Variable Length: an ESR and ENDOR Study

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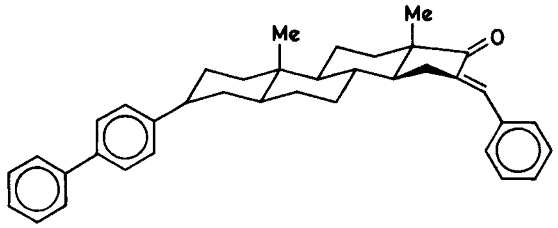
ESR, ENDOR, and TRIPLE-resonance studies are reported on the radical anions of **7(1,0)**, **7(2,0)**, and **7(1,1)** in which a completely rigid spacer separates two naphthalene π-moieties by 2, 4, and 6 C–C single bonds, respectively. Whereas $\mathbf{7(1,0)}^{\overline{\cdot}}$ has to be considered as a 'truly' charge- and spin-delocalized radical anion of a homobinaphthylene-like system, the frequency of intramolecular electron transfer in $\mathbf{7(2,0)}^{\overline{\cdot}}$ and $\mathbf{7(1,1)}^{\overline{\cdot}}$ is governed by the migration rate of the counterion (K^+) between two equivalent sites at the π-moieties. Under conditions of tight ion pairing (solvent 2-methyltetrahydrofuran), the unpaired electron in $\mathbf{7(2,0)}^{\overline{\cdot}}$ and $\mathbf{7(1,1)}^{\overline{\cdot}}$ is localized on one π-moiety and the pertinent spectra resemble that of the radical anion produced from an analogous mononaphthalene derivative **8**. On the other hand, with solvents of higher cation-solvating power (1,2-dimethoxyethane or its mixtures with *N,N,N',N',N'',N''*-hexamethylphosphoric triamide), delocalization of the electron spin over both π-moieties becomes evident, thus indicating that the electron-transfer rate exceeds the hyperfine time-scale (*ca.* 10^7 s^{-1}). Simultaneous occurrence of 'localized' and 'delocalized' radical anions is also observed, in particular for $\mathbf{7(1,1)}^{\overline{\cdot}}$. Previous findings for the radical anion of **6(1)** which, like $\mathbf{7(1,1)}^{\overline{\cdot}}$, contains two naphthalene π-moieties separated by 6 C–C single bonds are reinterpreted in the light of the results obtained in the present work. Exhaustive reduction of **7(2,0)** and **7(1,1)** leads to the formation of *triplet* dianions in which each of the two π-moieties houses one unpaired electron.

Introduction. – Recently, much experimental evidence has been gathered, demonstrating that both thermal and photoinduced electron transfer between a donor and an acceptor can occur over distances that are considerably greater than the sum of the donor and acceptor *van der Waals* radii. From the studies of this long-range electron transfer, a picture is emerging of how the transfer rate depends on such factors as the driving force, the solvent and vibrational reorganization energies, and, in particular, the distance and orientation of the donor and the acceptor [1]. The dependence of the transfer dynamics on the donor-acceptor distance and orientation can unambiguously be delineated when the donor and the acceptor are attached to a rigid spacer. Thus, in this respect, *intra*molecular electron transfer plays a pivotal role [2].

High rates (> 10^9s^{-1}) of intramolecular thermal electron transfer in donor-spacer-acceptor systems were determined from pulse radiolysis studies for the radical anions of **1** (donor = biphenyl radical anion, acceptor = cinnamoyl, spacer = steroid nucleus) and related compounds [3], and for those of even more rigid systems **2(m,n)** [4] with a variable length (donor = 1,4-dimethoxynaphthalene radical anion, acceptor = dicyanomethylidene, spacer = polynorbornyl/bicyclo[2.2.0]hexyl) [5]. These findings are remarkable, because the nearest edge-to-edge distance, relevant to the electron transfer between the donor and the acceptor, is *ca.* 1000 pm in **1**, and it is as much as 1350 pm in **2(1,2)** where the two moieties are separated by 12 C–C single bonds [6]. Comparably high rates were observed for a photoinduced intramolecular electron transfer in **2(m,n)** (donor = electronically excited *singlet* state of 1,4-dimethoxynaphthalene) [7]. Pulse-radiolysis studies of **3** [8] and other rigid donor-spacer-acceptor systems [9] have likewise shown that also a positive 'hole' can rapidly be transferred over large distances; *e.g.*, in **3** where the donor and acceptor are separated by 10 C–C single bonds, the transfer rate is higher than 10^8 s^{-1} [8].



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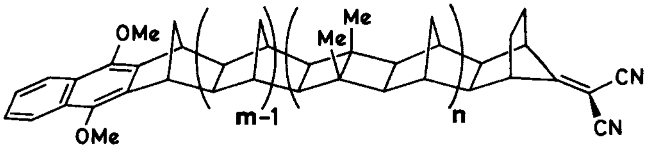
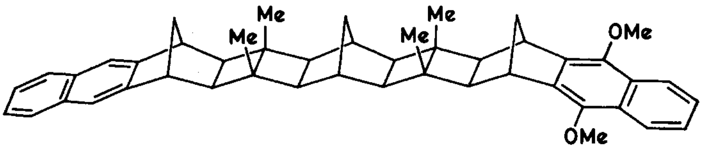


2(m,n)



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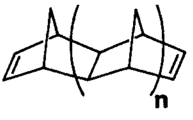

4(n)

The occurrence of surprisingly fast long-range intramolecular electron transfer in systems like **1**–**3** has been attributed [5][7][10][11] to a mechanism of through-bond coupling which mixes the orbitals of the donor and the acceptor with those of the intervening spacer [12][13][1]). In the case of **2(m,n)**, the notion of such a through-bond-mediated electron transfer is reinforced by photoelectron [15] and electron-transmission

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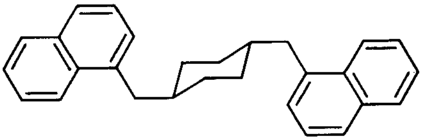
[1]) This mechanism was first suggested by *McConnell* [14] to account for the intramolecular electron transfer between the phenyl groups in more flexible radical anions of Ph–$(CH_2)_n$–Ph, especially for n = 1 and 2.

studies [16] on the dienes **4(n)** and the corresponding dibenzo analogues which contain spacers structurally similar to those in **2(m,n)**. Large π,π- and π^*,π^*-splitting energies of 0.32 [15b] and 0.25 eV [16], respectively, were observed for the diene **4(2)** in which the two ethene π-moieties are separated by 6 C–C single bonds. Considering the distance of *ca.* 700 pm between the two π-moieties in this diene, their through-space interaction should be negligible, and the observed splitting energies can only be due to the through-bond coupling of the ethene π-orbitals. In conjunction with the *Marcus* theory [17][18], these experimental energies (and analogous calculated values based on the *Koopmans'* theorem) [19] were used to estimate the transfer rates of a positive hole and an electron in $\mathbf{4(n)}^{\ddagger}$ and $\mathbf{4(n)}^{\bar{\cdot}}$, respectively [13][16][18][19]. Such estimates are noteworthy: for example, the electron transfer in $\mathbf{4(7)}^{\bar{\cdot}}$ could be as fast as 10^8 s^{-1}, even though the ethene π-moieties are *ca.* 1900 pm apart in this radical anion.

