(9,10-Dihydro-9,10-*o*-benzeno-2,6-anthrylene)di(phenylmethylene): A Ground State Quintet Molecule

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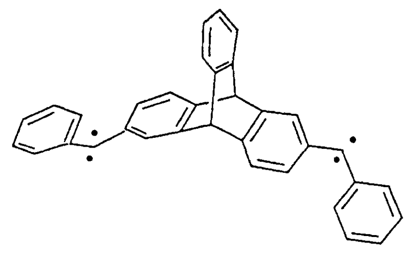
The title molecule, which has two diphenylmethylene moieties in a rigid triptycene skeleton, is photochemically generated from the corresponding diazo compound at cryogenic temperature in an ESR cavity, and the ESR spectra is identified with a quintet ground state, with ZFS parameters, $|D|/hc = 0.0665$ and $|E|/hc = 0.0043$ cm^{-1}, respectively.

Current interest in organo-ferromagnets requires the control of stacking of open-shell molecules in crystals.[1] For this purpose, it is necessary to examine spin–spin interactions in a variety of spatial arrangements in molecular assemblies. We tried to generate the title dicarbene as a model for a special case of molecular stacking.[2] Compound **1** has two diphenylmethylene (ground state triplet) moieties which are fixed in a rigid triptycene skeleton without direct conjugation.

Synthesis of the precursor, 2,6-bis(diazobenzyl)triptycene **2** is outlined in Scheme 1. 2,6-Dimethyltriptycene **3** was converted to dialdehyde **4** *via* the tetrabromide. The aldehyde was treated with phenyllithium, and then pyridinium chlorochromate to afford 2,6-dibenzoyltryptycene **5**. The hydrazone derivative of the ketone was oxidized with NiO_2 to give **2** as a red crystalline powder [ν_{CNN} (Nujol) = 2045 cm^{-1}].



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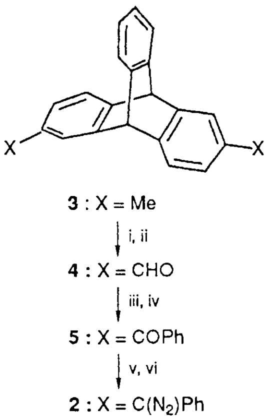

Scheme 1 *Reagents and conditions:* i, *N*-bromosuccinimide (5 equiv.), CCl_4; ii, aq. $AgNO_3$, $MeOC_2H_4OH$; iii, PhLi, diethyl ether; iv, pyridinium chlorochromate, CH_2Cl_2; v, anhydrous NH_2NH_2, EtOH; vi, NiO_2, CH_2Cl_2

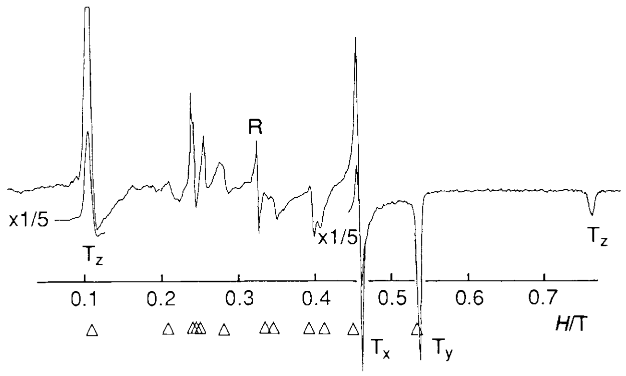

Fig. 1 ESR spectrum (frequency = 9.08206 GHz) of the dicarbene **1** in 2-MeTHF at 22 K. R and $T_{x,y,z}$ denote mono-radical and triplet carbene, respectively. Calculated resonance fields for quintet with zero field splitting parameters $|D|/hc$ = 0.0665 and $|E|/hc$ = 0.0043 cm^{-1} are indicated as $\triangle$.

When a *ca.* 0.2 mmol dm^{-3} 2-methyltetrahydrofuran solution (2-MeTHF) of **2** was irradiated with UV light (no filter) at 22 K for 15 min, a monotonic increase of the signals due to triplet monocarbene ($|D|/hc = 0.4073$, $|E|/hc = 0.01915$ cm^{-1}), doublet radical and quintet dicarbene (see Fig. 1) was observed, and no sign of stepwise generation of the dicarbene from the monocarbene was detected.

All the signal intensities show linear decrease with the reciprocal of temperature in the range 10–40 K, which indicates that the three species are independent and the observed triplet is not a thermally excited triplet of the dicarbene. The ground state quintet signals disappeared above *ca.* 80 K in 2-MeTHF matrix, and recooling to 20 K did not regenerate the ESR signals.

