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Geometric Conformers of 2,2-Dinaphthylcarbene in Shpol'skii Matrices Revealed by Electron Spin Resonance and Hole Burning*

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The ESR spectra of 2,2-dinaphthylcarbene in n-heptane and n-hexane at 3.5 K were studied. The spectra indicated that a single carbene conformer was present in the former matrix but that at least three geometric conformers of this carbene with different zero-field splitting parameters were present in the latter matrix. This observation was in good agreement with high resolution fluorescence spectra. D_0 parameters of 0.361 and 0.413 cm^{-1} were found for the pseudo-E/trans and Z/cis conformers of the carbene, respectively. The ESR results are in quantitative agreement with hole burning studies.

Key words: triplet carbenes, zero-field splitting of triplet state, electron spin resonance, hole-burning

Carbenes are a very important class of short-lived intermediates present in many chemical reactions. Their concentration in the gas or liquid phase is usually low, due to their high reactivity and consequently their short lifetime (typically of the order of a few microseconds) [1–3]. In a cryogenic matrix friction greatly restricts molecular motion of carbenes, which results in much longer lifetimes. Once created by photolysis with UV or visible light from diazo, diazirine or ketene precursors, many carbenes can be a subject of prolonged studies, usually as long as the matrix is kept frozen. Carbenes possess two nonbonding electrons and, therefore, may exist in either singlet or triplet electronic states. The energy separation between the lowest energy singlet and triplet states is usually small and certain carbenes have a singlet (S_0) and others a triplet (T_0) ground state.

In the present work we will be concerned with only a triplet ground state carbene. Triplet electronic states of organic molecules, even in the absence of an external magnetic field, are usually split into three spin components [4]. In carbenes, which contain only carbon and hydrogen atoms, this splitting is due to the magnetic dipolar spin-spin interaction between the unpaired electrons (spin-orbit contribution is negligible) and the zero-field splitting (ZFS) parameters D and E provide sensitive infor-

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* Dedicated to the memory of Professor Krzysztof Pigoń.
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mation on the spatial distribution of electron spins. Knowledge of the D and E parameters provides a deep insight into the geometric and electronic structure of triplet carbenes. Since the pioneering work of Wasserman and Trozzolo [1] the ZFS parameters D_0 and E_0 of the triplet ground state T_0 of many triplet carbenes have been determined by the conventional electron spin magnetic resonance (ESR) technique. However, the conventional ESR technique cannot detect short lived (typically nanoseconds) excited triplet state T_1 of carbenes. Furthermore, some problems can arise with attribution of the resonance fields of carbenes, which can exist in several geometric conformations.

Recently, we have proposed and developed a new experimental technique, which directly and with high precision investigates the ZFS parameters for both, the T_0 and T_1 states of carbenes in the same experiment [5–8]. This technique relies on burning holes on the $T_0 \rightarrow T_1$ fluorescence excitation (0,0) line of carbenes dissolved in a low-temperature (1.7 K) Shpol'skii matrix. Furthermore, the hole burning technique allows for an independent study of different geometric conformers of carbenes (and the sites they occupy), because the (0,0) lines of different conformers are usually spectroscopically separated.

In the present contribution we concentrate on 2,2-dinaphthylcarbene (2,2-DNC) in n-hexane and n-heptane matrices at cryogenic temperatures, where 2,2-DNC can exist in several geometric conformations. This system has been previously studied by the hole-burning technique [6,8]. A goal of the presented work was to compare the conclusions derived from these studies with those from the conventional ESR.

EXPERIMENTAL

The 2,2-DNC samples were obtained "in situ" by photolysis of 2,2-dinaphthyldiazomethane [6] dispersed at a concentration of 2×10^{-3} M in Shpol'skii matrices of n-hexane and n-heptane at 5 K. Photolysis was performed with the 366 nm line isolated from a HBO200 mercury lamp. Before being inserted into a liquid helium cryostat, all samples were degassed by the "freeze-pump-thaw" technique. The ESR spectra were collected with a Bruker ESP 300 E spectrometer equipped with a standard TE_{102} cavity, Model ER 4102 ST (microwave frequency – 9.42 GHz). To control the temperature of the sample in the range 2.7–300 K we used a liquid helium gas-flow cryostat, Oxford Instruments ESR 910, and a Temperature Controller ITC 503. Fluorescence spectra were observed at a right angle with respect to excitation. Samples were excited with the aid of the 366 or 404 nm line isolated from the spectrum of a HBO200 mercury lamp. Fluorescence spectra were collected with a 0.67 m monochromator McPherson 207, an EMI 9659 photomultiplier cooled to –20°C, and a LightScan PC pulse-counter.

