ORGANIC LETTERS

2001
Vol. 3, No. 21
3261−3264

N-(2-Methoxycarbonyl-2-yloethyl) (3-Nitrenophenyl)aminyl: EPR Observation of a Quintet Hetero-Spin Molecule

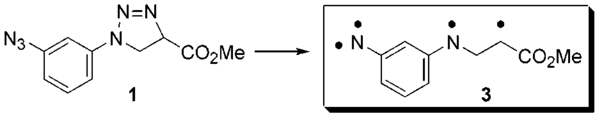
Hideyuki Tukada

Graduate School of Integrated Science, Yokohama City University,
Kanazawa-ku, Yokohama, 236-0027, Japan

htht@yokohama-cu.ac.jp

Received July 11, 2001

ABSTRACT



The EPR observation of a ground-state quintet hetero-spin molecule, *N*-(2-methoxycarbonyl-2-yloethyl) (3-nitreno-phenyl)aminyl 3, in a MTHF matrix at cryogenic temperatures is reported. The molecule has two different kinds of triplet sites, and the ZFS parameters of the quintet are $|D/hc| = 0.170\ \mathrm{cm}^{-1}$ and $|E/hc| = 0.004\ \mathrm{cm}^{-1}$. As a result of the nature of the 1,3-localized biradical, the quintet 3 was thermally labile over 5 K.

In the past two decades, organic high-spin molecules have attracted attention as a key to the design of molecule-based organic magnetic substances.[1] Thus a large number of non-Kekulé molecules and radical ions exhibit high-spin states, as expected from the degenerated singly occupied (or nonbonding) molecular orbitals (SOMOs or NBMOs) at the Hückel level of theory. Perturbation of the high-spin π-systems splits more or less the degeneration of the SOMOs and affects the energy gaps between the high- and low-spin states. These perturbed high-spin molecules have several electronic states in proximity and are good candidates for functional magnetic molecules that exhibit spin crossover, photomagnetism, pH-dependent magnetism, etc.[2] The perturbed high-spin molecules are also anticipated to exhibit reactivity depending on their spin states.[3] Hetero-spin molecules,[4] bearing different kinds of spin sites, are a family of the perturbed high-spin molecules. Therefore, we are interested in hetero-spin molecules such as *m*-nitrenophenyl carbene (carbene vs nitrene)[4a] and *m*-ylomethyphenyl nitrene ($S = 1$ vs 1/2),[4b] and here we report quintet molecules constructed with two different triplet sites (nitrenic atom vs 1,3-localized biradical or 2 spins on an atom vs 2 spins on different N and C atoms).

Photolysis (310−350 nm; 10 min) of methyl 1-(3-azidophenyl)-4,5-dihydro-1*H*-1,2,3-triazole-4-carboxylate **1**[5] (prepared from *m*-phenylenediazide and methyl acrylate) in

---

[1] (a) *Magnetic Properties of Organic Materials*; Lahti, P. M., Ed.; Marcel Dekker: New York, 1999. (b) *Diradicals*; Borden, W. T., Ed.; Wiley: New York, 1982. (c) Wentrup, C. *Organic Reactive Intermediates*; Wiley: New York, 1984; Chapter 3. (d) Iwamura, H. *Adv. Phys. Org. Chem.* **1990**, *26*, 179. (e) Berson, J. A. *Acc. Chem. Res.* **1997**, *30*, 238. (f) Rajca, A. *Chem. Rev.* **1994**, *94*, 871. (g) Nau, W. M. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2445.

[2] (a) Ishiguro, K.; Ozaki, M.; Sekine, N.; Sawaki, Y. *J. Am. Chem. Soc.* **1997**, *119*, 3625. (b) Hu, J.; Hill, B. T.; Squires, R. R. *J. Am. Chem. Soc.* **1997**, *119*, 11699.

[3] (a) Plattner, D. A. *Angew. Chem., Int. Ed.* **1999**, *38*, 82. (b) Abe, M.; Adam, W.; Ino, Y.; Nojima, M. *J. Am. Chem. Soc.* **2000**, *122*, 6508.

