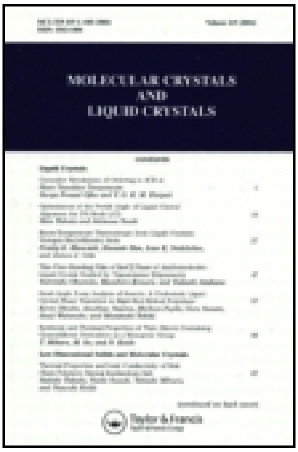

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New Classes of Organic High-Spin Molecules Generated with Electron-Doping

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New classes of organic high-spin molecules generated with electron-doping

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Abstract Two types of novel organic high-spin molecules are generated with electron doping; (1) 3-nitrenobenzyl, (2) 1,3-di(1-naphthyl)benzene dianion diradical.

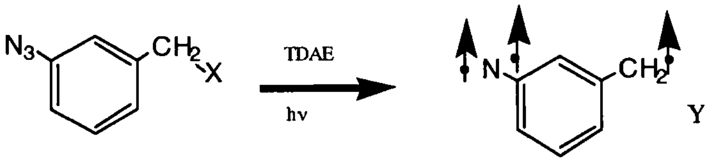
INTRODUCTION

So far numerous organic high-spin molecules have been reported,[1] however, most of them belong to the non-Kekulé molecules such as *m*-quinodimethane. In this paper, we describe new types of (ionic) high-spin-state species generated with electron doping.

3-NITRENOBENZYL: A Novel quartet having doubly heterogeneous spin sites (N and C atoms; S=1 and 1/2 center) in a π-conjugated molecule.

It is well known that photochemical σ-bond cleavage of benzyl halides is initiated with electron transfer from a suitable electron donor such as TDAE, and gives benzyl radicals.[2] Using the technique, we can observe 3-nitrenobenzyl **2**, which is the first reactive high-spin intermediate having both nitrene and methylene moieties. This molecule has a unique 3-spin system in which two of the spins are located on one atom and a spin on another atom. This type of molecule (e.g., 3-nitrenophenylaminyl) is may be a transient species in decomposition process of *m*-phenylene-dinitrene or -dicarbene via hydrogen abstraction in organic matrices, however, it is still unknown.

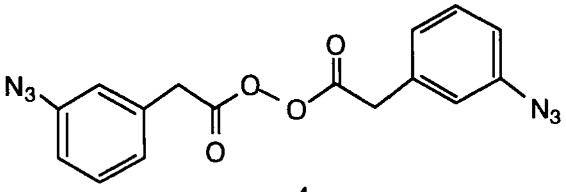
Photolysis of 3-azidebenzyl bromide (0.1M) (**1**; X=Br), in MTHF was performed at 20 ± 5 K for 70 min under the presence of tetrakis(dimethylamino)ethylene (TDAE, 0.4M) as an electron donor (Figure 1-b). Cleavage at benzylic carbon-halide bond along with azide group in **1** took place as is expected. In the absence of TDAE, **1** gave only a triplet nitrene.



1 2 ; Y^- 3 ; $Y^{\bullet\uparrow}$

In the Figure 1, T and R denote triplet mono-nitrene ($|D/hc| = 1.003\ cm^{-1}$, $|E/hc| \approx 0\ cm^{-1}$) and doublet radical(s), respectively. The rest of signals indicated as Q spread in a wide range of magnetic fields, which was characteristic for high spin ($S \geq 1$) species with a large D value, and are assigned to a quartet **2** (vide infra).

Independently, 3-azidephenylacetic peroxide **4** was selected for the precursor of **2** because of high efficiency for the generation of benzyl radical.[2, 3] Furthermore, the precursor will eliminate two CO_2 molecules between two radicals in a rigid glass, and which will separate the two radicals sufficiently. This is needed to eliminate complexity arisen from intermolecular interaction between radicals. In fact no indication to produce radical pairs was obtained from the ESR spectrum of unsubstituted phenylacetic peroxide photolized in an MTHF matrix at 20 K.