RESULTS AND DISCUSSION

The fluorescence spectra of 2,2-dinaphthylcarbene (2,2-DNC) in n-hexane and in n-heptane at 5 K are presented in Fig. 1. The spectra are composed of sharp bands with prominent origins at 590.5 and 634.4 nm in n-hexane and 637.6, 636.1, 635.1, 631.7 and 628.6 nm in n-heptane, which can be attributed to different geometrical

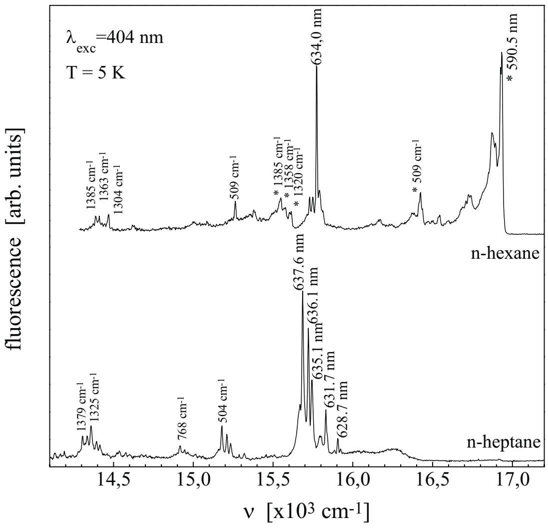
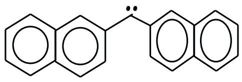
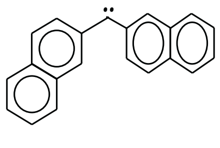


Figure 1. Fluorescence spectra of 2,2-DNC in n-hexane (upper spectrum) and in n-heptane (lower spectrum) at 5 K. Samples were excited with the 404 nm line isolated from the spectrum of a HBO200 lamp. Vibrational frequencies are indicated above the corresponding lines. Stars indicate lines attributed to the pseudo-E/trans conformer of 2,2-DNC observed in n-hexane.

conformations of 2,2-DNC and sites they occupy in the matrix. Theoretical calculations of the molecular structure of 2,2-DNC are still lacking. However, by analogy to the situation encountered for its relatives, diphenylcarbene [9] and 2-naphthylphenylcarbene (2-NPC) [10,11], we can postulate that the local energy minima in the ground state should have the conformers schematically presented below (these conformers are expected to be nonplanar with the dihedral angle between the planes of aromatic rings of about 30°).



1 (pseudo-E/trans)



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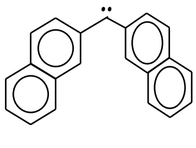

3 (pseudo-Z/cis)

Continuing with the analogy to the situation observed with 2-NPC, we may again postulate that the argument of "the nearest spin densities" [12] applies to 2,2-DNC and, thus, a lower ground state (T_0) energy, lower $T_0 \rightarrow T_1$ transition energy and larger zero-field splitting parameter D_0 characterize conformer **3** (called pseudo-Z/cis). Thus, the origin (0,0) lines at 634.0 nm in n-hexane and 637.6, 636.1 and 635.1 nm in n-heptane can be attributed to this conformer, whereas the (0,0) line at 590.5 nm in n-hexane to the conformer **1** (called pseudo-E/trans and having higher triplet ground state energy). Inspection of Figure 1 clearly indicates that both of these conformers of 2,2-DNC are present in the n-hexane matrix, whereas the conformer Z/cis dominates in n-heptane. The fluorescence (and fluorescence excitation) lines of 2,2-DNC in Shpol'skii matrices are narrow, with the full width at half maximum typically below 10 cm^{-1}, which indicates that they are the inhomogeneously broadened zero-phonon lines. This is a convenient situation for the hole burning experiment.

Typical holes burned within the fluorescence excitation (0,0) bands of the Z/cis and E/trans conformers of 2,2-DNC are presented in Figure 2A and 2B, respectively

