ESR Spectra of Para-Substituted Alkyl- and Alkenylbenzene Radical Cations in Halocarbon Matrices

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The ESR spectra of several para-substituted alkyl- and alkenylbenzene radical cations generated by ^{60}Co γ-ray irradiation in halocarbon matrices at 77 K have been studied with the aid of semiempirical MO calculations. It has been found that the ethyl conformation of 1,4-diethylbenzene radical cation (1,4-DEB$^{+\cdot}$) in CCl_2FCClF_2 is largely different from that in CCl_3CF_3. Further the ethyl and n-propyl groups in 4-ethyltoluene and 4-n-propyltoluene radical cations in CCl_2FCClF_2 take different conformations from that of 1,4-DEB$^{+\cdot}$. The conformations of the alkylbenzene radical cations depend strongly both on the matrices and on the substituent groups. A peculiar radiolytical reaction of 1,4-diisopropylbenzene to a deprotonation-type neutral radical in CCl_2FCClF_2 has been found, similarly to the case of photolysis.

1. Introduction

ESR spectra of alkylbenzene radical cations generated by ionizing irradiation in low temperature halocarbon matrices have been studied by several investigators with interest in substituent conformations and electronic structures [1–6]. The first studies of alkylbenzene radical cations in halocarbon matrices were carried out by Symons et al. [1] and Tabata et al. [2] with various methyl-substituted benzenes; the observed ESR spectra exhibited well resolved and relatively large proton hyperfine splittings [1–6]. Iwasaki et al. found that the benzene radical cation in halocarbon matrices is distorted at 4.2 K from a D_{6h} to a D_{2h} symmetry due to the Jahn-Teller effect [7]. Aromatic radical cations derived from diazabenzenes and halogenobenzenes have also been studied by several investigators [8, 9].

Symons et al. also studied various alkylbenzene radical cations in CCl_3F and discussed the conformations of alkyl chains, electronic structure, and molecular motion [3, 4]. According to their studies, the hyperfine coupling (hfc) constants of the methylene protons (β-protons) differ largely between the radical cations of ethylbenzene (EB$^{+\cdot}$) (29 G) (1 G = 0.1 mT) and 1,4-diethylbenzene (1,4-DEB$^{+\cdot}$) (ca. 11 G): the methylene groups in the former are more strongly coupled with the ring.

In contrast to the previous work [4], we have found that the methylene proton hfc constant in 1,4-DEB$^{+\cdot}$ in CCl_2FCClF_2 is 27.7 G, as large as that in EB$^{+\cdot}$ in CCl_3F, indicating that the ethyl-group conformation depends strongly on the matrix used. Here we report the ESR spectra of a series of para-substituted alkyl- and alkenylbenzene radical cations generated by ^{60}Co γ-ray irradiation at 77 K in CCl_2FCClF_2 matrix. All ESR parameters obtained are listed in Table 1.

2. Experimental

1,1,2-Trichloro-1,2,2-trifluoroethane, CCl_2FCClF_2, (Tokyo Kasei, GR) was used as matrix as received. All para-substituted benzenes studied were obtained from Tokyo Kasei, Wako and Aldrich, and were used as received, except for 1,4-di-n-propylbenzene (1,4-DPB) prepared from n-propylbenzene as follows: 1. 1,4-n-Propylpropiophenone (1,4-PPP) was synthesized from n-propylbenzene (Tokyo Kasei, GR) and propionic anhydride (Tokyo Kasei, GR) [10]. 2. 1,4-DPB

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Table 1. ESR parameters for para-substituted alkyl- and alkenylbenzene radical cations in CCl_2FCClF_2 at 77 K[a]

Parent benzenes	Hyperfine coupling constants/G		Line width/G
$(CH_3)C_6H_4(CH_3)$	18 (6)		–
$(CH_3CH_2)C_6H_4(CH_2CH_3)$	27.7 (4)		11.7
$(CH_3CH_2CH_2)C_6H_4(CH_2CH_2CH_3)$	17 (4)		–
$(CH_3)C_6H_4((CH_3)_2CH)$	17.5 (3)	20.5 (1)	5.8
$((CH_3)_2CH)C_6H_4(CH(CH_3)_2)$[b]	15.8 (6)	4.5 (2)	3.9
$(CH_3)C_6H_4(CH_3CH_2)$	17.5 (3)	57.9 (1)	6.0
$(CH_3)C_6H_4(CH_3CH_2CH_2)$	17.4 (3)	55.6 (1)	6.6
$(CH_3)C_6H_4((CH_3)_3C)$	18 (3)	3–5 (2)	–
$(CH_2{=}CH)C_6H_4(CH_2{=}CH)$	7.6 (4)		6.6
$(CH_2{=}C(CH_3))C_6H_4(C(CH_3){=}CH_2))$	10.0 (4)		9.6
$(CH_3)C_6H_4(CH{=}CH_2)$	11.3 (3)	11.3 (2)	5.4

[a] 1 G = 0.1 mT. The number of equivalent protons is given in parentheses. The line width refers fo the peak-to-peak Gaussian width determined by spectral simulation.