Zero field splitting parameters, *D* and *E*, for the quintet state constructed with two triplet sites can be estimated from the sum of *D* tensors of the two triplets after appropriate rotational operation to the triplet *D* tensors.[3] According to the approximation, $|D|/hc$ and $|E|/hc$ for the *syn* conformer of **1** are estimated as 0.083 and 0.011 cm^{-1}, respectively. Detailed simulation for resonance fields of quintet was done by the third-order perturbation method[3] around the estimated *D* value. The observed resonance fields for the quintet were best fitted to the calculated ZFS parameters of $|D|/hc = 0.0665$ and $|E|/hc = 0.0043$ cm^{-1}. Some weak signals cannot be assigned at this time; however, they might be attributed to the quintet.[3,4] The *D* value is similar to that of other quintet[4] dicarbenes, such as *m*-phenylenebis(phenylmethylene) ($|D|/hc = 0.07131$, $|E|/hc = 0.01902$ cm^{-1}). ZFS parameters for the thermally excited triplet are calculated from the *D* and *E* values for the quintet **1** as $|D|/hc = 0.1995$ and $|E|/hc = 0.0129$ cm^{-1}, respectively. No obvious signals corresponding to the *D* and *E* of the triplet were observed up to 80 K.

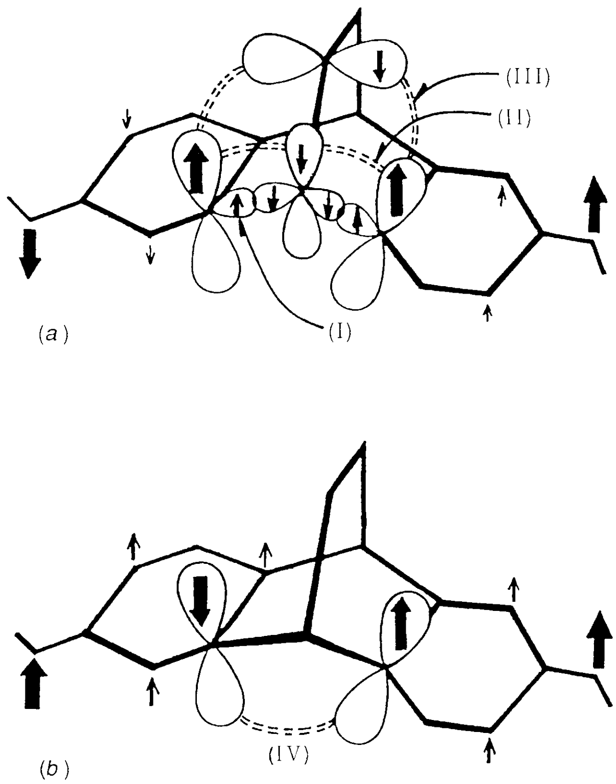

Fig. 2 Schematic spin polarization mechanisms (*a*) (I)–(III) *via* bridgehead and (*b*) through-space mechanism (IV)

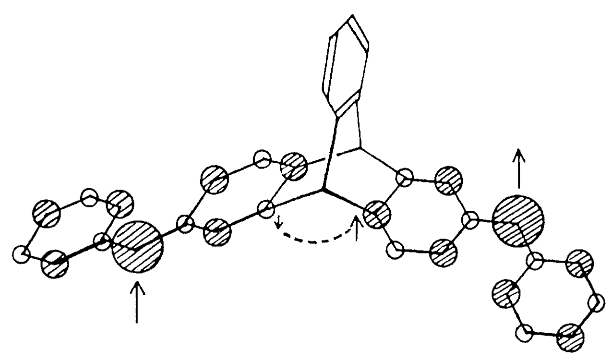

Fig. 3 Schematic spin populations with antiferromagnetic through-space interaction between two edges of diphenylmethylene units. Shaded and open circles represent α- and β-spin populations, respectively.

Triptycenes are known in which inter-ring interactions are observed.[5] We consider four possible mechanisms for the spin–spin interaction in **1**. The first mechanism (I) [Fig. 2(*a*)] is that two open shell units interact through two σ bonds at the bridgehead carbon atom by the usual π–σ spin polarization. This is effective in propane-1,3-diyls.[6] Mechanism (II) is hyperconjugation through the bridgehead carbon which may have high p-character. Mechanism (III) is that the spin–spin interaction occurs through the third benzene ring with no carbene unit. If spin populations on the diphenylmethylene units in **1** were similar to that of diphenylmethylene, alternative spin polarization around the benzene ring would be present, so that all these three mechanisms suggest a ground singlet state for the dicarbene **1**.

In contrast to these mechanisms, direct through-space interaction between two open shell units [Fig. 2(*b*)] reasonably predicts a ground quintet state as shown in Fig. 3. Antiferromagnetic interaction (a kind of a weak bond) between the two edges of the benzene rings in the diphenylmethylene units is suitable for totally ferromagnetic through-space interaction between two carbene centres.

Experimental results showed that ferromagnetic through-space interaction of McConnell's type[7] is dominant rather than through-bond interaction *via* bridgehead carbon or through-space interaction *via* the third benzene ring, at least in **1**.

Research on isomeric 2,7-dicarbene and tricarbene with a triptycene skeleton is currently in progress.

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