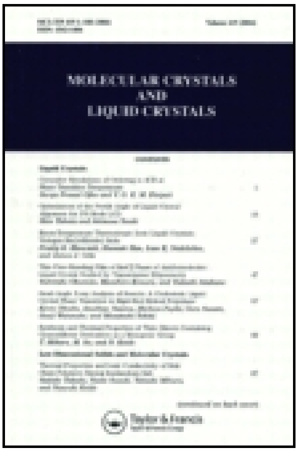

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Koya Tanaka [a] , Shigeaki Nakazawa [a] , Kazunobu Sato [a] , Daisuke Shiomi [a] , Takeji Takui [a] , Yoshihiro Nozaki [b] , Katsuyuki Hirai [b] & Hideo Tomioka [b]

[a] Department of Chemistry and Materials Science, Graduate School of Science, Osaka City University, Sumiyoshi-ku, Osaka, 558-8585, Japan

[b] Chemistry Department for Materials, Faculty of Engineering, Mie University, Tsu, Mie, 514-8507, Japan

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Extremely π-Delocalized Nature of Dianthrylcarbene-Based High Spin Systems as Studied by CW and Pulsed 2D Electron Spin Transient Nutation Spectroscopy

KOYA TANAKA[a], SHIGEAKI NAKAZAWA[a],
KAZUNOBU SATO[a], DAISUKE SHIOMI[a], TAKEJI TAKUI[a],
YOSHIHIRO NOZAKI[b], KATSUYUKI HIRAI[b] and
HIDEO TOMIOKA[b]

[a]*Department of Chemistry and Materials Science, Graduate School of Science, Osaka City University, Sumiyoshi-ku, Osaka 558-8585, Japan*
[b]*Chemistry Department for Materials, Faculty of Engineering, Mie University, Tsu, Mie 514-8507, Japan*

Abstract: Electronic and molecular structures of bis(9,9'-dianthrylcarbene) and tris(9,9'-dianthrylcarbene) coupled by 1,4-diethynylbenzene and 1,3,5-triethynylbenzene, respectively, have been investigated by cw and pulsed ESR spectroscopy. Their spin multiplicities were identified by two-dimensional electron spin transient nutation (2D-ESTN) method based on the pulsed ESR technique. The fine-structure ESR spectra observed after UV-irradiation of the corresponding diazo precursor were analyzed with the help of a hybrid eigenfield method. The biscarbene is spin-singlet in the ground state and a thermally accessible triplet state with an axial symmetry was detected, showing that the biscarbene undergoes a linear and perpendicular conformation of the two 9,9'-dianthrylcarbene moieties. Such a conformation gives rise to an extremely large amount of π-spin delocalization in ethynylbenzene-based 9,9'-dianthrylcarbene derivatives. The electronic and molecular structures of tris(9,9'-dianthrylcarbene) in the septet ground state are also discussed in this context. The oligocarbenes under study are a novel series of Skell-type high-spin carbenes characterized by extremely π-delocalized nature.

Keywords: Skell-type carbenes; high-spin carbenes; extreme π-delocalization; spin-spin interactions; hybrid eigenfield method

INTRODUCTION

In 1959, Skell and co-workers[1] suggested an orthogonal and delocalized structure for diphenylcarbene **1** (FIGURE 1). According to their proposal, the carbene center has *sp* hybrid orbitals, and $2p_x$ and $2p_y$ electrons are delocalized into two aromatic π-conjugation networks. Carbenes with orthogonally π-delocalized structures are designated as Skell-type carbenes. Contrary to Skell's suggestion, the bent and non-orthogonal structure of diphenylcarbene was derived on the basis of single-crystal ESR/ENDOR experiments. [2] In 1971, the ground-state triplet 9,9'-dianthrylcarbene (DAC) **2** has first been proven to have a Skell-type structure. [3] The reported fine-structure parameters, i.e. a very small *D* value and nearly vanishing *E* value, of **2** indicate extremely π-delocalized

