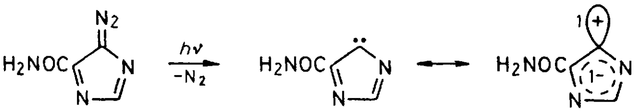
Triplet State Intermediate in the Low Temperature Photolysis of 5-Diazoimidazole-4-carboxamide

Hanna B. Ambroz,[a] **Bernard T. Golding,**[a] **Terence J. Kemp,***[a] **and Vishnu S. Shukla**[b]

[a] *Department of Chemistry and Molecular Sciences, University of Warwick, Coventry, CV4 7AL, U.K.*
[b] *Department of Radiotherapy and Oncology, Coventry and Warwickshire Hospital, Stoney Stanton Road, Coventry, CV1 4SH, U.K.*

U.v. photolysis of microcrystalline 5-diazoimidazole-4-carboxamide gives rise to *two* $S = 1$ species detected by e.s.r. spectroscopy, one of which is assigned to a radical-pair ($r_\perp = 3.14$ Å) while the other displays resonances indicative of a large D parameter typical of a carbene structure, supporting conclusions from solution photolysis.

5-Diazoimidazole-4-carboxamide (**1**) (DZC)[1] is a potent cytotoxic agent[2,3] and a powerful electrophile.[1b] Recently (**1**) has been shown to undergo both redox and addition processes with alkanols following nitrogen elimination on *thermolysis*, whereas *photolysis* of (**1**) in alkanols leads to C–H insertion products in addition to redox and addition processes:[4] the observation of insertion led to the proposed intermediate 5-carboxamido-4*H*-imidazolylidene (**2**), which could exist in either singlet or triplet states.[4] Species (**2**) has also been proposed as an intermediate in the photochemistry of (**1**) in water at 7.4 > pH > 1 by Horton and Stevens.[3] Although the insertion of (**2**) into C–H bonds implies singlet character[4] for the initially-produced species, its relaxed state could be triplet.



(**1**) (**2**)

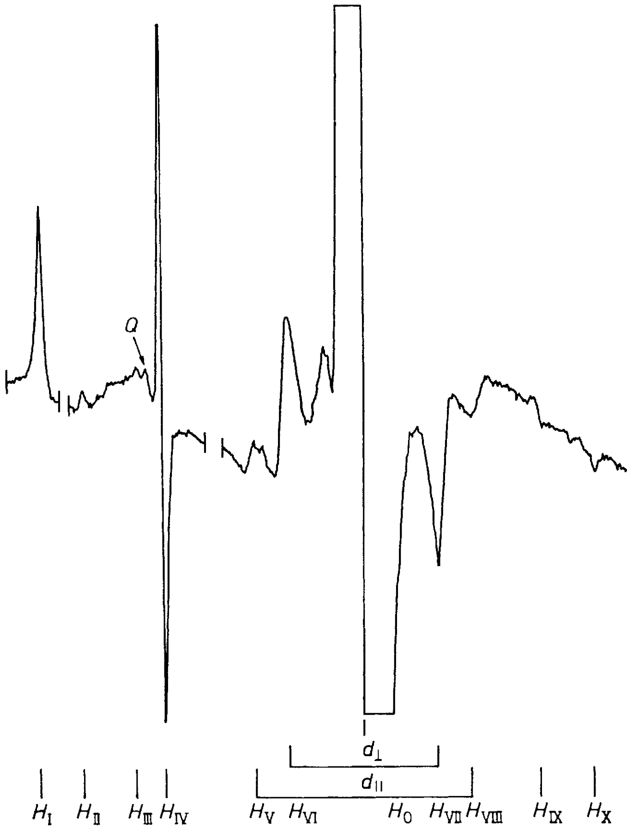


Figure 1. E.s.r. transitions in u.v.-irradiated microcystalline (**1**) (7 h photolysis at 77 K, bare Hg arc). For field positions see text (total scan 7 kG, Q = Quartz signal).

