# Spectroscopic Studies of Various Carbene–Radical-cations formed by Radiolysis of Solutions on Halogenocarbons

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Cationic species produced in the $\gamma$-radiolysis of the halogenocarbon–aryldiazomethane mixtures have been studied at 77 K by electron spin resonance (e.s.r.) and optical absorption spectroscopy. A diphenyldiazomethane radical-cation ($[(C_6H_5)_2CN_2]^{+\cdot}$) produced by the radiolysis of n-$C_4H_9Cl$–$(C_6H_5)_2CN_2$ (0.1 mol %) mixtures is found to have an absorption band at 650 nm. When the cation is irradiated with visible light, a different cation is produced which has an absorption spectrum at 390 nm, interpretable in terms of a diphenyl carbene radical-cation ($[(C_6H_5)_2C]^{+\cdot}$). A phenyldiazomethane radical-cation ($[C_6H_5CHN_2]^{+\cdot}$) and a phenylcarbene radical-cation ($[C_6H_5CH]^{+\cdot}$) have absorption bands at 515 and 475 nm, respectively. The e.s.r. spectrum of $[(C_6H_5)_2CN_2]^{+\cdot}$ cations, produced by the radiolysis of $CCl_3F$–$(C_6H_5)_2CN_2$ (0.2 mol %) mixtures at 77 K, shows a broad singlet spectrum. Upon irradiation with visible light the broad spectrum changes into a sharp singlet, which is ascribed to $[(C_6H_5)_2C]^{+\cdot}$ cations. Formation of $[C_6H_5CHN_2]^{+\cdot}$ and $[C_6H_5CH]^{+\cdot}$ cations has also been studied by e.s.r. spectroscopy. The effect of deuteriation on the e.s.r. spectra has been studied by use of deuteriated aryldiazomethanes, such as $(C_6D_5)_2CN_2$, $C_6H_5CDN_2$, and $C_6D_5CDN_2$.

A number of studies on arylcarbenes have been undertaken by chemical analysis of reaction products, electron spin resonance (e.s.r.) spectroscopy, and optical absorption spectroscopy.[1] Radical cations are also important reactive intermediates in organic reactions of diazo compounds.[2] Though carbene radical-cations are now thought to be the reactive species in some organic reactions, arousing much interest, detection of these cations has not been successful as yet.

It has been well established that exposure of dilute halogenocarbon solutions of certain compounds to $\gamma$-rays at 77 K gives solute cations, provided the ionization potential of the solute is less than that for the solvent. Using this phenomenon, e.s.r.[3] and optical[4] absorption spectra of various cations have been measured at low temperature. Most of the previous studies, however, are concerned with the cations of stable molecules.

Aryldiazomethanes are unstable molecules which decompose on exposure to light into arylcarbenes. In this work, in order to observe arylcarbene radical-cations, frozen solutions of halogenocarbons containing aryldiazomethane were $\gamma$-irradiated and the formation of cations was studied by e.s.r. and optical absorption spectroscopy.

## Experimental

*Materials.*—Butyl chloride and trichlorofluoromethane were more than 99.0 and 99.9 mol % pure, respectively and were used after distillation on a vacuum line. Phenyldiazomethane was prepared by pyrolysis of benzaldehyde tosylhydrazone with sodium methoxide in pyridine.[5] The purity of the phenyldiazomethane was more than 99 mol % as determined by n.m.r. spectroscopy. Diphenyldiazomethane was prepared by oxidation of benzophenone hydrazone with yellow mercuric oxide[6] which gave a purity of more than 99 mol %.

Since synthesis of deuteriated aryldiazomethanes has not been reported previously, their preparations are explained in some detail.

$[^2H_1]Phenyldiazomethane$ $(C_6H_5CDN_2)$.—$[^2H_1]$Benzaldehyde was prepared using $[^2H_4]$lithium aluminium hydride (Merck, 98%).[7] $[^2H_1]$Phenyldiazomethane was prepared by the reaction of sodium methoxide with $[^2H_1]$benzaldehyde tosylhydrazone, obtained easily from $[^2H_1]$benzaldehyde. The extent of deuteriation as analysed by n.m.r. spectroscopy was 80%.

