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Electron paramagnetic resonance study on the triplet species produced from 2-nitrobiphenyl derivatives by UV irradiation

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Abstract

The photochemical behavior of 2-nitrobiphenyl (NBP) derivatives was extensively studied by the electron paramagnetic resonance (EPR) technique. The molecules studied mainly are methyl-, fluoro-, carboxy-, ethoxycarbonyl-, hydroxymethyl- and methoxymethyl-NBPs and ethers possessing two NBP groups. Most of the triplet species produced were stable in ethanol glasses at 77 K after UV irradiation. The zero-field splittings (ZFSs) of these species are fairly close to those of the stable triplet species produced from NBP. Two sets of EPR signals were observed for the NBP derivatives with a relatively large substituent at the 2′-position of the biphenyl skeleton. The ZFS $|D|$ parameters of the stable triplet species giving strong EPR signals are a little larger than those giving weak signals. On the other hand, the ZFS $|E|$ parameters of the stable triplet species giving strong EPR signals are slightly smaller than those giving weak signals. For 3′-substituted NBPs, the EPR signals of methoxycarbonyl- and carboxy-NBPs were observed only during UV irradiation. These signals are attributed to the lowest excited triplet states of the precursors. For 4′-substituted NBPs studied except the methyl- and fluoro-NBPs, no stable triplet signals could be observed at 77 K in ethanol glasses after UV irradiation. From the precursors possessing two NBP groups, no signals of the quintet state could be observed, although the stable triplet signals were detected. The present study has no contradictions to the previous estimation that the stable triplet species is formed through the abstraction of a hydrogen atom from the 2′-position of the biphenyl skeleton by one of the oxygen atoms of the nitro group. Such a hydrogen-transfer process is inferred to occur for the nonplanar derivatives where the above hydrogen atom can approach one of the oxygen atoms rather easily.

Keywords: Electron paramagnetic resonance; Triplet state; Zero-field splitting; 2-Nitrobiphenyl; UV irradiation; Hydrogen atom abstraction

1. Introduction

2-Nitrobiphenyl (NBP) is a photochemically very interesting molecule, since a stable spin triplet species can be detected after cessation of its ultraviolet ray (UV) irradiation at temperatures below 120 K in its crystal or in various organic rigid glasses. The lowest triplet (Td1) state thus observed is located closely above the ground state of the produced species [1]. In the previous report, this triplet species was inferred to be formed through a triplet intermediate and the abstraction of a hydrogen atom from the 2′-position of the NBP skeleton by one of the oxygen atoms of the nitro group, as shown in Fig. 1 [1]. Similar reactions can be expected to occur for various derivatives of NBP and their related molecules. The knowledge of their photochemical behavior is essentially necessary in discussing the electronic and the structural properties of the stable triplet species in question.

In these circumstances, the present paper reports the steady-state electron paramagnetic resonance (EPR) studies on the stable triplet species produced from some of NBP derivatives after UV irradiation. Hereafter, such stable triplet species will be designated as the irradiated NBP derivatives and so on. In the present work, the precursors used are mainly 2′-, 3′- and 4′-substituted NBPs the substituents of which are connected with the benzene ring not possessing the nitro group. First, the three kinds of the irradiated methyl-substituted NBPs were examined mainly concerning their steric effect. Next, the irradiated fluorine-substituted NBPs were studied including the influence of their ^{19}F nuclear spins on the lineshape of the EPR spectra. In detecting the interaction between two triplet groups in a single molecular species, some of the precursors possessing two NBP groups were examined, but no signals of quintet state were observed. In the course of the syntheses of these

