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ESR and ENDOR Studies of Azulenophane Anion Radicals

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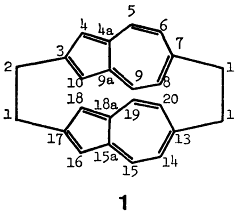
The anion radicals of *syn*- and *anti*-[2.2](2,6)azulenophane, (**1**) and (**2**), [2.2](1,3)azulenophane, (**3**), and [2](1,3)-azuleno[2]paracyclophane, (**4**), all produced by alkali metal reduction in various solvents, have been investigated by ESR and ENDOR spectroscopy. They exist in the ion pair with cations in the solutions, except for **4**$^{\overline{\cdot}}$ which exists in 1,2-dimethoxyethane with Na$^+$. Their ion pairing tendency is appreciably higher than that of the naphthalenophane anion radicals. The unpaired electron in these ion pairs localizes mostly on an azulene ring (in **1**$^{\overline{\cdot}}$, **2**$^{\overline{\cdot}}$, and **3**$^{\overline{\cdot}}$, close to a cation). The polarization effects due to the pairing with the cations are much larger than those in the naphthalenophane anion radicals, and increase in the order **1**$^{\overline{\cdot}}\leq$**2**$^{\overline{\cdot}}\leq$**3**$^{\overline{\cdot}}$, indicating that the smaller the inter-layer orbital overlap, the larger the polarizability. The unpaired electron of **4**$^{\overline{\cdot}}$ localizes mostly on the azulene ring even in the free anion.

Extensive studies have been carried out during the past decade on the distribution of unpaired electron in the anion radicals of paracyclophanes, because of the general interest in the transannular interaction in these layered compounds.[1—9] However, the compounds studied so far contain only alternant hydrocarbons with a few exceptions. In this paper, we describe the result of ESR and ENDOR spectroscopic studies on the anion radicals of *syn*- and *anti*-[2.2](2,6)azulenophanes (**1** and **2**), [2.2](1,3)azulenophane (**3**) and [2](1,3)azuleno[2]paracyclophane (**4**), all containing azulene rings. Investigation of these compounds seems significant, since they contain, as aromatic moieties, azulene which is a typical non-alternant hydrocarbon known to have unique physicochemical properties different from alternant hydrocarbons. We were interested in the evaluation of the difference in the unpaired electron delocalization found for **1**$^{\overline{\cdot}}$ and **2**$^{\overline{\cdot}}$ with opposite orientation of the azulene ring.



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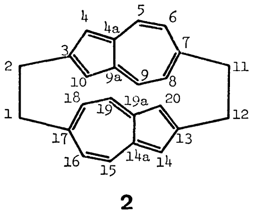

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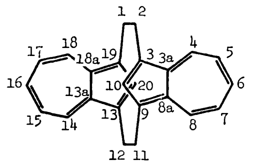

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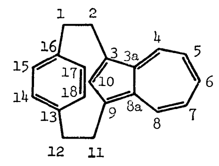

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Experimental

Compounds **1**, **2**, **3**, and **4** were synthesized by the method reported.[10] In order to prepare the anion radicals of the compounds, reduction with sodium or potassium in 1,2-dimethoxyethane (DME), tetrahydrofuran (THF), 2-methyltetrahydrofuran (MTHF), and mixture of the former two was carried out. ESR and ENDOR spectra of the anion radicals were measured with Varian E112 ESR and E1700 ENDOR spectrometers. However, no radicals **1**$^{\overline{\cdot}}$, **2**$^{\overline{\cdot}}$, and **3**$^{\overline{\cdot}}$ could be detected in DME because of their instability at *ca.* −85 °C, the freezing point of the solution.

