Diradical Diions of *m*-Bis(naphthyl) and (anthryl) Phenylenes as New High-spin Molecules

Hideyuki Tukada

Graduate School of Integrated Science, Yokohama City University, 22-2 Seto, Kanazawa-ku, Yokohama 236, Japan

Ferromagnetic spin alignment is observed in double one-electron-oxidized or -reduced conjugated molecules, *m*-bis(9-anthryl) phenylene dication diradical $\mathbf{1}^{2\cdot+}$ and *m*-bis(1-naphthyl) phenylene dianion diradical $\mathbf{2}^{2\cdot-}$, based on EPR experiments at cryogenic temperature.

Recently π-conjugated diradicals and homologous high-spin molecules[1] have received considerable attention not only as reactive intermediates but also as key building blocks for organic ferromagnets. Most of the high-spin molecules so far explored have non-Kekulé structures in the π-conjugated systems. Fukutome[2] predicted a different type of ferromagnetic polyradicals whose open-shell sites are derived from oxidation or reduction of the π-moieties. Dougherty[3] reported ferromagnetic interaction in doped polyenes, however, the average spin-concentration is low with regard to the biradical.

We describe here clear experimental evidence for the ferromagnetic interaction between ionic radical moieties in *m*-bis(9-anthryl) and -bis(naphthyl) phenylenes, **1** and **2**, as a new family of high-spin molecules.

The oxidation of **1** (0.2 mmol dm^{-3}) with $SbCl_5$ in CH_2Cl_2 at 0 °C for 10 s gave a blue–green solution (λ_{max} = 730 nm; *cf.* anthracene radical cation, 709 nm) and the EPR spectra (x-band) were immediately measured in the temperature range of 6.5–85 K (Fig. 1). The spectrum is characteristic of a randomly oriented triplet state biradical with a small zero field splitting (ZFS) $|E|$ value, except for a central peak attributed to mono-radicals. The triplet ZFS parameters are $|D/hc|$ = 0.00491 cm^{-1} and $|E/hc|$ = 0.0 cm^{-1}. The D value corresponds to an average distance of 0.81 nm between radical centres according to R_{av}/nm = 0.1375 $|D/\text{cm}^{-1}|^{-1/3}$. This distance is close to that between the two anthranyl groups in **1**.

The temperature dependence of the intensities of both the $|\Delta_m|$ = 1 and 2 signals showed a linear correlation to the reciprocal of absolute temperature in the above temperature range. Thus, the triplet is the ground state of $\mathbf{1}^{+\cdot}$ (or both the triplet and a singlet are nearly degenerated within 20 cal mol^{-1}).

