2B appears to consist of two radical species. A quartet with a proton splitting of 23 G (triangles in Figure 2) suggests the presence of the methyl radical; a triplet with two almost equivalent protons and a splitting of 24 G (circles) suggests the fragment N–CH$_2^\bullet$. The lines from the triplet are broader than for the quartet, suggesting an additional small splitting of <5 G, possibly from the ^{14}N nucleus. Both spectra are centered at $g = 2.0022$, as expected for organic radicals. An approximate ESR spectrum from the trapped electron, obtained by subtracting 2B from 2A, has a peak-to-peak line width of $\approx$12 G and is centered at $g = 2.0008$.

After bleaching the sample was annealed for 3 min at a given temperature, followed by measurement at 77 K, as shown in Figure 2C–E. The most dramatic change is seen in Figure 2D: After annealing at 150 K, the original spectrum given in Figure 2A is recovered and includes the bleachable central signal assigned to the trapped electron. The reappearance of this signal is accompanied by a blue coloration of the sample, thus providing additional proof for *the return of the trapped electron*. Further annealing leads to decay of all signals; above 220 K no signals are detected. The main features observed for the TMNOH hydrate clathrate are also detected for X-irradiated TBNOH.[8] In both hydrates the improved resolution of the spectra after optical bleaching suggests that the trapped electron and the alkyl radicals interact by magnetic dipole–dipole interaction, which causes line broadening. It is possible that the alkyl radicals *and* the electrons are trapped in the same cavity and are the result of the same radiolytic event. This conclusion is logical, in view of the crystal structure given in Figure 1: The cage diameter is about 9.2 Å, large enough to accommodate the electron and an alkyl radical.

The great stability of the trapped electrons, to about 200 K, and the return of the signal from trapped electrons after optical bleaching and annealing to $\approx$150 K are the most significant observations deduced in the present study. It is likely that the unusual stability of the electrons is due to their trapping in the vicinity of the peralkylammonium cation, which has a high reduction potential and is therefore a poor electron scavenger.[1a]

Symons et al. proposed a mechanism for the reappearance of the electrons: The electrons disappear on photobleaching due to reaction with O$^-$ to produce OH$^-$ and reappear by reaction of H atoms with OH$^-$.[9] Because we have not detected either O$^-$ or its acid form the OH radical in our system, we must seek an alternative explanation for the reappearance of the electrons. We propose that the diamagnetic species formed by optical bleaching is the electron pair e_{2t}^{2-}, which dissociates around $\approx$150 K and releases the trapped electron.

The existence of trapped electron pairs is well-documented experimentally and theoretically in ionic crystals;[10] in irradiated 6 M NaOH glasses, the disappearance of the signal from trapped electrons for a high irradiation dose was explained by the formation of the dielectron.[11-13] Evidence for the trapping of electron pairs has also been obtained in a polycrystalline K$^+$ (cryptand[2.2.2]) electride.[14,15] The vacancy size in the cryptand is $\approx$300 Å^3, similar to the cage size in the TMNOH hydrate, which is $\approx$400 Å^3. The cavity size appears to be important for the stability and reactivity of the electrons and of the electron pairs.

To the best of our knowledge we have reported here the first evidence for trapped electron pairs in polycrystalline hydrate clathrates. Further studies are in progress, in order to characterize in greater detail the electron site, the interaction between the radicals produced by irradiation, the stability of the electron pairs, and the conductivity at low temperatures.

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p-Phenylene-2,2′-bis(1,1:3,3-di-2,2′-biphenylenepropenyl): A Stable Non-Kekule Molecule as a Ground-State Singlet

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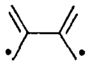
One of the interests in non-Kekule molecules[1] is to elucidate a relation between topological property of π-conjugation and ground-state spin multiplicity. For example, tetramethyleneethane (TME, **1**) is predicted to be a singlet ground state according to a classical formalism of $S = (n^* - n^\circ)/2$.[2] Ab initio calculations also confirm that the singlet state of **1** is slightly below the triplet state at any conformation about the central allyl–allyl bond.[3] However, conflict between theory and experiment is claimed by Dowd that the triplet is the ground state of both **1** and 2,3-dimethylenecyclohexa-1,3-diene based on ESR experiments.[4,5]



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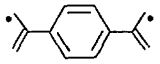

