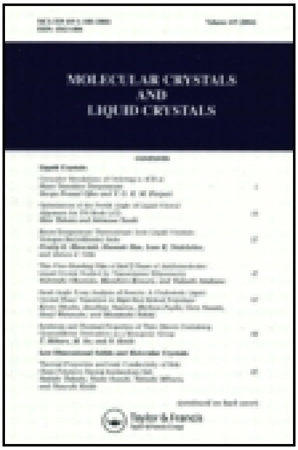


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

High-Spin Nitrenes with s-Triazine Skeleton

Takeo Nakai [a] , Kazunobu Sato [a] , Daisuke Shiomi [b] , Takeji Takui [a] , Koichi Itoh [b] , Masatoshi Kozaki [a] & Keiji Okada [a]

[a] Departments of Chemistry, Graduate School of Science, Osaka City University, Sumiyoshi-ku, Osaka, 558-8585, Japan

[b] Departments of Material Science, Graduate School of Science, Osaka City University, Sumiyoshi-ku, Osaka, 558-8585, Japan

Version of record first published: 24 Sep 2006

To cite this article: Takeo Nakai, Kazunobu Sato, Daisuke Shiomi, Takeji Takui, Koichi Itoh, Masatoshi Kozaki & Keiji Okada (1999): High-Spin Nitrenes with s-Triazine Skeleton, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 334:1, 157-166

To link to this article: http://dx.doi.org/10.1080/10587259908023313

Mol. Cryst. and Liq. Cryst., 1999, Vol. 334, pp. 157-166
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under the
Gordon and Breach Science Publishers imprint.
Printed in Malaysia

High-Spin Nitrenes with *s*-Triazine Skeleton

TAKEO NAKAI[a], KAZUNOBU SATO[a], DAISUKE SHIOMI[b], TAKEJI TAKUI[a], KOICHI ITOH[b], MASATOSHI KOZAKI[a] and KEIJI OKADA[a]

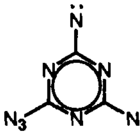
[a]*Departments of Chemistry and* [b]*Material Science, Graduate School of Science, Osaka City University, Sumiyoshi-ku, Osaka 558–8585, Japan*

Heteroatomic high-spin molecules are suitable for a model study of room-temperature stable molecular based magnetics. We studied high-spin nitrenes ($S = 1$ and 2) with s-triazine skeleton, which were generated by the photolysis of the polyazide precursor. We identified mononitrene **1** ($S = 1$) and bisnitrene **2** ($S = 2$) for the first time by single-crystal ESR measurements. The fine-structure parameters were determined by the angular dependence of resonance fields. The determined fine-structure parameters were $|D| = 1.402\ \mathrm{cm}^{-1}$ and $|D| = 0.280\ \mathrm{cm}^{-1}$ for mononitrene **1** and bisnitrene **2**, respectively. The large D values indicate that π-spin delocalization effects were hampered by introducing heteroatoms to π-spin systems. The hyperfine splittings due to the monovalent nitrogen nucleus of **1** were observed with magnetic field along the principal axis of the fine structure tensor. The hyperfine splitting constant was about $0.0018\ \mathrm{cm}^{-1}$. The temperature dependence of ESR signals showed that **1** and **2** were triplet and quintet in the ground state, respectively.

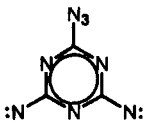
Keywords: high-spin nitrene; s-triazine; single-crystal; ESR; heteroatomic perturbation; hyperfine. splittings