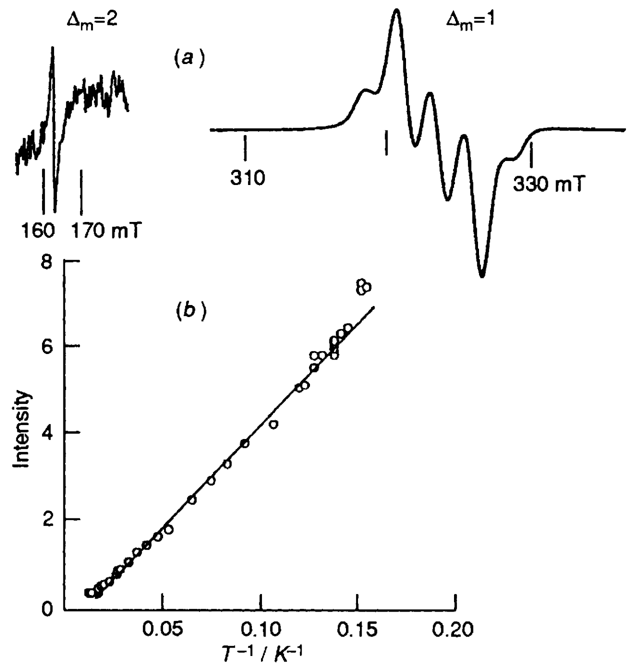


Fig. 1 (*a*) EPR spectrum of $\mathbf{1}^{2\cdot+}$ at 7 K in an MTHF matrix. The $|\Delta_{m_s}|$ = 2 signal was recorded with a higher amplitude than that for the $|\Delta_{m_s}|$ = 1 signals. A central signal is attributed to monoradical impurities: ν = 9.067 GHz, power = 0.005 mW, field modulation = 1 mT; (*b*) Curie plots of the intensity of the $|\Delta_{m_s}|$ = 1 signal.

In order to eliminate the possibility that the triplet arises from intermolecular mono-radical pairs,[4] anthracene **3**, 9-phenylanthracene **4**, and *m*-bis(9-methylanthryl) phenylene **5** were oxidized under the same conditions employed for $\mathbf{1}^{+\cdot}$. All of them gave a sharp single line in the EPR spectrum at g = 2.003 (ΔH_{pp} = 1.9 mT for $\mathbf{3}^{+\cdot}$ in an MTHF matrix). Thus, the possibilities that the triplet arises from the mono-radical pairs or dication of one anthracene moiety in **1** will be significantly reduced.

Furthermore, *p*-bis(9-anthryl) phenylene **6**, the *para*-isomer of **1**, did not give triplet species under the same oxidative conditions as **1**. If the central phenylenes only played a role to fix two cationic radicals in a close distance, **5** and **6** should yield triplets. These facts demonstrate the importance of the phenylene units and its topology (*meta*) for spin alignment.

Next, we examined a reductive introduction of two radical centres to **2**.

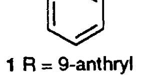
It is known that aromatic hydrocarbons and polyenes having no degenerated HOMOs give both mono- and di-anions by the reduction with alkali metals in ethereal solvents. The disproportionation constants ($2\,R^{\cdot-} \rightleftharpoons R + R^{2-}$) are affected by the solvents and the counter metals.[5] To minimize the disproportionation to the closed shell species, we chose the following system; naphthalene moieties **2** as the reductant and Na metal in 2-methyltetrahydrofuran (MTHF) as the reducing reagent.

Reduction of the precursor hydrocarbon **2** (0.3 mmol dm^{-3} in MTHF) with sodium metal at 10 °C for 15 min gave a dark green solution (λ_{max} = 698 nm). The EPR spectra of $\mathbf{2}^{2-\cdot}$ in MTHF were measured over the temperature range of 7–120 K (Fig. 2). A set of signals due to a triplet species was observed for both $|\Delta_m|$ = 1 and 2 transition (ZFS parameters, $|D/hc|$ = 0.00660 cm^{-1} and $|E/hc|$ = 0.0 cm^{-1}). Temperature dependence of these signals obeyed the Curie law (Fig. 2).

The triplet does not come from the dimeric monoradical because very concentrated sodium naphthalenide (20 mmol dm^{-3} in MTHF) gave only a sharp single line in the g = 2 region under the same conditions as mentioned above. Also, the reduction of **6** with sodium metal in MTHF showed doublet species with a sharp single line at the g = 2 position instead of triplet species.

Accordingly, the di(ion radical) of **1** and **2** can be obtained by double 1-electron-oxidation or -reduction of both the closed shell sites joined by a *m*-phenylene unit, and the resulting diionic diradicals have parallel spin alignment to give a triplet state.