A tool of choice for investigating electron transfer in paramagnetic species is ESR (and ENDOR) spectroscopy, because the frequency of such a transfer often lies within the hyperfine time-scale (10^6 to 10^8 s^{-1}). Consequently, this technique has been extensively applied to studies of intramolecular electron-spin transfer in radical anions containing two equivalent π-moieties separated by a spacer [20–24]. One of these moieties, which houses the unpaired electron, functions as donor, while the other (neutral) is an acceptor. However, as emphasized previously [20–23][24a, b, e, f], special care must be paid in such studies to experimental conditions, in order to ensure that the observed frequency of spin transfer corresponds to the true intramolecular rate. Above all, solvents of high cation-solvating power should be used to avoid formation of tight ion pairs by the radical anion and its positively charged counterion; otherwise, the electron-transfer rate is determined by the slower migration of the counterion between two equivalent sites at the radical anion. Also, low concentrations are required for the neutral precursor of the radical anion (to eliminate *inter*molecular transfer processes) and the reduction should not be pushed too far (to minimize the formation of tight ion pairs and dianions)[21a][22][24a, b].

Two earlier ESR studies of electron-spin transfer are particularly pertinent to the work described herein. In one study, performed on the radical anion of **5**, the electron-transfer rate was *ca.* 10^8 s^{-1}, even though the nearest edge-to-edge distance between the naphthalene π-moieties in the relatively flexible molecule **5** is *ca.*700 pm [20b]. More systematic ESR and ENDOR studies on the distance dependence of intramolecular electron-spin transfer was subsequently carried out on the radical anions of **6(n)** [22].

In the molecules **6(n)**, which are considerably more rigid than **5**, the two naphthalene π-moieties are attached to a variable-length spacer constructed from **n** = 1, 3, and 5 spirocyclobutane rings, *i.e.*, they are separated by 6, 10, and 14 C–C single bonds, respectively. Whereas the electron transfer in $\mathbf{6(3)}^{\bar{\cdot}}$ and $\mathbf{6(5)}^{\bar{\cdot}}$ was slow on the hyperfine time-scale, regardless of the experimental conditions, the ESR and ENDOR spectra of $\mathbf{6(1)}^{\bar{\cdot}}$ in solvent of high cation-solvating power were consistent with the presence of two distinct radical anions, one exhibiting a *slow*, and the other a *fast* spin transfer. It has been proposed that the transfer process is slow in *anti*-$\mathbf{6(1)}^{\bar{\cdot}}$ and fast in *syn*-$\mathbf{6(1)}^{\bar{\cdot}}$, because the π-moieties are further apart in the former than in the latter. This proposal will be reconsidered in the light of the results obtained in the present work (see *Discussion*).



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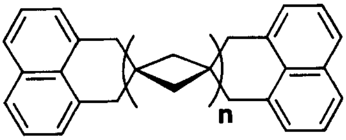
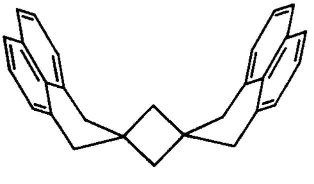
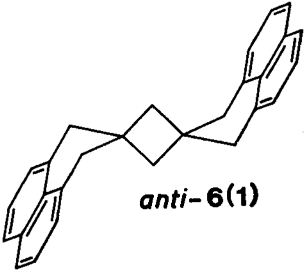


6(n)

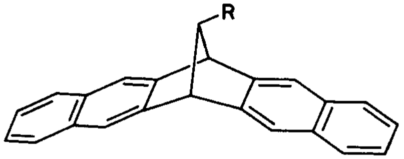


***syn*-6(1)**

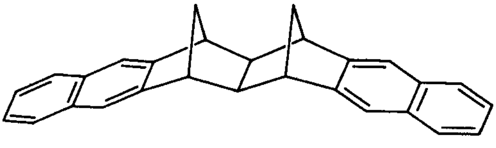


***anti*-6(1)**

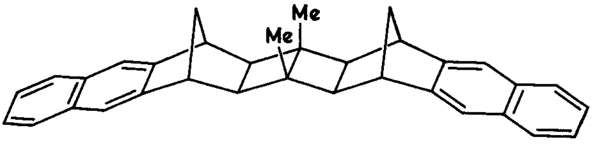
Here, we report on ESR and ENDOR studies of the radical anions and dianions in a series of norbornylogous systems **7(m,n)** [25] which, like **5** and **6(n)**, contain two equivalent naphthalene π-moieties. However, unlike **5** and **6(n)**, the spacer to which the two π-moieties are attached in **7(m,n)** is *completely rigid*. This spacer, of variable length, is closely related to that in the series **2(m,n)** and, consequently, the numbers **m** and **n** refer to



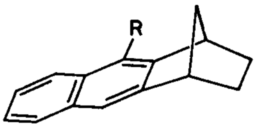
7(1,0) R=H
D-7(1,0) R=D



7(2,0)



7(1,1)



8 R=H
D-8 R=D

identical constituent groups. The three compounds dealt with in the present study are dinaphtho[2',3':2,3][2",3":5,6]bicyclo[2.2.1]hepta-2,5-diene (**7(1,0)**), dinaphtho[2',3':4,5]-[2",3":9,10]tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodeca-4,9-diene (**7(2,0)**), and 3,10-dimethyldinaphtho-[2',3':6,7][2",3":13,14]hexacyclo[10.2.1.1^{5,8}.0^{2,11}.0^{3,10}.0^{4,9}]hexadeca-6,13-diene (**7(1,1)**), in which the naphthalene π-moieties are separated by 2, 4, and 6 C–C single bonds, respectively. Included, as a reference species, is naphtho[2',3':2,3]bicyclo[2.2.1]hept-2-ene (**8**). For assignments of coupling constants, the deuterio derivatives D-**7(1,0)** and D-**8** have also been investigated.

As the spacer in **7(m,n)** is structurally similar to that in **4(n)**, the conclusions drawn from the experimental (electron-transmission spectroscopy) and calculated energies of **4(n)** for the electron transfer in the corresponding radical anions should also be meaningful for **7(m,n)**$^{\cdot-}$. Therefore, one may expect that, under appropriate conditions, an intramolecular electron transfer in **7(1,0)**$^{\cdot-}$, **7(2,0)**$^{\cdot-}$, and **7(1,1)**$^{\cdot-}$ will be sufficiently fast to be observed on the hyperfine time-scale.

Results. – *Radical Anions.* The compounds **7(1,0)**, D-**7(1,0)**, **7(2,0)**, **7(1,1)**, **8**, and D-**8** were reduced to their radical anions by K metal in 1,2-dimethoxyethane (DME) or 2-methyltetrahydrofuran (MTHF). In some experiments, *N,N,N',N',N",N"*-hexamethylphosphoric triamide (HMPT) was added to DME. All radical anions thus obtained were persistent below 293 K, so that ESR and ENDOR spectra could be taken up to this temperature. Optimal conditions for spectroscopic studies, in particular for those by the ENDOR technique, prevailed at *ca.* 203 K. The signs of the coupling constants were determined by general-TRIPLE resonance [26] combined with theoretical arguments. The g-factor of all radical anions was 2.0027±0.0001.

Naphthobicycloheptene **8**. *Fig. 1* shows the ESR and proton-ENDOR spectra of **8**$^{\cdot-}$ in DME. Assignments of the coupling constants derived therefrom to protons in individual positions (*Fig. 2*) have been based on comparison with structurally related radical anions, especially those of 2,3-dimethylnaphthalene (**9**) [27][28] and bicyclo[2.2.1]heptane-2,3-dione [29]. The assignment of –0.463 mT has been confirmed by the spectra of D-**8**$^{\cdot-}$, in which this value was due to one proton only and which exhibited an additional hyperfine interaction of –0.071 mT with one deuteron. Thus, in **8**$^{\cdot-}$, like in **9**$^{\cdot-}$, the two protons in the naphthalene *peri*-positions adjacent to the substituted C-atoms have the coupling constant with a smaller absolute value than those in the two more remote *peri*-positions (–0.483 mT), whereas an opposite relation holds for the radical anion of cyclobuta[*b*]naphthalene [28]. A second feature common to **8**$^{\cdot-}$ and **9**$^{\cdot-}$ is the similar dependence of the two coupling constants on temperature. For **8**$^{\cdot-}$, the difference in their absolute values increased from (0.483–0.463) mT = 0.020 mT at 203 K to (0.503–0.432) mT = 0.071 mT at 293 K. This effect was less pronounced with the use of MTHF instead of DME; otherwise only slight changes in the coupling constants were observed on passing from the latter to the former solvent.