INTRODUCTION

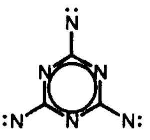
High-spin organic compounds have been suitable models for studying organic magnetism and molecular spin science[1]. In general, heteroatomic high-spin organic compounds are more stable than high-spin hydrocarbons[2-7]. Due to their stability, heteroatomic high-spin compounds have the potential to be models of new functionality materials. Recently, heteroatomic effects on spin alignment in π-conjugation systems have become an important issue for controlling spin alignment in heteroatomic π-spin systems. In order to study heteroatomic effects, we paid particular attention to 2,4,6-trinitreno-*s*-triazine **3**, which is expected to be septet in the ground state. We synthesized the corresponding precursor 2,4,6-triazide-*s*-triazine **4** and grew neat single crystals of **4**. The preliminary (powder-pattern) ESR measurements gave spectra characteristic of triplet species with a large *D* value. The spectra were due to mononitrene **1**. The fine-structure parameters ($|D|$ and $|E|$) were determined to be 1.445 cm^{-1} and 0.0045 cm^{-1} by spectrum simulation. On the other hand, both mononitrene **1** and bisnitrene **2** were observed in single-crystal ESR measurements. The analysis of angular dependence of resonance fields gave the fine-structure parameters ($|D|$ and $|E|$) of **1** and **2** to be 1.402 cm^{-1} and 0.011 cm^{-1}, 0.280 cm^{-1} and 0.058 cm^{-1}, respectively. The single-crystal ESR work on nitrenes was previously reported by J. A. Hebden and C. A. McDowell[7]. In this paper, the first observation of ESR signals from bisnitrene **2** (S = 2) is described and the electronic spin structure is discussed



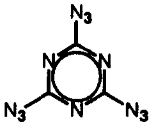
1



2



3



4

EXPERIMENTAL

The precursor **4** was synthesized by addition of the water solution of sodium azide into the acetone solution of cyanuric chloride. **4** was purified by recrystallization from ethanol and identified by mass spectroscopy and the melting point measurements. Single crystals of **4** were obtained from slow evaporation of benzene/ethanol solution of **4**. The crystallographic data of the single crystal of **4** was reported by E. W. Hughes[8]. The space group is $P6_3/m$ and

Z = 2 with a = b = 8.70 Å, c = 5.98 Å and α = 90.0 degrees.

The ESR spectra were obtained using a Bruker ESP300 spectrometer operating at X-band microwave frequency with 100 kHz modulation system. The single-crystal ESR measurements were carried out at 4 K. The temperature dependence of ESR signals was observed in the range from 3.5 K to 10.0 K. The sample for powder-pattern ESR measurements was prepared by magnetically diluting **4** in benzophenone. The single-crystal ESR measurements were carried out in the crystallographic ab plane only. The sample for ESR measurements was photolyzed in a cryostat at 4 K.

ANALYSES OF FINE-STRUCTURE SPECTRA

The observed powder-pattern ESR spectrum and angular dependence of resonance fields observed in the single-crystal ESR measurements were reproduced by spectral simulation and the calculated angular dependence using a spin Hamiltonian (1).

$$\mathcal{H} = \beta_e \underline{\mathbf{B}} \cdot \underline{\underline{\mathbf{g}}} \cdot \underline{\mathbf{S}} + D(S_Z^2 - \tfrac{1}{2}S^2) + E(S_X^2 - S_Y^2) \qquad (1)$$

All the analyses were performed by numerically diagonalizing spin Hamiltonian matrices with parameters (microwave frequency *ν*, spin multiplicity *S*, g value, and fine-structure parameters *D*, *E*). The calculation was based on the eigenfield methods[9-14] in order to avoid non-convergence problems in eigenenergy method. We assumed that g tensors were isotropic.

RESULTS AND DISCUSSION

Powder-Pattern ESR

The observed ESR spectrum was characteristic of triplet species with a large *D* value (> 0.3 cm^{-1}) and $E \neq 0$ (Fig.1). The strong signal at 330 mT of the top spectrum is due to doublet impurities generated by the photolysis. The observed

ESR signals at 800 mT were due to triplet mononitrene **1**. The fine-structure parameters of **1** were determined to be $|D| = 1.445$ cm^{-1} and $|E| = 0.0045$ cm^{-1} by spectral simulation. The experimentally determined fine-structure parameter D was much larger than those of phenylnitrenes ($|D| \approx 1.0$ cm^{-1})[6]. It indicates that the spin density on the monovalent nitrogen atom of molecule **1** is larger than those of phenylnitrenes; the π-spin localization or π-spin polarization in **1** is enhanced. The $|D|$ value is strongly dependent on the spin density on the monovalent nitrogen atom of nitrene, if one-center n-π spin–spin interaction is dominant[15]. From the comparison of DFT calculations (B3LYP) between mononitrene **1** with *s*-triazine skeleton and phenylnitrene, we concluded that the former mechanism is more effective. This finding was also supported by results from analyses of the single-crystal ESR measurements.