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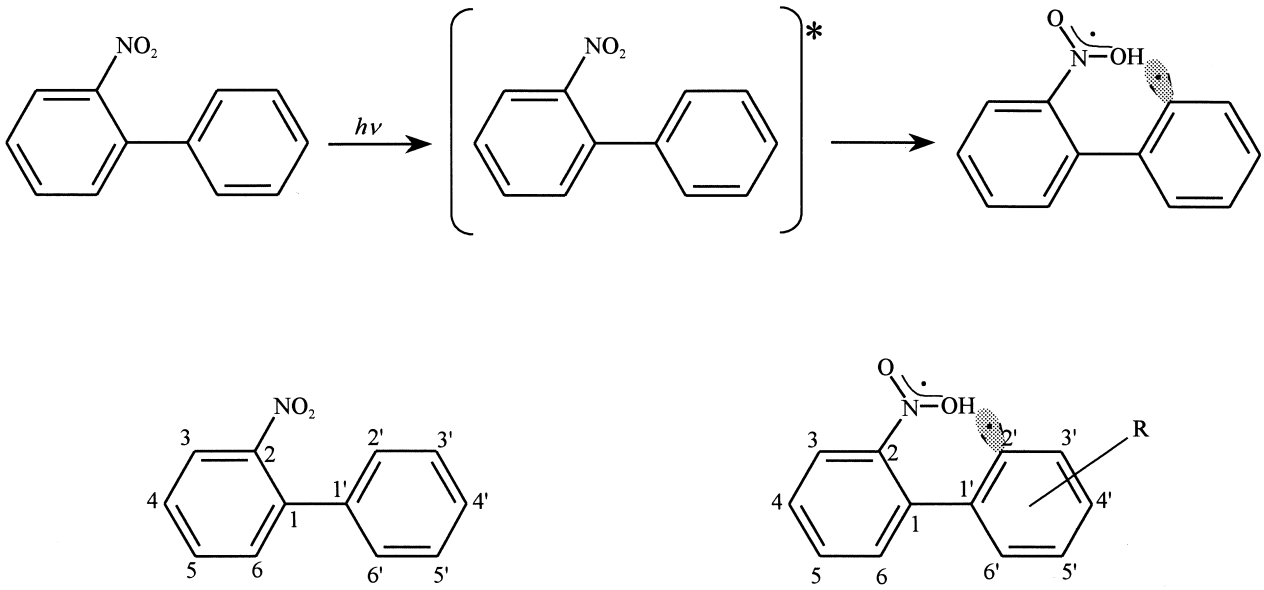


Fig. 1. Most probable process on the formation of the stable triplet species from NBP by UV irradiation. Numberings of atoms in the NBP skeleton and the stable triplet species produced from substituted NBP by UV irradiation.

precursors, several kinds of substituted NBPs were obtained as synthetic intermediates. In that case, triplet species produced photochemically from these derivatives and their related molecules were also studied for examining mainly the influence of their substituents and the substituted positions upon their molecular structures. For convenience, the numbering of atoms in the NBP derivatives used in the present paper are generally followed as shown in Fig. 1.

2. Experimental

2.1. Materials

Syntheses of the NBP derivatives were done with the modified procedures of the method reported previously [2] (see Appendix A). For solvents, ethanol (EtOH) (Wako, S.S. Grade) was used without further purification, and 2-methyltetrahydrofuran (MTHF) (Tokyo Kasei, E.P. Grade) was purified by passing through an active alumina column several times and thereafter by distillation.

2.2. Measurements

Most of the EPR spectra were measured in EtOH and in MTHF at 77 K by JEOL-JES-FE1XG spectrometer with 100 kHz magnetic field modulation at microwave frequencies close to 9.2 GHz. The excitations were carried out using an Ushio USH-500D 500 W mercury arc lamp or Canrad-Hanovia 1 kW Xe–Hg arc lamp through 5 cm of distilled water. If the intensity of the EPR signals was sufficiently strong, a Toshiba UV-D33S glass filter was additionally used.

3. Results and discussion

3.1. Spin Hamiltonian

In the presence of a magnetic field (magnetic induction $\boldsymbol{B}$), the EPR result can well be interpreted by the following spin Hamiltonian:

$$H_S = \mu_B \boldsymbol{B}\cdot\boldsymbol{g}\cdot\boldsymbol{S} + \boldsymbol{S}\cdot\boldsymbol{D}\cdot\boldsymbol{S} = \mu_B \boldsymbol{B}\cdot\boldsymbol{g}\cdot\boldsymbol{S} - XS_x^2 - YS_y^2 - ZS_z^2$$
$$= \mu_B \boldsymbol{B}\cdot\boldsymbol{g}\cdot\boldsymbol{S} + D\left[S_z^2 - \frac{S(S+1)}{3}\right] + E(S_x^2 - S_y^2) \quad (1)$$

Here, $\boldsymbol{D}$ is the zero-field splitting (ZFS) tensor with principal values of $-X$, $-Y$ and $-Z$, and D and E are the ZFS parameters. The other symbols have their usual meaning. The principal values are related by the following equation:

$$X + Y + Z = 0 \quad (2)$$

The lowest possible resonance field, $B_{\min}$, can be written as

$$B_{\min} = (2g\mu_B)^{-1}[(h\nu)^2 + 4(XY + YZ + ZX)]^{1/2} \quad (3)$$

The ZFS parameter parameters D and E are defined to be $D = -3Z/2$ and $E = (Y - X)/2$. The calculated ZFS parameter D^*(calc) is defined to be $D^*(\text{calc}) = (D^2 + 3E^2)^{1/2}$. The experimental D^* value can be obtained from the $B_{\min}$ signal with the aid of the following equation:

$$D^* = \left[\frac{3(h\nu)^2}{4} - 3(g\mu_B B_{\min})^2\right]^{1/2} \quad (4)$$

