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ESR Study on the σ- and π-Radical Cations Formed by One-Electron Oxidation of Phenyldiazomethanes

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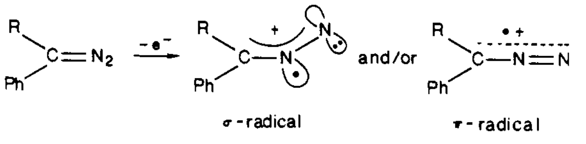
One-electron oxidations of diazomethanes have attracted much attention from mechanistic and synthetic standpoints.[1-4] The intermediacy of radical cations has often been suggested, but their direct observation could not be achieved spectroscopically[3] because of their short lifetimes as deduced from a voltammetric study.[4] Here, we report the first ESR study on the radical cations of phenyldiazomethanes in solution. Depending on substituents, the diazomethanes are shown to afford either σ- or π-radical cations of quite different electronic structures. The removal of one electron from the π-orbital (HOMO) of unhindered phenyldiazomethanes yields bent σ-radical cations by a turnover of the SOMO.

The ESR spectra of diazomethane radical cations were obtained during electrochemical oxidation[5] in a cavity at low temperature. When a degassed solution of diphenyldiazomethane (**1**) in CH_2Cl_2 containing 0.1 M n-Bu_4NBF_4 was electrolyzed at +1.3 V (vs. Ag/AgCl), a spectrum of $\mathbf{1}^{\bullet+}$ was observed (Figure 1a). The triplet of triplets pattern is due to the hyperfine coupling with two unequivalent nitrogens with large coupling constants, 1.72 and 1.01 mT.[6] When the electrolysis was stopped, this species decayed with half-lives of ~10 s at -33 °C and ~90 s at -83 °C. Similar spectra were observed for $(p\text{-}MeOC_6H_4)_2CN_2$ (**2**) and $Ph(Me)CN_2$ (**3**). Even when an α-methyl group is attached, couplings of protons were too small to resolve (Figure 1b). The coupling constants of two nitrogens are practically unchanged by substituents (Table I) and close to those (2.25 and 0.94 mT) of phenyldiazenyl, a reported σ-radical.[7] Thus, the radical cations of **1**–**3** seem to have a "σ-radical" structure, where an unpaired electron is localized on two nitrogens.



(1)