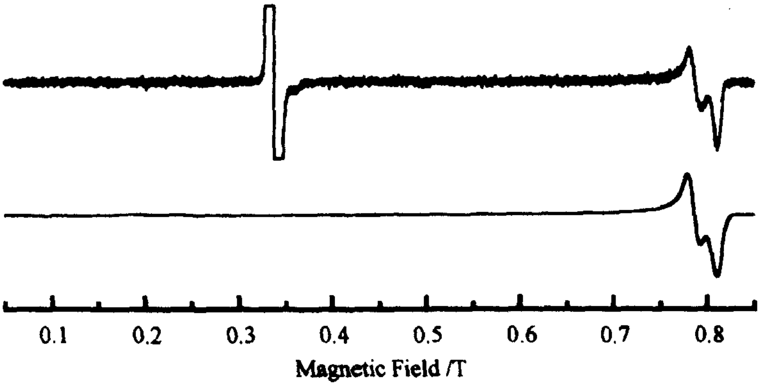


FIGURE 1 Powder-pattern ESR spectra after photolysis of **4**.
Top: The observed spectrum after photolysis of **4** at 3.5 K.
Bottom: The simulated spectrum with $\nu = 9.48717$ GHz, $S = 1$, $g = 2.003$, $|D| = 1.445$ cm^{-1} and $|E| = 0.0045$ cm^{-1}.

Single-Crystal ESR Measurements

The observed ESR spectrum at $\theta_{ab} = 60$ degrees and the angular dependence of resonance fields are shown in Fig. 2 and 3, respectively. The same spectrum

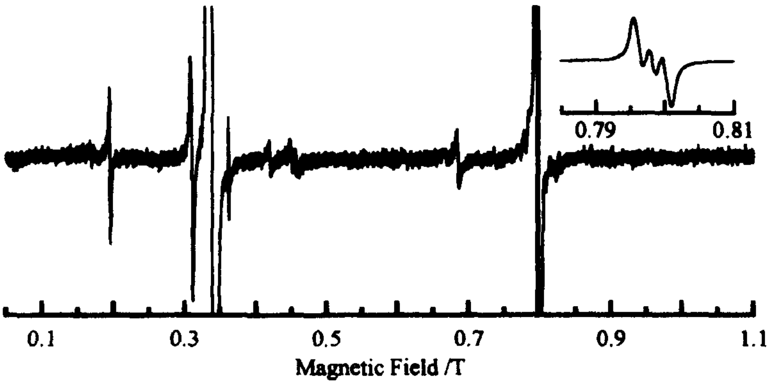


FIGURE 2 The ESR spectrum at θ_{ab} = 60 degrees observed at 3.9K with ν = 9.050838 GHz

appears in every 60 degrees in the ab plane, reflecting the C_3 symmetry of the precursor **4**. The photolysis of **4** gave three high-spin molecules **1**, **2**, and **3**. **1** and **2** have three kinds of orientations A, B, and C according to the decomposition site of azide (Fig. 4). It indicates that the observed ESR spectra in the single-crystal ESR measurements were a mixture of the spectra arising from mononitrene **1**, bisnitrene **2**, and trinitrene **3**. We analyzed the angular dependence of all the resonance fields. The analyses were based on the results of the preliminary experiment (S = 1; $|D|$ = 1.445 cm^{-1} and $|E|$ = 0.0045 cm^{-1}). We determined the fine-structure parameters to be $|D|$ = 1.402 cm^{-1} and $|E|$ = 0.011 cm^{-1} for **1** (S = 1), and $|D|$ = 0.280 cm^{-1} and $|E|$ = 0.058 cm^{-1} for **2** (S = 2), respectively (Fig.3). The calculated resonance fields for A, B, and C are shown for both **1** and **2** in Fig. 3. Because of sensitivity problems the number of the observed resonance peaks is not many in Fig. 3. The experimentally determined fine-structure parameter D of **2** ($|D|$ = 0.280 cm^{-1}) is much larger than that of *m*-phenylenebisnitrene ($|D| \approx 0.20$ cm^{-1})[16] as mononitrene **1** is. The large D value indicates that the spin density on each monovalent nitrogen atom increases, because the one-center spin-spin interaction on each spin-carrying atom dominates the D value. The increase in the spin densities on the monovalent