Dinaphthobicycloheptadiene **7(1,0)**. ESR and proton-ENDOR spectra of **7(1,0)**$^{\cdot-}$ in DME are displayed in *Fig. 3*. The pertinent coupling constants stem from the protons in *both* naphthalene π-moieties, and they bear resemblance to the corresponding values for the radical anion of binaphthylene (**10**)[30]. This relation has served as a reliable guide for assigning the coupling constants to the protons in the π-moieties of **7(1,0)**$^{\cdot-}$ (*Fig. 2*). The

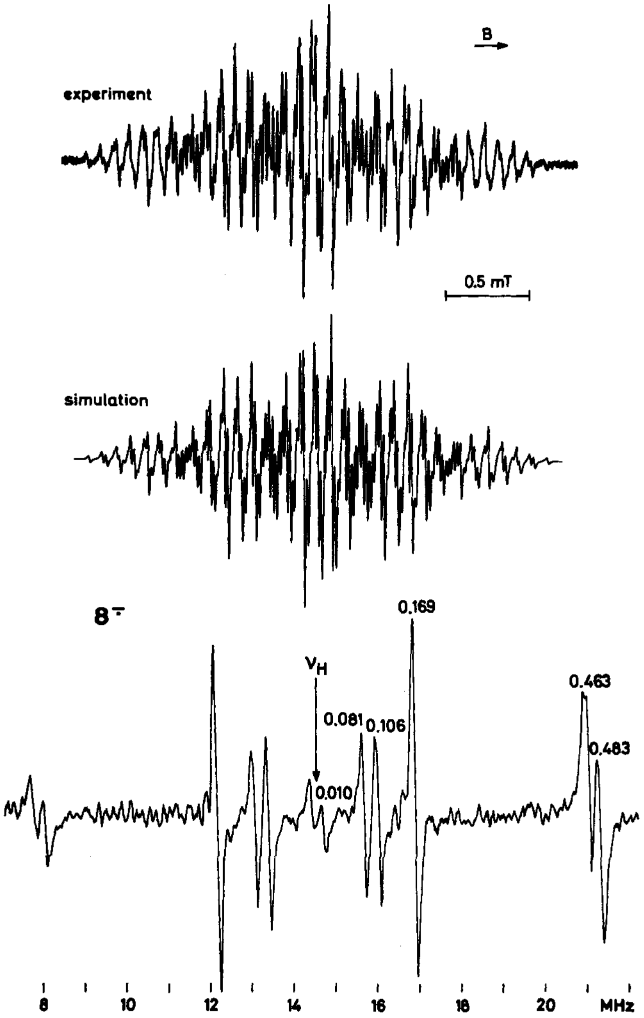


Fig. 1. *ESR* (top) *and proton-ENDOR spectra* (bottom) *of* **8**$^{\cdot -}$. Solvent: DME; counterion: K$^+$; temp.: 203 K. The numbers above the ENDOR signals refer to proton-coupling constants [mT] associated with them. The simulation made use of these values and their assignments to sets of equivalent protons as indicated for **8**$^{\cdot -}$ in *Fig.* 2; line-shape: *Lorentz*ian; line-width: 0.020 mT.

assignment of +0.133 mT to the two protons in the bridgehead positions of the norbornadiene unit (and not to those in the methano bridging group) has been based on the identity of the spectra of D-**7(1,0)**$^{\cdot -}$ and **7(1,0)**$^{\cdot -}$; the hyperfine splitting from the protons in the methano bridge is obviously too small to be detected either by ESR or ENDOR technique. Raising the temperature from 183 to 293 K had only a negligible effect on the coupling constants, as had the replacement of the solvent DME by MTHF.

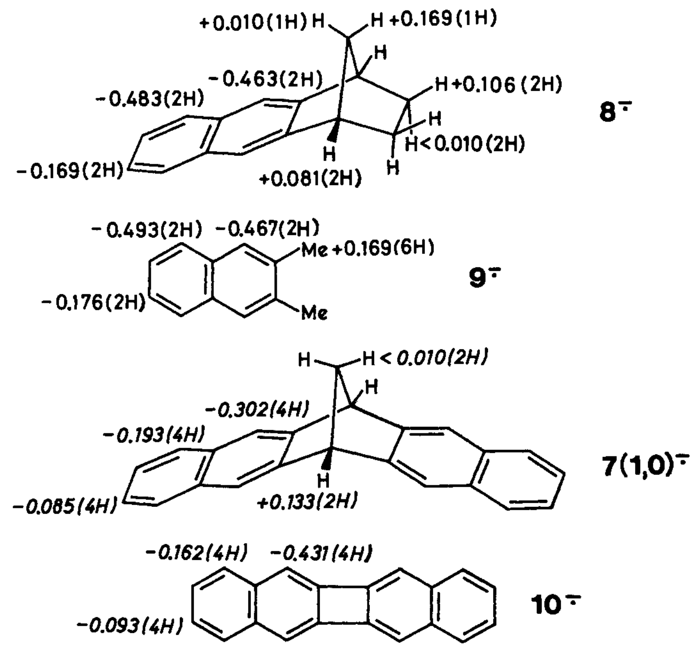


Fig. 2. *Assignments of coupling constants* [mT] *to protons in* $\mathbf{8}^{\cdot-}$ *and* $\mathbf{7(1,0)}^{\cdot-}$. Solvent: DME; counterion: K^+; temp.: 203 K. Experimental error in the coupling constants: ±0.002 and ±0.001 mT in (absolute) values larger and smaller than 0.2 mT, respectively. Corresponding data for $\mathbf{9}^{\cdot-}$ [27] and $\mathbf{10}^{\cdot-}$ [30] are given for comparison. Numbers in italics refer to protons interacting with two naphthalene π-moieties.

Dinaphthotetracyclododecadiene **7(2,0)**. Cautious reduction of **7(2,0)** in DME yielded the radical anion, of which the ESR and proton-ENDOR spectra are presented in *Fig. 4*. Although the ESR spectrum was barely resolved, the coupling constants could readily be determined from the positions of the ENDOR signals associated with them. These coupling constants are approximately *half as large* as the corresponding values for $\mathbf{8}^{\cdot-}$ and, in order to account for the total width of the ESR spectrum, they must belong to sets of *twice as many* equivalent protons (*Fig. 5*). The unpaired electron, thus, interacts with the protons in *both* naphthalene moieties, which is consistent with its *delocalization* over the entire system. This finding justifies the notation $\mathbf{7(2,0)}_{\mathrm{del}}^{\cdot-}$ for the radical anion in question.

Renewed contact of the DME solution with the potassium mirror led to gradual displacement of the ESR and ENDOR spectra of $\mathbf{7(2,0)}_{\mathrm{del}}^{\cdot-}$ by those exhibiting coupling constants very similar to the corresponding values for $\mathbf{8}^{\cdot-}$ and, thus, pointing to a hyperfine interaction with the protons in *only one* naphthalene π-moiety (*Fig. 5*). Because of the apparent spin *localization* on this moiety, the pertinent radical anion is denoted $\mathbf{7(2,0)}_{\mathrm{loc}}^{\cdot-}$. It is remarkable that the coupling constant of +0.018 mT observed for $\mathbf{7(2,0)}_{\mathrm{del}}^{\cdot-}$ has no counterpart in the hyperfine data for $\mathbf{7(2,0)}_{\mathrm{loc}}^{\cdot-}$. An obvious candidate for this value are the two protons in the bridgehead positions at the joint of the two norbornene units (*Fig. 5*).