3.2. Methyl-substituted triplet species

From 2′-, 3′-, and 4′-methyl-NBPs [n'-Me-NBPs ($n' = 2'$, 3′ and 4′, respectively)], stable triplet species are detected in

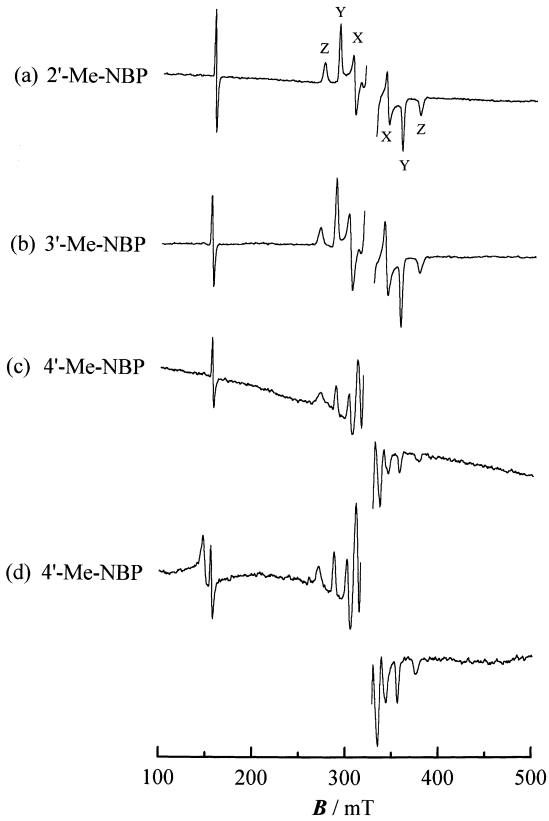


Fig. 2. EPR spectra of the $\Delta M_S = \pm 1$ and B_{min} transitions for the stable triplet species produced from (a) 2′-Me-NBP; (b) 3′-Me-NBP; (c) 4′-Me-NBP observed after UV irradiation and (d) for the excited triplet species from 4′-Me-NBP observed before the signals from 4′-Me-NBP reaches the maximized intensities. The chemical formulas shown are the precursors.

EtOH glasses after UV irradiation at 77 and 4.2 K. In general, the photochemical behavior of these molecules is similar to that of NBP, although the phosphorescence was observed at the early stage in UV irradiation. The EPR spectra are generally similar to that of the irradiated NBP as shown in Fig. 2. In the present work, therefore, the assignments of the resonance fields were assumed to be the same as those of the irradiated NBP [1], including the species discussed in the succeeding sections. Therefore, the order of the triplet sublevels was assumed to be T_y, T_x and T_z from the top. The ZFS parameters thus obtained are listed in Table 1. In this case, the D value of the irradiated 3′-Me-NBP was determined to be positive from the temperature dependence of the EPR signals as in the irradiated NBP [1].

The ZFS parameters of the irradiated 3′- and 4′-Me-NBPs are fairly close to those of the irradiated NBP. However, each of the absolute values of the ZFS parameters obtained for 2′-Me-NBP is relatively smaller than the corresponding one of 3′- and 4′-Me-NBPs. This can be well explained from the fact that the twist angle around the central C–C bond of the biphenyl group increases with the increase of steric hindrance arising from the *ortho*-methyl substitution and the conjugation between these two benzene rings is weakened. In this case, the methyl group should be located at the 6-position of the benzene ring not possessing NO(OH) group, in order to reduce the steric hindrance of the nitro group before UV irradiation. Such a trend has already been observed for the stable triplet species produced from 2,2′-dinitrobiphenyl (2,2′-DNBP) after UV irradiation [3].

For the present stable triplet species, one of the singly occupied orbitals possess mainly a π character, while another one is largely localized at the carbon atom of the 2′-position of the NBP skeleton, as in the unpaired electron of the phenyl radical [4]. Nevertheless, a similar tendency of the D value was observed for the lowest excited triplet [$T_1(\pi\pi^*)$] states of 2,2′-dimethylbiphenyls [5]. In the T_1 states of the methyl-substituted biphenyls, the ZFS parameters are generally close to those of the unsubstituted biphenyl. For *s-cis*-2,2′-dimethylbiphenyl, however, the absolute values of ZFS are relatively smaller than the corresponding ones of the unsubstituted biphenyl. This is due to the increase of the twist angle around the central C–C bond, because of the increase of the steric hindrance between the two methyl groups.