Results and Discussion

ESR Spectra. All the ESR spectra of anion radicals produced from **1**—**4** at temperatures below −90 °C in various solvents are well defined (Figs. 1—4). However, in mixed DME–THF with concentration of DME higher than 3:1 (volume), radical

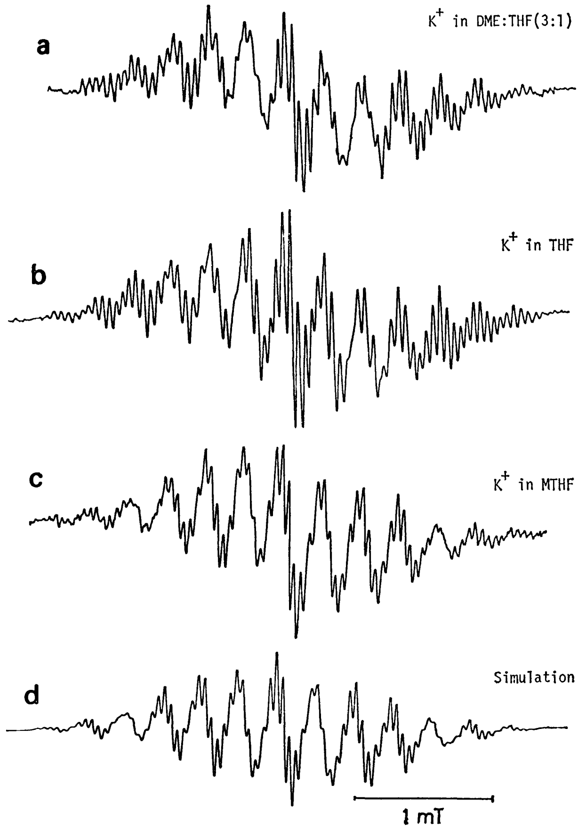

Fig. 1. ESR spectra of **1**$^{\overline{\cdot}}$ observed at −95 °C in a) K$^+$ in DME:THF (3:1), b) K$^+$ in THF, and c) K$^+$ in MTHF, and d) simulated spectrum for c) using the hf coupling constants in Table 1.

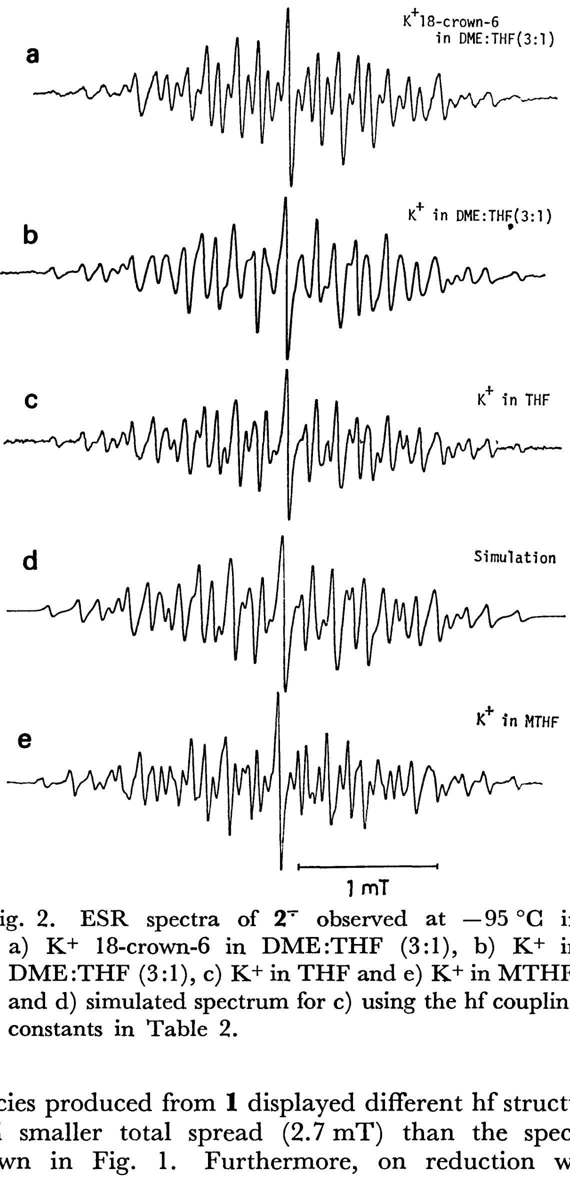

Fig. 2. ESR spectra of $\mathbf{2}^{\overline{\cdot}}$ observed at −95 °C in a) K^{+} 18-crown-6 in DME:THF (3:1), b) K^{+} in DME:THF (3:1), c) K^{+} in THF and e) K^{+} in MTHF, and d) simulated spectrum for c) using the hf coupling constants in Table 2.

species produced from **1** displayed different hf structure and smaller total spread (2.7 mT) than the spectra shown in Fig. 1. Furthermore, on reduction with sodium, **1** and **2** exhibit spectra due to two different radical species, one showing a very broad pattern with no hf splitting and the other a sharp one with many hf lines. In all cases, no reliable analysis was possible and no radical species could be identified.