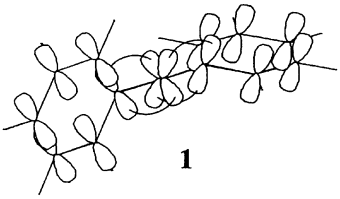

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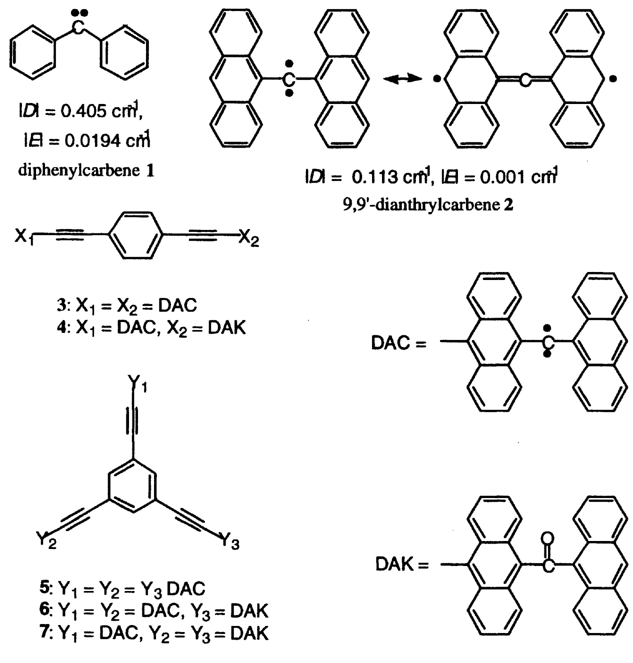
FIGURE 1 Molecular structure of diphenylcarbene suggested by Skell et al.

nature and D_{2d} symmetry of the spin density distribution, compared with any other carbenes ever studied[4].

EXPERIMANTAL AND RESULTS

1,4-Bis(9,9'-dianthrylcarbene)

A 2-methyltetrahydrofran solution of the diazoprecursor of 1,4-bis(9,9'-dianthrylcarbene) **3** and ketone **4** as impurity was prepared in an ESR cell and the diazoprecursor was photodenitrogenized to 1,4-bis(9,9'-dianthrylcarbene) by an USHIO UI-501C high pressure mercury lamp at 4K. Randomly oriented fine-structure spectra were measured on a Bruker ESP 300 spectrometer at various temperatures. The non-oriented fine-structure CW-ESR spectrum at 4K was attributed to be a triplet ground state from ketone **4** with parameters listed in TABLE 1. On increasing the temperature, new triplet pattern signals appeared. The signals were reversible in the range of 4 K to 100 K, and they were attributed to a thermally accessible triplet state of **3**.



SCHEME

TABLE 1 Observed and calculated parameters of carbenes.

		3	**4**	**7**	**6**	**5**
	S	1	1	1	2	3
	g	2.0023	2.0023	2.0023	2.0023	2.0023
experimental	$\lvert D\rvert$ / cm^{-1}	0.0025	0.079	0.0830	0.0233	0.0045
	$\lvert E\rvert$ / cm^{-1}	0.000	0.000	< 0.0010	0.0022	0.000
calculated[1]	D / cm^{-1}	-	-	-	-0.0277	+0.0083
	E / cm^{-1}	-	-	-	< 0.0001	0
calculated	D / cm^{-1}	-	-	-	-0.0261	+0.0061
	E / cm^{-1}	-	-	-	+0.0016	0

1) The spin-spin interactions between the triplet spin units are neglected.

The 2-dimensional electron spin transient nutation (2D-ESTN) technique was applied to the mixture of the seemingly triplet states in order to determine spin multiplicities unequivocally. The observed nutation frequencies indicate that all transitions but those of radical impurities are due to triplet states.

1,3,5-Tris(9,9'-dianthrylcarbene)

A 2-methyltetrahydrofran solution of the diazoprecursor of 1,3,5-tris(9,9'-dianthrylcarbene) **5** (and ketones **6** and **7** as impurity) was prepared in an ESR cell and the precursor was photodenitrogenized to 1,3,5-tris(9,9'-dianthrylcarbene) by UV irradiation with a Spectra Physics BeamLok 2065 argon ion laser at 4K. 2D-ESTN spectroscopy was also applied to disentangle overlapping spectra. The sample was contaminated by both monoketone **6** and diketone **7**. The observed fine-structure ESR spectra were simulated by a hybrid eigenfield method. The experimentally determined spin Hamiltonian parameters are summarized in TABLE 1.