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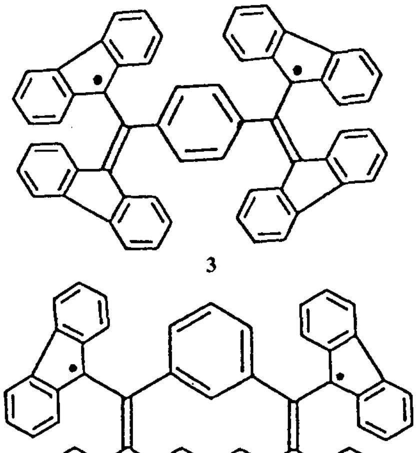

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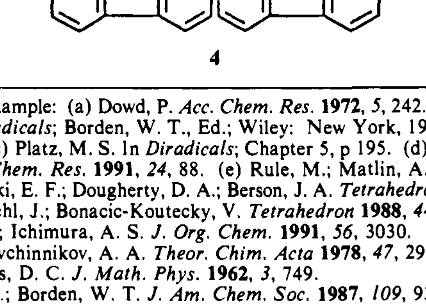

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[5] Several experimental results were reported on diradicals isomorphic to TME. (a) *m*-Phenylenebis(phenylmethylene) (singlet ground state, $\Delta E_{(S-T)} = 45$ cm^{-1}): Itoh, K. *Pure Appl. Chem.* **1978**, *50*, 1251. (b) 2,3,5,6-Tetramethylene-1,4-cyclohexanediyl (triplet ground state): Roth, W. R.; Langer, R.; Bartmann, M.; Stevermann, B.; Maier, G.; Reisenauer, H. P.; Sustmann, R.; Muller. W. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 256. (c) 2,6-Dimethyleneanthracenediyl-4,8-dioxy (triplet ground state): Seeger, D. E.; Berson, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 5146.

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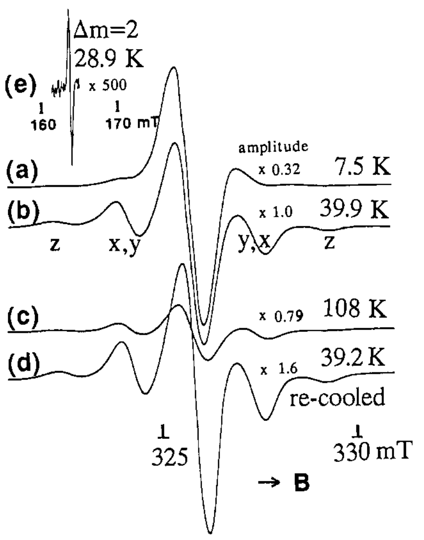

Figure 1. ESR spectrum of **3** in MTHF matrix. These were recorded at (a) 7.5 K, (b) 39.9 K, and (c) 108 K, and (d) measured after recooling at 39.2 K. Central peak is due to impurity of monoradical(s). $|\Delta m| = 2$ line (163.4 mT) was obtained at 28.9 K (frequency = 9.13136 GHz, field modulation = 0.5 mT, microwave power = 10^{-3} mW for $|\Delta m| = 1$ lines and 1 mW for $|\Delta m| = 2$ line).

A biradical **2** is a conceptual benzolog of TME and yet received no attention neither theoretically nor experimentally.[6,7] Here we show ESR experiments on a diradical **3**, in which the π-system of **2** was stabilized with fluorene rings. Our conclusion is that a thermally accessible triplet state of **3** lies over a single state in contrast with the case of TME.

Synthesis of **3** was performed by Neugebauer's method,[8] and the obtained biradical was purified with chromatography of florisil. The biradical **3** is stable in a solid state which is the same as the Koelsch's radical.[8,11]

ESR spectra of **3** in 2-methyltetrahydrofuran (MTHF) matrix (6 mM) were measured in the temperature range 7.9–125 K (Figure 1). The spectra can be assigned to triplet species with a small E value. The central peak may be ascribed to be a monoradical impurity. The assignment is consistent with different thermal behavior between the central peak and all others (Figure 1-a vs c, vide infra). Zero-field splitting parameters are obtained as $|D|/hc = 0.00334\ \mathrm{cm}^{-1}$ (35.7 G) and $|E| = 0\ \mathrm{cm}^{-1}$ ($g = 2.0022$). In addition to the $|\Delta m| = 1$ signals, $|\Delta m| = 2$ transition was observed at 0.1634 T as is characteristic for a triplet species (Figure 1e). The average distance between two radical centers is estimated from the D value as $R_{\mathrm{av}} = 0.92$ nm [$R_{\mathrm{av}}(\mathrm{nm}) = 0.138|D(\mathrm{cm}^{-1})|^{-1/3}$] and reasonably corresponds to a canonical formula **3**.