$[^2H_6]Phenyldiazomethane$ $(C_6D_5CDN_2)$.—$[^2H_6]$Benzaldehyde was prepared by a modified general procedure for the preparation of p-nitrobenzaldehyde.[8] Chromium trioxide (3 g) was added slowly to a solution of $[^2H_8]$toluene [Atomic Energy Commission of France (CEA); 99.6%; 1 ml], in glacial acetic acid (20 ml), acetic anhydride, (20 ml) and concentrated sulphuric acid (1 ml) at 0 °C. The mixture was stirred for 10 min, when the solution was poured into cold water, extracted with ether, and the organic layer was washed with water. Removal of solvent yielded $[^2H_6]$benzal diacetate. The diacetate was hydrolysed by reflux in ethanol (20 ml) and 1M-sulphuric acid (10 ml) acid to give $[^2H_6]$benzaldehyde. $[^2H_6]$Phenyldiazomethane was then prepared according to the literature method[6] from $[^2H_6]$benzaldehyde tosylhydrazone, obtained from $[^2H_6]$benzaldehyde. The extent of deuteriation, as determined by mass spectrometry after the conversion into benzaldehyde, were 98% for the phenyl group and 73% for the $\alpha$-carbon.

$[^2H_{10}]Diphenyldiazomethane$ $[(C_6D_5)_2CN_2]$.—$[^2H_{10}]$Benzophenone was prepared by the reported procedure[9] from $[^2H_6]$benzene (Merck, 99.5%). $[^2H_{10}]$Diphenyldiazomethane was then prepared from $[^2H_{10}]$benzophenone hydrazone, obtained easily from $[^2H_{10}]$benzophenone. The extent of deuteriation was 96%.

*Irradiation and Measurement.*—The sample was irradiated at 77 K with $\gamma$-rays from $^{60}Co$ at a dose rate of 7.4 × $10^5$ rad h$^{-1}$ to a dose of 3.7 × $10^5$ rad. The irradiation with visible light was carried out with a xenon lamp. The irradiation at wavelengths
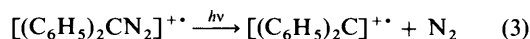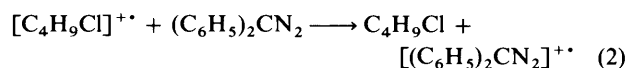
longer than 560 nm was carried out with the xenon lamp equipped with a Toshiba V-O 56 filter.

Optical absorption spectra were measured at 77 K on a Hitachi Model 323 Recording Spectrophotometer. E.s.r. spectra were measured at 77 K on a JES-FE2XG ESR spectrometer at a microwave power level of 0.2 mW which does not result in signal saturation. The e.s.r. signals were analysed using a Nippon -Univac digitizer personal computer system.

## Results and Discussion

*Optical Absorption Spectra of γ-Irradiated Butyl Chloride–Aryldiazomethane Mixtures.*—Figure 1 shows the optical absorption spectra of the γ-irradiated $n\text{-}C_4H_9Cl\text{-}(C_6H_5)_2CN_2$ (0.1 mol %) mixtures at 77 K. Butyl chloride when γ-irradiated in the absence of diphenyldiazomethane (DDM) shows a broad and weak absorption spectrum at around 540 nm as reported previously.[4] When an $n\text{-}C_4H_9Cl\text{-}DDM$ (0.1 mol %) mixture was γ-irradiated at 77 K, the broad absorption spectrum disappeared and an intense absorption spectrum appeared at 650 nm (the solid line in Figure 1) which is different from the absorption spectrum (a very weak one around 520 nm and a strong one below 330 nm) of the DDM molecule itself. Since γ-irradiation of the butyl chloride frozen solution produces cations of the solute by hole migration from butyl chloride to the solute,[4] the absorption at 650 nm is ascribed to the cation of DDM. The absorption at 650 nm appears also in the spectrum run at very low DDM concentration (0.025 mol %). Thus, the spectrum at 650 nm is not due to the dimer cation of DDM, but probably to the monomer cation.

