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The Radical Cation of 4,5-Diphenylimidazole, an EPR and ENDOR Study†

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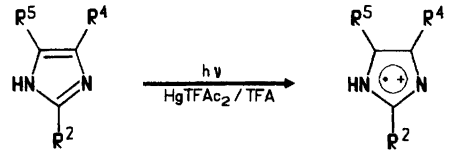
EPR parameters of the radical cation of 4,5-diphenylimidazole are given. The analysis of the data indicates a coplanar conformation of one of the phenyl rings with the imidazole system and a nearly perpendicular arrangement of the second phenyl substituent.

The EPR spectra of radical cations of numerous hetero[5]annulenes derived from pyrrole have been recorded in fluid solution[1,2] and in the solid state[3,4] over the last few years. The hyperfine splittings are similar to those derived from substituted cyclopentadienyl radicals which are isoelectronic systems with 5 π electrons. Concerning the related imidazole system, only the radical cation of 1-methylimidazole **1** is described in the literature.[5,6] The values of the splitting parameters which are given in the solid state[5] and in liquid solution[6] are different, see Table 1. An additional imidazole radical cationic system will therefore be studied in solution. The 4,5-diphenyl substituted radical cation ($2^{\cdot+}$) was chosen which was generated by UV irradiation of the parent compound **2** with $Hg(CF_3COO)_2$ ($HgTFAc_2$) in trifluoroacetic acid (TFA)[7] (Scheme 1).

The radical cations are stabilized by the phenyl rings allowing their investigation by ENDOR spectroscopy. For confirmation of the assignment of the splittings, the radical cation of 4,5-diphenylimidazole-d_{10} **3** was also studied and trifluoroacetic acid-d_1 was used as a solvent.

Experimental

Materials. 4,5-Diphenylimidazole **2**, trifluoroacetic acid, trifluoroacetic acid-d_1, benzaldehyde-d_6 and $Hg(CF_3COO)_2$ were commercial products and were used without further purification. 4,5-Diphenylimidazole-d_{10} **3** was synthesized from benzil-d_{10} following the procedure of Davidson *et al.*[8] Benzil-d_{10} was prepared from benzaldehyde-d_6 via a benzoin condensation and oxidation with $CuSO_4$. Benzil-d_{10} (1.13 g, 5.13 mmol), hexamethylenetetramine (3.02 g, 39.2 mmol) and ammonium acetate (3.02 g, 39.2 mmol) were stirred and refluxed with 25 cm^3 acetic acid. After 1 h, 220 cm^3 acetic acid and 270 cm^3 concentrated aqueous ammonia were added. The precipitate was recrystallized from a mixture of pyridine and water (9 cm^3, 1:1); yield 2.87 mmol, 56%; m.p. 232 °C; ^{1}H NMR (300 MHz): δ(*N*-methylpyrrolidone) 7.26 (s, 1 H, NCHN) and 10.42 (s, 1 H, NH); MS (70 eV): *m/z*(%), 230 (100, M^+), 173 (15, $C_{13}HD_8^+$), 94 (7, $C_7D_5^+$). Instrumentation: ^{1}H NMR [$Si(CH_3)_4$ as internal standard], Bruker AM 300; MS, Finnigan Mat 8230.



Scheme 1.

EPR and ENDOR measurements.[9] $Hg(CF_3COO)_2$ (20 mg), 20 mg of the parent compound and 0.2 cm^3 trifluoroacetic acid were placed in glass tubes, degassed using freeze–thaw cycles and closed under argon. The tubes were irradiated at −15 °C in the cavity of an EPR spectrometer (VARIAN E-109) with the light of a 1000 W Hg–Xe high pressure lamp (Hanovia 977 B-1). After the EPR spectra had been recorded, the tubes were stored at dry-ice temperature. ENDOR spectra were then taken using a Bruker ESP 300 E spectrometer with ENDOR equipment ESP 360 D and a 200 W RF amplifier.

Results and discussion

The EPR spectrum given in Fig. 1(a) was taken after UV irradiation of **2** with $Hg(CF_3COO)_2$ in CF_3COOH at −15 °C and is assigned to $2^{\cdot+}$, as will be discussed in

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Table 1. EPR parameters of radical cations from substituted imidazoles (splitting constants in mT).

Radical cation	a(1)	a(2)	a(3)	a(4)[a]	a(5)[a]	g-value
$\mathbf{1}^{\cdot+}$ [b]	N: 0.533 3H: 1.200		N: 1.000			2.004
[c]	N: 0.068 3H: 0.160	H: 1.189	N: 0.160	H: 1.025	H: 0.225	2.0035
$\mathbf{2}^{\cdot+}$ [d]	H: 0.158	H: 0.158		H: 0.073 0.266 0.284	H: 0.019	
[e]	H: 0.157 N: 0.019	H: 0.161	N: 0.146	2H: 0.073 2H: 0.266 1H: 0.284	2H: 0.019	2.0032
[f]	H: −0.078 N: −0.050	H: −0.688	N: −0.242	H(7′): −0.439 H(8′): 0.255 H(9′): −0.487 H(10′): 0.249 H(11′): −0.410	H(7): −0.031 H(8): 0.133 H(9): −0.010 H(10): 0.128 H(11): −0.039	
$\mathbf{3}^{\cdot+}$ [d] [g]	H: 0.158	H: 0.158				2.0032

[a] Phenyl proton splittings are included, for assignment see Fig. 1. [b] Ref. 5. [c] Ref. 6. [d] ENDOR data in CF_3COOH at −15 °C. [e] EPR data in CF_3COOH at −15 °C. [f] INDO calculations (see the text). The signs of the coupling constants were not obtained experimentally. [g] The EPR spectrum shows a broad singlet (linewidth ≃ 0.5 mT).