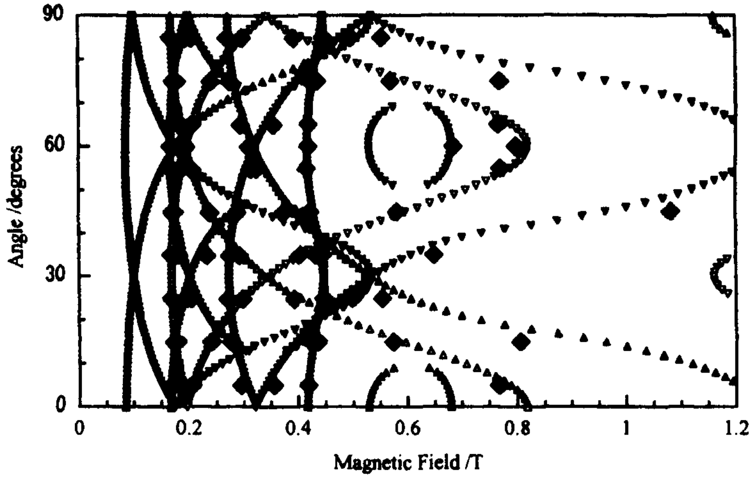


FIGURE 3 Angular dependence of resonance fields.
◆ : The observed resonance fields
△ and ▽ : The simulated resonance fields of orientation A and B, and C with $S = 1$, $g = 2.003$, $|D| = 1.402$ cm^{-1} and $|E| = 0.011$ cm^{-1} for mononitrene **1**, respectively.
▲ and ▼ : The simulated resonance fields of orientation A and B, and C with $S = 2$, $g = 2.003$, $|D| = 0.280$ cm^{-1} and $|E| = 0.059$ cm^{-1} for bisnitrene **2**, respectively.

nitrogen atoms arises from the π-spin localization for the present case.

The fine-structure parameters of bisnitrene **2** were reproduced by a semiempirical calculation of the fine-structure tensor[12,16,17], where Eq.2 and the fine-structure parameters of mononitrene **1** ($|D| = 1.402$ cm^{-1} and $|E| = 0.011$ cm^{-1}) with $2\theta = 118.3$ degrees were used. θ is defined in Fig. 5. The calculation proves that the π-spin delocalization effects are hampered by introducing heteroatoms into π-conjugation systems for high-spin molecule. A decrease in the π-spin delocalization was also supported by results from DFT calculations (B3LYP) of bisnitrene with *s*-triazine skeleton and *m*-phenylenebisnitrene.

$$\underline{\underline{D}}_{S=2} = \underline{\underline{D}}^{(1)}_{S=1} + \underline{\underline{D}}^{(2)}_{S=1} \qquad (2)$$

The hyperfine splittings due to the monovalent nitrogen atom of **1** were well resolved at θ_{ab} = 60 degrees only (Fig. 3). The observed hyperfine constant at 60degrees is 0.0018 cm^{-1}. The hyperfine splittings were not well resolved at other angles, but the linewidth (ΔB_{pp}) is dependent on angle as shown in Fig. 6, indicating that the hyperfine tensor $\underline{\underline{A}}$ has a colinear principal-axes system with the fine-structure tensor $\underline{\underline{D}}$, reflecting the molecular structure of mononitrene **3**, if the linewidth variation arises dominantly from the hyperfine anisotropy of nitrogen nucleus.