When the γ-irradiated $n\text{-}C_4H_9Cl\text{-}DDM$ mixture is exposed to visible light λ > 560 nm, the intensity of the absorption at 650 nm decreases and a new absorption appears at around 390 nm (the dashed line in Figure 1). The difference between the two spectra gives the new spectrum (–·–·–·–). Since a DDM molecule is not itself decomposed by visible light (λ > 560 nm), the new absorption at 390 nm must be due to a species produced by the photolysis of the DDM cation. The photodetachment of an $N_2$ molecule, which is a well known process in the photolysis of diazo compounds, probably occurs in the photolysis of the DDM cation. The reaction scheme is represented as follows.

$$n\text{-}C_4H_9Cl \rightsquigarrow [C_4H_9Cl]^{+\bullet} + e^- \qquad (1)$$

$$[C_4H_9Cl]^{+\bullet} + (C_6H_5)_2CN_2 \longrightarrow C_4H_9Cl + [(C_6H_5)_2CN_2]^{+\bullet} \qquad (2)$$

$$[(C_6H_5)_2CN_2]^{+\bullet} \xrightarrow{h\nu} [(C_6H_5)_2C]^{+\bullet} + N_2 \qquad (3)$$

The DDM cation, produced by γ-irradiation [equation (1)] and a subsequent hole migration [equation (2)], is decomposed photochemically to a diphenylcarbene radical-cation [equation (3)] which has an absorption band at 390 nm.

Figure 2 shows the optical absorption spectra of γ-irradiated $n\text{-}C_4H_9Cl\text{-}C_6H_5CHN_2$ (*ca.* 0.1 mol %) mixtures at 77 K. By analogy to the DDM system, the absorption spectrum at 515 nm is ascribed to a phenyldiazomethane radical-cation ($[C_6H_5CHN_2]^{+\bullet}$). When the γ-irradiated mixture is then exposed to visible light, the intensity of the absorption at 515 nm decreases and a new absorption at 475 nm appears simultaneously. This new absorption may be ascribed to the phenylcarbene radical-cation ($[C_6H_5CH]^{+\bullet}$). The wavelength of this absorption is longer than that (390 nm) of the diphenylcarbene radical-cation, though this may perhaps be expected. One plausible explanation is as follows. The structure of the phenylcarbene radical-cation is a tropylium-cation type, whereas that of the diphenylcarbene radical-cation is a benzyl-cation type. The specific structure of the phenylcarbene radical-

cation may give the absorption spectrum at a longer wavelength than that of the diphenylcarbene radical-cation.

*E.s.r. Spectra of γ-Irradiated Trichlorofluoromethane–Aryldiazomethane Mixtures.*—Figure 3 shows e.s.r. spectra of a γ-irradiated $CCl_3F\text{-}(C_6H_5)_2CN_2$ (0.2 mol %) mixture at 77 K. In order to simplify the overlapping spectra, the spectrum due to a colour centre of a γ-irradiated quartz cell has been omitted by graphic analysis with a personal computer. Thus only the spectra due to the solute are shown. A broad singlet (solid line) can be ascribed to the $[(C_6H_5)_2CN_2]^{+\bullet}$ cations which are produced by hole migration from $CCl_3F$ to diphenyldiazomethane. When the γ-irradiated sample is subsequently irradiated with visible light at wavelengths longer than 560 nm, the broad line changes into a sharp one centred at $g$ 2.0024. This spectral change corresponds to the change in the optical absorption spectra shown in Figure 1. The illumination of diphenyldiazomethane molecules with visible light (λ > 560 nm) does not give e.s.r. spectra of free radicals under the present conditions. Thus the new species might perhaps be a di-



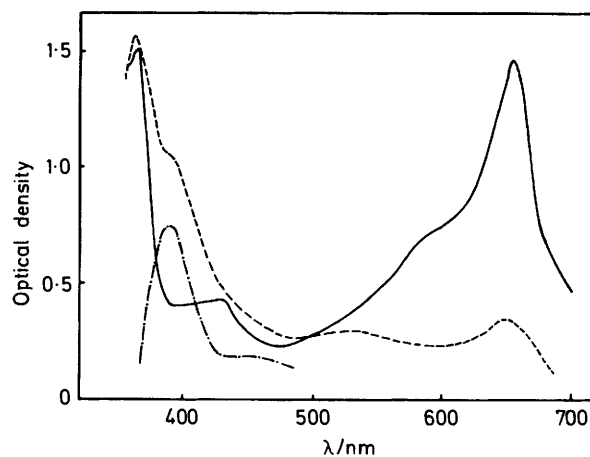**Figure 1.** Optical absorption spectra of γ-irradiated $n\text{-}C_4H_9Cl\text{-}(C_6H_5)_2CN_2$ (0.1 mol %) at 77 K. —— After γ-irradiation to a dose of $3.7 \times 10^5$ rad. – – – – After photobleaching of the γ-irradiated sample with visible light at λ > 560 nm. —·—·—·— Absorption spectrum of the new species produced by the photobleaching