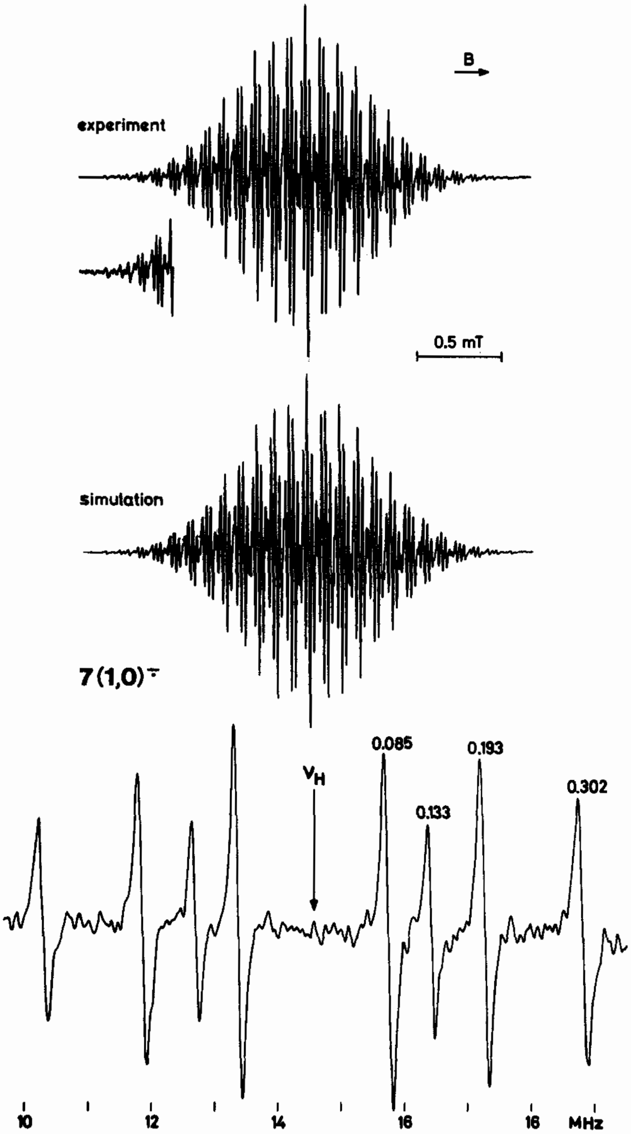


Fig. 3. *ESR* (top) *and proton-ENDOR spectra* (bottom) *of* $\mathbf{7(1,0)}^{\overline{\cdot}}$. Solvent: DME; counterion: K^+; temp.: 203 K. The numbers above the ENDOR signals refer to proton-coupling constants [mT] associated with them. The simulation made use of these values and their assignments to sets of equivalent protons as indicated for $\mathbf{7(1,0)}^{\overline{\cdot}}$ in *Fig.* 2; line-shape: *Lorentz*ian; line-width: 0.015 mT.

No clear-cut changes in the appearance of $\mathbf{7(2,0)}_{\mathrm{del}}^{\overline{\cdot}}$ and $\mathbf{7(2,0)}_{\mathrm{loc}}^{\overline{\cdot}}$ were ascertained, when the temperature was raised from 183 to 293 K. By contrast, replacement of DME by MTHF had a striking effect: with MTHF as solvent, *exclusively* spectra of $\mathbf{7(2,0)}_{\mathrm{loc}}^{\overline{\cdot}}$ were observed, irrespective of the extent of reduction.

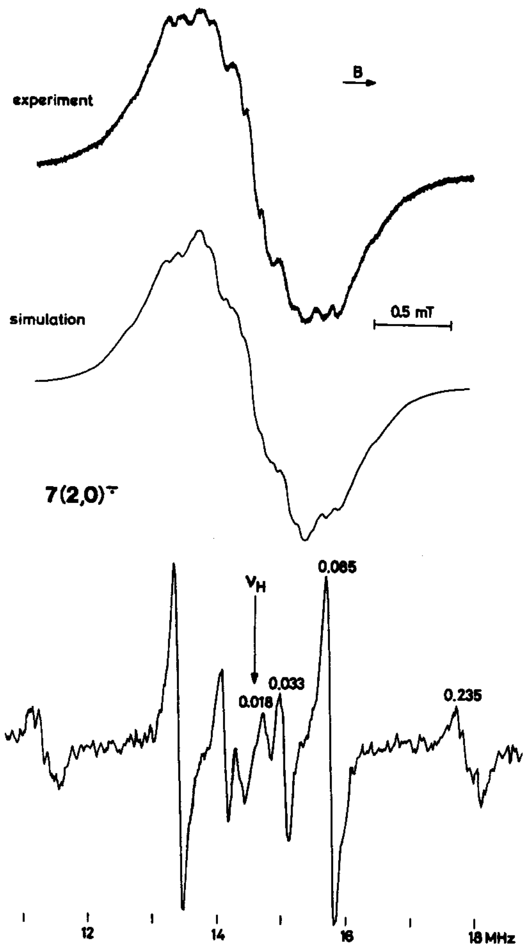


Fig. 4. *ESR* (top) *and proton-ENDOR spectra* (bottom) *of* **7(2,0)**$^{\overline{\cdot}}$. Solvent: DME; counterion: K$^+$; temp.: 203 K. The numbers above the ENDOR signals refer to proton-coupling constants [mT] associated with them. The simulation made use of these values and their assignments to sets of equivalent protons as indicated for **7(2,0)**$^{\overline{\cdot}}$ in *Fig.* 5; line-shape: *Lorentzian*; line-width: 0.080 mT.

Dinaphthohexacyclohexadecadiene **7(1,1)**. ESR and ENDOR spectra obtained upon cautious reduction of **7(1,1)** in DME arose from a mixture of two radical anions. One of them was characterized by *halved* coupling constants of *doubled* numbers of equivalent protons in *both* naphthalene π-moieties, as required for **7(1,1)**$_{\mathrm{del}}^{\overline{\cdot}}$, whereas the other exhibited hyperfine data similar to those for **8**$^{\overline{\cdot}}$ and diagnostic of **7(1,1)**$_{\mathrm{loc}}^{\overline{\cdot}}$ with interacting protons restricted to *only one* π-moiety (*Fig. 5*). The concentration ratio of **7(1,1)**$_{\mathrm{del}}^{\overline{\cdot}}$ to **7(1,1)**$_{\mathrm{loc}}^{\overline{\cdot}}$ was *ca.* 1:2, and it increased to almost 1:1 when DME contained *ca.*10% of HMPT (addition of larger amounts of HMPT to DME proved inconvenient to a controlled