It should be noted here that in the early stage of the UV irradiation of 4′-Me-NBP another weak B_{min} signal was

Table 1
ZFS parameters observed from methyl- and fluoro-NBPs by UV irradiation in EtOH glasses

Precursor	$\|X\|$ (cm^{-1})	$\|Y\|$ (cm^{-1})	$\|Z\|$ (cm^{-1})	$\|D\|$ (cm^{-1})	$\|E\|$ (cm^{-1})	D^*(calc) [a] (cm^{-1})	D^* [b] (cm^{-1})
NBP	0.0116	0.0212	0.0327	0.0491	0.0048	0.0498	0.0520
2,2′-DNBP	0.0114	0.0201	0.0314	0.0472	0.0044	0.0478	0.0484
2′-Me-NBP	0.0110	0.0209	0.0319	0.0478	0.0050	0.0486	0.0509
3′-Me-NBP	0.0116	0.0214	0.0330	0.0494	0.0049	0.0502	0.0533
4′-Me-NBP	0.0118	0.0214	0.0331	0.0496	0.0048	0.0503	0.0525
2′-F-NBP	0.0114	0.0214	0.0328	0.0493	0.0050	0.0500	0.0550
3′-F-NBP	0.0119	0.0219	0.0338	0.0506	0.0050	0.0514	0.0576
4′-F-NBP	0.0117	0.0215	0.0332	0.0499	0.0049	0.0596	0.0530
4-F-NBP	0.0114	0.0213	0.0327	0.0491	0.0049	0.0498	0.0525
5-F-NBP	0.0114	0.0210	0.0324	0.0485	0.0048	0.0493	0.0517
6-F-NBP	0.0105	0.0209	0.0314	0.0471	0.0052	0.0480	0.0507

[a] Calculated from D and E.
[b] Obtained from the B_{min} signal.

detected at a resonance field near 150 mT ($D^* \approx 0.1\ cm^{-1}$) as shown in Fig. 2(d). Under the continued UV irradiation, however, the weak B_{min} signal near 150 mT ($D^* \approx 0.1\ cm^{-1}$) could not be detected after when the aforementioned $\Delta M_S = \pm 1$ transition signals ($|D| = 0.0496$ and $|E| = 0.0048\ cm^{-1}$) reached the maximized intensity (for longer than 3 min), as shown in Fig. 2(c). This may suggest the fact that the weak B_{min} signal is attributed to the T_1 state of the precursor that was produced before the formation of the stable triplet species discussed here. Further, a pair of peaks giving $|D| \approx 0.03\ cm^{-1}$ was observed at the inner sides of the low- and high-field $\Delta M_S = \pm 1$ transition signals. From a brief calculation of the resonance field, these signals appear to be not due to the double quantum transitions of the irradiated 4′-Me-NBP. Therefore, they are inferred to be attributed by the other stable triplet species, such that arising from the abstraction of a hydrogen atom of the methyl group by one of the oxygen atoms of the nitro group.

3.3. Fluorine-substituted triplet species

From 2′-, 3′-, and 4′-fluoro-NBPs [n'-F-NBPs ($n' = 2'$, $3'$ and $4'$, respectively)], stable triplet EPR signals can similarly be detected in EtOH glasses at 77 K after UV irradiation as in the irradiated NBP. To clarify the line broadening due to the ^{19}F spin, Fig. 3(a–c) show the EPR spectra of the low-field $\Delta M_S = \pm 1$ transitions. The ZFS parameters obtained are fairly close to those of the irradiated NBP as listed in Table 1.

For the irradiated n'-F-NBPs ($n' = 2'$, $3'$ and $4'$), the $|D|$ values are slightly larger than those of the irradiated NBP and its methyl-substituted derivatives. This may mainly be due to the electronegativity difference of the fluorine atom from the methyl group. Similarly to the cases of the irradiated n'-Me-NBPs ($n' = 2'$, $3'$ and $4'$), the $|D|$ value is smallest for the *ortho*-substituted species, owing to the increase of the nonplanarity of the molecule due to the steric effect of the fluorine atom. Such a trend was also observed in the $T_1(\pi\pi^*)$ states of the conformers of 2,2′-difluorobiphenyl [6], as was described previously in the case of 2,2′-dimethylbiphenyl.

Next, the ^{19}F hyperfine structures (hfs) of these species were examined from their EPR spectra. For the irradiated 2′- and 3′-F-NBPs, the ^{19}F hfs in their Z signals and the line broadening due to the ^{19}F spin in their B_{min} signals were actually observed, but appreciable splitting in the X and Y signals could scarcely be detected, as shown in Fig. 3. For the irradiated 4′-F-NBP, the ^{19}F hfs was barely detectable, although the line broadening of the X peak was observed by the overlapping with the triplet signals corresponding to $D^* \approx 0.02\ cm^{-1}$.