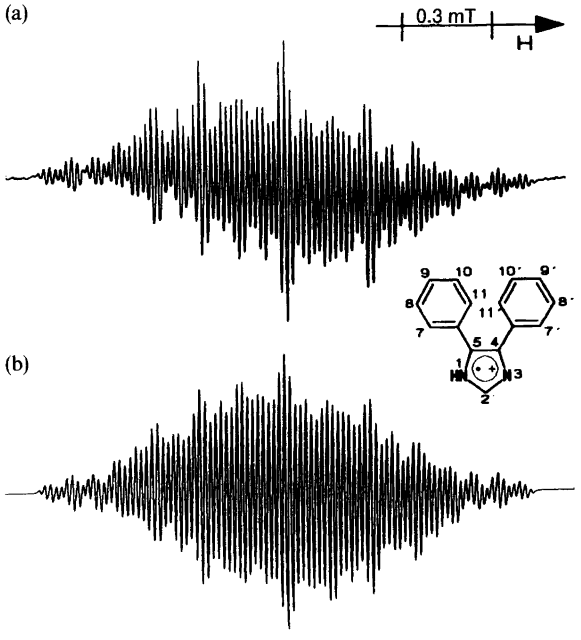

Fig. 1. (a) EPR spectrum of $\mathbf{2}^{\cdot+}$ in TFA at −15 °C after irradiation of **2** with $Hg(CF_3COO)_2$; (b) EPR spectrum of $\mathbf{2}^{\cdot+}$ calculated with the hyperfine coupling constants given in Table 1.

detail. The only feature that can be unambiguously identified from the EPR spectrum is a multiplet of at least five signals with a small coupling of 0.019 mT which might be caused by one or two nitrogens and/or an even number of protons. To obtain further information concerning the splitting constants, an ENDOR spectrum was taken under the same conditions, which gave proton couplings of 0.019, 0.073, 0.158, 0.266 and 0.284 mT, which should be due to the phenyl protons, $a_H(1)$ and $a_H(2)$. ^{14}N splittings were not observed.

The EPR spectrum of $\mathbf{2}^{\cdot+}$ shows a marked temperature dependence up to +40 °C, which might be the consequence of dynamic processes. It was not possible to obtain ENDOR spectra at temperatures higher than −15 °C. The temperature dependence of the EPR spectra has therefore not been analysed.

After UV irradiation of **3** with $Hg(CF_3COO)_2$ in CF_3COOH at −15 °C, only a broad EPR signal with a linewidth of 0.5 mT was observed. The ENDOR spectrum exhibited a single proton splitting of 0.158 mT. It is therefore concluded that the splittings of 0.019, 0.973, 0.266 and 0.284 mT observed in the ENDOR spectrum of $\mathbf{2}^{\cdot+}$ have to be assigned to the phenyl protons. The ratio of the three bigger splittings resembles that of the *m*-, *o*- and *p*-splittings of the benzyl radical (1:3:4). They are therefore assigned to one of the phenyl rings which must be coplanar with the imidazole system. The small splitting of 0.019 mT is assigned to the *m* protons of the second ring and to one of the nitrogens. As *m* protons are known to show the biggest couplings in highly twisted phenyl systems,[10–12] it is concluded that the second ring is perpendicular to the imidazole system. This is supported by a geometry optimization by MNDO RHF calculations,[13] which give twist angles of 87° for the ring at C-5 and of 3° for the ring at C-4.

The values for the second ^{14}N splitting, $a_H(1)$ and $a_H(2)$ were determined by comparing simulated spectra with the observed spectrum. The EPR spectrum shown in Fig. 1(b) was calculated with the splitting constants listed in Table 1. The best fit was obtained with slightly different values for $a_H(1)$ and $a_H(2)$. The agreement with the observed spectrum is satisfactory. In order to assign

the splitting constants, an INDO calculation was performed.[14] The results do not show a quantitative agreement with the experiment, but allow the assignment given in Table 1.

For confirmation of the magnitude $a_H(1)$, CF_3COOD was used as a solvent for **2**. The NH proton of $\mathbf{2}^{\cdot+}$ should then be exchanged for deuterium, leading to definite changes in the EPR spectrum. The observed EPR spectrum could not be analysed. The intensity allowed the determination of the spectral width (1.537 mT), which is as expected with $a_D = 0.1535 a_H$.

The splitting constants of $\mathbf{2}^{\cdot+}$ are similar to those of $\mathbf{1}^{\cdot+}$ in the liquid state, but not to those observed in the solid state, see Table 1. $a_H(2)$ exhibits the most severe discrepancy between $\mathbf{2}^{\cdot+}$ and $\mathbf{1}^{\cdot+}$ and the experimental and the calculated values of $\mathbf{2}^{\cdot+}$. This might be a consequence of deviations of the imidazole ring system from planarity not taken into account in the calculations.

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