ChemComm

N-(2-Methoxycarbonyl-2-yloethyl)phenylaminyl: EPR observation of a triplet nonconjugated 1,3-diradical with two different kinds of radical centers

Hideyuki Tukada

Graduate School of Integrated Science, Yokohama City University, Kanazawa-ku, Yokohama 236-0027, Japan.
E-mail: htht@yokohama-cu.ac.jp

Received (in Cambridge, UK) 6th October 1999, Accepted 24th November 1999

EPR observation of *N*-(2-methoxycarbonyl-2-yloethyl)phenylaminyl at cryogenic temperature shows that the diradical has a triplet ground state, and is thermally labile for ring-closure reaction with low and distributive activation energies centered around 3.2 kJ mol^{-1}.

Diradicals,[1] reactive intermediates frequently appearing in both thermal and photochemical reactions, are unique in that they show dichotomous reactivities depending on their spin states. Recently numerous conjugated diradicals have been explored in efforts to develop building blocks for organic magnetic substances.[2] On the other hand, localized diradicals linked with σ-bonds have not yet received sufficient attention as magnetic molecules. Among the localized diradicals, 1,3-diradicals, such as trimethylene,[3] are the simplest and representative.[1] Here we report *N*-(2-methoxycarbonyl-2-yloethyl)phenylaminyl **1**, a diradical with two different kinds of formal radical centers,[4] localized and conjugated, on N and C atoms. To the best of our knowledge this is the first example of EPR observation of an open-chain nonconjugated 1,3-diradical. It is of interest how the energy gap between the singlet and the triplet in **1** is affected by heteroatom substitution on one side of the radical site in trimethylene, and how the lone pair on the nitrogen atom affects the kinetic stability of **1**.

Photolysis (330 ± 20 nm) of methyl 1-phenyl-4,5-dihydro-1*H*-1,2,3-triazole-4-carboxylate **2**[5] in a 1 : 1 mixture of C_2D_5OD–CD_3OD (50 mmol dm^{-3}) was performed in an EPR cavity (X-band) with a 500 W super-high-pressure mercury lamp and glass filters at 5 K. The EPR spectrum after irradiation for 5 min persisted for at least 1 h at this temperature, and showed a set of signals characteristic of a triplet biradical (half-field signal; 0.1569 mT) with zero-field-splitting (ZFS) parameters of $|D| = 3|E|$[6] (Fig. 1).

The signals at 2516 and 3953 mT were assigned to overlapping signals due to transition of Z and Y with the ZFS parameters $|D/hc| = 0.06716$ cm^{-1} and $|E/hc| = 0.02239$ cm^{-1}. The D value is close to those of 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}), and is fully consistent with a localized 1,3-diradical structure with an average distance of 0.34 nm between two unpaired electrons.[8]

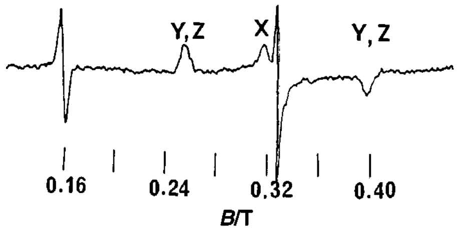


Fig. 1 X-Band EPR spectrum of **1** obtained after UV irradiation (330 ± 20 nm) to methyl 1-phenyl-4,5-dihydro-1*H*-1,2,3-triazo-4-carboxylate **2** in a 1 : 1 mixture of C_2D_5OD–CD_3OD matrix for 5 min at 5 K ($\nu = 9.0067$ GHz, power = 0.2 mW, modulation = 1 mT). Asterisk denotes doublet impurities.

EPR measurements were then performed on warming from 5 to 50 K in the dark. At each temperature (T_i) the signal intensity (I) stabilized within 3 min. Re-cooling from T_i to 5 K did not regenerate the initial intensity, which indicates that the biradical was irreversibly diminished by the reactions. However, no further decrease in signal intensity was observed between T_i and 5 K. The temperature dependence of the signal intensity for the annealed sample obeyed the Curie law (IT = constant) between 5 and T_i.

Consequently, the IT *vs.* T plot for the warming process did not become flat [line (i) in Fig. 2], whereas the plot for the post-annealed process showed a constant value [line (ii) in the Fig. 2]. The latter indicates that the triplet is the ground state of biradical **1**.

It seems reasonable that the initial decrease in signal intensity of the triplet can be attributed to decay through a ring-closure reaction to give methyl 1-phenylaziridine-2-carboxylate, which is the main photo-product at room temperature in solution (Scheme 1).[5] Decay by hydrogen abstraction from the matrix can probably be excluded because no new signals and no increase in the doublet species (indicated as * in Fig. 1) were observed up to 50 K. At 35 K, the triplet EPR signals originating from the biradical dissappeared immediately and simultaneously.

The same thermal behaviour of **1** was observed using 2-methyltetrahydrofuran as the matrix, indicating that the hardness of the surroundings of the diradical had little influence on ring-closure.

