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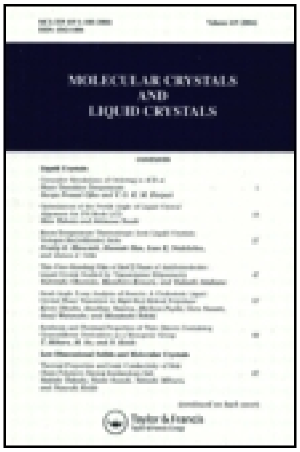

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Electronic and Molecular Structures of a Stable Triplet Species Generated from 2-Nitrobiphenyl after UV Irradiation

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ELECTRONIC AND MOLECULAR STRUCTURES OF A STABLE TRIPLET SPECIES GENERATED FROM 2-NITROBIPHENYL AFTER UV IRRADIATION

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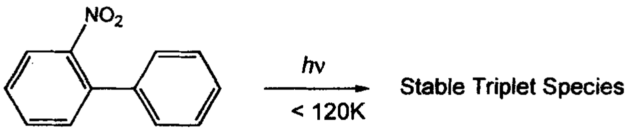
Abstract A stable triplet species of 2-nitrobiphenyl generated by UV irradiation below 120K has been studied by single-crystal ESR and ENDOR spectroscopies. From the angular dependence of ENDOR spectra, all the ^{1}H-hyperfine coupling tensors were determined. Based on the consideration of the anisotropic terms of the hyperfine coupling tensors, it was concluded that the stable triplet state was formed by the abstraction of a hydrogen atom from the 2'-position of the biphenyl skeleton by the 2-nitro group.

INTRODUCTION

The quest for stable and novel high-spin organic systems has been an important issue in a rapidly developing multi-disciplinary field of organic molecule-based magnetics. UV irradiation of 2-nitrobiphenyl (2-NBP) at 120K in organic rigid glasses or its neat crystals generates stable spin-triplet species. The fine-structure parameters of the triplet species in the single crystal of 2-NBP have been determined and the probable molecular structure of the triplet species has been proposed.[1] In this paper we report the



2-Nitrobiphenyl
(2-NBP)

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single-crystal ENDOR spectroscopy applied to the stable triplet state of 2-NBP generated by UV irradiation in order to determine the spin density distribution and the probable molecular structure of the triplet species. The fundamental knowledge of the electronic structure of the stable triplet state serves for molecular design and synthesis for extended analogues of 2-NBP and for the understanding of the spin alignment of heteroatomic organic systems, where σ–π interaction is taken into account. The system under study exemplifies spin alignment mechanisms different from those controlling high-spin opened shell systems with homoatomic π-conjugation.

EXPERIMENTAL

2-Nitrobiphenyl was magnetically diluted into perdeuterated benzophenone-d_{10} single crystals. Mixed single crystals of benzophenone-d_{10} incorporating 2-nitrobiphenyl were grown from a diethylether solution by slowly cooling the solution. Benzophenone-d_{10} was used in order to decrease the spectral density of the ^{1}H-ENDOR transitions arising from protons of the surrounding host molecules. UV irradiation of 2-NBP was performed at liquid helium temperature using a SAN-EI UVF-351S 300W high-pressure mercury lamp. Single-crystal ESR and ENDOR measurements were carried out on Bruker ESP350 spectrometer equipped with an Oxford helium gas flow variable temperature controller ESR910. The angular dependence of single-crystal ESR and ENDOR spectra was measured by rotating the single crystal using a uniaxial goniometer.

RESULTS AND DISCUSSION

Figure 1 shows a typical ESR spectrum of UV irradiated 2-NBP observed at 15K in the crystallographic *bc* plane of the benzophenone-d_{10} single crystal, indicating allowed ESR transitions occurred from a triplet spin state. From the angular dependence of the ESR spectra we determined the fine-structure tensor of the triplet state of the irradiated 2-NBP summarized in Table I. The negative sign of the fine-structure parameter D was derived from ENDOR measurements described below. The fine-structure parameter D in benzophenone-d_{10} single crystals is smaller in magnitude than those (0.049 ~ 0.055