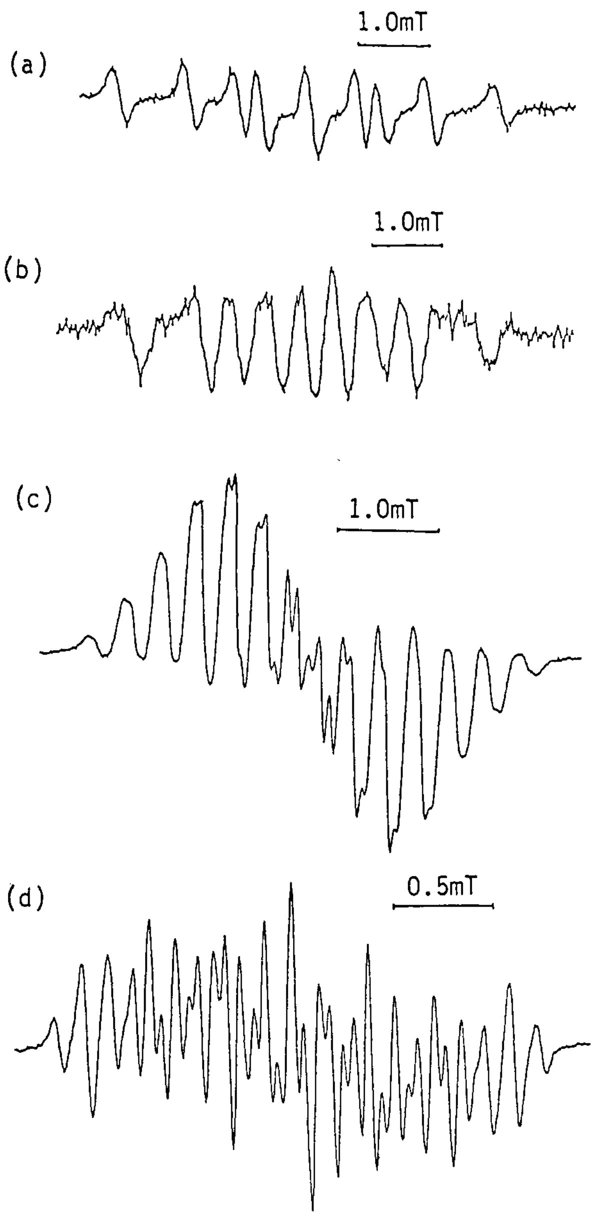


Figure 1. ESR spectra observed during the electrochemical oxidation of (a) **1** at -33 °C, (b) **3**, (c) **4**, and (d) **5** at -90 °C, in CH_2Cl_2 containing 0.1 M n-Bu_4NBF_4.

The one-electron removal from the π-orbital (HOMO) of phenyldiazomethanes[8] surely changes the resulting electronic configuration into a σ-radical structure. This interesting turnover is assumed to be due to a significant stabilizing interaction between phenyl and the resulting cation center. In order to reduce such an interaction, we studied diazomethanes with a *tert*-butyl substituent. In fact, a different type of ESR spectrum was observed in the case of $\mathbf{4}^{\bullet+}$ and $\mathbf{5}^{\bullet+}$ (Figure 1c and 1d). These radical cations were relatively stable with half-lives of ~10 and ~30 min, respectively, at -90 °C. These well-resolved spectra could be nicely simulated by using the hyperfine coupling constants of nitrogens and protons on the phenyl group (see Table I). Radical cations $\mathbf{4}^{\bullet+}$ and $\mathbf{5}^{\bullet+}$ have clearly a "π-radical" structure, the spin density being delocalized on both diazo and phenyl groups.

The turnover of electronic structures by one-electron oxidation has been documented recently,[9] but the present case is the only clear-cut example. Relevant σ-radicals, e.g., iminoxyl,[10] benzoyl,[11]

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Table I. ESR Spectral Data for Diazomethane Radical Cations[a]

diazo compd	g^b	a_N,[c] mT	a_H,[d] mT ortho H	meta H	CH_3	electronic structure assigned
Ph_2CN_2 (**1**)	2.0009	1.72, 1.01				σ
(p-$MeOC_6H_4)_2CN_2$ (**2**)	2.0012	1.65, 1.02				σ
$Ph(Me)CN_2$ (**3**)	2.0015	1.49, 1.01				σ
p-$MeC_6H_4(t\text{-}Bu)CN_2$ (**4**)	2.0017	0.47,[d] 0.35[d]	0.35 (2H)	0.08 (2H)	0.67 (3H)	π
p-$MeOC_6H_4(t\text{-}Bu)CN_2$ (**5**)	2.0021	0.39,[d] 0.34[d]	0.33 (1H) 0.26 (1H)		0.14 (3H)	π

[a] Generated in an ESR cavity by electrolysis of 20–100 mM diazomethane at 1.2–1.6 V vs. Ag/AgCl in CH_2Cl_2 containing 0.1 M n-Bu_4NBF_4 at −70 to ca. −90 °C. [b] g value, ±0.0001. [c] Coupling constant, ±0.01 mT (**1**–**3**). [d] Coupling constant from computer simulation.

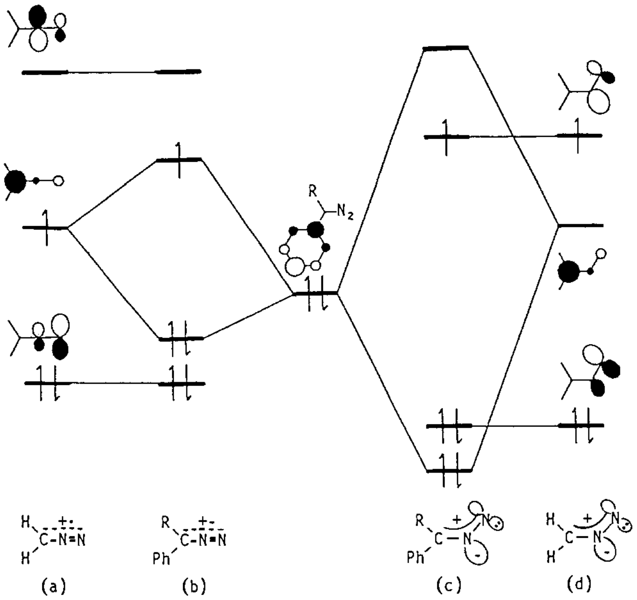

Figure 2. Schematic drawing of MOs of (a) diazomethane linear π-radical cation, (b) *tert*-butylphenyldiazomethane π-radical cation (R = t-Bu), (c) phenyldiazomethane σ-radical cation, and (d) hypothetical diazomethane bent σ-radical cation.