[b] The radical derived is the deprotonation-type neutral radical. See text.

was prepared by reducing the 1,4-PPP with hydrazine (Tokyo Kasei, GR) and KOH (Wako, practical grade) [11], and its purity was checked by NMR.

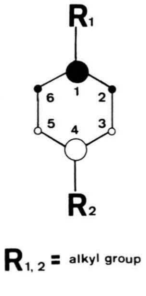
Liquid-solute volume fractions were ca. 0.01, and the concentration of 1,4-diisopropenylbenzene (1,4-DIPEB) was 8.3×10^{-3} mol dm^{-3}. Sample solutions were fully degassed in suprasil ESR capillary cells and were exposed to ^{60}Co γ-rays at 77 K.

ESR spectra were recorded at 77 K on an X band ESR spectrometer (Echo Electronics) combined with a JEOL JM-360 electromagnet operating with 100 kHz field modulation. The magnetic fields were measured by means of a proton NMR gaussmeter (JEOL, JMF-3).

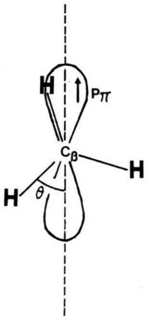
3. Results and Discussion

3.1. 1,4-Xylene radical cation (1,4-XYL$^{+\cdot}$)

The ESR spectrum of 1,4-XYL$^{+\cdot}$ observed in CCl_2FCClF_2 consists of seven isotropic lines with an hfc constant of 18 G associated with the freely rotating methyl protons (or β-protons) [1, 2, 4]. As established, the relevant hfc mechanism is hyperconjugation, e.g., [12]. With the effective molecular symmetry D_{2h}, the singly occupied molecular orbital (SOMO) is a b_{3g} π-orbital:



The open and solid circles represent the positive and negative AO coefficients, respectively, and the unpaired electron is largely localized on C_1 and C_4 [2–4]. The end-of-view of the π-orbital and the methyl group visualizes the hyperconjugation on β-protons:



Here, θ is the angle of twist between the α-carbon $2p\pi$ orbital and the plane containing the β-proton C–H σ-bond, which is estimated from the observed β-proton hfc constant, a_β^H, and the UHF-INDO spin density on the $2p\pi$ orbital of the ring α-carbon, ϱ_α, with the relation [12],

$$a_\beta^H = (B_0 + B_2 \cos^2\theta)\,\varrho_\alpha, \tag{1}$$

where B_0 and B_2 are the constants originating from spin polarization and hyperconjugation, respectively. For the β-proton, the spin polarization is negligible, and (1) is reduced to

$$a_\beta^H = B_2 \cos^2\theta\,\varrho_\alpha. \tag{2}$$

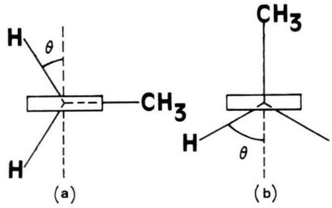
For a freely rotating methyl group, the orientation average $\langle\cos^2\theta\rangle = 1/2$ can be used, and B_2 is evaluated as 132 G by substituting into (2) $a^{CH_3} = 20.0$ G and $\varrho_\alpha = 0.303$ in the toluene radical cation [2]. It may be noted that this B_2 value is also valid for the

1-methyl-1-cyclopentene and 1-methyl-1-cyclohexene radical cations [13].

The equivalence of the six methyl protons in 1,4-XYL$^{+\cdot}$ in the three different matrices CCl_2FCClF_2, CCl_3F [1, 4] and CCl_3CF_3 at 77 K [2] indicates the free rotation of the methyl groups, as has generally been observed for π-type radical cations (π-character of SOMO) [14], whereas this is not necessarily the case for σ-type radicals (σ-character of SOMO) [15].

3.2. 1,4-Diethylbenzene and 1,4-di-n-propylbenzene radical cations (1,4-DEB$^{+\cdot}$, 1,4-DPB$^{+\cdot}$)

Figure 1 (a) shows the ESR spectrum of 1,4-DEB$^{+\cdot}$ in CCl_2FCClF_2, exhibiting isotropic five lines separated by 27.7 G. The spectrum simulated with the hfc constant of 27.7 G is shown in Figure 1 (b). This hfc constant is reasonably attributed to the four equivalent methylene protons of two ethyl groups and is fairly larger than that in 1,4-XYL$^{+\cdot}$ (18.0 G), reflecting the somewhat hindered rotation of the methylene protons in 1,4-DEB$^{+\cdot}$. The θ value in 1,4-DEB$^{+\cdot}$ in CCl_2FCClF_2 is estimated to be ca. 30° with $\varrho_\alpha = 0.312$ for the trans-form (C_{2h}). Conformation (a):