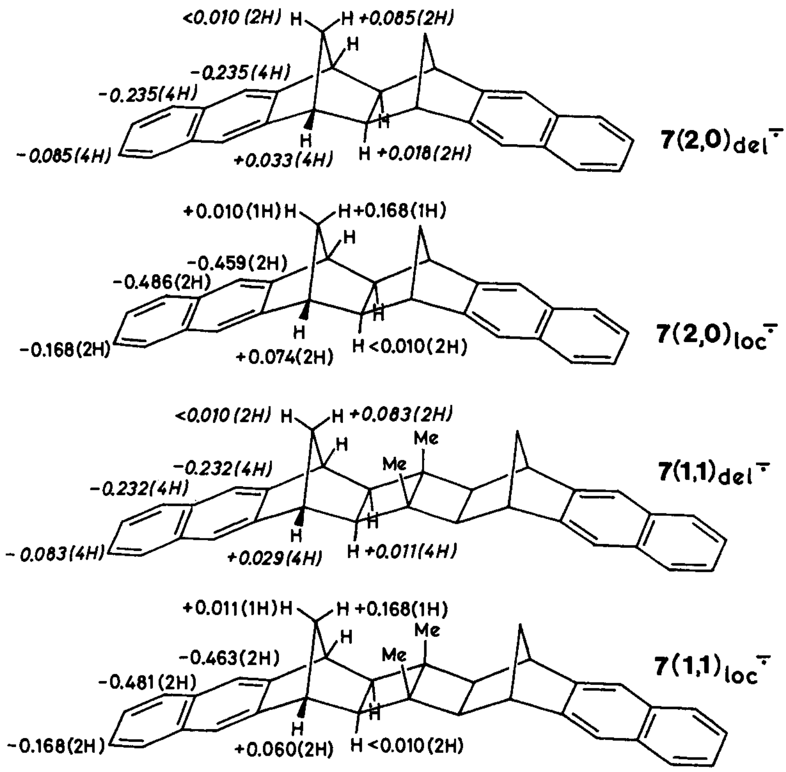


Fig. 5. *Assignments of coupling constants* [mT] *to protons in* $\mathbf{7(2,0)}^{\cdot-}$ *and* $\mathbf{7(1,1)}^{\cdot-}$. Solvent: DME; counterion: K$^+$; temp.: 203 K. Experimental error in the coupling constants: ±0.004 and ±0.002 mT in (absolute) values larger and smaller than 0.1 mT, respectively. Numbers in italics refer to protons interacting with both naphthalene π-moieties. The coupling constants of the Me protons in both $\mathbf{7(1,1)}_{\mathrm{del}}^{\cdot-}$ and $\mathbf{7(1,1)}_{\mathrm{loc}}^{\cdot-}$ are too small to be resolved.

reduction process and detrimental to the persistence of the radical anion). As illustrated by *Fig. 6*, which shows the ESR and proton-ENDOR spectra of $\mathbf{7(1,1)}_{\mathrm{del}}^{\cdot-}$/ $\mathbf{7(1,1)}_{\mathrm{loc}}^{\cdot-}$ in DME/HMPT, the ENDOR signals belonging to either one of the two species can clearly be distinguished. An exception is the signal associated with the smallest coupling constant of +0.011 mT which has been assumed to arise both from a proton in the *syn*-position of a methano bridge in $\mathbf{7(1,1)}_{\mathrm{loc}}^{\cdot-}$ and from four protons in the bridgehead positions at the joints of norbornene and cyclobutane units in $\mathbf{7(1,1)}_{\mathrm{del}}^{\cdot-}$ (*Fig. 5*).

Further contact of the DME or DME/HMPT solution with the potassium mirror caused a gradual increase in the intensity of the ESR and ENDOR signals of $\mathbf{7(1,1)}_{\mathrm{loc}}^{\cdot-}$ at the expense of those of $\mathbf{7(1,1)}_{\mathrm{del}}^{\cdot-}$. As in the case of $\mathbf{7(2,0)}^{\cdot-}$, the concentration ratio of the two species was not distinctly changed by varying the temperature, but it strongly depended on the solvent. Using MTHF instead of DME or DME/HMPT resulted in the *sole* appearance of $\mathbf{7(1,1)}_{\mathrm{loc}}^{\cdot-}$, even upon a very short reduction time.

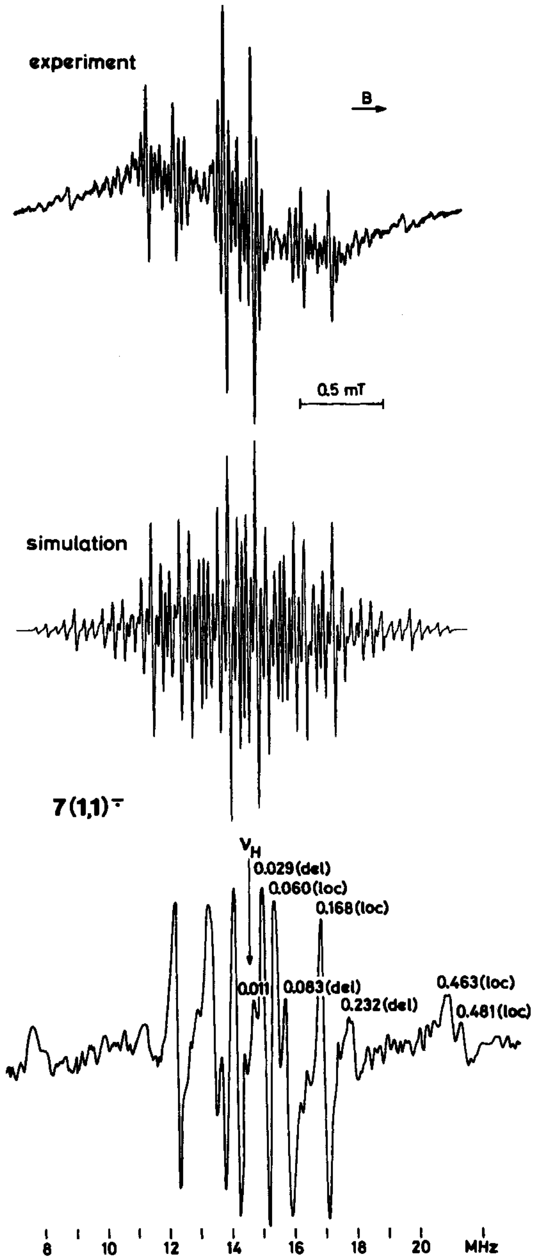


Fig. 6. *ESR* (top) *and proton-ENDOR spectra* (bottom) *of* **7(1,1)**$^{\cdot-}$. Solvent: DME/HMPT (10:1); counterion: K$^+$; temp.: 203 K. The numbers above the ENDOR signals refer to proton-coupling constants [mT] associated with them. The simulation made use of these values and their assignments to sets of equivalent protons as indicated for **7(1,1)**$_{\text{del}}^{\cdot-}$ and **7(1,1)**$_{\text{loc}}^{\cdot-}$ in *Fig. 5*; concentration ratio of **7(1,1)**$_{\text{del}}^{\cdot-}$ to **7(1,1)**$_{\text{loc}}^{\cdot-}$ is 4:5; line-shape: *Lorentz*ian; line-width: 0.020 mT.

Triplet *Dianions*. When solutions of **7(2,0)** or **7(1,1)** in MTHF were frozen down after an exhaustive reduction, ESR signal diagnostic of *triplet* states appeared on both sides of the central absorption due to $\mathbf{7(2,0)}_{\mathrm{loc}}^{\overline{\cdot}}$ or $\mathbf{7(1,1)}_{\mathrm{loc}}^{\overline{\cdot}}$. These signals, displayed in *Fig. 7*, represent *x*,*y*- and *z*-features of an axial or a nearly axial anisotropy tensor. They are attributed to *triplet* dianions $\mathbf{7(2,0)}^{\overline{\cdot}\overline{\cdot}}$ and $\mathbf{7(1,1)}^{\overline{\cdot}\overline{\cdot}}$. From the spacing $2D'$ of the *z*-features, average separations *r* of the two unpaired electrons were calculated using the relation [31]

$$\bar{r} = \sqrt[3]{278 \cdot 10^{9}/D'}$$

where D' is in mT and $\bar{r}$ in pm. The resulting values $\bar{r}$, 787 pm for $\mathbf{5(2,0)}^{\overline{\cdot}\overline{\cdot}}$ and 1036 pm for $\mathbf{5(1,1)}^{\overline{\cdot}\overline{\cdot}}$, compare favourably with the distances between the centres of the two naphthalene π-moieties in these systems, as estimated from molecular-mechanics calculations (*Table*).