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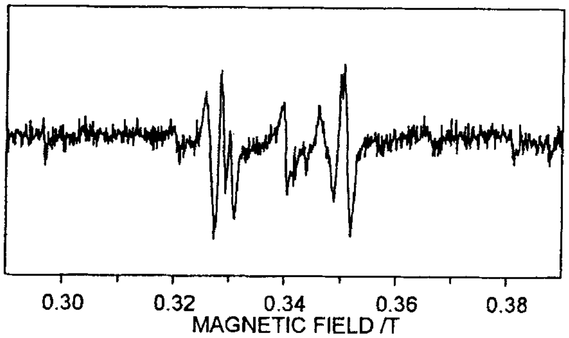

FIGURE 1. Single crystal ESR spectrum of the stable triplet state of the irradiated 2-NBP observed at 15K in the benzophenone-d_{10} single crystal.

TABLE I. Experimentally determined fine-structure tensor of the irradiated 2-NBP in the benzophenone-d_{10} single crystals.

g value	Fine-Structure Parameters			Direction Cosine		
	D value /cm^{-1}	E value /cm^{-1}		*a*	*b*	*c*
2.003 (isotropic)	-0.04460	0.00272	x	0.91615	-0.35848	-0.17935
			y	-0.30813	-0.91600	0.25690
			z	-0.25638	-0.18010	-0.94965

cm^{-1}) observed in neat single crystals of 2-NBP or in ethanol glasses[1]. The dependence of the fine-structure parameter D on organic matrices may be caused by the molecular structure of the triplet state. The difference of the fine-structure parameter is expected to arise from that of the dihedral angle between two phenyl rings of the biphenyl skeleton.

Figure 2 shows a typical ENDOR spectrum observed at 15K in the benzophenone-d_{10} single crystal, where an $|M_S=0\rangle \leftrightarrow |M_S=1\rangle$ ESR transition measured in the crystallographic *bc* plane of the benzophenone-d_{10} single crystal was monitored. The ESR transition monitored is indicated by an arrow in Figure 1. There were observed nine ENDOR transitions arising from all the proton atoms of 2-NBP, excepted for the transition appearing close to a free proton NMR frequency (ν_n=13.9MHz). ENDOR transitions observed at about 2MHz was assigned to those arising from the nitrogen atom of the 2-nitro group. The shift of the proton ENDOR transition (ν_{ENDOR}) from ν_n is given by

$$\nu_{ENDOR} - \nu_n = -A_{ZZ} M_S / h \qquad (1)$$

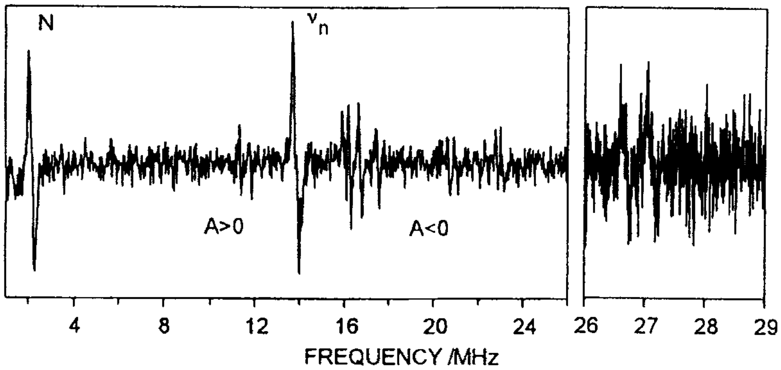

FIGURE 2. Typical ENDOR spectrum of the stable triplet state of the irradiated 2-NBP observed at 15k in the crystallographic *bc* plane of the benzophenone-d_{10} single crystal.

in terms of the first-order perturbation treatment of the spin Hamiltonian including both fine-structure and hyperfine-structure terms. As the observed nine ENDOR transitions belong to the $|M_S=1>$ sublevel of the triplet state, the corresponding shifts are given by

$$\nu_{ENDOR} - \nu_n = -A_{ZZ} / h \ . \qquad (2)$$

Therefore, the observed transitions give two positive and seven negative hyperfine couplings (hfc's) according from Equation (2).