The UHF-INDO hfc constant of the methylene proton, 27.1 G, evaluated for the conformation (a) (tans-form) with $\theta = 30°$ by use of

$$a^{\mathrm{H}} = 508\,\varrho_{\mathrm{H}}, \tag{3}$$

ϱ_{H} denoting the hydrogen 1s orbital spin density, is in good agreement with the observed (27.7 G) [12]. Throughout the present paper, the UHF-INDO proton hfc constant is derived by substituting the UHF-INDO ϱ_{H} value into (3) [16]. The proportionality constant, 508 G, corresponds to the theoretical hfc constant for $\varrho_{\mathrm{H}} = 1$ evaluated by Whiffen [17]; the constant is evaluated as 506.8 G by Carrington et al. [12] and 539.86 by Pople et al. [16]. The standard geometrical parameters of Pople and Beveridge were used in the UHF-INDO calculations [16]. Since the UHF-INDO hfc constant evaluated for the cis-form (C_{2v}) is 27.1 G, we cannot conclude which form is present, trans or cis. In contrast to the present results, Symons et al. reported that the ESR spectrum of 1,4-DEB$^{+\cdot}$ in CCl_3F is composed of at least two conformational isomers, the major species having hfc constants, $a_1^{\mathrm{CH_2}} = 7$ G and $a_2^{\mathrm{CH_2}} = 15$ G, ascribable to the respective ethyl groups [4]. The spectrum became a quintet with $a^{\mathrm{CH_2}} \approx 11$ G at 140 K; they suggested that the major cation has conformation (b) with $\theta \approx 60°$ [4].

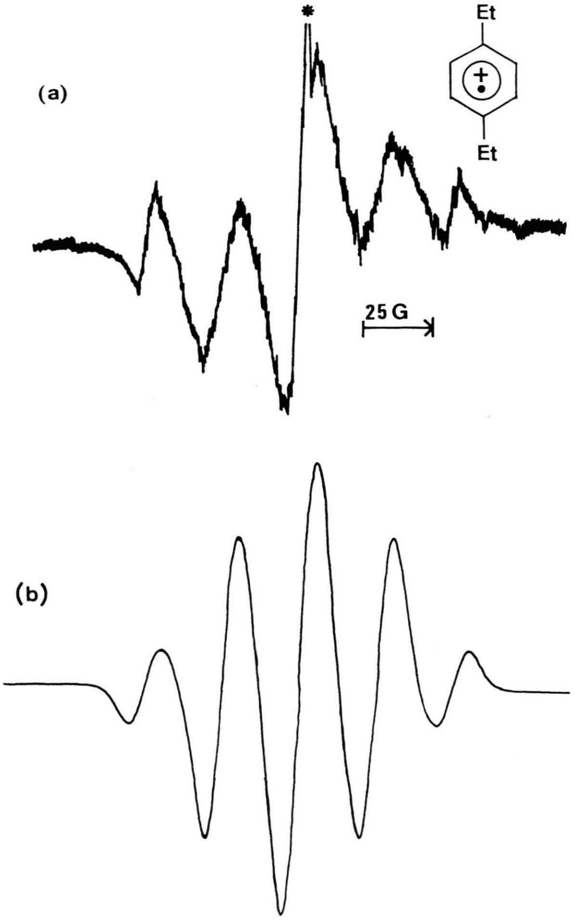


Fig. 1. ESR spectrum of the 1,4-diethylbenzene radical cation in CCl_2FCClF_2 at 77 K (a). The simulation spectrum (b) was computed using the hfc constant and peak-to-peak Gaussian line width listed in Table 1. The signal marked with asterisk comes from the damaged sample tube.

In the CCl_2FCClF_2 matrix, only one radical species was observed, and the ethyl-group conformation (a) is similar to that of EB$^{+\cdot}$ in CCl_3F proposed by Symons et al. [3]. To sum up, the above facts suggest that the ethyl-group conformation strongly depends on matrices. The matrix dependence of the ethyl-group conformation in 1,4-DEB$^{+\cdot}$ has been discussed elsewhere [18].

The ESR spectrum of 1,4-DPB$^{+\cdot}$ consists of five lines with an average hfc constant of 17 G, which is fairly smaller than that of 1,4-DEB$^{+\cdot}$ (27.7 G). The conformation of 1,4-DPB$^{+\cdot}$ could not be determined and will be a subject of future study.

3.3. 1,4-Methylisopropylbenzene and 1,4-diisopropylbenzene radical cations (1,4-MIB$^{+\cdot}$, 1,4-DIPB$^{+\cdot}$)

Figure 2 shows the ESR spectrum of 1,4-MIB$^{+\cdot}$, apparently composed of five hyperfine lines. The hfc constant of the three methyl protons is estimated to be 17.5 G, while that of the isopropyl methine proton is 20.5 G. Judging from these hfc constants, the methyl group rotates freely, while the isopropyl group takes the structure of $\theta \approx 45°$, with $\varrho_\alpha = 0.311$ as illustrated below. It may be noted that only one conformation was detected in CCl_2FCClF_2 matrix, in contrast to the results in CCl_3F reported by Symons et al. [3, 4]. The UHF-INDO hfc constants of the methyl and isopropyl methine protons are evaluated to be 16.0 G and 15.5 G for the geometry with $\theta = 45°$, respectively, in good agreement with the observed.