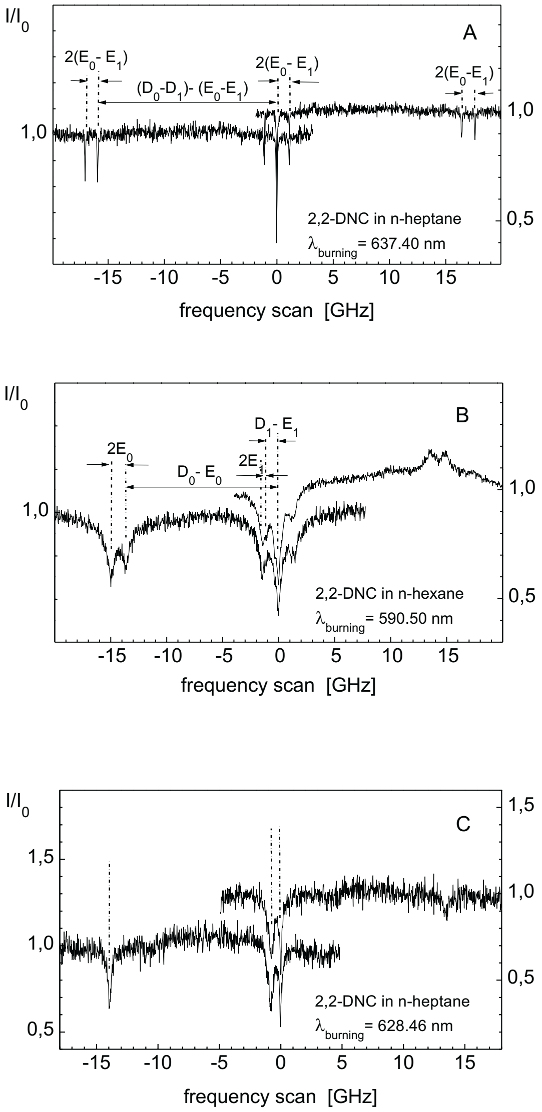

Figure 2. Typical holes burned within the inhomogeneous (0,0) fluorescence excitation line with maximum at 637.5 nm in n-heptane (A), at 590.5 nm in n-hexane (B) and at 628.5 nm in n-heptane (C). The experiment was performed at 1.7 K. Energy separations between holes, in terms of ZFS parameters D_0, E_0, D_1 and E_1, are given according to the models discussed in [6] and [8].

[6,8]. The different pattern of holes clearly proves that these lines correspond to different conformers of 2,2-DNC. We should add that the holes burned on the origin lines with maxima at 636.1 and 635.1 nm in n-heptane and at 634.0 nm in n-hexane were similar to the holes presented in Figure 1A [8]. It indicates that they correspond to the same conformer (**3**). The hole pattern was different and hole burning efficiency was 4 orders of magnitude greater (as compared with the both conformers considered before) for the 628.5 nm line of 2,2-DNC in n-heptane. This line was related to the conformer **2**, which is undergoing geometrical transformation [8].

The origin of burned holes in 2,2-DNC was analyzed previously in detail [6,8]. The spectral positions of the observed holes were attributed to the ZFS of both, the T_0 and T_1 states, as indicated in Figure 2. It was important to realize that only in the case of the pseudo-E/trans conformer could the four ZFS parameters, D_0, E_0, D_1 and E_1 be experimentally determined. For the Z/cis conformer **3**, which appeared to be planar, the experiment could only provide the difference of the ZFS parameters, $(D_0 - D_1)$ and $(E_0 - E_1)$. The ZFS parameters of the ground T_0 state obtained from the hole burning experiment [6,8] are collected in Table 1.

The acquired ESR spectra are shown in Figure 3. It is clearly seen that the spectrum observed in n-heptane is simpler than that in n-hexane.

The axial resonance magnetic fields observed in n-heptane (Figure 3B) indicate a single triplet species [4] with: $H_{z1} = 999$ G, $H_{x2} = 4799$ G, $H_{y2} = 5415$ G and $H_{z2} = 7735$ G. Using the well known formulas, which provide the relationship between the resonance fields and the D_0 and E_0 parameters of the triplet state [13], we found that $D_0 = 0.413 \pm 0.002\ \mathrm{cm}^{-1}$ and $E_0 = 0.016 \pm 0.001\ \mathrm{cm}^{-1}$. These parameters were attributed to the Z/cis geometric conformer **3** of 2,2-DNC.