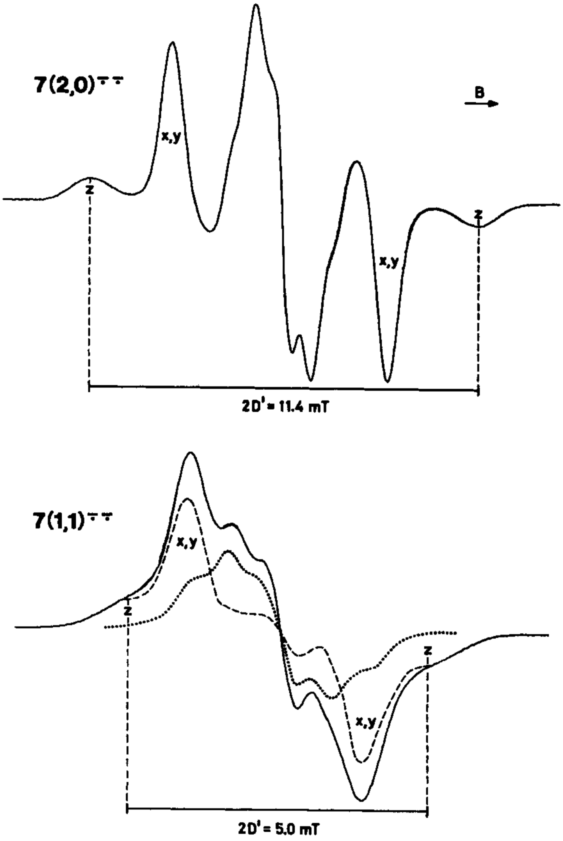


Fig. 7. *ESR spectra of the* triplet *dianions* $\mathbf{7(2,0)}^{\overline{\cdot}\overline{\cdot}}$ *and* $\mathbf{7(1,1)}^{\overline{\cdot}\overline{\cdot}}$. Solvent: MTHF; counterions: K$^+$; temp.: 115 K. For $\mathbf{7(1,1)}^{\overline{\cdot}\overline{\cdot}}$, the contribution of the radical anion $\mathbf{7(1,1)}^{\overline{\cdot}}$(···) was deducted from the experimental curve. Note the different magnetic-field scale in the two spectra.

Table. *Nearest Edge-to-Edge and Centre-to-Centre Distances* [pm] *of the Two Naphthalene Moieties in* syn- *and* anti-**6(1)**, **7(1,0)**, **7(2,0)**, *and* **7(1,1)**, *as Calculated by Molecular Mechanics*

	syn-**6(1)**	*anti*-**6(1)**	**7(1,0)**	**7(2,0)**	**7(1,1)**
Edge-to-edge	575	631	236	474	711
Centre-to-centre	734	874	629	796	1033

^{1}H-NMR spectra, which would reveal the presence of the corresponding *singlet* dianions **7(2,0)**$^{2-}$ and **7(1,1)**$^{2-}$, were not observed upon exhaustive reduction of the neutral precursors with an alkali metal in (D_8)THF at low temperatures. In the case of **7(1,0)**, neither the signals of the *triplet* dianion **7(1,0)**$^{\cdot-\cdot-}$ nor those of its *singlet* counterpart **7(1,0)**$^{2-}$ could be detected by ESR and NMR spectroscopy, respectively.

Discussion. – The hyperfine data for **7(1,0)**$^{\cdot-}$ are consistent with those for a radical anion of a homobinaphthylene-like system which is a 'truly' charge- and spin-delocalized species of C_{2v} symmetry. Due to the relatively small edge-to-edge separation of the naphthalene π-moieties (*Table*), the homoconjugative or through-space interaction is effective in **7(1,0)**. It can be estimated from the π^*,π^*-energy splittings of the lowest antibonding MO's in bicyclo[2.2.1]hepta-2,5-diene (1.52 eV [32]) and its 2,3:5,6-dibenzo derivative (0.98 eV [16]). Using an approximate dependence of these values on the squared LCAO coefficients at the interacting π-centres in the LUMO (0.5 for ethene, 0.25 for a 1,2-dialkylbenzene, and 0.07 for naphthalene), one obtains a predicted value of 0.21 to 0.27 eV for the π^*,π^*-energy splitting in **7(1,0)**$^{\cdot-}$. This value could well be large enough to ensure that **7(1,0)**$^{\cdot-}$ is a homoconjugatively delocalized species[13b][33]. Since the ESR and ENDOR spectra do not depend on the solvent, ion pairing has little effect on the dynamics of the spin transfer. This observation suggests that the counterion K^+ is situated midway between the two naphthalene π-moieties, *i.e.* in the '*endo*' cavity of the radical anion. The centre-to-centre distance of the two moieties in **7(1,0)** (*Table*) seems to be favourable for such a structure of the ion pair, as the centre of the cation should be *ca.* 350–400 pm remote from the π-plane of the radical anion [34].

In contrast to **7(1,0)**$^{\cdot-}$, the striking dependence of the ESR and ENDOR spectra of **7(2,0)**$^{\cdot-}$ and **7(1,1)**$^{\cdot-}$ on the solvent indicates that the frequency of the electron-spin transfer between the two naphthalene π-moieties in both radical anions is determined by the rate of synchronous counterion migration between two equivalent sites at these moieties. In MTHF, a solvent of low cation-solvating power, the counterion K^+ is strongly associated with such a site, forming a *tight* ion pair with the radical anion. Consequently, its migration is *slow* on hyperfine time-scale (*ca.* 10^7 s^{-1}), yielding the spectra of **7(2,0)**$_{\mathrm{loc}}^{\cdot-}$ and **7(1,1)**$_{\mathrm{loc}}^{\cdot-}$ with the unpaired electron *localized* on one naphthalene π-moiety. Upon replacement of MTHF by DME or DME/HMPT, the cation-solvating power of the solvent is greatly enhanced, and the association of K^+ with the radical anion is weakened. In the *loose* ion pairs thus formed, the counterion migration becomes *fast* on the hyperfine time-scale, and the electron-spin transfer is less strongly tied in with this motion. The ESR spectra of **7(2,0)**$_{\mathrm{del}}^{\cdot-}$ and **7(1,1)**$_{\mathrm{del}}^{\cdot-}$, observed under such conditions, exhibit charge and spin delocalization over both π-moieties; the rate of electron transfer must, therefore, be higher than 10^7 s^{-1}.

The edge-to-edge separations of the naphthalene π-moieties in **7(2,0)** and **7(1,1)** *(Table)* are too large for an effective through-space interaction. The respective π^*,π^*-splitting energies of 0.15 and 0.05 eV in the two systems, as estimated from the electron-transmission spectroscopic data for the corresponding dienes **4(1)** and **4(2)**, should exclusively be due to through-bond coupling. Even in the absence of tight ion pairing, this coupling is probably too weak to permit **7(2,0)**$_{\mathrm{del}}^{\bar{\cdot}}$ and **7(1,1)**$_{\mathrm{del}}^{\bar{\cdot}}$ to exist as truly delocalized species, but it is certainly strong enough to mediate an electron transfer between the two naphthalene π-moieties with a rate exceeding the hyperfine time-scale. A through-bond coupling mechanism of electron-spin transfer would also account for the finding that the bridgehead protons at the joint of the two norbornene units give rise to an observable hyperfine splitting (+0.018 mT) for **7(2,0)**$_{\mathrm{del}}^{\bar{\cdot}}$, but not for **7(2,0)**$_{\mathrm{loc}}^{\bar{\cdot}}$ (if our tentative assignment is correct (see *Fig. 4*), an analogous statement could be made for the coupling constant (+0.011 mT) of the correspondingly positioned protons in **7(1,1)**$_{\mathrm{del}}^{\bar{\cdot}}$ relative to **7(1,1)**$_{\mathrm{loc}}^{\bar{\cdot}}$).