The ESR spectrum of irradiated 1,4-DIPB in CCl_2FCClF_2 is shown in Fig. 3 (a), together with the spectrum of Fig. 3 (b) simulated with the hfc constants, 15.8 G (6H) and 4.5 G (2H), and peak-to-peak Gaussian line width ΔH of 3.9 G. The ESR spectrum consists of a septet of triplets. Symons et al. reported two conformers for the isopropylbenzene radical cation (IPB$^{+\cdot}$) generated by ^{60}Co γ-ray irradiation of IPB, one with a small hfc constant of 6 G (1 H) and the other with a larger hfc constant of 21 G (1 H) [3]. The ESR spectrum in Fig. 3 (a) cannot be assigned to 1,4-DIPB$^{+\cdot}$ since the spectral pattern implies six equivalent protons. The most probable species is the neutral radical, $(CH_3)_2CHC_6H_4C^{\cdot}(CH_3)_2$, formed by hydrogen detachment from a methine carbon.

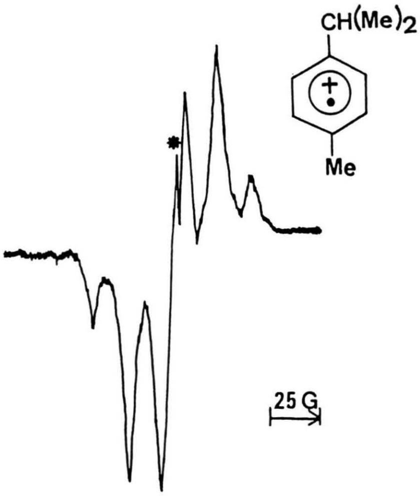
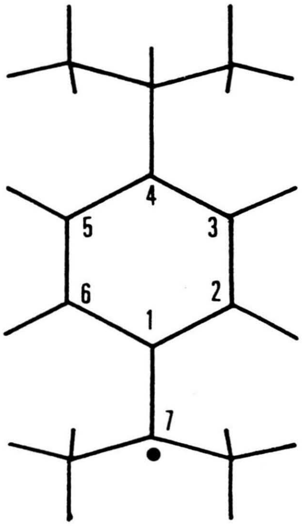


Fig. 2. ESR spectrum of the 1,4-methylisopropylbenzene radical cation observed in CCl_2FCClF_2 at 77 K. For the asterisk see Figure 1.



The UHF-INDO hfc constants calculated for the neutral radical, 15.8 G for a^{CH_3} at C_7, 2.4 G for $a^{H_{2,6}}$ and 1.6 G for $a^{H_{3,5}}$, seemingly support this interpretation; the larger and smaller experimental hfc constants are assigned to six methyl protons at C_7 and two protons at C_2 and C_6, respectively. This interpretation is also supported by an ESR investigation of substituted benzyl radicals generated photochemically [18]. The mechanism of the peculiar neutral-radical formation in 1,4-DIPB deserves to be studied further in detail.

3.4. 4-Ethyltoluene and 4-n-propyltoluene radical cations (4-ET$^{+\cdot}$, 4-PT$^{+\cdot}$)

The ESR spectra of 4-ET$^{+\cdot}$ and 4-PT$^{+\cdot}$ observed at 77 K are shown in Figure 4. These spectra are of the doublet of quartets, with the same quartet hfc constant of 17.5 G and slightly different doublet ones of 58 G for 4-ET$^{+\cdot}$ and 56 G for 4-PT$^{+\cdot}$. In these cations, the SOMO's are of the symmetric type with larger spin densities on the positions next to the substituents. The quartet hfc constant is readily attributed to the freely rotating methyl protons, and the large doublet ones to the respective one proton in the ethyl-methylene and n-propyl-methylene protons (β-pro-

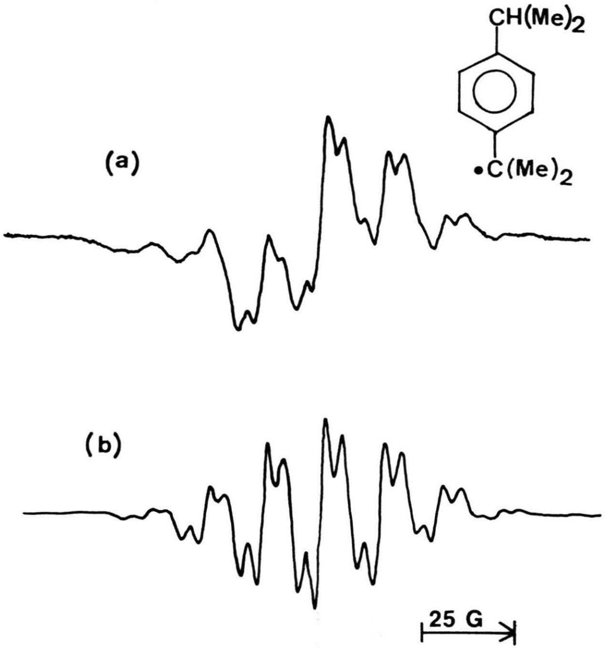
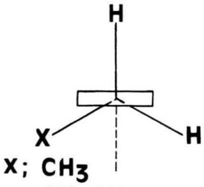