DISCUSSION

Electronic Structure of 9,9'-Dianthrylcarbene

Compared with the observed D value of **1**, the smaller D value of **3** indicates that an extreme amount of π-spin delocalization takes place in the thermally accesible triplet state of **3**, where both the π-π and n-π interactions dominate. In contrast to one-center n-π interactions dominating in ordinary carbenes, two-center π-π interactions play a dominant part in Skell-type carbenes. Thus, even in semiempirical calculations for their fine-structure tensors, interacting tensors between triplet spin moieties are not negligible. In the procedure of the semiempirical calculations for determing molecular structures of the Skell-type high-spin carbenes, we estimated the interacting tensors by invoking spin dipolar interaction models. The density functional method was applied to obtain an optimized structure of DAC **2** and the spin density distribution. The calculated spin density at the divalent carbon of DAC is about half as large as that of diphenylcarbene. The *D* value of DAC was calculated from equation **1** using the calculated spin density distribution;

$$D=\frac{3}{4}g_e^{2}\beta^{2}\sum_{i,j}\frac{r^{2}_{ij}-3m^{2}_{ij}}{r^{5}_{ij}}\rho_i\rho_j \qquad (1)$$

where m_{ij} is the distance vector along the principal z axis. The direction of the principal z axis is along the symmetry axis of DAC, shown in SCHEME. The *E* value is vanishing for the optimized structure.

Semiempirical Calculations of Fine-Structure Tensors for Bis- and Tris(9,9'-dianthrylcarbene)

We calculated the fine-structure tensors of quintet molecule **6** and septet molecule **5** using the following equations[5]; equation 2 for quintet molecule **6** and equation 3 for septet molecule **5**, respectively;

$$\mathbf{D}_{quint}=\frac{1}{6}\,{}^{t}\mathbf{U}_A\mathbf{D}_A\mathbf{U}_A+\frac{1}{6}\,{}^{t}\mathbf{U}_B\mathbf{D}_B\mathbf{U}_B+\frac{1}{3}\,{}^{t}\mathbf{U}_{AB}\mathbf{D}_{AB}\mathbf{U}_{AB} \qquad (2)$$

$$\begin{aligned}\mathbf{D}_{sept}&=\frac{1}{15}\left({}^{t}\mathbf{U}_A\mathbf{D}_A\mathbf{U}_A+{}^{t}\mathbf{U}_B\mathbf{D}_B\mathbf{U}_B+{}^{t}\mathbf{U}_C\mathbf{D}_C\mathbf{U}_C\right)\\&\quad+\frac{2}{15}\left({}^{t}\mathbf{U}_{AB}\mathbf{D}_{AB}\mathbf{U}_{AB}+{}^{t}\mathbf{U}_{BC}\mathbf{D}_{BC}\mathbf{U}_{BC}+{}^{t}\mathbf{U}_{CA}\mathbf{D}_{CA}\mathbf{U}_{CA}\right) \qquad (3)\end{aligned}$$

where $\mathbf{D}_i$ represents the fine-structure tensor of the DAC triplet spin unit and $\mathbf{D}_{ij}$ the interacting tensor of spin-spin interaction between the spin units. $\mathbf{U}_i$ or $\mathbf{U}_{ij}$ is a unitary matrix, which rotates the local tensors into those in a molecular-frame coordinate system. Calculation for the $\mathbf{D}_{ij}$

tensor was carried out by the spin dipolar model mentioned above. The $\mathbf{D}_i$ tensors were constructed with the help of the observed D_i and E_i values and the assumed molecular structure for the *i*-th triplet DAC. The semiempirical calculations considering the interacting term reproduce well the observed values for both **6** (S = 2) and **5** (S = 3), giving a rationale for the extremely small D values.

CONCLUSIONS

The ground-state triplet ketone **4** and thermally excited triplet state of 1,4-bis(9,9'-dianthrylcalbene) **3** were identified. The π-spins are extremly delocalized via ethynylbenzene, illustrating that ethynylbenezene-based oligodianthrylcarbenes are a new series of Skell-type triplet carbenes.

A ground-state high-spin Skell-type biscarbene (S = 2) and triscarbene (S = 3) were identified. The spin-spin interactions between the triplet spin units are not negligible in the tensorial calculations for the fine-structure parameters of the Skell-type high-spin oligocarbenes. This is due to the highly delocalized nature arising from the orthogonal molecular structures at the divalent carbon atoms.

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