The ^{19}F hf coupling constants were roughly estimated from the difference between the line widths of each B_{min} signal, $\lambda_{min}(X)$, and that of the irradiated NBP, $\lambda_{min}(NBP)$, assuming the same structures of these carbon skeletons

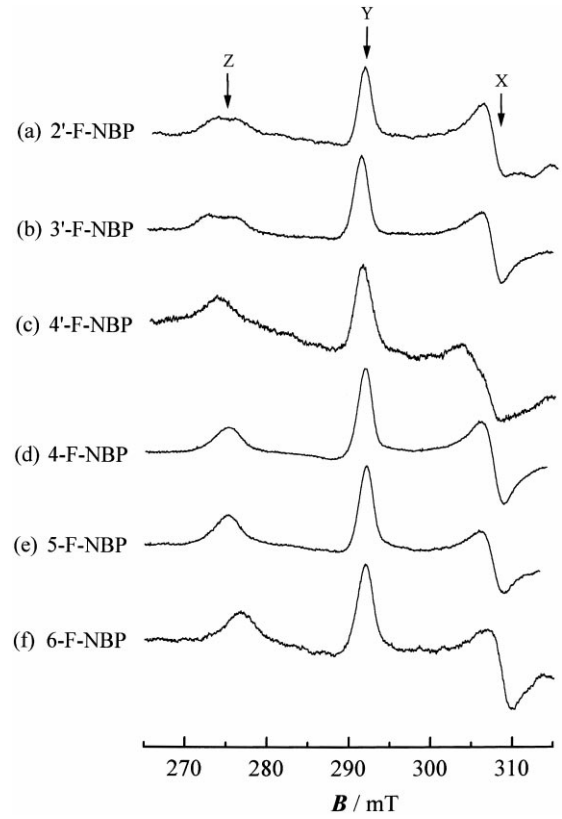


Fig. 3. EPR spectra of the low-field $\Delta M_S = \pm 1$ transitions for the stable triplet species produced from (a) 2′-F-NBP, (b) 3′-F-NBP, (c) 4′-F-NBP, (d) 4-F-NBP, (e) 5-F-NBP and (f) 6-F-NBP, observed after UV irradiation. The chemical formulas shown are the precursors.

[7,8]. The obtained results of δB_{min} are listed in Table 2. In this procedure, the results estimated for the irradiated NBP with *ortho*-substituted fluorine are less reliable because of the decrease of their planarity. For the irradiated 2′-F-NBP, the fluorine atom was assumed to be connected at the 6-position of the benzene ring not possessing NO(OH) group where the steric hindrance between the fluorine atom and the nitro group is smaller before UV irradiation. The isotropic ^{19}F hf constant of the irradiated 3′-F-NBP is the largest among the species studied. According to the preliminary result of the single-crystal ENDOR study of the irradiated NBP [9], the π electron spin density is fairly large at the 3′-position, but very small at the 5′-position in the NBP skeleton. Therefore, the above ^{19}F hfs may be due to the ^{19}F nucleus at the 3′-position and the ZFS parameters obtained from the irradiated 3′-F-NBP may be those of the irradiated 3′-F-NBP, but not the irradiated 5′-F-NBP. The corresponding ^{19}F hf coupling constants obtained from the Z signals are relatively close to those of the B_{min} signals. The π-electron spin distribution thus obtained for the benzene ring not possessing NO(OH) group shows generally similar trend to that obtained from the ENDOR study of the irradiated NBP [9]. From the angular dependence of the ^1H-ENDOR transitions, it was concluded that the stable triplet

Table 2
Linewidth (λ_{min}) in the B_{min} EPR signals and ^{19}F hyperfine constants (δB_{min}) for the irradiated fluorine-substituted NBPs [a]

	NBP	2′-F-NBP	3′-F-NBP	4′-F-NBP	4-F-NBP	5-F-NBP	6-F-NBP
λ_{min} (mT)	1.65	2.73	3.34	1.73	1.71	1.75	1.61
δB_{min} (mT)	–	1.08[b]	1.69	0.08	0.06	0.10	−0.04[b]

[a] $\delta B_{min}(X) = \lambda_{min}(X) - \lambda_{min}(NBP)$.
[b] These values are underestimated because of the more twisted structure than the irradiated NBP.

species was formed by the abstraction of a hydrogen atom from the 2′-position of the NBP skeleton.