Fig. 3. ESR spectrum of the deprotonation-type neutral radical derived from 1,4-diisopropylbenzene in CCl_2FCClF_2 at 77 K (a). The simulation spectrum (b) was computed as in Figure 1. See text.

tons). The theoretical β-proton hfc constants, $a^H(1\,H) = 42.6$ G ($\varrho_\alpha = 0.320$) for $4\text{-}ET^{+\cdot}$ and $a^H(1\,H) = 41.9$ G ($\varrho_\alpha = 0.315$) for $4\text{-}PT^{+\cdot}$ have been obtained by applying the $\cos^2\theta$ rule with the conformation of $\theta = 0°$; these values are fairly larger than observed (58 G and 56 G), but are the closest to the observed. Thus, we propose a conformation illustrated below for the ethyl group of $4\text{-}ET^{+\cdot}$ and the n-propyl group of $4\text{-}PT^{+\cdot}$ in the CCl_2FCClF_2 matrix.

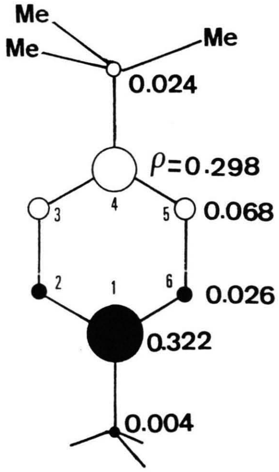


The UHF-INDO hfc constants of ethyl and n-propyl protons calculated for this conformation ($\theta = 0°$) are 34.6 G for $4\text{-}ET^{+\cdot}$ and 32.3 G for $4\text{-}PT^{+\cdot}$, and smaller than observed (58 and 56 G, respectively); in this conformation, the angle between the C–X (X: CH_3, C_2H_5) bond and the ring plane is ca. 30°. As mentioned above, there are two strongly coupled methylene protons in $1,4\text{-}DEB^{+\cdot}$ (27.7 G), where the angle θ is also close to 30°. The results for $4\text{-}ET^{+\cdot}$ and $1,4\text{-}DEB^{+\cdot}$ (as well as for $4\text{-}PT^{+\cdot}$ and $1,4\text{-}DPB^{+\cdot}$) make an interesting contrast. However the reason is not known at present.

3.5. 4-tert-Butyltoluene radical cation ($4\text{-}t\text{-}BT^{+\cdot}$)

Figure 5 shows the ESR spectrum of $4\text{-}t\text{-}BT^{+\cdot}$ observed at 77 K, which is composed of four lines due to $a^{CH_3} =$ ca. 18 G of the three equivalent methyl protons at C_1 with superposed small hyperfine splittings, 3–5 G, probably ascribable to the ring protons. Symons et al. have reported that the ESR spectrum of the tert-butylbenzene radical cation in CCl_3F is a broad triplet at 77 K with a hfc constant of ca. 13 G, and on warming the triplet is reversibly altered to a quartet and then to a doublet with a hfc constant of ca. 12 G [3]; the doublet has been attributed to the para proton, but the other splittings have been left to be assigned [3].

The UHF-INDO SOMO is illustrated below:



The UHF-INDO hfc constants of methyl protons and ring protons at $C_{3,5}$ and $C_{2,6}$ are 15.8 G (3H), −1.5 G (2H) and −0.6 G (2H), respectively. The hfc constant of methyl protons estimated by the $\cos^2\theta$ rule is 21.4 G (3H), while those of ring protons at $C_{3,5}$ and $C_{2,6}$ by McConnell's formula ($Q = -22.5$ G) [12] are −1.5 G (2H) and −0.6 G (2H), respectively. The UHF-INDO hfc constants of tert-butyl protons are too small (0.1–0.5 G) to be experimentally accessible. Thus, the superposed small hyperfine splittings of 3–5 G can be attributed to two ring protons at C_3 and C_5.

