3-Ylomethylphenylnitrene† a Novel Quartet Species having Doubly Heterogeneous Radical Sites (N and C Atom; $S = 1$ and 1/2 Centre) in a π-Conjugated Molecule

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The ground-state quartet species, 3-ylomethylphenylnitrene **1**, is photochemically generated from two precursors, **2** and **3**, and is characterized using ESR spectroscopy in the temperature range 8–80 K in a 2-methyltetrahydrofuran (MTHF) matrix.

The relationship between ground-state spin-multiplicities and the topology of spin-connecting systems in π-conjugated high-spin molecules is of importance in developing organic ferromagnets.[1]

Here, we report 3-ylomethylphenylnitrene **1**, which is the first reactive high-spin intermediate having both nitrene and methylene moieties. This species has a unique three-spin system in which two of the spins are located on one atom and one on another. This type of species has been suggested to be a transient species in the decomposition of *m*-phenylene-dinitrene or -dicarbene *via* hydrogen abstraction in organic matrices.

For the precursor of **1**, 3-azidophenylacetic peroxide **2** was selected because it should have high efficiency in the generation of benzyl radicals.[2,3] Furthermore, the precursor will eliminate two CO_2 molecules between two radicals in a rigid glass, which will produce two separated radicals—this is needed in order to eliminate complexity, which may arise from intermolecular interaction between radicals.

When a 2-methyltetrahydrofuran (MTHF) matrix of 3-azidophenylacetic peroxide **2** (0.03 mol dm^{-3})‡ was irradiated with UV light through cut-off filters (310–400 nm) at 18 ± 2 K for 2 h, several sets of ESR signals appeared with monotonic increase of intensities [Fig. 1(*a*)]. In Fig. 1, T and R denote triplet mononitrene ($|D/hc| = 1.003$ cm^{-1}, $|E/hc|$ *ca.* 0 cm^{-1}) and doublet radical(s), respectively. The remaining signals indicated as Q spread in a wide range of magnetic fields, which is characteristic of high spin ($S \geqslant 1$) species with a large D value. The ESR spectrum was assigned to the quartet **1**.[4]

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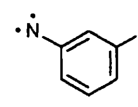
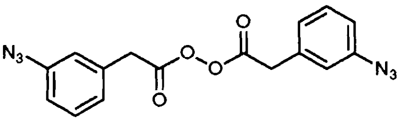
† *Revised Nomenclature for Radicals, Ions, Radical Ions and Related Species*, W. H. Powell, *Pure and Appl. Chem.*, IUPAC, 1993, in the press.

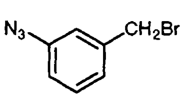
‡ The peroxide **2** was obtained from 3-azidophenylacetic chloride and sodium peroxide [IR (neat) ν/cm^{-1}), ν_{CO} = 1740, 1810, ν_{N3} = 2120]; See also ref. 2.



1



2



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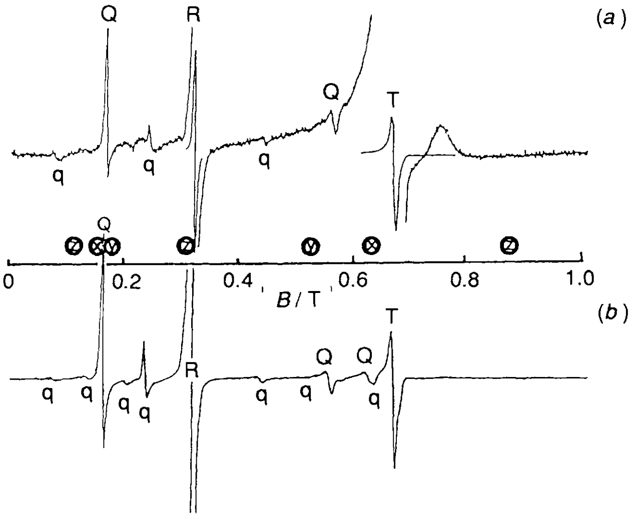

Fig. 1 (*a*) ESR spectrum photochemically obtained from **2** (0.03 mmol dm^{-3}) in an MTHF matrix at 22 K (after UV irradiation at 18 ± 2 K for 2 h; frequency = 9.0804 GHz, power = 0.8 mW, field modulation = 1 mT). Q, T and R denote the quartet **1**, triplet mononitrene(s), and doublet monoradical impurities, respectively. (*b*) Photolysis of **3** (0.1 mol dm^{-3}) was performed in the presence of TDAE (0.4 mol dm^{-3}) in MTHF at 20 ± 5 K for 70 min, and the spectrum was recorded at 20 K (frequency = 9.09013 GHz, power = 0.6 mW, field modulation = 1 mT). About the circled letters, see text. q = quintet species.