[4] Heterospin molecules, for example: (a) Rule, M.; Matrinand, A. R.; Dougherty, D. A.; Hilinski E.; Berson, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 5098. (b) Tukada, H.; Mutai K.; Iwamura, H. *J. Chem. Soc., Chem. Commun.* **1987**, 1159. (c) Tukada, H. *J. Chem. Soc., Chem. Commun.* **1993**, 302. (d) Matsuda, K.; Iwamura, H. *J. Chem. Soc., Chem. Commun.* **1996**, 1131. (e) Lahti, P. M.; Esat B.; Walton, R. *J. Am. Chem. Soc.* **1998**, *120*, 5122. (f) Shultz, D. A.; Farmer, G. T. *J. Org. Chem.* **1998,** *63*, 6254.

[5] **Spectroscopic data for 1:** ^{1}H NMR (270 MHz, $\mathrm{CDCl_3}$) δ 7.34 (1H, t, J = 8.1 Hz), 7.02 (1H, dd, $J = 8.1$, 2.0 Hz), 6.97 (1H, t, $J = 2.0$ Hz), 6.78 (1H, dd, $J = 8.1$, 2.0 Hz), 5.26 (1H, dd, $J = 13.2$ 9.8 Hz), 3.94(1H, t, $J = 9.8$ Hz), 3.88 (3H, s), 3.75 (1H, dd, $J = 13.2$, 9.8 Hz); ^{13}C NMR (67.5 MHz, $\mathrm{CDCl_3}$) δ 168.14, 141.45, 140.83, 130.71, 113.49, 111. 06, 105.44, 78.43, 53.26, 44.01; IR (neat, $\mathrm{cm^{-1}}$) 2109, 1746, 1603, 1287, 1262, 1111.

10.1021/ol016421i CCC: $20.00

2-methyl-tetrahydrofuran (MTHF, 0.1 mol dm^{-3}) was performed at 4.2 K in an EPR cavity (X-band) with a 500 W super-high-pressure mercury lamp and glass filters (Toshiba UV-D33S, UV-31, and IRA-25S). The EPR spectrum after irradiation persisted for at least 1 h at this temperature and consisted of several sets of signals (Figure 1a). Besides a peak attributable to mononitrene (665.5 mT, *X*-, *Y*-transitions, $|D/hc| = 0.9887$, $|E/hc| = 0.000$ cm^{-1}), peaks at 156.9 (a half-field signal), 251.6, and 395.3 mT were assigned to **2** because they are superimposed on that of a triplet diradical, *N*-(2-methoxycarbonyl-2-yloethyl)-phenylaminyl as reported recently by us.[6] The zero-field-splitting (ZFS) parameters of **2** are $|D/hc| = 0.06716$ cm^{-1} and $|E/hc| = 0.02239$ cm^{-1} (Figure 1d). The *D* value is close to that of 1,3-diradicals such as cyclobutane-1,3-diyls[7] ($|D/hc| = 0.050-0.11$ cm^{-1}) and cyclopentane-1,3-diyls[8] ($|D/hc| = 0.041-0.084$ cm^{-1}).