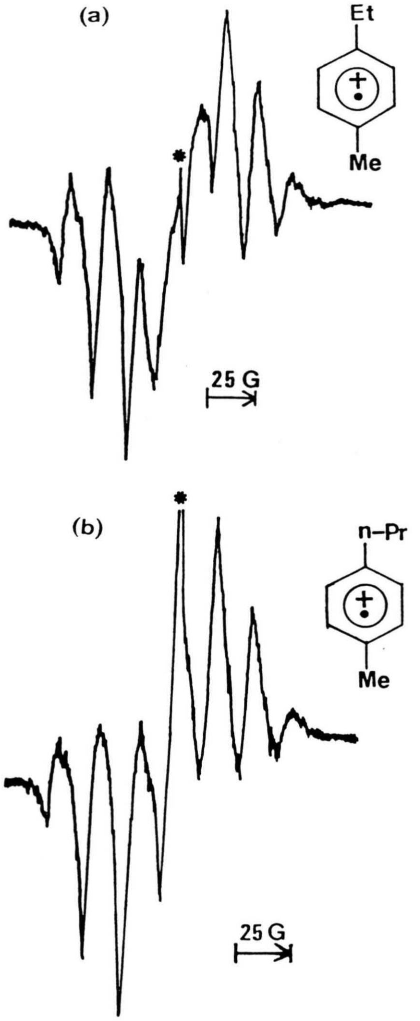


Fig. 4. ESR spectra of the 4-ethyltoluene (a) and 4-n-propyltoluene (b) radical cations in CCl_2FCClF_2 at 77 K. For the asterisks see Figure 1.

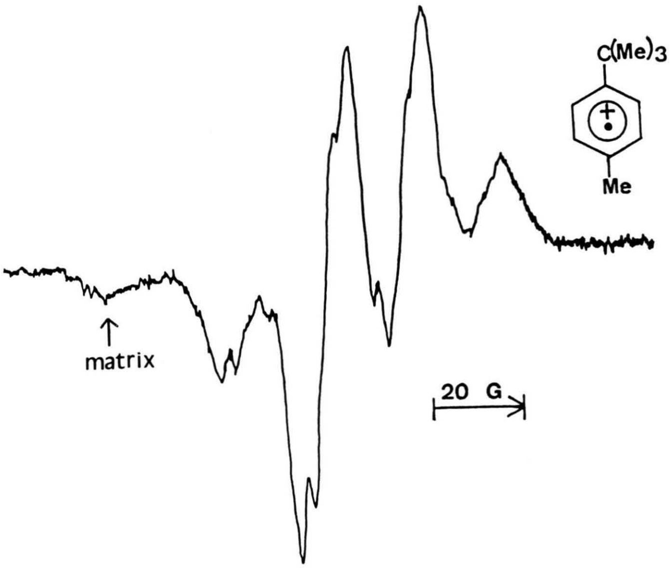
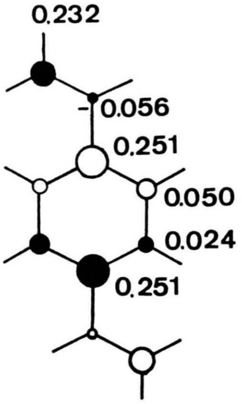


Fig. 5. ESR spectrum of the 4-tert-butyltoluene radical cation in CCl_2FCClF_2 at 77 K. An extra low-field line is due to the matrix.

3.6. 1,4-Divinylbenzene, 1,4-diisopropenylbenzene and 4-methylstyrene radical cations ($1,4\text{-}DVB^{+\cdot}$, $1,4\text{-}DIPEB^{+\cdot}$, $4\text{-}MST^{+\cdot}$)

Figure 6 (a) shows the ESR spectrum of $1,4\text{-DVB}^{+\cdot}$ observed at 77 K. The spectrum consists of five lines. Figure 6 (b) gives the spectrum simulated with an isotropic hfc constant of 7.6 G. The styrene radical cation ($ST^{+\cdot}$) observed in CCl_3F at 77 K has been reported to yield the hfc constants of 9.5 G (2H) and 11 G (1H), ascribable to the CH_2 protons and para proton, respectively [4]. Thus, it is reasonable to attribute the quartet of 7.6 G to the four CH_2 protons of the two vinyl groups. The UHF-INDO spin densities in $1,4\text{-DVB}^{+\cdot}$ were evaluated for two planar geometries, i.e., the trans- and cis-forms. The former SOMO and carbon $2p\pi$ spin densities are illustrated below:



The UHF-INDO hfc constants of CH_2 protons are -5.4 G and -5.5 G for the both planar structures, trans-form (C_{2h}) and cis-form (C_{2v}), which are a little underestimated in absolute value. The hfc constants and total energies as functions of the dihedral angle ϕ between the vinyl group plane and the benzene ring