Photolysis (100 W, u.v., bare Hg arc, several h) of (**1**) as a microcrystalline powder at 77 K produced the complex wide-field e.s.r. spectrum shown in Figure 1; the resonances appeared at the following field positions (in G; 1 mT = 10 G): H_{I} 427.8, H_{II} 1132, H_{III} 1460, H_{IV} 1615, H_{V} 2729, H_{VI} 2928, H_0 3392, H_{VII} 3830, H_{VIII} 4043, H_{IX} 4409, and H_{X} 4767 for an applied microwave frequency of 9.500 GHz. We associate the two main peaks (excluding H_0) denoted H_{I} and H_{IV} with two *different* $S = 1$ species because their *relative* intensities change gradually on storage at 77 K by up to a factor of four over 13 h (with H_{I} disappearing faster than H_{IV}). Furthermore, a 7 h photolysis gave a stronger H_{IV} resonance (Figure 1), whereas a 1 h photolysis gave a stronger H_{I} resonance: warming the latter sample to 300 K, recooling to 77 K, and irradiating a second time for 1 h, increased the ratio $H_{\mathrm{I}}/H_{\mathrm{IV}}$ further.

Peak H_{IV} is typical in shape and field position of the so-called $H_{\min}$ component of the $\Delta m = 2$ transition of a triplet state.[5] Inspection led us to associate H_{IV} with peaks H_{V}, H_{VI}, H_{VII}, and H_{VIII} as the $\Delta m = 2$ and $\Delta m = 1$ components, respectively, of an $S = 1$ species with a small D parameter. The most likely candidate in assignment is a radical-pair with $d_\perp = 902$, $d_\parallel = 1314$ G, and inter-spin distances $r_\perp = 3.14$ Å ($r_\parallel = 3.49$ Å).[6] This is attributed to pairs of the major radical expected,[4] *i.e.* the 4-yl radical, which is centred at H_0 (Figure 1).

Analysis of the other peaks is less unequivocal. The lineshape of the dominant H_{I} peak is unusual for a $\Delta m = 2$ transition: these are normally quite narrow and highly symmetrical (H_{IV} itself is a good example), but less symmetrical cases have been recorded, *e.g.* that of *N*-phenyliminocyclohexadienylidene in its high-temperature rotameric form.[7] If H_{I} is indeed a $\Delta m = 2$ transition despite its asymmetry, then D^* may be calculated to be 0.2655 cm^{-1}: the associated $\Delta m = 1$ transitions would be H_{II}, H_{III}, H_{IX}, and H_{X} [corresponding to $H_{y(1)}$, $H_{x(1)}$, $H_{x(2)}$, and $H_{y(2)}$][5] from which D^* can be determined as 0.2672 cm^{-1}, *i.e.* in good agreement with that calculated from H_{I}. The alternative view is to regard H_{I} as an $H_{z(1)}$ transition (its lineshape closely resembles the corresponding transition in the triplet spectrum of irradiated 9-diazo-10-anthrone[8]): H_{IX} and H_{X} would then be the corresponding $H_{x(2)}$ and $H_{y(2)}$ peaks, the resulting D parameter would be 0.33 cm^{-1}. [The figure for cyclopentadienylidene[8] is 0.41 cm^{-1} but the presence of the heteroatoms and the amide group in (**2**) would be expected to lower the value.[9]] The disadvantages of the latter assignment are (i) that no $H_{z(2)}$ peak could be detected (this would, however, be weak and possibly located beyond the 10 kG range of the spectrometer) and (ii) that peaks H_{II} and H_{III} would have to be assigned to yet another species such as a quintet state.[8]

Whichever analysis is correct, there is no doubt that a triplet species of large *D*-value is generated on irradiation of (**1**), which is probably (**2**) in its triplet form.

Experiments on *solutions* of (**1**) irradiated at 77 K revealed the presence of the H_{IV} resonance (of the radical-pair species) in water, tetrahydrofuran, methanol, and acetone. The H_I resonance was present only in methanol, but this single observation confirms that it emanates from a molecular triplet state and not a type of crystal defect.

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