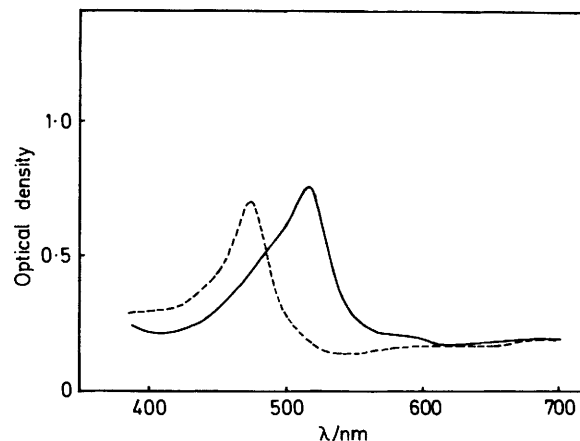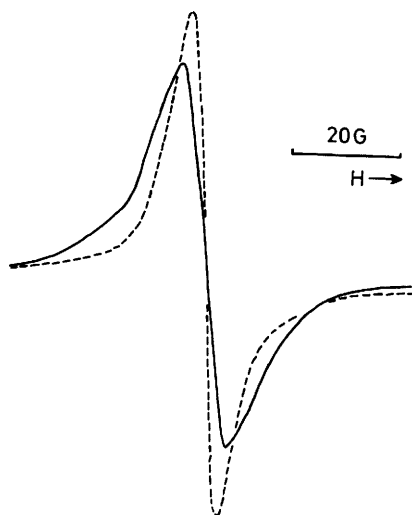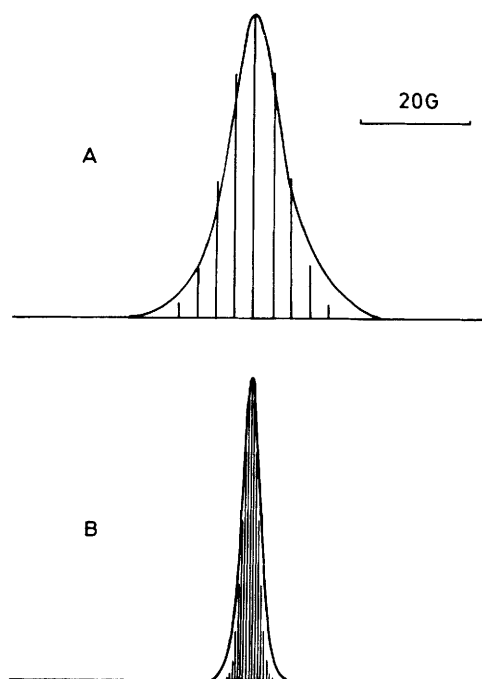**Figure 2.** Optical absorption spectra of γ-irradiated $n\text{-}C_4H_9Cl\text{-}C_6H_5CHN_2$ (*ca.* 0.1 mol) at 77 K. —— After γ-irradiation to a dose of $3.7 \times 10^5$ rad. – – – – After photobleaching of the γ-irradiated sample with visible light

**Figure 3.** E.s.r. spectra of γ-irradiated $CCl_3F$–$(C_6H_5)_2CN_2$ (0.2 mol %) at 77 K. The e.s.r. spectra due to a colour centre of a γ-irradiated quartz cell are omitted from the spectra. The gain setting of the two spectra is the same. —— After γ-irradiation to a dose of $3.7 \times 10^5$ rad. – – – – After photobleaching of the γ-irradiated sample with visible light at $\lambda > 560$ nm