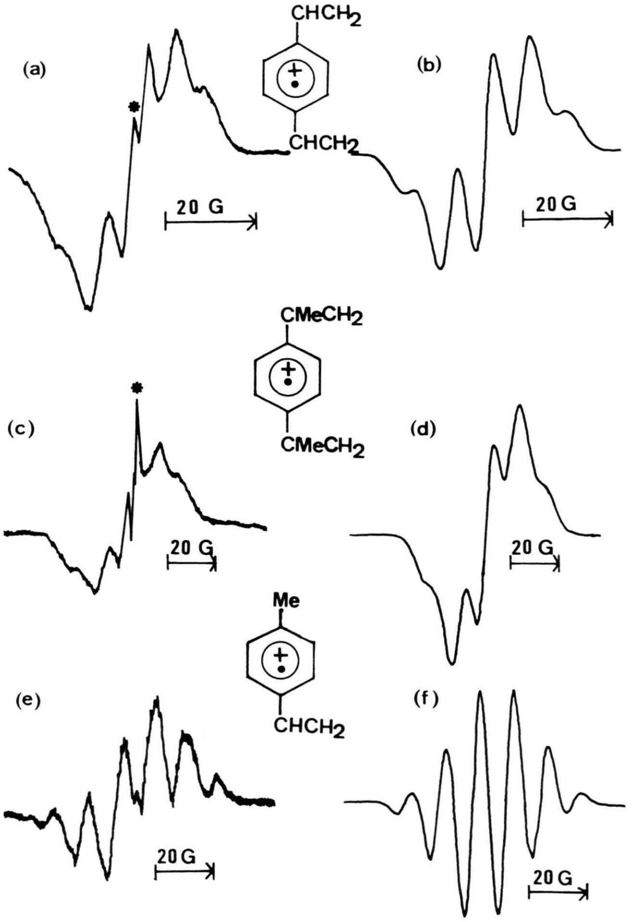
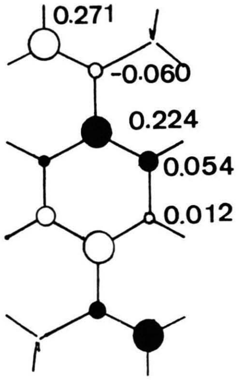


Fig. 6. ESR spectra of the 1,4-divinylbenzene (a), 1,4-diisopropenylbenzene (c), and 4-methylstyrene (e) radical cations in CCl_2FCClF_2 at 77 K. The respective simulation spectra, (b), (d), (f), were computed as in Figure 1. For the asterisks see Figure 1.

plane are given in Figs. 7 (a) and (b), for the trans- and cis-form, respectively.

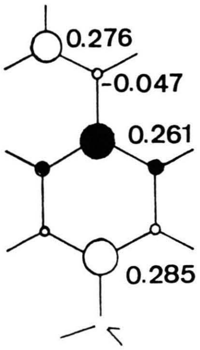
The difference between $a_1^{CH_2}$ and $a_2^{CH_2}$ increases with increasing angle ϕ, in a contrast to the observation that the four CH_2 protons are equivalent. Therefore, we conclude that 1,4-$DVB^{+\cdot}$ has a planar structure, although the total energy curves give the minima at ϕ = ca. 30° for both structures. We cannot determine which form is the case, the trans-form or the cis-form, since there is no significant energy difference between them. In the planar 1,4-$DVB^{+\cdot}$ there occurs strong conjugation between the benzene ring and vinyl group. The theoretical spin densities on the CH_2 carbons of 1,4-$DVB^{+\cdot}$ are a little smaller than that of $ST^{+\cdot}$ [4], as expected from the molecular symmetry.

Figure 6(c) shows the ESR spectrum of 1,4-$DIPEB^{+\cdot}$ exhibiting isotropic five lines associated with the four equivalent CH_2 protons; the hfc constant is estimated to be 10.0 G from spectral simulation as shown in Fig. 6(d). The UHF-INDO SOMO and carbon $2p\pi$ spin densities for an assumed planar geometry are illustrated below:



The UHF-INDO hfc constants of CH_2 protons are estimated to be -6.1 G and -6.4 G for two planar structures, trans-form (C_{2h}) and cis-form (C_{2v}), respectively, which are underestimated in absolute value similarly to the case of 1,4-$DVB^{+\cdot}$. The experimental hfc constants of CH_2 protons are slightly larger than those in 1,4-$DVB^{+\cdot}$. This tendency is reproduced by the present UHF-INDO calculation.

Figure 6(e) shows the ESR spectrum of 4-$MST^{+\cdot}$ observed at 77 K. The ESR spectrum is composed of six lines with an equal hfc constant of 11.3 G (5H). Thus, the three methyl protons and two CH_2 protons are equivalent. The spectral simulation with this hfc constant is shown in Figure 6(f). The UHF-INDO SOMO is illustrated below for a geometry where the vinyl group and the benzene ring are coplanar:



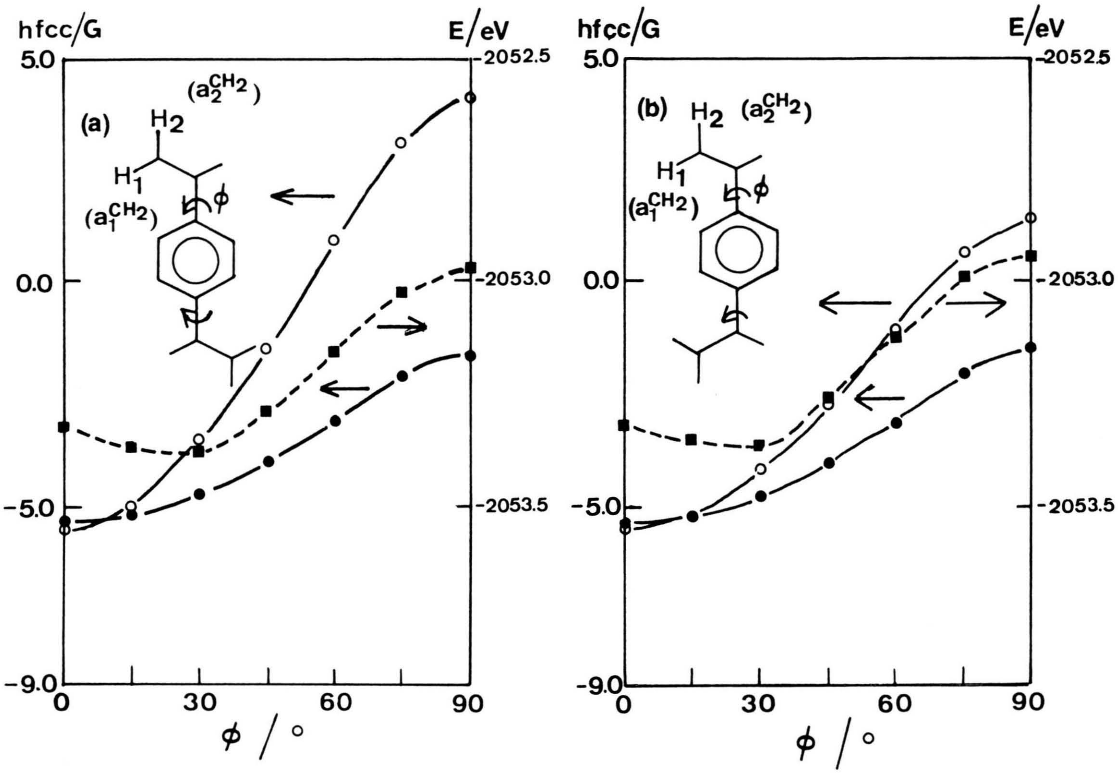


Fig. 7. The UHF-INDO hfc constants (hfcc) and total energies for the trans-form (a) and cis-form (b) of the 1,4-divinylbenzene radical cation. The symbols ●, ○, and ■ refer to $a_1^{\mathrm{CH_2}}$, $a_2^{\mathrm{CH_2}}$ and total energy, respectively. ϕ is the dihedral angle between the vinyl-group plane and the benzene ring (see text).

The UHF-INDO hfc constants of methyl and CH_2 protons are evaluated to be 13.6 G, −6.4 G and −6.5 G, respectively. In contrast to the experimental result, the UHF-INDO hfc constant of the methyl protons is about twice as large as those of the CH_2 protons. No significant improvement has been achieved when the calculations were made for various angles ϕ. Nevertheless, we believe that 4-MST$^{+\cdot}$ has a planar structure by referring to the results for 1,4-DVB$^{+\cdot}$ and 1,4-DIPEB$^{+\cdot}$.

It is interesting to note that the ϱ_α's in 1,4-DVB$^{+\cdot}$, 1,4-DIPEB$^{+\cdot}$ and 4-MST$^{+\cdot}$ (0.251, 0.225, and 0.261) are remarkably smaller than those of alkylbenzene radical cations (0.3). This comes from the extended conjugation between the benzene ring and alkenyl groups. The decrease of ϱ_α in 1,4-DIPEB$^{+\cdot}$ results from increased interaction between the benzene ring and alkenyl group due to hyperconjugation.

The theoretical spin density on the CH_2 carbon, $\varrho_{\mathrm{CH_2}}$, increases in the order of 1,4-DVB$^{+\cdot}$, 1,4-DIPEB$^{+\cdot}$ and 4-MST$^{+\cdot}$, and the pertinent proton hfc constants are −5.2 G, −6.1 G, and −6.2 G with $Q = -22.5$ G for McConnell's formula [12]. These values are consistent with the observed ones as far as the decreasing order is concerned, but are considerably smaller in absolute value. This probably comes from the adoption of a large C−C bond length (1.54 Å) between the benzene ring and alkenyl group.

Conclusion and Remarks

The electronic and molecular structure of some alkyl- and alkenylbenzene radical cations have been studied by ESR and semiempirical MO calculations. Though the matrix dependence of the alkyl conformation and the radiochemical reaction in some alkylbenzenes have been established for the first time, the mechanism has not yet been clarified. For elucidation of the interaction between radical species and matrices, optical approaches such as IR and resonance Raman spectroscopy as well as theoretical approaches would be promising.

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