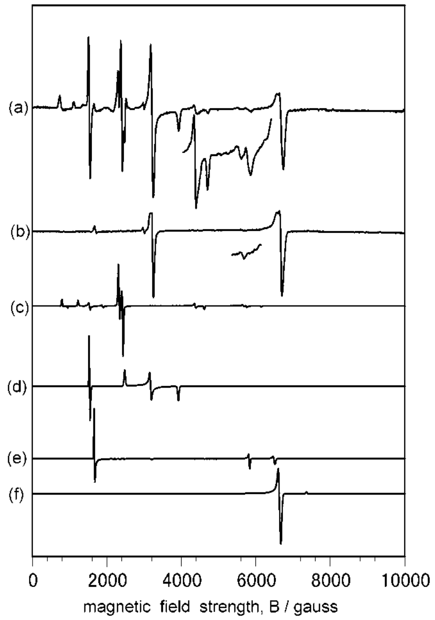


Figure 1. X-band EPR spectrum obtained after UV irradiation (310−350 nm; 10 min) of methyl 1-(3-azidophenyl)-4,5-dihydro-1*H*-1,2,3-triazole-4-carboxylate **1** in a MTHF matrix at 5 K (ν = 9.0024 GHz, power = 0.1 mW, modulation = 1 mT; inset, gain ×10) (a) and a spectrum after annealing at 46 K (observed at 18 K; inset, gain ×40, power ×4) (b). Simulated spectra[9] for quintet state (spin Hamiltonian = eq 1, $g = 2.003$) with ZFS parameters of $|D/hc| = 0.170$ cm^{-1} and $|E/hc| = 0.004$ cm^{-1} (c), for a triplet 1,3-biradical with ZFS parameters of $|D/hc| = 0.06716$ cm^{-1} and $|E/hc| = 0.02239$ cm^{-1} (d), for a quartet with $|D/hc| = 0.345$ cm^{-1} and $|E/hc| = 0.0003$ cm^{-1} (e), and for a triplet nitrene with $|D/hc| = 0.9887$ cm^{-1} and $|E/hc| = 0.0$ cm^{-1} (f), respectively.

The remaining signals are attributable to quintet **3** having two triplet sites, a nitrenic atom, and a localized 1,3-biradical. Computer simulation[9] by a full-matrix diagonalization method for randomly oriented quintet molecules (spin Hamiltonian in eq 1) produced the spectrum shown in Figure 1c ($|D/hc| = 0.170$ cm^{-1} and $|E/hc| = 0.004$ cm^{-1}).

$$H = D\{Sz^2 - S(S+1)/3\} + E(Sx^2 - Sy^2) + g\beta BS \quad (1)$$

The *D* value of the quintet agrees with that predicted by Itoh's model[10] [eq 2),

$$D^q = (D^t_{\mathrm{A}} + D^t_{\mathrm{B}})/6 \quad (2)$$

0.17 cm^{-1} estimated from the numerical sum of *D* values; 0.16 cm^{-1} (*syn*-conformer;[11] rotational angle = 90°) and 0.17 cm^{-1} (*anti*-conformer; rotational angle = 142°) estimated from the sum of *D* tensors] for the quintets constructed with weakly interacting two triplet sites, of which the *D* values are D^t_{A} and D^t_{B}.

The quintet spectrum resembles that of transient unidentified species we have observed previously in two independent EPR experiments[12] involving the photolysis of 3-azidobenzyl bromide in the presence of tetrakis(dimethylamino)ethylene and the photolysis of (3-azidophenyl)acetyl peroxide in MTHF. Thus, these species can be attributed to quintets ($|D/hc| = 0.16$ cm^{-1}) composed of a triplet nitrene and an intramolecular radical pair. The *D* value of these species is slightly smaller than that of **3**. This is in good accord with D^t (intramolecular radical pair) being smaller than D^t (1,3-localized biradical).

EPR measurements for **3** were then carried out on warming from 5 to 50 K in darkness. At each temperature (T_i) the signal intensity (*I*) became almost steady within 3 min. The initial intensity (5 K) did not regenerate upon cooling from T_i to 5 K (open circles in Figure 2). The decrease occurred primarily at about 14 K, and the recooled (16 → 5 K) sample exhibited half the initial intensity. Quintet **3** did not survive

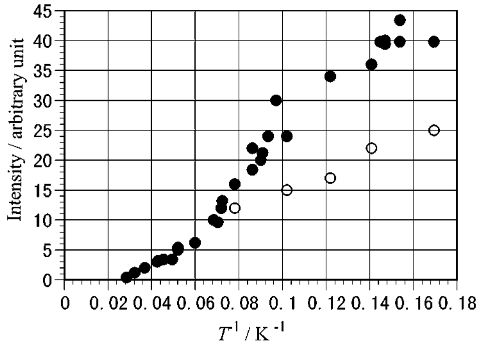


Figure 2. Intensity of EPR signals vs reciprocal absolute temperature for **3** in MTHF. Closed circles indicate heating process from 5 to 50 K, and open circles represent temperature dependence of signal intensity between 5 and 16 K after annealing at 16 K.