Temperature dependence of singal intensity is shown in Figure 2. Intensities of both $|\Delta m| = 1$ and $|\Delta m| = 2$ signals reached a maximum at about 18 K, and the curve was fitted with the following equation[9] with an energy gap of $\Delta E_{(\mathrm{S-T})} = 60$ cal/mol, $I = \mathrm{const} \times \exp(X)\,[1 + 3\exp(X)]^{-1}\,T^{-1}$, where $X = -\Delta E_{(\mathrm{S-T})}/RT$ and T is absolute temperature. The thermal behavior was reversible for all temperatures examined, and no significant change of the D value was observed (Figure 1a vs d). A possibility of saturation in intensity at lower temperature was excluded by careful experiments of microwave power dependence on intensities.

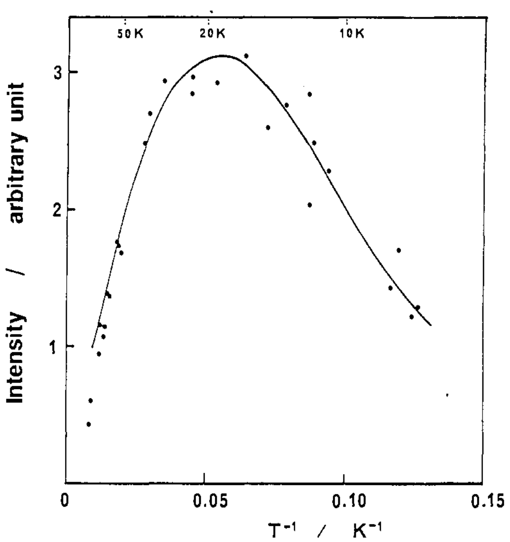

Figure 2. Curie plot of the signal intensity of the $|\Delta m| = 2$ line of **3** vs the reciprocal absolute temperature. The solvent was 2-methyltetrahydrofuran. The solid line is a simulation curve with an S–T energy gap of 60 cal/mol (see text).

Thus the observed triplet is unequivocally the thermally exited state. The thermal attitude of **3** is in marked contrast to that of a isomeric diradical **4**, which shows linear Curie plots between 7 and 85 K.[10]

In general, there are two factors determining ground-state spin multiplicity of non-Kekule molecules: (A) pair-wise spin correlation giving alternative spin polarization and (B) extended Hund's rule based on exchange interaction. In a class of non-Kekule molecules such as trimethylenemethane, both factors A and B align spins parallel to give a triplet ground state. In TME, however, the factor A stabilizes the singlet state, whereas B stabilizes the triplet state. Thus the small energy gap between singlet and triplet for TME[3] and **3** will be rationalized by the above reason.

In any canonical structures of **3**, radical centers are written on fluorene rings and are not written on a central phenyl ring. The NBMOs of **3** reflect the nature, thus the coefficients of NBMOs are found primarily at terminal positions of two allyl moieties by the simple HMO level of argument. Such a spatial localization of radical centers is the characteristic of the non-Kekule molecule **3**. An ENDOR experiment[11] for the Koelsch's radical supports the fact that most of the spin population exists on the fluorene moieties.

Furthermore, bulkiness of fluorene rings will distort **3** to nonplanar geometry around Ar–C(allyl) and ArC–C(fluorene) bonds, which forces **3** to be a localized biradical.

These arguments lead to a conclusion that alternative spin polalization will be weaker in **3** and **4** than in TME. Nevertheless, the experimental facts show that spin polalization is effectively larger than the exchange interaction in **3** and **4** to give the singlet ground state and the triplet ground state, respectively. These situations are summarized as the following energy relations: factor A > B in **3** and **4**; both factors in **1** > in **3** and **4**; factor A < B in **1**.

Our findings will help in understanding ground-state spin multiplicity of non-Kekule molecules and will expand synthetic choices toward organoferromagnets.

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