From Figs. 1—4 we see that the spectra of $\mathbf{1}^{\overline{\cdot}}$ and $\mathbf{3}^{\overline{\cdot}}$ are hardly affected at all by solvents, the spectrum of $\mathbf{2}^{\overline{\cdot}}$ changing slightly, while that of $\mathbf{4}^{\overline{\cdot}}$, which is similar to that of $\mathbf{3}^{\overline{\cdot}}$, changes a great deal with solvent. The spectrum of $\mathbf{4}^{\overline{\cdot}}$ also changes with temperature. The hf pattern produced with potassium in DME at −50—−60 °C is very similar to that in THF or MTHF, but on cooling to *ca.* −85 °C, the pattern becomes similar to that in DME with sodium ion.

ENDOR Spectra. Measurements of ENDOR spectra of $\mathbf{1}^{\overline{\cdot}}$—$\mathbf{4}^{\overline{\cdot}}$ were undertaken, but except for $\mathbf{4}^{\overline{\cdot}}$ no spectra could be obtained because of insufficient radical concentration. A typical spectrum observed for $\mathbf{4}^{\overline{\cdot}}$ is shown in Fig. 5.

Analysis of the ESR Spectra. The ESR spectra of $\mathbf{1}^{\overline{\cdot}}$ can be interpreted in terms of six sets of triplet splittings, those of $\mathbf{2}^{\overline{\cdot}}$ by four sets of triplets and those of $\mathbf{3}^{\overline{\cdot}}$ and $\mathbf{4}^{\overline{\cdot}}$ by two sets each of triplets and doublets.

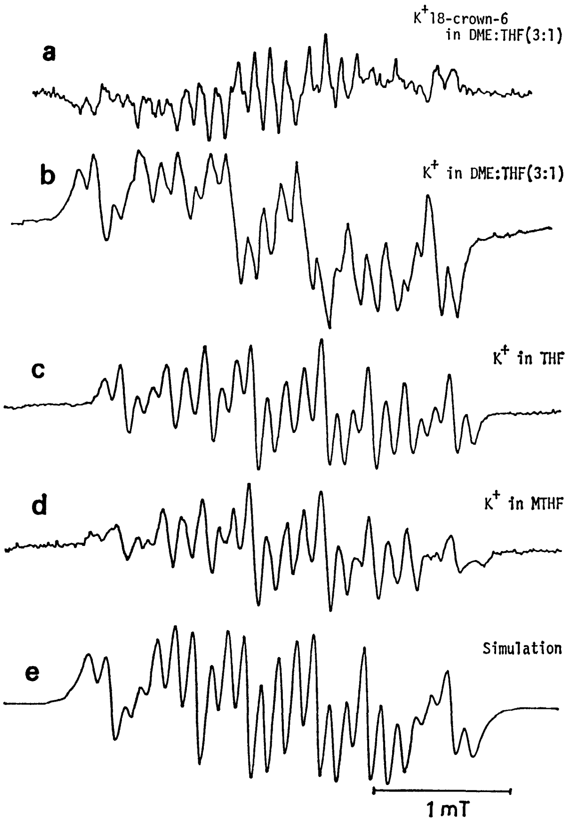

Fig. 3. ESR spectra of $\mathbf{3}^{\overline{\cdot}}$ observed at −95 °C in a) K^{+} 18-crown-6 in DME:THF (3:1), b) K^{+} in DME:THF (3:1), c) K^{+} in THF, d) K^{+} in MTHF, and e) simulated spectrum for d) using the hf coupling constants in Table 3.