**Figure 4 A.** Integrated e.s.r. spectrum after photobleaching of the γ-irradiated $CCl_3F$–$(C_6H_5)_2CN_2$ (0.2 mol %) at 77 K. The stick diagram represents a calculated spectral pattern for a $[(C_6H_5)_2C]^{+\bullet}$ cation (see the text). **B.** Integrated e.s.r. spectrum after photobleaching of the γ-irradiated $CCl_3F$–$(C_6D_5)_2CN_2$ (0.2 mol %) at 77 K. The stick diagram represents a calculated spectral pattern for a $[(C_6D_5)_2C]^{+\bullet}$ cation (see the text)

phenylcarbene radical-cation $[(C_6H_5)_2C]^{+\bullet}$, produced by the photodetachment of $N_2$ from the DDM cation.
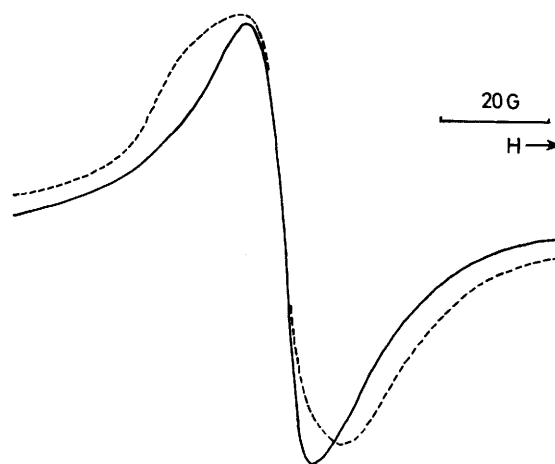
Hyperfine splitting of protons was not observed in the e.s.r. spectra in Figure 3 because of broadening of the spectra. Although the e.s.r. spectra were measured at 110 K, the hyperfine splitting of protons could not be measured. In order to obtain further information from the e.s.r. spectra, deuteriated diphenyldiazomethane $[(C_6D_5)_2CN_2]$ was used in place of $(C_6H_5)_2CN_2$. The e.s.r. spectrum of $[(C_6D_5)_2CN_2]^{+\bullet}$ produced by γ-irradiation of a $CCl_3F$–$(C_6D_5)_2CN_2$ mixture is sharper singlet than that of $[(C_6H_5)_2CN_2]^{+\bullet}$. Moreover, the spectrum of $[(C_6D_5)_2C]^{+\bullet}$ produced by photolysis of the γ-irradiated sample is significantly sharper than that of $[(C_6H_5)_2C]^{+\bullet}$. Integrated e.s.r. spectra of $[(C_6H_5)_2C]^{+\bullet}$ and $[(C_6D_5)_2C]^{+\bullet}$ cations are shown in Figures 4A and B, respectively. In Figure 4A a stick diagram represents a spectral pattern for the $[(C_6H_5)_2C]^{+\bullet}$ cation calculated on the assumption that all the protons have the same hyperfine splitting constant of 3.4 G as determined to best fit the experimental spectrum. Then a hyperfine splitting constant of the deuterons in the $[(C_6D_5)_2C]^{+\bullet}$ cation is evaluated as 0.5 G and thus a spectral pattern for the $[(C_6D_5)_2C]^{+\bullet}$ cation can be calculated. The calculated spectral pattern for the $[(C_6D_5)_2C]^{+\bullet}$ cation coincides well with the experimental spectrum as shown in Figure 4B.

Figure 5 shows the e.s.r. spectra of γ-irradiated $CCl_3F$–$C_6H_5CHN_2$ (ca. 0.2 mol %) mixture at 77 K. The broad spectrum (solid line) is due to $[C_6H_5CHN_2]^{+\bullet}$ cations, produced by hole migration from $CCl_3F$ to phenyl-diazomethane. When the γ-irradiated sample is exposed to visible light, the spectrum changes into a broader singlet spectrum (dashed line) centred at $g$ 2.0046 and ascribed to the phenylcarbene radical-cation ($[C_6H_5CH]^{+\bullet}$).