4

When an MTHF matrix of 3-azidephenylacetic peroxide **4** (0.03 M) was uv-irradiated through filters (310 - 400 nm) at 18 ± 2 K for 2 hr, several sets of ESR signals appeared with monotonous increase of intensities (Figure 1-a). Thus the same ESR spectrum was obtained from **1** and **4** except for a minor high spin species which we assign to a quintet **3** (denoted as q in the figure 1) constructed with a pair of the

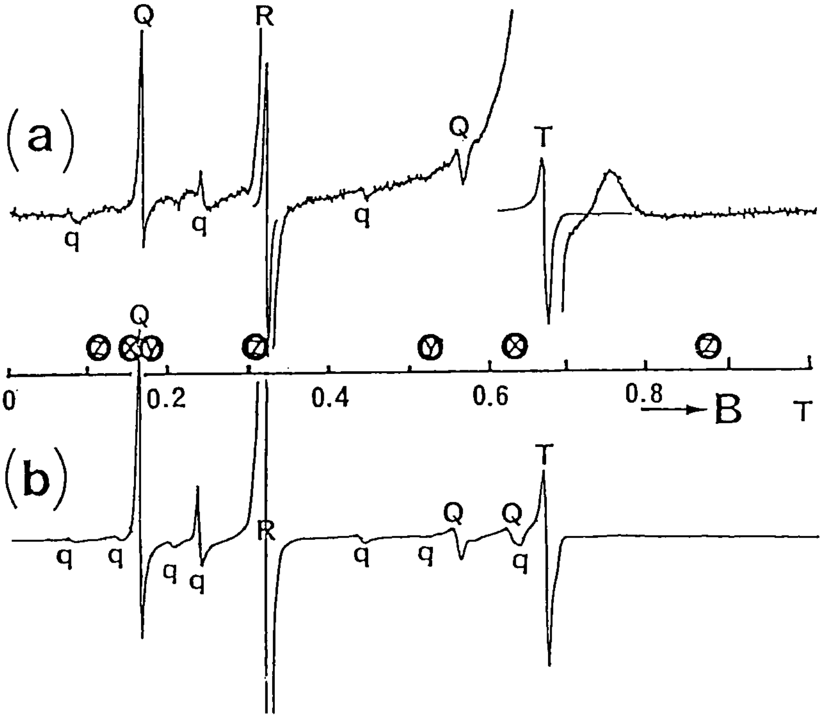


Figure 1. (a) ESR spectrum photochemically obtained from **4** (0.03 mM) in an MTHF matrix at 22 K (after uv irradiation at 18 ± 2 K for 2 hs; frequency = 9. 0804 GHz, power= 0.8 mW, field modulation = 1 mT). Q, T, and R denote the quartet **2**, triplet mono-nitrene(s), and doublet mono-radical impurities, respectively. (b) Photolysis of **1** (0.1M) was performed in the presence of TDAE (0.4M) in MTHF at 20± 5K for 70min, and the spectrum was recorded at 20 K (frequency = 9.09013 GHz, power = 0.6 mW, field modulation = 1 mT).

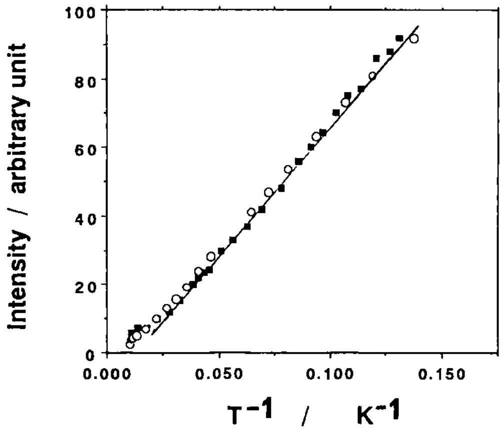


Figure 2. Temperature dependence of the intensities of a quartet ESR signal at 0.169 T vs. reciprocal of absolute temperatures (■, from a precursor **4** : ○, from a precursor **1**).

quartet **4** and a nearby doublet (Y=TDAE radical cation or bromine radical). The speculation of radical pairs agrees with an observation of a biradical triplet from photo-irradiated benzyl bromide in the presence of TDAE. Distinction of ESR signals of **2** from that of **3** is based on a difference of yields depending on photolitic conditions. Further investigation on the quintet **4** will be published elsewhere.