This indicates that the unpaired electrons in $\mathbf{1}^{\overline{\cdot}}$, $\mathbf{2}^{\overline{\cdot}}$, and $\mathbf{3}^{\overline{\cdot}}$ are distributed unequally on the two azulene rings in the molecules since the quintet splittings would be observed if the unpaired electrons are distributed equally on the two azulene rings. The observed distribution suggests that the anion radicals interact with the counter ion in the solutions. $\mathbf{4}^{\overline{\cdot}}$ is also considered to have interaction with the counter ion. The coupling constants were determined from the ESR and ENDOR (for $\mathbf{4}^{\overline{\cdot}}$) spectra and assigned to the respective protons on the basis of MO calculation (*vide infra*), referring to the hf interaction in the azulene anion radical ($\mathbf{5}^{\overline{\cdot}}$), since the relative ratio of the spin densities in the azulene should not change so much by the transannular interaction or ion pairing. No calculation was carried out for $\mathbf{3}^{\overline{\cdot}}$, but the assignment was easily made by comparison with that of $\mathbf{4}^{\overline{\cdot}}$, which gives very similar ESR spectra.

MO Calculation for the Hf Coupling Constants. The unpaired electron distribution and the hf coupling constants of the anion radicals in the ion pair form were calculated by the method reported.[9] The geometry of the anion radicals was estimated from the X-ray data for the neutral molecules,[10] the exchange integrals being assumed to be proportional to the overlap integrals, and the proportional constant for the exchange integrals between the layers one and half times the constant within the layers. Only the sets of atomic orbitals which gave larger overlap in-

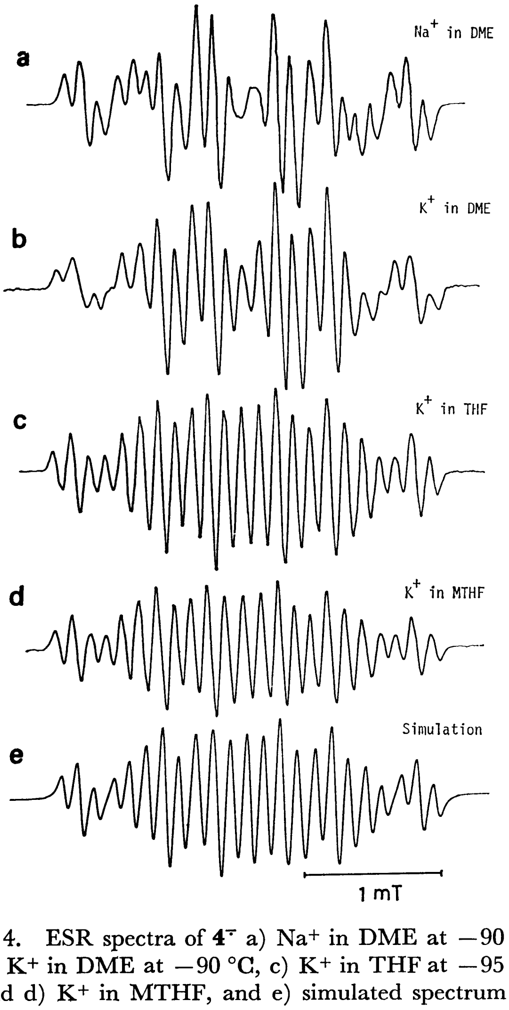

Fig. 4. ESR spectra of $\mathbf{4}^{\overline{\cdot}}$ a) Na$^+$ in DME at −90 °C, b) K$^+$ in DME at −90 °C, c) K$^+$ in THF at −95 °C, and d) K$^+$ in MTHF, and e) simulated spectrum for c) using the hf coupling constants in Table 4.

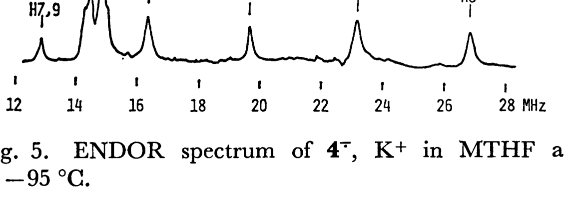

Fig. 5. ENDOR spectrum of $\mathbf{4}^{\overline{\cdot}}$, K$^+$ in MTHF at −95 °C.

tegrals than 0.02 were taken into account for the interlayer exchange integrals.