The *m*-phenylene junction between radical centres has been skillfully used in Itoh and Iwamura's origocarbenes to realize up to S = 9.[1] The topology promises the origocarbenes to give (1) degenerated non-bonding MOs and (2) alternative up and down spin-populations in the whole π-framework. A variety of high spin molecules, constructed with a π-conjugated chain



1 R = 9-anthryl
2 R = 1-naphthyl

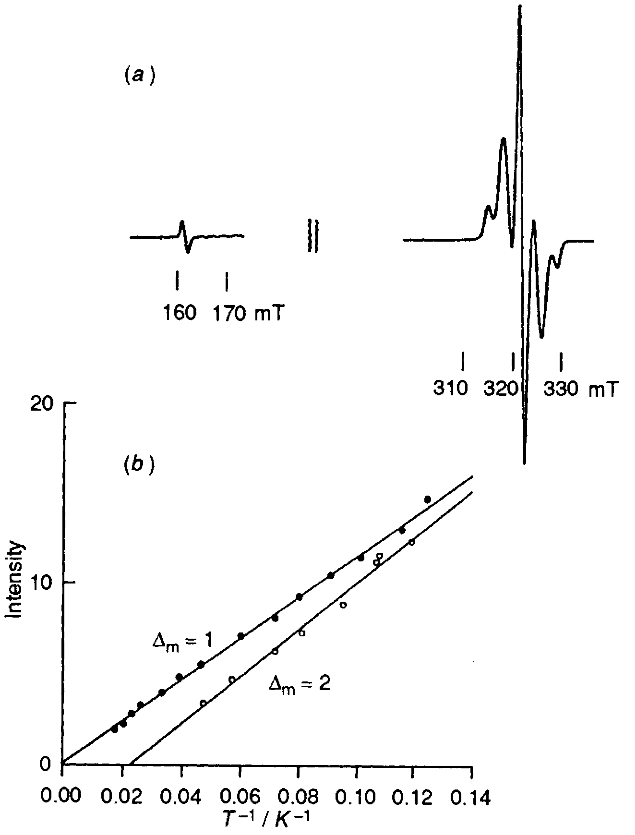


Fig. 2 (*a*) EPR spectrum of **2**$^{2\cdot-}$ at 65 K in an MTHF matrix. The $|\Delta m_s| = 2$ signal was recorded with higher amplitude than that for the $|\Delta m_s| = 1$ signals: $\nu = 9.073$ GHz, power = 0.05 mW, field modulation = 1 mT. (*b*) Curie plots of the intensity of both the $|\Delta m_s| = 1$ and 2 signals.

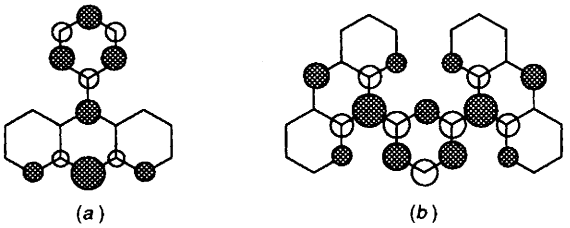


Fig. 3 Spin populations of cationic radicals according to the PM3 calculation (UHF); (*a*) 9-phenylanthracene$^{\cdot+}$ (*b*) **1**$^{2\cdot+}$ (triplet). The closed and open circles represent up and down spins, respectively. Small spin populations were omitted for clarity and the limit of the calculation.

and pendant spins, are thus designed based on the two factors.[1]

On the other hand, diradicals like **1**$^{2\cdot+}$ and **2**$^{2\cdot-}$ do not meet these points *a priori*. Even for the Hückel level of calculation, **1**$^{2\cdot+}$ and **2**$^{2\cdot-}$ have no degenerate SOMOs. It is in marked contrast to non-Kekulé molecules and highly symmetric π-ionic-radicals[6] such as coronene^{2+} and $C_{60}{}^{2-}$. Degeneracy of NBMOs is, however, not necessary for spin ordering in several non-Kekulé molecules containing heteroatoms.[7] Small energy gaps between NBMOs or SOMOs (like **1**$^{2\cdot+}$ and **2**$^{2\cdot-}$) permit the high spin state to be a ground state due to stabilization by exchange interactions.