The seven negative hfc's are relatively larger in magnitude than the two positive ones. The isotropic hfc of the proton bonded to a carbon atom with positive π-spin gives a negative coupling constant for an α-proton via the spin polarization of the paired electron of C-H bond.[2] Here we neglected a contribution from an anisotropic hfc because it was quite small. When we put the sign of the fine-structure parameter *D* to be negative, the seven hfc's observed above ν_n give positive π-spin densities on the carbon atoms. If we assume a positive *D* value, the stable triplet state has large negative π-spin density on the whole molecule. As the total spin density on the whole molecule is usually positive, such negatively polarized picture is not acceptable. We can, therefore, conclude that the fine-structure parameter *D* is positive.

The angular dependence of the ^{1}H-ENDOR transitions was examined in order to determine the ^{1}H-hfc tensors of the irradiated 2-NBP. The determined ^{1}H-hfc tensors were summarized in Table II. The hfc tensors were assigned to constituent protons based on the consideration of the direction cosines and anisotropic terms of the hfc

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tensors. The ^{1}H-assignments include some ambiguities. The anisotropic term of the hfc tensor which results from a dipole-dipole interaction between nuclear spin on a hydrogen atom and unpaired electron spin in the $2p_\pi$ orbital on a carbon atom neighboring to the hydrogen atom was discussed using Slater orbital as the $2p_\pi$ orbital.[3,4] When the shape of the $2p_\pi$ orbital is considered, the anisotropy of the hfc tensor for the α-proton bonded to the carbon atom with positive spin density was approximately given by $B_{xx} : B_{yy} : B_{zz} = -1 : -9 : 10$ where z, x, and y were defined as directions of the C-H bond, p_π orbital, and the axis perpendicular to both the z and x axes, respectively. In Table II, one of the protons (8) has positive sign of B_{xx} in spite of the negative isotropic term which gives positive spin density on the carbon atom neighboring to the hydrogen atom. We concluded that this hydrogen atom is not bonded to the carbon atom, but abstracted from the 2'-position of the biphenyl skeleton by the 2-nitro group in the stable triplet state. In order to discuss the anisotropic term of the abstraction of the hydrogen atom, we have to take effects from p orbitals of the nitrogen atom as well as those of the oxygen atoms into account.

The π-spin density (ρ_π) on the carbon atom is related to the isotropic hfc term (A_{iso}) of the ^{1}H-hfc tensor of the adjacent α-proton by a generalized McConnell's Equation,[5,6]

$$A_{iso} = Q\rho_\pi / 2S, \tag{3}$$

where 1/2S is a projection factor in order to normalize the spin density to be unity. We used -66.9MHz for the Q value which was determined for the excited triplet state of naphthalene.[7] The determined π-spin densities and the possible spin density distribution of the irradiated 2-NBP were shown in table II.

In conclusion, we studied the stable triplet state of 2-NBP after UV irradiation by single crystal ENDOR spectroscopy in order to determine the π-spin density distribution and the possible molecular structure of the stable triplet state. From the anisotropic term of the hfc tensors we concluded that the stable triplet state of 2-NBP was formed by the abstraction of the hydrogen atom of 2'-position of the biphenyl skelton by the nitro group.

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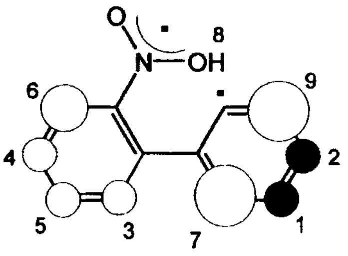
TABLE II. Experimentally determined ^{1}H-hyperfine coupling tensors of the irradiated 2-NBP in the benzophenone-d_{10} single crystals.

Site No.	Isotropic Term A_{iso} /MHz	Anisotropic Term /MHz			π-Spin Density
		B_{xx}	B_{yy}	B_{zz}	
1	3.0994	0.5733	2.3188	-2.8921	-0.0927
2	3.5219	0.0715	2.1646	-2.2361	-0.1053
3	-2.1716	-0.0737	-1.53341	1.6074	0.0649
4	-3.0413	-0.2542	-1.9253	2.1795	0.0909
5	-2.2013	-0.2753	-1.3141	1.5894	0.0658
6	-2.6192	-0.3588	-1.7682	2.1270	0.0780
7	-9.0254	-0.6058	-3.4197	4.0256	0.2698
8	-9.4837	0.1490	-4.8231	4.6740	(0.2835)
9	-13.1550	-0.0833	-5.5352	5.6185	0.3933



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