In order to obtain further information on the e.s.r. spectra of the carbene radical-cation, the effect of deuteriation on the spectra was studied using $C_6H_5CDN_2$ and $C_6D_5CDN_2$. Figure 6 shows the integrated e.s.r. spectra of $[C_6H_5CH]^{+\bullet}$, $[C_6H_5CD]^{+\bullet}$, and $[C_6D_5CD]^{+\bullet}$ cations, produced by the photolysis of the corresponding phenyldiazomethane cations. Replacement of the α-proton with deuterium does not cause a
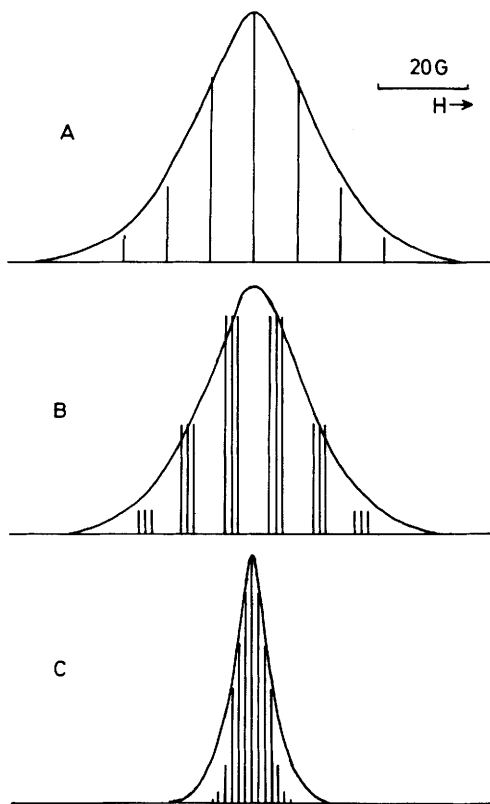


**Figure 5.** E.s.r. spectra of γ-irradiated $CCl_3F$–$C_6H_5CHN_2$ (ca. 0.2 mol %) at 77 K. The e.s.r. spectra due to a colour centre of a γ-irradiated quartz cell are omitted from the spectra. The gain setting of the two spectra is the same. —— After γ-irradiation to a dose of $3.7 \times 10^5$ rad. – – – – After photobleaching of the γ-irradiated sample with visible light

drastic spectral change, and the spectrum (Figure 6B) of $[C_6H_5CD]^{+\bullet}$ is only slightly sharper than that (Figure 6A) of $[C_6H_5CH]^{+\bullet}$. The spectrum of $[C_6D_5CD]^{+\bullet}$, however, is very narrow (Figure 6C). Thus it can reasonably be assumed that all the protons in $[C_6H_5CH]^{+\bullet}$ have the same hyperfine splitting constant of 9.6 G which is determined from the best fit with the experimental spectrum (Figure 6A). This assumption may be acceptable if the $[C_6H_5CH]^{+\bullet}$ cation is a tropylium-

**Table.** Spectral data for arylcarbene radical-cations

| Cation | Optical absorption $\lambda_{max.}$/nm | E.s.r. absorption | |
| --- | --- | --- | --- |
| | | $g$-values | $\Delta H_{\frac{1}{2}}{}^a$/gauss |
| $[(C_6H_5)_2C]^{+\cdot}$ | 390 | 2.0024 | 11 |
| $[C_6H_5CH]^{+\cdot}$ | 475 | 2.0046 | 30 |

$^a$ Half-height width of e.s.r. spectrum.

**Figure 6 A.** Integrated e.s.r. spectrum after photobleaching of the γ-irradiated $CCl_3F–C_6H_5CHN_2$ (ca. 0.2 mol %) at 77 K. The stick diagram represents a calculated spectral pattern for $[C_7H_6]^{+\cdot}$ cation (see the text). **B.** Integrated e.s.r. spectrum after photobleaching of the γ-irradiated $CCl_3F–C_6H_5CDN_2$ (ca. 0.2 mol %) at 77 K. The stick diagram represents a calculated spectral pattern for a $[C_7H_5D]^{+\cdot}$ cation (see the text). **C.** Integrated e.s.r. spectrum after photobleaching of the γ-irradiated $CCl_3F–C_6D_5CDN_2$ (ca. 0.2 mol %) at 77 K. The stick diagram represents a calculated spectral pattern for a $[C_7D_6]^{+\cdot}$ cation (see text)

splitting constant of 1.4 G for deuteron. The calculated spectral patterns coincide with the experimental spectra shown in Figures 6B and C. Although the evidence for the structures of $[C_6H_5CH]^{+\cdot}$ is not conclusive at present, the benzyl-cation type seems to be less probable on the basis of its absorption maximum being of longer wavelength than that of diphenyl-carbene radical-cation (Figures 1 and 2).

Spectral data for arylcarbene radical-cations obtained in this work are summarized in the Table.

cation type or alternatively if the $[C_6H_5CH]^{+\cdot}$ cation is a benzyl-cation type and a spin density at the α-carbon is a sixth of that of phenyl group. The spectral patterns for $[C_6H_5CD]^{+\cdot}$ and $[C_6D_5CD]^{+\cdot}$ cations can then be calculated by using a

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