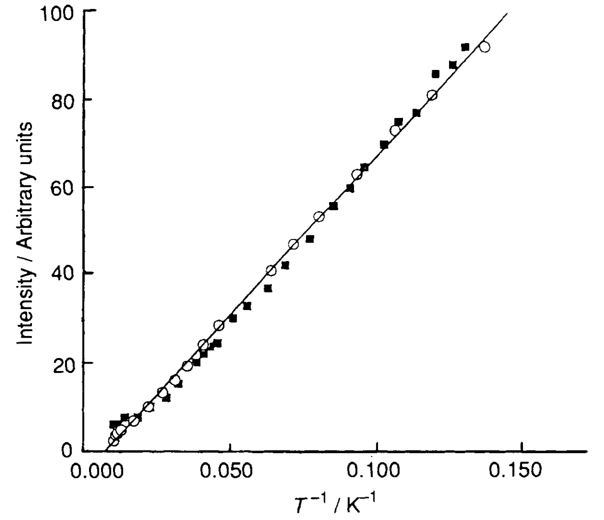

Fig. 2 Temperature dependence of the intensities of a quartet ESR signal at 0.169 T *vs.* reciprocal of absolute temperatures (■ for a precursor **2**; ○ for a precursor **3**).

The quartet ESR signals were persistent up to 88 K in MTHF. At 92 K, the quartet signal (and a quintet, see below) decreased and a new triplet diradical signal was observed (presumably radical pairs of aminyl and MTHF radicals; $|D/hc| = 0.02045\ cm^{-1}$, $|E/hc|$ *ca.* 0 cm^{-1}; $|\Delta m_s| = 2$ signal at 161.6 mT) were observed within 30 s, and the change was not reversed by cooling to 10 K. Some of the triplet mononitrene survived at 92 K. This thermal behaviour is consistent with the assisgnments of the ESR signals.

Photolysis of 3-azidobenzyl bromide (0.1 mol dm^{-3}) **3**, in MTHF at 20 ± 5 K for 70 min in the presence of tetrakis(dimethylamino)ethylene (TDAE, 0.4 mol dm^{-3}) as an electron donor [Fig. 1(*b*)] resulted in cleavage at the benzylic carbon–halogen bond together with azide group. This is a well-known photochemical reaction for benzylic halides mediated by electron transfer either in solution or in matrix.[2] Thus, the same ESR spectrum was obtained from **2** and **3** except for a minor high-spin species which we assign to a quintet§ (denoted by q in Fig. 1) due to a radical pair of the quartet **1** and a nearby monoradical.

In general, zero-field-splitting (z.f.s.) parameters for the quartet[4] can be estimated from an observed highest field H_z signal using $2D = H_z - H_0$, where $H_0 = h\nu/(g_e\beta)$. Also, the resonance fields for a randomly oriented quartet can be calculated.¶ Thus, the z.f.s. parameters of **1** were estimated as $|D/hc| = 0.26\ cm^{-1}$ and $|E/hc| = 0.015\ cm^{-1}$ (see Fig. 1; calculated resonance fields parallel to the x, y and z axes are indicated as circles in Fig. 1). The D value of the quartet is a function of the average distance between radical electrons, and is expressed as in eqn. (1), where r_{12} is the distance

$$D(\text{quartet}) = (1/4)(\mu/4\pi)(g_e\beta)^2 \langle\phi|\,[(r_{12}^2 - 3z_{12}^2)/r_{12}^5 + (r_{23}^2 - 3z_{23}^2)/r_{23}^5 + (r_{31}^2 - 3z_{31}^2)/r_{31}^5]|\phi\rangle \quad (1)$$

between electron 1 and 2. In a similar way, that of the triplet is given by eqn. (2).[4] Because a one-centre diradical has a

$$D(\text{triplet}) = (3/4)(\mu/4\pi)(g_e\beta)^2 \langle\phi|\,(r_{12}^2 - 3z_{12}^2)/r_{12}^5]|\phi\rangle \quad (2)$$

shorter average distance between electrons than that of a delocalized diradical [*cf.* D(triplet nitrenes) *ca.* 1.0 cm^{-1}, D(triplet *m*-quinodimethanes) *ca.* 0.01 cm^{-1}], D(quartet) of **1** approximates to D(quartet **1**) *ca.* (1/3)D(nitrene) *ca.* 0.3 cm^{-1}—this value agrees with that obtained above.||

A Curie law plot (Fig. 2) for the intensity of the quartet ESR signal (based on the signal at 0.169 T) shows a linear dependence in the temperature range 8 to 80 K, which implies that the quartet state is the ground state of **1**.