The quartet ESR signals were persistent up to 88 K in MTHF. As the temperature was kept at 92 K, simultaneous decrease of the quartet (and a quintet, vide infra) and increase of new triplet diradical (presumably radical pairs of aminyls and MTHF radicals ; $|D/hc| = 0.02042\ \mathrm{cm}^{-1}$, $|E/hc| \approx 0\ \mathrm{cm}^{-1}$; $|\Delta m_S| = 2$ signal at 161.6 mT) were observed within 30 sec, and the change was not reversed by re-cooling to 10 K. A part of triplet mono-nitrene survived at 92 K. These thermal behavior were consistent with the assignments of the ESR signals to R, T, and Q.

In general, zero-field-splitting parameters for the quartet[4] can be estimated from an observed highest field Hz signal using $2D = H_z - H_0$, where $H_0 = h\nu / (g_e\beta)$. Also, the resonance fields for a randomly oriented quartet are calculated by equations, e.g., W[energy for m_S (// z axis) = +3/2] $= g_e\beta H + [(D + g_e\beta H)^2 + 3E^2]^{1/2}$, where H is an applied magnetic field. Thus the z.f.s parameters of **2** were estimated as $|D/hc| = 0.26\ \mathrm{cm}^{-1}$ and $|E/hc| = 0.015\ \mathrm{cm}^{-1}$ (See Figure 1; Calculated resonance fields are indicated by circles).

A Curie plot (Figure 2) for the intensity of the quartet ESR signal (a signal at 0.169 T) shows a linear line in the temperature range 8 to 80 K, and which means the quartet is the ground state of **2**.

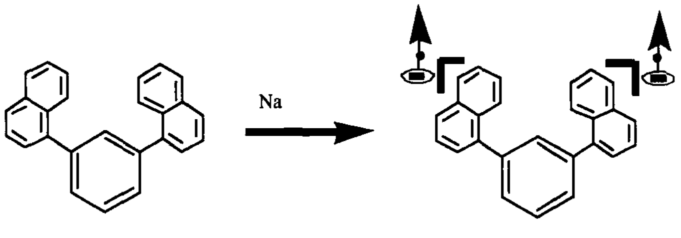
Lack of the degeneracy of energy levels of SOMOs in **2** is shown by PM3 (RHF) calculation.[5] The gaps among the three SOMOs of **2** is 0.55 eV at the level of calculation. One of principles for parallel spin alignment in non-Kekulé molecules is based on degeneracy of nonbonding MOs. Perturbation by heteroatom upon trimethylenemethane gives rise to large splitting of NBMOs, and then some derivatives of oxyallyl [$\bullet CR_2(C{=}O)CR_2\bullet$] are reported to be ground state singlet. Nevertheless highest spin state was observed in **2** as the ground state. It is similar to the case of *m*-benzoquinomethane and *m*-nitrenophenylmethylene.[6] Researches are still needed to clear how degree of perturbation diverse the ground state spin multiplicity.

Finally it is noteworthy that the quartet **2** is constructed with S=1 and S=1/2 spin centers as the first organic example. So far several organic quartet species were observed, most of them have three C_3-symmetrical π-radical sites.[4] Although attentions are well paid to the topology of π systems which connect spin sites, it is also interested in the symmetry on the inter-spin-sites and spin quantum number at each spin site.