The axial resonance magnetic fields observed in n-hexane (Figure 3A) indicate the presence of several triplet species with slightly different D and E values. A close inspection of the z1 magnetic field range shows axial resonance fields at 423, 522, 774 and 1010 G. These lines can be attributed to different geometric conformations of 2,2-DNC. For two of the conformers we were able to identify all of the available axial fields, and estimate the ZFS parameters. For the "low-field" conformer: $H_{z1} = 423$ G, $H_{x2} = 4570$ G, $H_{y2} = 5348$ G and $H_{z2} = 7193$ G, which correspond to $D_0 = 0.361 \pm 0.004\ \mathrm{cm}^{-1}$ and $E_0 = 0.020 \pm 0.002\ \mathrm{cm}^{-1}$. For the "high-field" conformer: $H_{z1} = 1010$ G, $H_{x2} = 4875$ G, $H_{y2} = 5376$ G and $H_{z2} = 7754$ G, that correspond to $D_0 = 0.411 \pm 0.004\ \mathrm{cm}^{-1}$ and $E_0 = 0.013 \pm 0.002\ \mathrm{cm}^{-1}$. We identify the former parameters with those of the pseudo-E/trans conformer **1** whereas the latter with the Z/cis conformer **3**. Both conformers of 2,2-DNC are expected to be present in n-hexane, as they contribute to the fluorescence spectrum presented in Figure 1. We also attempted to estimate the ZFS parameters of the "intermediate field" resonances. The axial resonance fields $H_{z1} = 522$ G and $H_{x2} = 4642$ G correspond to a triplet species with $D_0 = 0.366\ \mathrm{cm}^{-1}$ and $E_0 = 0.016\ \mathrm{cm}^{-1}$. The carrier of the spectrum is attributed to a conformer of **1** located in a different matrix site. The axial fields $H_{z1} = 774$ G and $H_{x2} = 4803$ G correspond to the $D_0 = 0.387\ \mathrm{cm}^{-1}$ and $E_0 = 0.011\ \mathrm{cm}^{-1}$, which we attribute to the conformer of **2**.

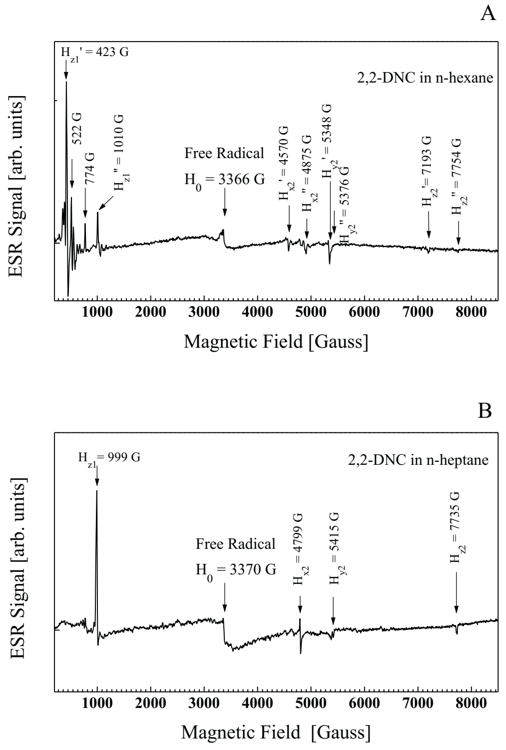

Figure 3. ESR spectra of 2,2-DNC in n-hexane (upper spectrum) and in n-heptane (lower spectrum) at 3.5 K. The axial resonance magnetic fields discussed in the text are indicated by arrows.

Table 1. The ZFS parameters D_0 and E_0 of the triplet ground (T_0) state of 2,2-DNC estimated from the hole burning and ESR experiments. The hole burning data from references [6] and [8]. The data for the Z/cis conformer of 2,2-DNC in n-heptane are indicated by *, the data for this conformer in n-hexane are given in parentheses. The data attributed to the conformer **1** in different site of n-hexane are indicated by $^+$.

Carbene conformer	hole burning experiment		ESR experiment	
	D_0 [cm^{-1}]	E_0 [cm^{-1}]	D_0 [cm^{-1}]	E_0 [cm^{-1}]
1 (pseudo-E/trans)	0.477	0.022	0.361 (0.366)$^+$	0.020 (0.016)$^+$
2			0.387	0.011
3 (Z/cis)	0.558* (0.560) + D_1	0.018* (0.0178) + E_1	0.413* (0.411)	0.016* (0.013)

The ZFS parameters of 2,2-DNC in n-hexane and n-heptane, estimated from this ESR study and those taken from previous hole burning work [6,8], are collected in Table 1. It is easy to see the qualitative agreement between the data, showing the lower

D_0 value for the pseudo-E/trans conformer as compared with that for the Z/cis conformer. However, the ZFS parameters derived by hole burning are systematically higher (by more than 30%), which is outside of the experimental error inherent to parameters obtained by both experimental techniques. We should stress that during the hole burning and ESR experiments the energy scales were carefully calibrated and there is no simple explanation to this unexpected observation. The hole burning approach to study triplet carbenes is a very new experimental method and more systematic studies are needed to understand this discrepancy.

Acknowledgments

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