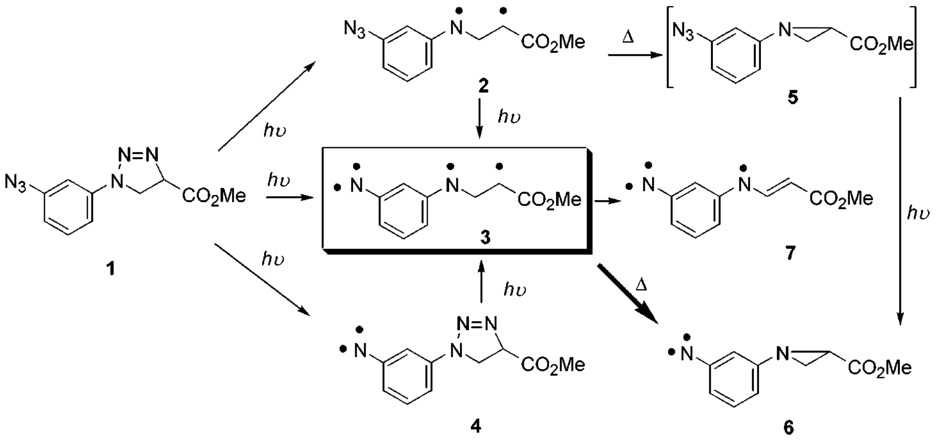
---

[6] Tukada, H. *J. Chem. Soc., Chem. Commun.* **2000**, 63.

[7] Sponsler, M. B.; Jain, R.; Coms, F. D.; Dougherty, D. A. *J. Am. Chem. Soc.* **1989**, *111*, 2240; **1988**, *110*, 1356.

[8] (a) Buchwalter, S. L.; Closs, G. L. *J. Am. Chem. Soc.* **1975**, *97*, 3857; **1979**, *101*, 4688. (b) Adams, W.; Emmert, O.; Heidenfelder, T. *J. Org. Chem.* **1999**, *64*, 3417. (c) Adam, W.; van Barneveld, C.; Bottle, S. E.; Engert, H.; Hanson, G. R.; Harrer, H. M.; Heim, C.; Nau, W. M.; Wang, D. *J. Am. Chem. Soc.* **1996**, *118*, 3974.

Scheme 1. Possible Mechanism of the Photochemical Decomposition of **1**



at temperatures greater than 40 K. Between T_i and 5 K, the signal intensity of the annealed sample obeyed the Curie law, and no further decrease of intensity was observed between T_i and 5 K (Figure 2).

This behavior can be interpreted as (1) the quintet is the ground state of **3** (or the quintet state and lower spin states are nearly degenerated within 30 J mol^{-1}), (2) the irreversible decay arises from a ring-closure reaction of the 1,3-diradical moiety (Scheme 1), and (3) the process proceeds through transition states with distributive activation energies rather than through classical or tunneling processes with a single activation energy. This thermal behavior is identical to that of *N*-(2-methoxy-carbonyl-2-yloethyl)phenylaminyl.[6]

The transition states having distributive activation energies should be accounted for by both the result of matrix site effects and the existence of conformers of **3** and can be analyzed using a "distribution slicing" method, which was successively used for the ring closure of cyclobutane-1,3-diyls by Dougherty's group.[7] Applying this method to our case gave an average activation energy of $E_a = 3$ kJ mol^{-1}, under the assumption that $A = 10^8$ and $t = 180$ s, where A is a frequency factor in the Arrhenius equation and t is the slicing time. The activation energy, which possibly corresponds to that required for spin inversion (ISC), is the same as that of *N*-(2-methoxycarbonyl-2-yloethyl)phenylaminyl (3.2 kJ mol^{-1}) and is smaller than that of cyclobutane-1,3-diyls ($E_a = 4.0-9.7$ kJ mol^{-1})[7] and cyclopentane-1,3-diyls ($E_a = 8$ to >20 kJ mol^{-1}).[8]

The lower activation energy for ring closure in **3** compared with that for cyclobutane-1,3-diyls is attributable primarily to the flexible open chain structure of **3** and secondarily to the interaction between a lone pair on the aminyl radical and the p-orbital of the counterpart carbon radical.