1,3-DI(1-NAPHTHYL)BENZENE DIANION DIRADICAL

An open-shell species **6** can be derived from double one-electron reduction of both the closed-shell sites connected with a *m*-phenylene unit in **5**. However, scarce is known for the type of diradicals such as **6**, except for Fukutome's theoretical[7] and Dougherty's experimental[8] works on conjugated polymers. We describe here experimental evidences for ferromagnetic interaction between ionic-radical moieties in **6**, as a new family of high-spin molecules.

It is known that the reduction of aromatic hydrocarbons and polyenes with alkali metals in etherial solvents give both mono- and di-anions depending on the reaction conditions, and the dissociation constant ($2\,R^{\bullet -} \rightleftharpoons R^{0} + R^{2-}$) also affected by the solvents and the counter metals.[9] To minimize the formation of closed shell dianion, we choose the following system; naphthalene moieties as reductant and Na in 2-methyltetrahydrofuran (MTHF) as reducing reagent.



5 **6**

After reduction of the precursor hydrocarbon **5** with sodium metal at 10 °C for 15 min giving a dark green solution (λmax =698nm), an esr spectrum of **6** in MTHF was measured over the temperature range 7 - 120 K. A set of signals due to a triplet species was observed for both $|\Delta m_S| = 1$ and $|\Delta m_S| = 2$ transition (Figure 3: zfs parameters, $|D/hc| = 70.6$ G and $|E/hc| = 0.0$ G). A possibility that the triplet comes from dimeric monoradical pairs may be rejected because sodium naphthalenide in MTHF gave only a sharp single line at g=2.003 region under the same conditions as was measured for **6**. The Curie plot for both $|\Delta m_S| = 1$ and $|\Delta m_S| = 2$ signals of **6** gave linear lines in the above temperature range. It shows that the ground state of **6** is triplet (or the triplet and a singlet are nearly degenerated within 20 cal/mol).

Topological requirement of meta-phenylene junction is essential for the preparation of those diionic species and the parallel spin-alignment. Thus the reduction of the para isomer of **5** with sodium metal in MTHF showed no triplet species, only a sharp single line was observed at the g=2.003 position.