The potential energy maps for the cation placed at a distance of 0.38 nm above the nearest azulene ring were calculated for ion pairs of $\mathbf{1}^{\overline{\cdot}}$, $\mathbf{2}^{\overline{\cdot}}$, and $\mathbf{4}^{\overline{\cdot}}$. The results are shown in Fig. 6, together with a similar map for $\mathbf{5}^{\overline{\cdot}}$. Another model of $\mathbf{4}^{\overline{\cdot}}$ examined in which the cation was placed above the benzene ring gave less stable potential energies. The results show that the most stable position of cation in $\mathbf{1}^{\overline{\cdot}}$ is above the center of the five-membered ring. The position shifts toward the seven-membered ring on going from $\mathbf{1}^{\overline{\cdot}}$ to $\mathbf{2}^{\overline{\cdot}}$ and then to $\mathbf{4}^{\overline{\cdot}}$.

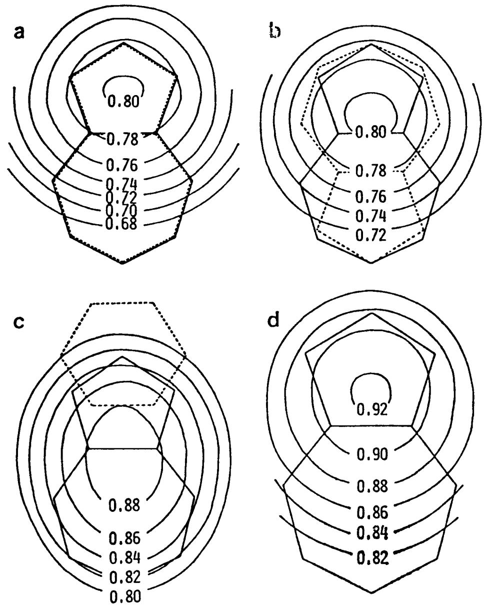

Fig. 6. Electrostatic interaction energies between a cation and anion radicals, a) $\mathbf{1}^{\overline{\cdot}}$, b) $\mathbf{2}^{\overline{\cdot}}$, c) $\mathbf{4}^{\overline{\cdot}}$, and d) $\mathbf{5}^{\overline{\cdot}}$ (in unit of β). The cation is placed at the distance of 0.38 nm from the nearest aromatic plane (drawn by solid lines).

The spin density distribution and the hf coupling constants were calculated[11] as a function of the distance between the cation and the anion radicals by placing the former above the potential minimum points. The potential minimum position of the cation has been shown to change slightly with distance which may cause some effect on the hf constants.[12] However, such an effect was ignored because it would not be so large as to give a wrong assignment of the hf coupling constants.

Spin Distribution in $\mathit{1}^{\overline{\cdot}}$ and $\mathit{2}^{\overline{\cdot}}$. The observed proton hf coupling constants could reasonably be assigned to the protons (Tables 1 and 2) of the anion radicals in the ion pair form on the basis of the above calculation. The MO calculation showed that the hf coupling constants change drastically with the distances between the cation and the anion radicals. The calculated coupling constants are for the distance 0.35 nm which give the best fit with the experimental values.

In order to observe the ESR spectra of $\mathbf{1}^{\overline{\cdot}}$ and $\mathbf{2}^{\overline{\cdot}}$ in the free anion state, generation of the anion radicals

Table 1. Hf coupling constants of $\mathbf{1}^{\overline{\cdot}}$

Position, i	$\lvert a_i^H \rvert$/mT			
	DME:THF, (3:1) K$^+$	THF, K$^+$	MTHF, K$^+$	Calcd[a)]
5, 9	0.557	0.567	0.568	0.6010
11	0.517	0.524	0.523	0.5180
2	0.291	0.292	0.292	0.2689
6, 8	0.251	0.247	0.252	0.1503
15, 19	0.094	0.095	0.091	0.1245
12	0.050	0.050	0.047	0.0908
1	—	—	—	0.0601

a) The distance between the cation and the anion radical was taken to be 0.35 nm.