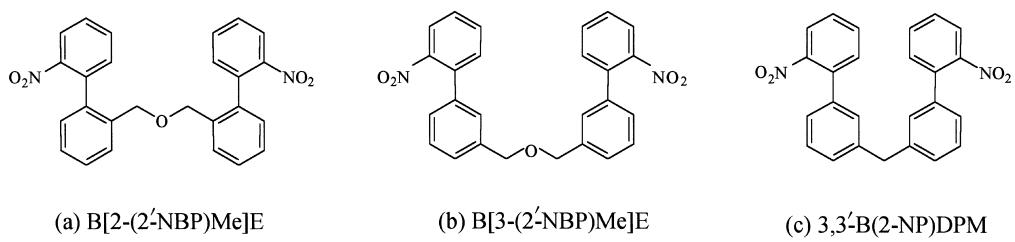
In addition, similar experiments were carried out for the irradiated 4-, 5- and 6-fluoro-NBPs (*n*-F-NBPs) ($n = 4$, 5 and 6, respectively) in which the fluorine atom is connected with the benzene ring possessing NO(OH) group. These EPR spectra of the low-field $\Delta M_S = \pm 1$ transitions are shown in Fig. 3(d–f), and the ZFS parameters obtained are listed in Table 1. These $|D|$ values are generally smaller than those of the irradiated *n*′-F-NBPs. The line shape of each peak is not largely changed from that of the irradiated NBP and the line broadenings due to the ^{19}F spin were barely detectable. We tried to synthesize 3-F-NBP, but could not obtain a sufficient amount of it for the EPR measurement.

3.4. Species produced from molecules possessing two NBP groups

Molecular systems possessing two triplet sites are of special interest in studying the interactions between these active groups. For examining such a magnetic interaction, we synthesized *bis*[2-, 3-, and 4-(2′-nitrobiphenyl)methyl]-ethers (B[*n*-(2′-NBP)Me]Es) ($n = 2$, 3 and 4, respectively) which are obtainable by rather easier procedures. The EPR measurements were carried out through UV irradiation of these molecules at 77 K in MTHF glasses because of low solubility in EtOH.

In the case of B[4-(2′-NBP)Me]E, no signals of quintet state and triplet state could actually be detected through UV irradiation at 77 K. For B[2-(2′-NBP)Me]E (see Fig. 4(a)), however, the signals arising from two kinds of triplet states were clearly observed at 77 K during UV irradiation, as shown in Fig. 5(a). The D^* values obtained from the B_{min} signals are 0.1279 and 0.1019 cm^{-1}. This may arise from the two kinds of conformers in the excited triplet states of the precursor in which the twist angles around the central C–C bond of the NBP group are different from each other. In the case of B[3-(2′-NBP)Me]E (see Fig. 4(b)), a set of stable triplet signals was observed after UV irradiation at 77 K, as shown in Fig. 5(b). The ZFS parameters thus obtained are fairly close to those of the irradiated *meta*-substituted NBPs, as listed in Table 3, especially for the irradiated 3′-hydroxymethyl-NBP in an EtOH glass (see Table 4). However, no signals of a quintet state could be detected by UV irradiation of these three precursors.

Here, one should re-examine the possibility that the spin multiplet species are actually detectable from the photochemical products of these precursors. At first, we examined the fact that a little long linkage part (–CH_2–O–CH_2–) may weaken the interaction between the two triplet sites. Then, we synthesized 3,3′-*bis*(2-nitrophenyl)diphenylmethane (3,3′-B(2-NP)DPM) (see Fig. 4(c)), as a promising precursor of spin multiplet. After its UV irradiation at 77 K in an MTHF glass through 5 cm of distilled water and Toshiba UV-25 glass filter, EPR signals of triplet state were observed as shown in Fig. 5(c). To examine the formation of another intermediate, a similar experiment was performed at 4.2 K, but no significant change could be observed. The ZFS parameters thus obtained are also listed in Table 3. These absolute values are fairly close to those of the irradiated NBP and 3′- and 4′-Me-NBPs in spite of the different solvent used, and are slightly smaller than most of the corresponding values of the irradiated B[3-(2′-NBP)Me]E. This may show the fact that the influence of the oxygen in the linkage part disappears. The EPR spectrum of the irradiated 3,3′-B(2-NP)DPM is observed as if the irradiated 3′-methylene-NBP (3′-CH_2-NBP) group exists almost independently from another part of the species separated by the C–C bond in the linkage part. The ZFS parameters of the triplet states of these separated groups are expected to be very close to each other. This is similar to the case of the irradiated B[3-(2′-NBP)Me]E where the irradiated 3′-oxymethyl-NBP (3′-



(a) B[2-(2′-NBP)Me]E (b) B[3-(2′-NBP)Me]E (c) 3,3′-B(2-NP)DPM

Fig. 4. Precursors possessing two NBP groups from which the stable triplet species are produced after UV irradiation.