Lack of the degeneracy of energy levels of the SOMOs in **1** is shown by PM3 (RHF) calculation.[5] The spread between the three SOMOs is 0.55 eV. One of the principles for parallel spin alignment in non-Kekulé molecules is based on degeneracy of nonbonding MOs. Perturbation by a heteroatom in the trimethylenemethane series gives rise to a large splitting of the NBMOs, such that some derivatives of oxyallyl [$\cdot CR_2(C{=}O)CR_2\cdot$] are reported to be ground state singlets. However, the highest spin state of **1** was found to be the ground state. It is similar to the case of *m*-benzoquinomethane and *m*-nitrenophenylmethylene.[6] Research is still needed to clarify the way in which the degree of perturbation affects the ground-state spin multiplicity.

Finally, it is noteworthy that the quartet **1** is the first organic example constructed with $S = 1$ and $S = 1/2$ spin centres. So far several organic quartet species have been observed, most of which have three C_3-symmetrical π-radical sites.[4] Although attention must be paid to the topology of the π system that connects spin sites, interest also lies in the symmetry of the

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§ To be published elsewhere. The quintet signals were distinguished from the quartet by the dependence of yields on the photolysis wavelength.

¶ For example, W[energy for $m_s = +3/2$ (|| z axis)] = $g_e\beta H + [(D + g_e\beta H)^2 + 3E^2]^{1/2}$.

|| Owing to difficulty in the assignment of *x*-, *y*- and *z*-transition and a limited applicability of the equations described in the text, the D and E values should be read as preliminary.

inter-spin sites and in the spin quantum number at each spin site.

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References

1 H. Iwamura, *Adv. Phys. Org. Chem.*, 1990, **26**, 179; D. A. Dougherty, *Acc. Chem. Res.*, 1991, **24**, 88; *Diradicals*, ed. W. T. Borden, Wiley, NY, 1982; P. M. Lahti and A. S. Ichimura, *J. Org. Chem.*, 1991, **56**, 3030; J. A. Berson, *Pure Appl. Chem.*, 1987, **59**, 1571.

2 K. W. Haider, E. Migirdicyan, M. S. Platz, N. Soundararajan and A. Despres, *J. Am. Chem. Soc.*, 1990, **112**, 733.

3 *The Chemistry of Peroxides*, ed. S. Patai, Wiley, New York, 1983, pp. 235 and 685.

4 S. I. Weissman and G. Kothe, *J. Am. Chem. Soc.*, 1975, **97**, 2537; J. Brickmann and G. Kothe, *J. Chem. Phys.*, 1973, **59**, 2807; G. Koth, S. S. Kim and S. I. Weissman, *Chem. Phys. Lett.*, 1980, **71**, 445; Von C. Nowak, G. Kothe and H. Zimmermann, *Ber. Bunsenges. Phys. Chem.*, 1974, **78**, 25; G. Kothe and H. Zimmermann, *Tetrahedron*, 1973, **29**, 2305; V. G. Koth and E. Ohmes, *Ber. Bunsenges. Phys. Chem.*, 1974, **8**, 924; Ishida and H. Iwamura, *J. Am. Chem. Soc.*, 1991, **113**, 4238; M. Matsushita, T. Nakamura, T. Momose, T. Shida, Y. Teki, T. Takui, T. Kinoshita and K. Itoh, *J. Am. Chem. Soc.*, 1992, **114**, 7470; inorganic quartet, for example, R. J. van Zee, C. M. Brown, K. J. Zaringue and W. Weltner, Jr., *Acc. Chem. Res.*, 1980, **13**, 237.

5 J. J. P. Stewart, *J. Comput. Chem.*, 1989, **10**, 209 and 221.

6 D. E. Seeger, P. M. Lahti, A. R. Rossi and J. A. Berson, *J. Am. Chem., Soc.*, 1986, **108**, 1251; H. Tukada, K. Mutai and H. Iwamura, *J. Chem. Soc., Chem. Commun.*, 1987, 1159.