The PM3 (UHF) calculation[8] for 9-phenylanthracene$^{\cdot+}$, as the half part of **1**$^{2\cdot+}$, showed large spin populations at the 9- and 9′-positions [See Fig. 3(*a*)]. Moderately large and alternative spin populations appeared on the phenyl ring. Such spin distributions, especially the alternative spin alignment on the phenylene unit, fit the overall parallel spin alignment between two radical centres in **1**$^{2\cdot+}$ [Fig. 3(*b*)]. It will be expected that if π-radical ions were connected with *m*-phenylene (or topologically equivalent units) at the positions having large spin populations, the highest spin-state would be the ground state in spite of the nondegeneracy of SOMOs.

In conclusion, EPR experiments on **1**$^{2+}$ and **2**$^{2\cdot-}$ demonstrate the possibility of producing highly ionic species by either oxidative or reductive doping, and to align spins in parallel.[9] It gives clear experimental support for the ferromagnetic doped-polyenes proposed by Fukutome and Dougherty. Further investigations on the dopable sites is currently being investigated.†

Professor K. Müllen and Dr M. Baumgarten (Max-Planck Institute) are gratefully acknowledged for their valuable information on anionic high-spin molecules. This work was financially supported by the Nishida Research Fund for Fundamental Organic Chemistry (1993) and a Grant-in-Aid from the Japan Ministry of Education, Science, and Culture (1992, No. 04640492).‡

Received, 22nd June 1994; Com. 4/03791J

Footnotes

† In our preliminary EPR experiments, the following π-radical systems gave triplet species: reduction of the disodium salts of *m*-bis-(3-phenylpropane-1,3-dione) phenylene and *m*-bis-(4,4′-dimethylpentane-1,3-dione) phenylene, whereas the following systems produced no obvious triplets: oxidation of *m*-bis(tetrathiafulvalene) phenylene; oxididation and reduction of *m*-bis(4-phenyl-1,3-butadienyl) phenylene.

‡ This work was partly performed at the University of Tokyo.

References

1 D. A. Dougherty, *Acc. Chem. Res.*, 1991, **24**, 88; H. Iwamura and N. Koga, *Acc. Chem. Res.*, 1993, **26**, 346; K. Itoh, *Pure. Appl. Chem.*, 1978, **50**, 1251; *Diradicals*, ed. W. T. Borden, Wiley, N.Y., 1982.

2 H. Fukutome, A. Takahashi and M. Ozaki, *Chem. Phys. Lett.*, 1987, **133**, 34.

3 D. A. Kaisaki, W. Chang and D. A. Dougherty, *J. Am. Chem. Soc.*, 1991, **113**, 2764.

4 K. M. Kadish, G. Moninot, Y. Hu, D. Dubois, A. Ibnlassi, J.-M. Barbe and R. Guilard, *J. Am. Chem. Soc.*, 1993, **115**, 8153.

5 *Comprehensive Organometallic Chemistry*, ed. G. Wilkinson, vol. 1, 1982, Pergamon, p. 109.

6 R. Breslow, B. Jaun, R. Q. Kluttz and C.-Z. Xia, *Tetrahedron*, 1982, **38**, 867; P. J. Krusic and E. Wasserman, *J. Am. Chem. Soc.*, 1991, **113**, 2322; B. Servet, S. Ries, M. Trotel, P. Alnot, G. Horowitz and F. Garnier, *Adv. Mater.*, 1993, **5**, 461.

7 M. Rule, A. R. Matlin, D. E. Seeger, E. F. Hilinski, D. A. Dougherty and J. A. Berson, *Tetrahedron*, 1982, **38**, 787; H. Tukada, K. Mutai and H. Iwamura, *J. Chem. Soc., Chem. Commun.*, 1987, 1159.

8 MOPAC ver. 6 was used for the PM3 calculation. J. P. Stewart, *J. Comput. Chem.*, 1989, **10**, 209 and 221.

9 M. Baumgarten, U. Müller, A. Bohnen and K. Müllen, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 448.