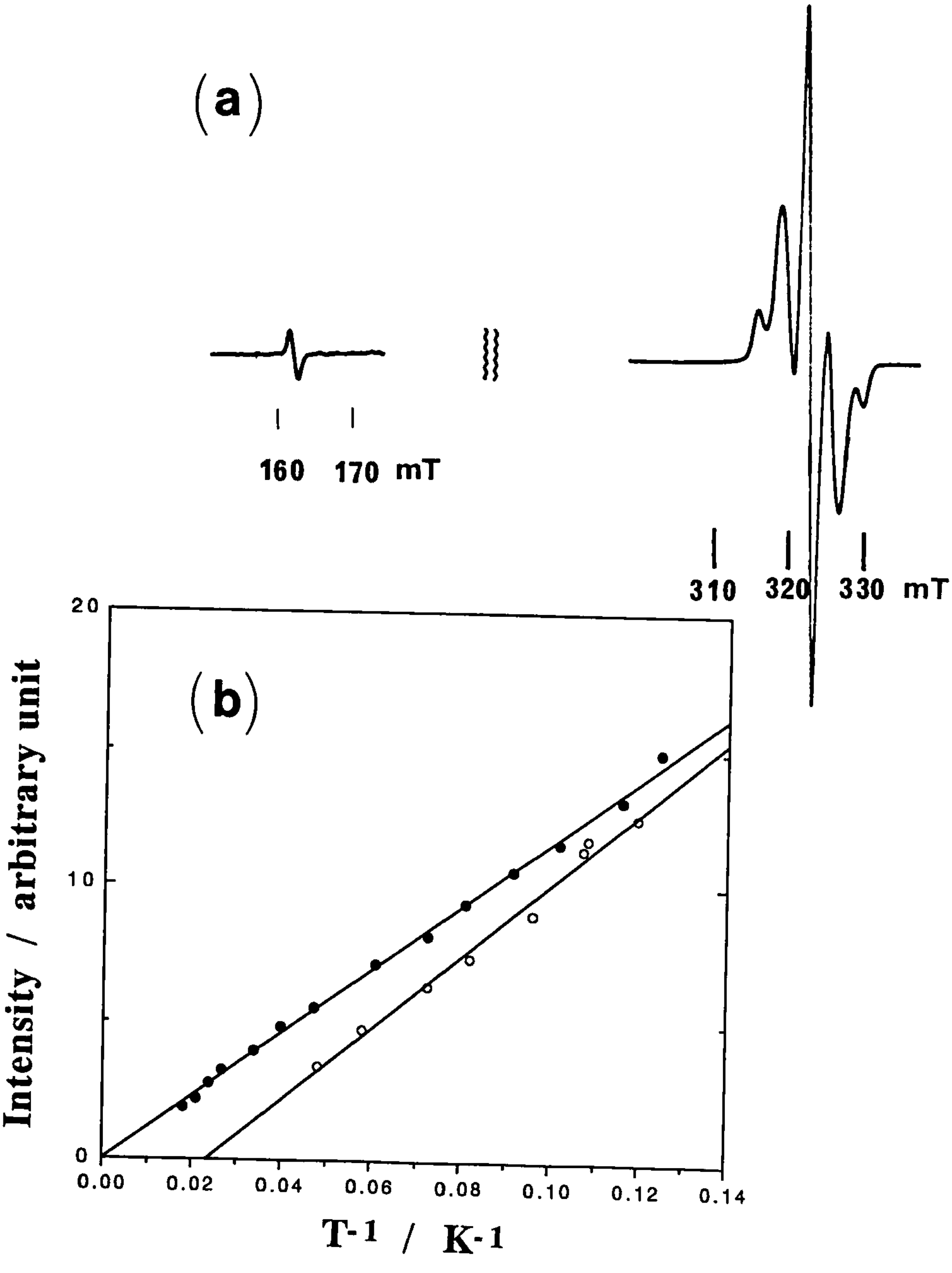
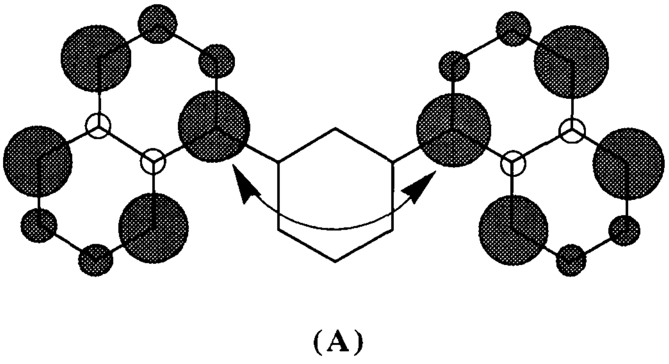


Figure 3. (a) ESR spectrum of **6** at 65 K in an MTHF matrix ($|\Delta m_S| = 2$ signal was recorded with higher amplitude than that for $|\Delta m_S| = 1$ signals).(b) Curie plot of the intensity of both $|\Delta m_S| = 1$ (•) and $|\Delta m_S| = 2$ signal (o).

In contrast to the non-Kekule molecules, the ion-radicals such as **6** have (1) no formal radical centers and (2) no degenerated SOMOs even at Hückel level of calculation. (3) The spin populations of the SOMOs of **6** have lack of spin-alternancy. These three factors are unfavorable for spin-alignment. Anion radical of the naphthalene part in **6** is expected to have large spin population at the peri-positions (see below). The positions correspond to the radical centers of *m*-quinodimehane, and which is favorable to spin-alignment.


(A)

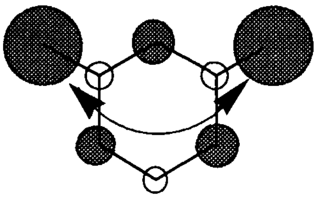

(B)

Figure 4 Schematic drawing of spin populations in (A) diradical dianion of di(1-naphthyl)benzene and (B) *m*-quinodimethane. Filled and open circles represent up- and down spins, respectively.

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