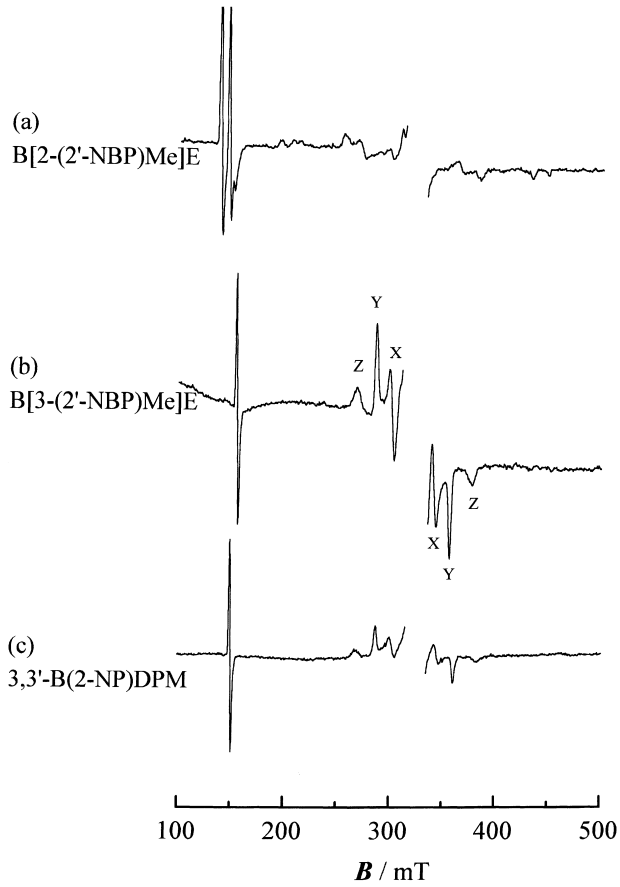


Fig. 5. EPR spectra of the excited triplet state produced from (a) B[2-(2′-NBP)Me]E observed during UV irradiation, and those for the stable triplet species produced from (b) B[3-(2′-NBP)Me]E and (c) 3,3′-B(2-NP)DPM, observed after UV irradiation. The chemical formulas shown are the precursors.

OCH_2-NBP) group is apparently separated from the 3′-CH_2-NBP group by the C–O bond of the linkage part. These facts may possibly suggest that the two benzene rings connected by the linkage part are not coplanar with each other and the conjugation between these groups almost disappears.

Under the present circumstances, we could not actually observe the interaction between the two active triplet sites in the irradiated 3,3′-B(2-NP)DPM and B[3-(2′-NBP)Me]E. For the observation of the triplet signals only, there may be the following two possibilities that the observed spectrum arises either from an intermediate produced by a photochemical reaction localized only a single NBP group or from species possessing two reacted NBP groups. The former process is possible when it is difficult for the hydrogen atom at the 2′-position of one of the NBP groups to approach any oxygen atom of this nitro group. On the other hand, the occurrence of the triplet intermediate in the latter case can be elucidated by the fact that the ground state of the irradiated NBP group is a singlet state being closely located to the excited triplet state [1]. The produced active sites are largely separated from each other and the conjugation between these groups is fairly small. As a result, the exchange integral between the unpaired orbitals localized separately in these sites should be very small. Therefore, the quintet state of the present species is higher than the lowest singlet and triplet states, and the EPR spectrum of the quintet state is difficult to be observed in rigid glasses. At present, however, we could not determine the possibility of either of these processes. To know the photo-produced paramagnetic species in detail, the EPR measurement should be carried out using a suitable host crystal containing the above precursor as a guest.

By the UV irradiation of synthesized 4,4′ bis(2-nitrophenyl)biphenyl, a B_{min} signal giving $D^* = 0.08\ cm^{-1}$ was observed at 77 and 4.2 K in MTHF. However, we could not obtain further information from this precursor.

3.5. Species produced from other NBP derivatives

In the course of the syntheses of B[*n*-(2′-NBP)Me]E ($n = 2$, 3 and 4), several kinds of substituted NBPs were obtained as the synthetic intermediates. In these substitution products, the molecules used for the EPR measurements are *n*′-ethoxycarbonyl-, carboxy-, hydroxymethyl- and methoxymethyl-NBPs ($n' = 2'$, 3′ and 4′). Similarly to the NBP derivatives described in the previous sections, EPR studies of these molecules were carried out under UV irradiation at 77 K in EtOH glasses. The ZFS parameters obtained are listed in Table 4.