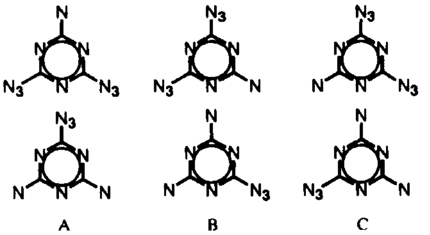


FIGURE 4 Orientations of **1** and **2** depending on the decomposition site of azide.

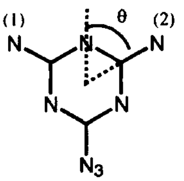


FIGURE 5 Definition of θ.

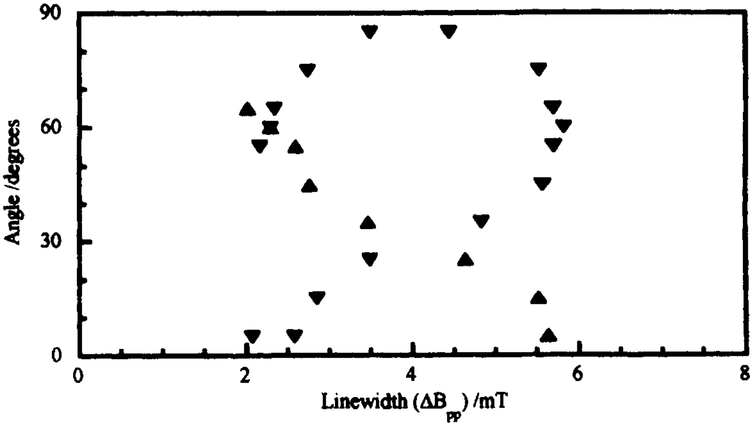


FIGURE 6 Angular dependence of the linewidth of the monovalent nitrogen nucleus.

Variable-Temperature ESR Measurements

Variable-temperature ESR measurements were carried out in the rage of 3.5-10 K in order to determine the ground states of the observed compounds **1** (S = 1) and **2** (S = 2). The temperature dependences of signal intensities were shown in Fig. 7. The intensities of both the triplet and the quintet states increase in proportion to the inverse of temperature. It proves that the triplet state of **1** and the quintet state of **2** are ground states or they are nearly degenerate with singlet states within small energy gaps (< 3 cm^{-1}).

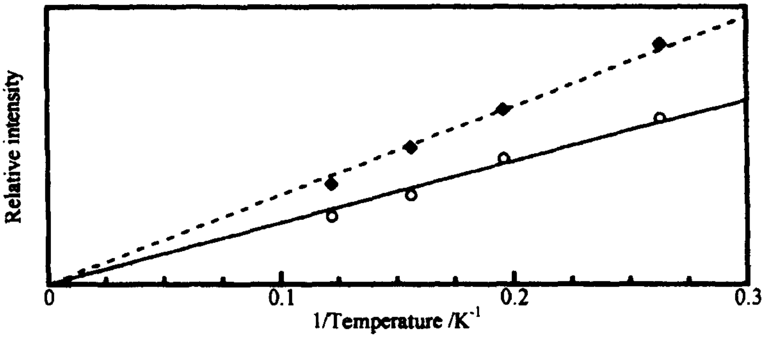


FIGURE 7 Temperature dependence of the signal intensities of **1** (S = 1) and **2** (S = 2).

SUMMARY

Electronic and molecular structure of mononitrene **1** and bisnitrene **2** generated by photolysis of **4** have been investigated by powder-pattern and single-crystal ESR spectroscopy. Mononitrene **1** was identified by both powder-pattern and single-crystal ESR measurements, and bisnitrene **2** was identified by single-crystal ESR measurements. But septet species **3** were not completely identified because of low concentration of the septet species generated under the present conditions. The experimentally determined fine-structure parameters are summarized in Table I. The D values of **1** and **2** are much larger than those of phenylnitrenes and *m*-phenylenebisnitrenes, respectively. The fine-structure parameters of **2** were interpreted by those of **1** and a semiempirical calculation of the fine-structure tensor, where one-center spin-spin interactions at the monovalent nitrogen atoms are assumed to be dominant. It is concluded that π-spins are more localized on monovalent nitrogen atoms by introducing *s*-triazine skeleton into π-conjugation systems.