A structural feature shared by **7(1,1)** with **6(1)** is the separation of the two naphthalene π-moieties by 6 C–C single bonds. Although the edge-to-edge distances in *syn*- and *anti*-**6(1)** fall short of those in **7(1,1)** (*Table*), they are also too large for a significant through-space interaction between the two moieties. Intramolecular electron transfer in *syn*- and *anti*-**6(1)**$^{\bar{\cdot}}$ must thus be mediated by a through-bond mechanism which is particularly effective in spiro-bonded cyclobutane bridges [35]. Calculations on bis-allyl analogues of **6(1)** as model systems indicate that through-bond interactions are almost equally strong in the *syn*- (0.061 eV) and *anti*-conformers (0.064 eV) of these systems [36], a statement which should also be valid for *syn*- and *anti*-**6(1)**.These considerations shed a new light on the previously observed [22] simultaneous occurrence of 'localized' and 'delocalized' radical anions, **6(1)**$_{\mathrm{loc}}^{\bar{\cdot}}$ and **6(1)**$_{\mathrm{del}}^{\bar{\cdot}}$, in solvents of high cation-solvating power. The proposed identification of the former and the latter with *anti*- and *syn*-**6(1)**$^{\bar{\cdot}}$, respectively, can hardly be traced back to differing through-bond interactions in the two conformers. In this respect, it is important to note the present finding that **7(1,1)**$_{\mathrm{loc}}^{\bar{\cdot}}$ and **7(1,1)**$_{\mathrm{del}}^{\bar{\cdot}}$ also coexist in the same DME or DME/HMPT solutions, though, unlike **6(1)**, the molecule **7(1,1)** is completely rigid. Similar reports on 'localized' and 'delocalized' radical anions in the same solution of a high solvating power have been known for other rigid systems containing two equivalent π-moieties separated by C–C single bonds, such as spirobifluorene [21a] and several [2.2]paracyclophanes [23]. A possible rationalization of this phenomenon is in terms of electron transfer being still (weakly) governed by the rate of counterion migration even in the absence of tight ion pairing. Thus, in the case of **6(1)**, previous identification of the 'delocalized' and 'localized' radical anions as the *syn*- and *anti*-conformers, respectively, might still be valid, albeit their differences in the distances between the two naphthalene π-moieties should affect the electron transfer 'indirectly' *via* counterion migration rather than 'directly' through orbital interaction. It is conceivable that the cation migrates more rapidly in *syn*-**6(1)**$^{\bar{\cdot}}$ than in *anti*-**6(1)**$^{\bar{\cdot}}$, because its displacement is smaller in the former than in the latter (relevant to this migration of the cation are its preferred sites which should be better represented by the centres of the π-moieties than by their edges; clearly, the centre-to-centre distances in *syn*- and *anti*-**6(1)** differ more strongly than edge-to-edge separations, see the *Table*).

Concluding Remarks. – The results of the present studies on **7(m,n)**$^{\overline{\cdot}}$ bear out the expectation that the rate of intramolecular electron transfer between two π-moieties can exceed 10^7 s^{-1}, even when a rigid spacer separates these moieties by as many as 6 C–C single bonds and holds them at a distance larger than 700 pm. There is some indication that a synchronous migration of the counterion might still influence the electron transfer in solvents of high cation-solvating power, *i.e.*, in the absence of tight ion pairing.

Experimental. – *Source of Compounds.* The syntheses of **7(1,0)**, **7(2,0)**, **7(1,1)**, and **8** have been described in [5][25]. Compound D-**8** was prepared from **8** by *i*) bromination with Br_2, *ii*) *Grignard* reaction, and *iii*) quenching with D_2O, following the standard procedure (see, *e.g.*, [28a]). The D-content was better than 95%, according to ^{1}H-NMR. Compound D-**7(1,0)** was synthesized by the same method as **7(1,0)** [25a], but using 7-deuterionorbornadiene [37] instead of norbornadiene. ^{1}H-NMR and MS revealed that the D-content was at least 90%.

Instrumental. The ESR spectra were taken on a *Varian-E9* ESR instrument, while a *Bruker ESP-300* spectrometer served for ENDOR and TRIPLE-resonance studies.

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REFERENCES

[1] V. Balzani, ed., 'Supramolecular Photochemistry', Reidel, Dordrecht, 1987.

[2] a)'Covalently Linked Donor-Acceptor Species for Mimicry of Photosynthetic Electron and Energy Transfer', Eds. D. Gust, T. A.Moore,Tetrahedron Symposium-in-Print, No. 39, *Tetrahedron* **1989**, *45* ; M.R. Wasielewski in 'Photoinduced Electron Transfer', Part A, Eds. M .A. Fox, M. Chanon, Elsevier, Amsterdam, 1988, Chapt. 1.4.

[3] a) L. T. Calcaterra, G. L. Closs, J. R. Miller, *J. Am. Chem. Soc.* **1983**, *105*, 670; b) J. R. Miller, L. T. Calcaterra, G. L. Closs, *J. Am. Chem. Soc.* **1984**, *106*, 3047; c) G. L. Closs, L. T. Calcaterra, N. J. Green, K. W. Penfield, J. R. Miller, *J. Phys. Chem.* **1986**, *90*, 3673; d) G. L. Closs, J. R. Miller, *Science* **1988**, *240*, 440.

[4] K. W. Penfield, J. R. Miller, M. N. Paddon-Row, E. Cotsaris, A. M. Oliver, N. S. Hush, *J. Am. Chem. Soc.* **1987**, *109*, 5061.

[5] M. N. Paddon-Row, E. Cotsaris, H. K. Patney, *Tetrahedron* **1986**, *42,* 1779.

[6] D. C. Craig, M. N. Paddon-Row, *Aust. J. Chem.* **1987**, *40*, 1951.

[7] a) N. S. Hush, M. N. Paddon-Row, E. Cotsaris, H. Oevering, J. W. Verhoeven, M. Heppener, *Chem. Phys. Lett.* **1985**, *117*, 8.; b) J. M. Warman, M. P. de Haas, M. N. Paddon-Row, E. Cotsaris, N. S. Hush, H. Oevering, J. W. Verhoeven, *Nature* **1986**, *320*, 616; c) H. Oevering, M. N. Paddon-Row, M. Heppener, A. M. Oliver, E., Cotsaris, J. W. Verhoeven, N. S. Hush, *J. Am. Chem. Soc.* **1987**, *109*, 3258; d) A. M. Oliver, D. C. Craig, M. N. Paddon-Row, J. Kroon, J. W. Verhoeven, *Chem. Phys. Lett.* **1988**, *150*, 366; e) J. M. Lawson, D. C. Craig, M. N. Paddon-Row, J. Kroon, J.W. Verhoeven, *Chem. Phys. Lett.*.**1989**, *164*, 120.

[8] J. M. Warman, M. Hom, M. N. Paddon-Row, A. M. Oliver, J. Kroon, *Chem. Phys. Lett.*, in press..

[9] a) M. D. Johnson, J. R. Miller, N. S. Green, G. L. Closs, *J. Phys. Chem.* **1989**,*93*, 1173; b) G. L. Closs, M. D. Johnson, J. R. Miller, P. Piotrowiak, *J. Am. Chem. Soc.* **1989**, *111*, 3751.