The former behavior [line (i)] can be interpreted as decay through transition states with distributive activation energies due to matrix site effects and conformers of **1**, rather than classical or tunneling processes having a single activation

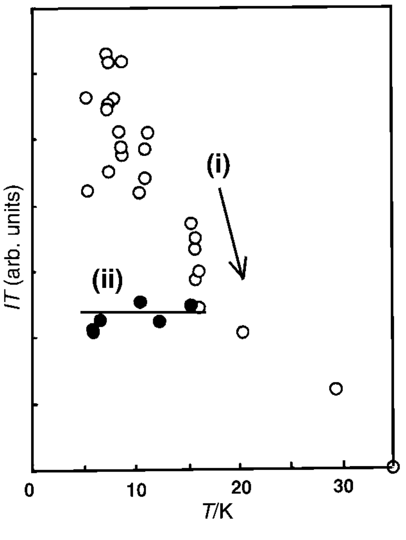
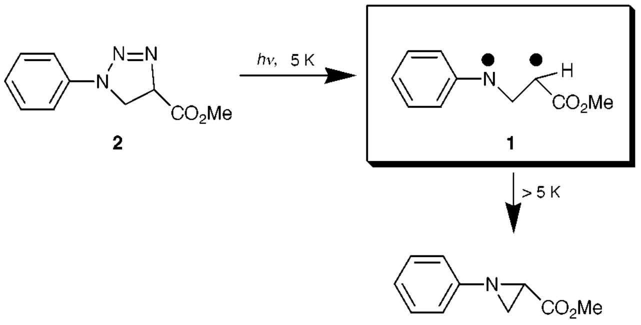


Fig. 2 IT *vs.* T plots, where I is the EPR signal intensity of the $|\Delta M_s| = 2$ transition of **1** in a 1 : 1 mixture of C_2D_5OD–CD_3OD, and T is the absolute temperature. (i) Open circles indicate a heating process from 5 to 35 K, and closed circles show the temperature dependence of the signal intensity between 5 and 18 K after annealing at 18 K.



Scheme 1

energy. Such a mechanism with distributive activation energies was successively analyzed by a 'distribution slicing method' in the case of cyclobutane-1,3-diyls by Dougherty's group.[7] Applying this method to our case (50% of **1** decayed at 16 K) gave an average activation energy, $E_a = 3.2$ 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 slightly smaller than that in the case of cyclobutane-1,3-diyls ($E_a = 4.0$–9.7 kJ mol^{-1}) or cyclopentane-1,3-diyls ($E_a = 8$–>20 kJ mol^{-1}).

The low activation energy in the case of **1** is attributable primarily to the flexible open chain structure and secondly 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/6-13G*)[9] for the biradical **1**, the triplet has a (0,0) conformation (following the notation for trimethylene)[3] and lies below the singlet by 1.3 kJ mol^{-1} (vertically; the singlet biradical has no minimum on the energy surface, and the optimization of the structure gives methyl 1-phenylaziridine-2-carboxylate). The computed energy gap $\Delta E_{\text{S-T}}$ is consistent with the result of the EPR experiment. Most of the spin populations of triplet **1** are distributed on both the formal radical centers (spin/charge = 0.63/−0.47 on the N atom, and 0.90/−0.16 on the C2′ atom), and agree with the average distance between unpaired electrons as estimated from the experimental D parameter.

In conclusion, we have been able to detect triplet diradical **1**, a heteroatom analogue of trimethylenemethane, and found that the diradical is thermally labile above 5 K with low and distributive activation energies.

The present work was financially supported by the Nagase Science and Technology Foundation, and by a Grant-in-Aid for Scientific Research on Priority Areas 'Creation of Delocalized Electronic Systems' (10146244) from the Ministry of Education, Science, Sports, and Culture, Japan.

Notes and references

1 *Diradicals*, ed. W. T. Borden, Wiley, New York, 1982; C. Wentrup, *Organic Reactive Intermediates*, Wiley, New York, 1984, ch. 3.

2 H. Iwamura, *Adv. Phys. Org. Chem.*, 1990, **26**, 179; J. A. Berson, *Acc. Chem. Res.*, 1997, **30**, 238; A. Rajca, *Chem. Rev.*, 1994, **94**, 871; W. M. Nau, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2445.

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

4 Heterospin molecules: for examples, see M. Rule, A. R. Matrinand, D. A. Doughtery, E. Hilinski and J. A. Berson, *J. Am. Chem. Soc.*, 1979, **101**, 5098.; H. Tukada, K. Mutai and H. Iwamura, *J. Chem. Soc., Chem. Commun.*, 1987, 1159; H. Tukada, *J. Chem. Soc., Chem. Commun.*, 1993, 302; K. Matsuda and H. Iwamura, *Chem. Commun.*, 1996, 1131; P. M. Lahti, B. Esat and R. Walton, *J. Am. Chem. Soc.*, 1998, **120**, 5122; D. A. Shultz and G. T. Farmer, *J. Org. Chem.*, 1998, **63**, 6254.

5 R. Huisgen, G. Szeimies and L. Mobius, *Chem. Ber.*, 1966, **99**, 475.

6 Diradicals having ZFS parameters of $D = 3E$, for example: T. Hirano, T. Kumagai, T. Miyashi, K. Akiyama and Y. Ikegami, *J. Org. Chem.*, 1992, **57**, 876.

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

8 W. Adams, O. Emmert and T. Heidenfelder, *J. Org. Chem.*, 1999, **64**, 3417; S. L. Buchwalter and G. L. Closs, *J. Am. Chem. Soc.*, 1975, **97**, 3857; 1979, **101**, 4688.

9 The DFT calculations were performed using a Gaussian98 program package (Revision A7, Gaussian, Inc., USA).

Communication a908039b