phenyldiazenyl,[7] and nitrosobenzene radical cation,[12] have been reported but without turnover. The present turnover may be analyzed on the basis of MO calculations. Thus, electronic structures for $CH_2N_2^{\bullet+}$ were calculated according to the ab initio UHF-MO method[13] (STO-3G basis).[14] The calculated π-radical cation has a linear C–N–N geometry with a three-centered allylic orbital, which corresponds to the HOMO of CH_2N_2[8] (Figure 2a). On the other hand, the σ-radical cation[15] takes on a planar bent geometry in which an unpaired electron is localized in the in-plane π_{np}*-orbital (Figure 2d). The energy of the optimized σ-radical is 53.7 kcal/mol higher than that of the π-radical. However, the difference for the case of $PhCHN_2^{\bullet+}$ is dramatically reduced down to ~10 kcal/mol. The observed turnover of energy levels seems to be reasonable since the calculated difference is so small and solvation should be significant in solution.

The dramatic effect of phenyl substituent can be well understood as shown in Figure 2. When R = aryl or Me, the energy of the upper C–N–N π-orbital should be significantly raised by interaction with the coplanar phenyl group, resulting in the reversion of the SOMO to the N–N π_{np}*-orbital to afford bent σ-radicals (Figure 2c). But when R = t-Bu, the diazo group is forced by steric repulsion to be twisted out of the phenyl plane, the π-radical structure being retained as observed (Figure 2b). Thus, we have uncovered two contrasting σ and π electronic structures for phenyldiazomethane radical cations.

Further studies on related radical cations are in progress.

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Proton-Transfer Spectroscopy of Benzanilide. The Amide-Imidol Tautomerism

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We report the photoinduced proton-transfer tautomerization of benzanilide (N-phenylbenzamide) to its imidol form (N-phenylbenzimidic acid), structures I and II, Figure 1. The study compares the UV fluorescence (F_1), the violet phosphorescence (P), and a strong blue-green fluorescence (F_2) observed at 293 K in Na-dried, Ar-degassed hydrocarbon solvent. F_2 is identified as the transient fluorescence of the excited imidol tautomer produced by double proton transfer in the H-bonded dimer of *cis*-benzanilide.

The photochemistry of aryl amides and urethanes has generated spectroscopic interest.[1-3] The spectra on one species, benzanilide, if taken at face value, would represent an anomaly to the spectroscopist. For example, the fluorescence maximum reported[4] is 1200 cm^{-1} lower in frequency than the phosphorescence maximum, although the onsets of the singlet–singlet and triplet–singlet emissions seem to be normal in order.

Benzanilide spectra include UV absorption, onset 320 nm, first maximum 265 nm (ϵ 13000), discrete shoulder 222 nm (10^{-4} M, methylcyclohexane (MCH), 293 K); normal fluorescence F_1, onset 280 nm, maximum 307 nm (10^{-6} M, MCH, 293); and phosphorescence, onset 370 nm, maximum 410 nm (ethanol glass, 77 K). These data generally agree with those published,[4] except that F_1 was not previously observed as a discrete emission; it is very weak and is rapidly replaced by photoproduct emission at slightly longer wavelengths.

The F_2 proton-transfer fluorescence is shown in Figure 2. This luminescence has an onset at 410 nm and maximum at 474 nm at 293 K in MCH. At 77 K the band observed at 444 nm maximum in MCH glass solvent and in ethanol glass at 438 nm and at[4] 435 nm for EPA at 77 K represents a total emission: $P + F_2$ (cf. Figure 2). The previous observation of fluorescence by time-resolved spectrometry[4] for benzanilide in EPA at 77 K we

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