[10] a) P. Pasman, J. W. Verhoeven, Th. J. de Boer, *Tetrahedron* **1976**, *32*, 2827; b) P. Pasman, J. W. Verhoeven, Th. J. de Boer, *Tetrahedron Lett.* **1977**, 207.

[11] K. Ohta, G. L. Closs, K. Morokuma, N. J. Green, *J. Am. Chem.Soc.* **1986**, *108*, 1319.

[12] a) R. Hoffmann, A. Imamura, W. J. Hehre, *J. Am. Chem. Soc.* **1968**, *90*, 1499; b) R. Hoffmann, *Acc. Chem. Res.* **1971**, *4*, 1.

[13] a) M. N. Paddon-Row, *Acc. Chem. Res.* **1982**, *15*, 245; b) M. N. Paddon-Row, K. D. Jordan, in: 'Modern Models of Bonding and Delocalization', eds. J. F. Liebman, A. Greenberg,VCH Publishers, New York, 1988, Chapt. 3.

[14] H. M. McConnell, *J. Chem. Phys.* **1961**, *35*, 508.

[15] a) M. N. Paddon-Row, H. K. Patney, R. S. Brown, K. N. Houk, *J. Am. Chem. Soc.***1981**, *103*, 5575; b) F. S. Jørgensen, M. N. Paddon-Row, H. K. Patney, *J. Chem. Soc., Chem. Commun.* **1983**, 573; c) M. N. Paddon-Row, H. K. Patney, J. B.Peel, G. W. Willett, *J. Chem. Soc., Chem. Commun.* **1984**, 564; d) E. Heilbronner, H.-D. Martin, *Helv. Chim. Acta* **1972**, *55*, 1490.

[16] V. Balaji, L. Ng, K. D. Jordan, M. N. Paddon-Row, H. K. Patney, *J. Am. Chem. Soc.* **1987**, *109*, 6957.

[17] a) R. A. Marcus, N. Sutin, *Biochim. Biophys. Acta* **1985**, *811*, 265; b) N. S. Hush, *Trans. Farad. Soc.* **1961**, *57*, 557.

[18] N. S. Hush, *Coord. Chem. Rev.* **1985**, *64*, 135.

[19] M. N. Paddon-Row, S. S. Wong, *Chem. Phys. Lett.* **1990**, *167*, 432.

[20] a) M. Szwarc, J. Jaguar-Grodzinski, in 'Ions and Ion Pairs in Organic Reactions', Vol. 2, ed., M. Szwarc, J. Wiley, New York, 1974, Chapt. 1; b) K. Shimada, M. Szwarc, *Chem. Phys. Lett.* **1974**, *28*, 540.

[21] a) F. Gerson, B. Kowert, B. M. Peake, *J. Am. Chem. Soc.* **1974**, *96*, 118; b) P. Fürderer, F. Gerson, J. Heinzer, S. Mazur, H. Ohya-Nishiguchi, A. H. Schröder, *ibid.* **1979**, *101*, 2275; c) S. Mazur, V. M. Dixit, F. Gerson, *ibid.* **1980**, *102*, 5343.

[22] F. Gerson, W. Huber, W. B. Martin, J., P. Caluwe, T. Pepper, M. Szwarc, *Helv. Chim. Acta* **1984**, *67*, 416.

[23] a) F. Gerson, *Topics Curr. Chem.* **1983**, *115*, 57, and ref. cit. therein; b) F. Gerson, W. B. Martin, H. N. C. Wong, C. W. Chan, *Helv. Chim. Acta* **1987**, *70*, 79; c) A. de Meijere, F. Gerson, B. König, O. Reiser, T. Wellauer, *J. Am. Chem. Soc.*, in press.

[24] a) W. Huber, H. Unterberg, K. Müllen, *Angew. Chem.* **1983**, *95*, 239; *ibid. Int. Ed.*. **1983**, *22*, 242; b) W. Irmen, W. Huber, J. Lex, K. Müllen, *Angew. Chem.* **1984**, *96*, 800; *ibid. Int. Ed.* **1984**, *23*, 818; c) J. Fiedler, W. Huber, K. Müllen, *Angew. Chem.* **1986**, *98*, 444; *ibid. Int. Ed.* **1986**, *25*, 443; d) G. Krummel, W. Huber, K. Müllen, *Angew. Chem.* **1987**, *99*, 1305; *ibid. Int. Ed.* **1987**, *26*, 1290; e) J. Alexander, M. Ehrenfreund, J. Fiedler, W. Huber, H.-J. Räder, K. Müllen, *Angew. Chem.* **1989**, *101*, 1530; *ibid. Int. Ed.* **1989**, *28*, 1531; f) W. Huber, K. Müllen, *Acc. Chem. Res.***1986**, *19*, 300.

[25] M. N. Paddon-Row, H. K. Patney, *Synthesis* **1986**, 328.

[26] H. Kurreck, B. Kirste, W. Lubitz, 'Electron Nuclear Double Resonance Spectroscopy of Radicals in Solution', VCH Publishers, New York, 1988, Chapt. 2.

[27] F. Gerson, B.Weidmann, E. Heilbronner, *Helv. Chim. Acta* **1964**, *47*, 1951.

[28] a) R. D. Rieke, C. F. Meares, L. I. Rieke, *Tetrahedron Lett.* **1968**, 5275; b) R. D. Rieke, S. E. Bales, C. F. Meares, L. I. Rieke, C. M. Milliren, *J. Org. Chem. Soc.* **1974**, *39*, 2276.

[29] G. A. Russell, G. W. Holland, K.-Y. Chang, R. G. Keske, J. Mattox, C .S. C. Chung, K. Stanley, K. Schmitt, R. Blankespoor, Y. Kosugi, *J. Am. Chem. Soc.* **1974**, *96*, 7237.

[30] A.Carrington, J. dos Santos-Veiga, *Mol. Phys.* **1962**, *5*, 285.

[31] a) S. S. Eaton, K. M. More, B. M. Sawant, G. R. Eaton, *J. Am. Chem. Soc.* **1983**, *105*, 6560; b) G. R. Luckhurst, in 'Spin Labelling: Theory and Applications', ed. L. J. Berliner, Academic Press, New York, 1976, Chapt. 4.

[32] K. D. Jordan, J. A. Michejda, P. D. Burrow, *Chem. Phys. Lett.* **1976**, *42*, 227.

[33] N. S. Hush, 'Electron Delocalization, Structure and Dynamics in Mixed-Valence Systems' in 'Mixed-Valence Compounds, eds. D. B. Brown, D. Reidel, Co, Dordrecht, 1980, 151.

[34] a) A. H. Reddoch, *J. Chem. Phys.* **1965**, *43*, 225; b) M. Iwaizumi, M. Suzuki, T. Isobe, H. Azumi, *Bull. Chem. Soc. Jpn.* **1967**, *40*, 1325; c) A. H. Reddoch, *J. Magn. Reson.* **1974**, *15*, 75; d) M. Iwaizumi, Y. Fukazawa, N. Kato, S. Itô, *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1299.

[35] a) C. A. Stein, H. Taube, *J. Am. Chem. Soc.* **1981**, *103*, 693; b) C. A. Stein, N. A. Lewis, G. Seitz, *ibid.* **1982**, *104*, 2596; c) A. D. Baker, R. Scharfman, C. A. Stein, *Tetrahedron Lett.* **1983**, *24*, 2957; d) A. P. L. Rendell, G. B. Bacskay, N. S. Hush, *J. Am. Chem. Soc.* **1988**, *110*, 8343.

[36] S. S.Wong, private communication to M. N. Paddon-Row.

[37] S. C. Clarke, B. L. Johnson, *Tetrahedron* **1968**, *24*, 5067.