Table 2. Hf coupling constants of $\mathbf{2}^{\cdot-}$

Position, i	$\lvert a^{\rm H}_{\rm i}\rvert$/mT				
	DME:THF(3:1), K$^+$-(18-crown-6)	DME:THF, K$^+$ (3:1)	THF, K$^+$	MTHF, K$^+$	Calcd$^{\rm a)}$
5, 9	0.5826	0.5993	0.6029	0.6095	0.6487
11	0.5048	0.5046	0.5081	0.5187	0.5495
2	0.3600	0.3485	0.3589	0.3633	0.2875
6, 8	0.2177	0.2216	0.2167	0.2139	0.1671
15, 19	—	—	—	—	0.1317

a) The distance between the cation and the anion radical was taken to be 0.35 nm.

Table 3. Hf coupling constants of $\mathbf{3}^{\cdot-}$

<table>
<tr><th rowspan="2">Position, i</th><th colspan="4">|a^H_i|/mT</th></tr>
<tr><th>DME:THF(3:1), K+-(18-crown-6)</th><th>DME:THF, K+ (3:1)</th><th>THF, K+</th><th>MTHF, K+</th></tr>
<tr><td>6</td><td>0.832</td><td colspan="3">0.840</td></tr>
<tr><td>4, 8</td><td>0.590</td><td colspan="3">0.610</td></tr>
<tr><td>10</td><td>0.362</td><td colspan="3">0.367</td></tr>
<tr><td>5, 7</td><td>0.115</td><td colspan="3">0.110</td></tr>
</table>

in the presence of 18-crown-6 was examined. However, the ESR spectrum observed for $\mathbf{2}^{\cdot-}$ was still due to the ion pair, and that attributable to $\mathbf{1}^{\cdot-}$ was not observed under these conditions.

It is apparent from the hf coupling constants obtained that the unpaired electron largely localized on the azulene ring at the cation side. By comparison with the hf coupling constants of the azulene anion radical ($a^{\rm H}_{1,3}=0.0274$ mT, $a^{\rm H}_{2}=0.3948$ mT, $a^{\rm H}_{4,8}=0.6219$ mT, $a^{\rm H}_{5,7}=0.1338$ mT, $a^{\rm H}_{6}=0.8829$ mT),[13] the unpaired electron densities on the azulene ring at the cation side were estimated to be *ca.* 87—91% for $\mathbf{1}^{\cdot-}$ and 89—93% for $\mathbf{2}^{\cdot-}$. The [2.2](1,4)naphthalenophane anion radical also shows a similar large polarization in the spin distribution by the formation of ion pairs.[5b)] In the ion pair of the *syn* isomer($\mathbf{6}^{\cdot-}$), the unpaired electron densities on the naphthalene ring close to a cation can be estimated as *ca.* 72—77% by comparison of its hf coupling constants with those of naphthalene anion radical.[14] The polarization in the azulenophane anion radicals is appreciably larger than that in the naphthalenophane anion radical.

The hf coupling constants of 11 position in $\mathbf{1}^{\cdot-}$ is larger than that for the corresponding position in $\mathbf{2}^{\cdot-}$, while that of 2 position in $\mathbf{1}^{\cdot-}$ is smaller than that for the same position in $\mathbf{2}^{\cdot-}$, indicating that the unpaired electron distribution in $\mathbf{1}^{\cdot-}$ is polarized more from the head position (3 position) to the tail (7 position) than in $\mathbf{2}^{\cdot-}$.

Spin Distribution in $\mathbf{3}^{\cdot-}$. The observed hf coupling constants (Table 3) apparently show that the unpaired electrons are mostly distributed on one of the azulene ring. The situation did not change with the presence of 18-crown-6. As in $\mathbf{1}^{\cdot-}$ and $\mathbf{2}^{\cdot-}$, the observed polarization in the spin distribution can be attributed to the ion pairing of the anion radical. From a comparison with the hf coupling constants of the azulene anion radical, the unpaired electron densities on the azulene ring at the cation side are estimated to be *ca.* 94—95%; larger polarization than that in $\mathbf{1}^{\cdot-}$ and $\mathbf{2}^{\cdot-}$.