TABLE I The fine-structure parameters of nitrenes **1** ($S = 1$) and **2** ($S = 2$)

Compounds	S	$\lvert D\rvert$ /cm^{-1}	$\lvert E\rvert$ /cm^{-1}
1 (powder-pattern ESR)	1	1.445	0.0045
1 (single-crystal ESR)	1	1.402	0.011
Phenylnitrenes	1	≈ 1.0[6]	-
2 (observed)	2	0.280	0.058
2 (calculated with 2θ = 118.3degrees)	2	0.281	0.058
m-Phenylenebisnitrenes	2	≈ 0.20[16]	-

The hyperfine splittings due to the monovalent nitrogen nucleus of **1** were observed at θ_{ab} = 60 degrees. The hyperfine tensor $\underset{\sim}{A}$ has a colinear principal-axes system with the fine-structure tensor and one of the principal value is 0.0018 cm^{-1}.

The analyses of temperature dependence of the signal intensity confirmed that both the triplet state of **1** and the quintet state of **2** are ground states or they are nearly generate with singlet states within very small energy gaps.

Acknowledgment

The authors acknowledge the Ministry of Education, Science, and Culture, Japan for financial supports. One of the authors (T. NAKAI) thanks the Japan Society for the Promotion of Science for a research fellowship for young scientists.

References

[1] *Bunshi-jisei (Molecure Magnetism)*,edited by K. Itoh (Gakkenshuppan, Tokyo, 1996).

[2] K. Furukawa, T. Takui, K. Itoh, I. Miyahara, K. Hirotsu, T. Watanabe, K. Hirai, and H. Tomioka, *Mol. Cryst. Liq. Cryst.*, **306,** 185, (1997).

[3] G. Smolinsky, E. Wasserman, and W.A. Yager, *J. Am. Chem. Soc.*, **84,** 3220, (1962).

[4] A.M. Trozzolo, R.W. Murray, G. Smolinsky, W.A. Yager, and E. Wasserman, *J. Am. Chem. Soc.*, **85,** 2526, (1963).

[5] E. Wasserman, G. Smolinsky, and W.A. Yager, *J. Am. Chem. Soc.*, **86,** 3166, (1964).

[6] J.A. Rcoope, J.B. Farmer, C.L. Gargner, and C.A. McDowell, *J. Chem. Phys.*, **42,** 54 (1965).

[7] J.A. Hebden and C.A. McDowell, *J. Mag. Reson.*, **5,** 115 (1971).

[8] E.W. Hughes, *J. Chem. Phys.*, **3,** 1 (1935).

[9] C.N. Banwell and H. Primas, *Mol. Phys.*, **6,** 225, (1963).

[10] G.G. Belford, R.L. Belford, and J.F. Brukkhalter, *J. Mag. Reson.*, **11,**251, (1973).

[11] K.T. McGregor, R.P. Scaringe, and W.E. Hatfield, *Mol. Phys.*, **30,** 1925, (1975).

[12] Y. Teki, I. Fujita, T. Takui, T. Kinoshita, and K. Itoh, *J. Am. Chem. Soc.*, **116,** 11499, (1994).

[13] C.B. Moler and G.W. SteWart, *SIAM J. Num. Anal.*, **10,** 241 (1973).

[14] K. Sato, Doctoral Thesis, Osaka City University, 1994.

[15] J. Higuchi, *J. Chem. Phys.*, **39,** 1847 (1963).

[16] T.A. Fukuzawa, Master's Thesis, Osaka City University, 1997.

[17] Y. Teki, T. Takui, K. Itoh, H. Iwamura, and K. Kobayashi, *J. Am. Chem. Soc.*, **108,** 2147, (1986).