According to density functional theory calculations (U-B3LYP/6-31G*),[11] which are known to give reliable structures and energies for open-shell molecules, the quintet[13] **3**

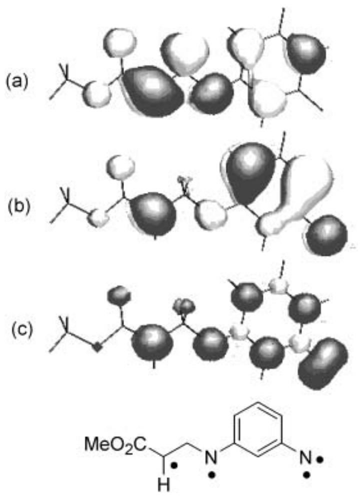


Figure 3. The HOMO(α) of quintet **3** and an optimized structure at U-B3LYP/6-31G* level of calculations (a), HOMO-1(α) (b), and the spin population (α−β) (c). Black and white surfaces in (c) indicate α and β spins, respectively. Surfaces of the spin population and MOs are drawn with density of 0.01 and 0.03 electrons/au^3, respectively. Calculations were performed with Gaussian98W,[11] and the results were visualized with WinMOPAC (v.3, Fujitsu Ltd.).

---

(9) Computer simulations were performed with an EPR simulation program suite, XSophe-Sophe-XeprView (v.1.0.1) developed by Prof. G. R. Hanson (University of Brisbane, Australia) and Bruker Analytik GmbH, using a full-matrix diagonalization method for $S = 2$ and the following parameters; $g = 2.003$, $\nu = 9.005$ GHz. Wang, D.; Hanson, G. R. *J. Magn. Res., Ser. A* **1995**, *117*, 1.

(10) (a) Itoh, K. *Pure Appl. Chem.* **1978**, *50*, 1251. (b) Kalgutkar, R. S.; Lahti, P. M. *J. Am. Chem. Soc.* **1997**, *119*, 4771.

(11) The DFT calculations at the B3LYP/6-31G* level of theory were carried out by a Gaussian98W program package: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998. The *anti*-conformer (shown in Figure 3) about a RCH_2-NAr bond in the quintet **3** is slightly more stable (0.2 kJ mol^{-1}) than the *syn*-conformer.

(12) Tukada, H. *Mol. Cryst. Liq. Cryst.* **1993**, *233*, 9.

has a flat and (0,0) conformation (following the notation for trimethylene,[14] Figure 3a). The flat structure is appropriate for a hyperconjugative interaction between the isolated 1,3-biradicals and a methylene group. In fact, the HOMO(α) has a hyperconjugative orbital interaction expressed as π_a− pseudo $\pi(CH_2)$. The next HOMO(α) is expressed as π_s and has a node at the methylene position (Figure 3b). Most of the spin populations of quintet **3** are distributed around the formal radical centers and alternatively around an aromatic ring (Figure 3c; the Mulliken spin populations are 1.60/nitrenic atom, 0.63/N (aminyl) atom, and 0.91/C2′ atom). The values are consistent with the sum of spin populations in phenyl nitrene and *N*-(2-methoxycarbonyl-2-yloethyl)-phenylaminyl.

The intensity of an EPR signal (665.5 mT) of the triplet mononitrene **6** did not change practically at the diminishment of **3** (40 K). Considering the low activation energy for ring closure, it is reasonable that the primary photoproduct from **1** is **6** (via a singlet 1,3-localized biradical state; Scheme 1) and far less **3** is produced than **6**.

After the disappearance of quintet signals a set of signals (167.6, 302.4, 568.5, and 656.1 mT) remained up to 70 K. The intensities of these signals obeyed the Curie law between 4.5 and 70 K. The species could be assigned to a quartet ($|D/hc| = 0.345$, $|E/hc| = 0.0003$ cm^{-1}; Figure 2e); a candidate for the quartet is **7**.

In summary, we have observed a quintet molecule composed of different kinds of triplet sites, which exhibited an inter-spin reaction for ring closure with very small and distributive activation energies centered at 3 kJ mol^{-1}.

Acknowledgment. The present work was financially supported by a Grant-in-Aid for Scientific research from Japan Society for the Promotion of Science (C-12640524) and by the Nagase Science and Technology Foundation.

OL016421I

---

(13) The eigenvalue of S^2 is 6.09 (6.00) before (after) annihilation.

(14) (a) Skancke, A.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1998**, *120*, 7079. (b) Getty, S. J.; Davidson E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1992**, *114*, 2085. (c) Baldwin, J. E.; Yamaguchi Y.; Schaefer, H. F., III. *J. Phys. Chem.* **1994**, *98*, 7513.