Spin Distribution in $\mathbf{4}^{\cdot-}$. The ESR spectrum at −50—−60 °C of $\mathbf{4}^{\cdot-}$ in DME with potassium ion is similar to spectra observed for $\mathbf{4}^{\cdot-}$ in THF or MTHF, becoming similar to that observed in DME with sodium ion with lowering in temperature. This suggests that $\mathbf{4}^{\cdot-}$ in DME with sodium ion exists mostly as a free anion; it is associated with the cation in THF and MTHF, and $\mathbf{4}^{\cdot-}$ in DME with potassium ion is in an equilibrium between these two forms. The equilibrium shifts toward the free anion state by lowering in temperature. The hf coupling constants obtained for $\mathbf{4}^{\cdot-}$ both in the free anion and in the ion pair are given in Table 4.

We see that the unpaired electrons are distributed mostly on the azulene ring even when the anion radical is in a free anion state. By ion pairing the spin density is polarized more from the benzene ring to the azulene ring. This indicates that the cation is associated with $\mathbf{4}^{\cdot-}$ at the azulene ring side, in line with the result of calculation of the cation-anion interaction energies. The unpaired electron densities on the azulene ring are *ca.* 91—95% in the free anion state and *ca.* 98—99% in the ion pair form.

In contrast to the increase of spin density of the azulene ring as a whole, the density of carbon 10 is reduced by the interaction with the counter ion. Such polarization effect by ion pairing can be shown by MO calculation using the ion-pair model in which the cation is placed above the potential minimum point. The calculation using the other ion pair model does not reproduce the observed effect (Table 4).

Polarization of Unpaired Electron Distribution and the Interlayer Interaction. The unpaired electron in $\mathbf{1}^{\cdot-}$, $\mathbf{2}^{\cdot-}$, and $\mathbf{3}^{\cdot-}$ is localized in one of the azulene rings. The unpaired electrons in the anion radical of [2.2]-

Table 4. Hf coupling constants of $\mathbf{4}^{\cdot-}$

Position, i	$\lvert a_i^H \rvert$/mT			Effect of Cation, $\Delta\lvert a_i^H \rvert$/mT[a]			
	DME, Na$^+$	MTHF, K$^+$	Calcd[b]	Obsd	Calcd[b]		
					Model I[c]	II[c]	III[c]
6	0.8357	0.8746	0.8575	+0.0383	−0.0091	−0.0041	−0.0023
4, 8	0.5751	0.6180	0.6910	+0.0429	+0.0791	+0.0357	−0.0391
10	0.3865	0.3612	0.2777	−0.0253	−0.0031	−0.0141	+0.0011
5, 7	0.1070	0.1254	0.1546	+0.0184	+0.0587	+0.0094	−0.0360
2, 11[d]	0.0328	0.0294	0.0636	−0.0034	−0.0283	−0.0033	+0.0245
14, 15[d]	0.0241	0.0220	0.0046	−0.0021	−0.0018	−0.0007	+0.0000
17, 18[d]	0.0162	0.0106	0.0023	−0.0056	−0.0001	−0.0001	+0.0001
1, 12	—	—	0.0018	—	+0.0025	+0.0057	+0.0089

a) The difference between the hf coupling constants of the free anion state and the ion pair form. b) The distance between the cation and the anion radical was taken to be 0.35 nm. c) In models I, II, and III, the cation is placed above the center of the five-membered ring, the potential minimum point and the center of the seven-membered ring, respectively. d) The empirical hf coupling constants were tentatively assigned to the proton positions. The hf interactions were not observed in the ESR spectra and the coupling constants were obtained from the ENDOR specta.

paracyclophanes with the identical aromatic rings are distributed equally on both rings unless there is interaction with a counter ion.[1–7] The observed localization (polarization) might arise from such an interaction. The results indicate that polarization due to a cation increases in the order $\mathbf{1}^{\cdot-} \leq \mathbf{2}^{\cdot-} < \mathbf{3}^{\cdot-}$. Since the geometry of these molecules indicates the decreasing order $\mathbf{1}^{\cdot-} > \mathbf{2}^{\cdot-} > \mathbf{3}^{\cdot-}$ in the interlayer π-π interaction,[10] the observed order of the polarization shows that smaller interlayer π-π interaction gives larger polarization in the electron spin distribution.

The unpaired electron in $\mathbf{1}^{\cdot-}$ and $\mathbf{2}^{\cdot-}$ is polarized to a greater extent than in $\mathbf{6}^{\cdot-}$. Such a difference may be attributed to the nature of the two aromatic ring systems.

Tendency to Ion Pairing. While $\mathbf{6}^{\cdot-}$ exists as a free anion in THF with potassium ion,[5b] $\mathbf{1}^{\cdot-}$ and $\mathbf{2}^{\cdot-}$ exist in the ion pair form under the same conditions. This indicates that $\mathbf{1}^{\cdot-}$ and $\mathbf{2}^{\cdot-}$ have higher tendency of ion pairing than $\mathbf{6}^{\cdot-}$. It seems of interest to compare the ion pairing tendencies of the azulenophane anion radicals with those of other relating anion radicals. By taking into account the fact that anion radicals tend to associate more at higher temperature with the alkali metal cations in various solvents in the order $\mathrm{Li}^+ < \mathrm{Na}^+ < \mathrm{K}^+$, and DME<THF<MTHF, the following order for ion pairing tendency is estimated: $\mathbf{6}^{\cdot-}$<*anti*-[2.2](1,4)naphthalenophane$^{\cdot-}$ ($\mathbf{7}^{\cdot-}$)<$\mathbf{1}^{\cdot-}$, $\mathbf{2}^{\cdot-}$, $\mathbf{3}^{\cdot-}$, $\mathbf{4}^{\cdot-}$≤naphthalene$^{\cdot-}$($\mathbf{8}^{\cdot-}$)<$\mathbf{5}^{\cdot-}$.[15] Thus, the anion radicals corresponding azulene rings have higher tendency of ion pairing than the naphthalene counterparts. Such a pronounced tendency of ion pairing of azulenophane anion radicals may be mainly attributed to the nature of the azulene ring which tends to accumulate a high negative charge on its five-membered ring. The estimated order for the ion pairing agrees with the order in the electrostatic interaction energies calculated for the most stable ion pair structures for the anion radicals: $\mathbf{6}^{\cdot-}$(0.752)<$\mathbf{7}^{\cdot-}$(0.787)<$\mathbf{1}^{\cdot-}$(0.802)≤$\mathbf{2}^{\cdot-}$(0.806)<$\mathbf{4}^{\cdot-}$(0.893)<$\mathbf{8}^{\cdot-}$(0.895)<$\mathbf{5}^{\cdot-}$(0.920).[16]

Table 5. Calculated spin densities in $\mathbf{1}^{\cdot-}$ and $\mathbf{2}^{\cdot-}$ in the free anion state

Position	$\mathbf{1}^{\cdot-}$	$\mathbf{2}^{\cdot-}$
3	0.0729	0.0694
4, 10	−0.0099	0.0028
4a, 9a	0.0376	0.0195
5, 9	0.1497	0.1610
6, 8	−0.0308	−0.0372
7	−0.1338	0.1382

Spin Distribution in $\mathbf{1}^{\cdot-}$ *and* $\mathbf{2}^{\cdot-}$ *in the Free Anion State.* The spin density distributions in $\mathbf{1}^{\cdot-}$ and $\mathbf{2}^{\cdot-}$ in the free anion state were not clarified experimentally in the present work. However, the electron spin distribution (Table 5) predicted by MO calculation shows that the unpaired electron in $\mathbf{2}^{\cdot-}$ is localized more on the seven-membered ring than in $\mathbf{1}^{\cdot-}$, in view of the finding that in ion pairs the unpaired electron in $\mathbf{2}^{\cdot-}$ is localized more on the five-membered ring than in $\mathbf{1}^{\cdot-}$.

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11) It was assumed that $Q_{\text{alkyl}}=2.30\,\text{mT}$ and $Q_{\text{arom.}}=2.25\,\text{mT}$ for $\mathbf{1}^{\cdot-}$, $\mathbf{2}^{\cdot-}$, and $\mathbf{3}^{\cdot-}$, and $Q_{\text{alkyl}}=2.30\,\text{mT}$ and $Q_{\text{arom.}}=2.50\,\text{mT}$ for $\mathbf{4}^{\cdot-}$.

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15) The order of tendency among $\mathbf{1}^{\cdot-}$, $\mathbf{2}^{\cdot-}$, $\mathbf{3}^{\cdot-}$, and $\mathbf{4}^{\cdot-}$ has not been made clear in the present work.

16) In unit of β. The cation-anion distances are taken to be 0.38 nm.