After UV irradiation of these *para*-substituted NBPs at 77 K, the stable triplet EPR signals giving $D^* \approx 0.05\ cm^{-1}$ could be barely observed with sufficient intensity. For the irradiated 4′-hydroxymethyl-NBP, weak signals were detected near resonance fields giving $|D| = 0.021$ and $|E| = 0.001\ cm^{-1}$. These signals may possibly be due to a similar species to that observed in 4′-F-NBP as an origin of

Table 3
ZFS parameters observed from molecules possessing two NBP groups by UV irradiation in MTHF glasses

Precursor	$\|X\|$ (cm^{-1})	$\|Y\|$ (cm^{-1})	$\|Z\|$ (cm^{-1})	$\|D\|$ (cm^{-1})	$\|E\|$ (cm^{-1})	D^*(calc) [a] (cm^{-1})	D^* [b] (cm−1)
B[2-(2′-NBP)Me]E	–	–	–	–	–	–	0.1279
	–	–	–	–	–	–	0.1019
B[3-(2′-NBP)Me]E	0.0124	0.0216	0.0337	0.0507	0.0046	0.0513	0.0540
3,3′-B(2-NP)DPM	0.0119	0.0214	0.0332	0.0498	0.0047	0.0505	0.0526

[a] Calculated from *D* and *E*.
[b] Obtained from the B_{min} signal.

Table 4
ZFS parameters observed from substituted NBPs by UV-irradiation in EtOH glasses[a]

Precursor		$\|X\|$ (cm^{-1})	$\|Y\|$ (cm^{-1})	$\|Z\|$ (cm^{-1})	$\|D\|$ (cm^{-1})	$\|E\|$ (cm^{-1})	D^*(calc) [b] (cm^{-1})	D^* [c] (cm^{-1})
NBP		0.0116	0.0212	0.0327	0.0491	0.0048	0.0498	0.0520
2′-COOEt-NBP	S	0.0115	0.0202	0.0315	0.0473	0.0044	0.0479	-
	W	0.0145	0.0221	0.0350	0.0533	0.0038	0.0537	0.0524
2′-COOH-NBP	S	0.0112	0.0203	0.0313	0.0470	0.0046	0.0477	-
	W	0.0145	0.0222	0.0357	0.0541	0.0039	0.0545	0.0525
2′-CH_2OH-NBP	S	0.0111	0.0208	0.0318	0.0478	0.0048	0.0485	–
	W	0.0141	0.0231	0.0368	0.0554	0.0045	0.0559	0.0553
2′-CH_2OMe-NBP	S	0.0110	0.0210	0.0319	0.0479	0.0050	0.0487	–
	W	0.0144	0.0238	0.0375	0.0566	0.0047	0.0572	0.0527
3′-COOEt-NBP		–	–	–	–	–	–	0.1078
3′-COOH-NBP		–	–	–	–	–	–	0.1085
3′-CH_2OH-NBP		–	–	–	–	–	–	0.1074
		0.0122	0.0216	0.0337	0.0506	0.0047	0.0512	0.0539
3′-CH_2OMe-NBP		0.0120	0.0214	0.0330	0.0497	0.0047	0.0504	0.0538
3′-OMe-NBP	S	0.0114	0.0234	0.0348	0.0522	0.0060	0.0532	0.0542
	W	0.0103	0.0214	0.0317	0.0475	0.0055	0.0485	–

[a] S: strong signal; W: weak signal.
[b] Calculated from D and E.
[c] Obtained from the B_{min} signal..

the line broadening of its X peaks. On the other hand, the weak B_{min} signals giving $D^* \approx 0.05\ cm^{-1}$ were observed for the irradiated 4′-carboxy- and 4′-methylcarbonyl-NBP. For the irradiated *ortho*-substituted NBPs, however, the situation was different from the above cases. In these species, two sets of stable triplet EPR signals were observed at 77 K after UV irradiation, as shown in Fig. 6. The absolute values of ZFS parameters obtained from the set of the signals with higher intensities are relatively small and in a range of $|D| = 0.0475 \pm 0.0005$ and $|E| = 0.0047 \pm 0.0003\ cm^{-1}$, while those with lower intensities are relatively large and in a range of $|D| = 0.0550 \pm 0.0017$ and $|E| = 0.0042 \pm 0.0005\ cm^{-1}$. The observation of two sets of stable triplet signals may be due to the conformers arising from the different orientation of the substituent. In the two species with different ZFS parameters, the former group giving smaller $|D|$ values is more stable and the conformation of NBP group is possibly close to that of the irradiated 2′-Me-NBP with nonplanar biphenyl skeleton (the irradiated 6′-Me-NBP), while the latter group giving larger $|D|$ values is less stable and has smaller twist angles around the central C–C bond in its biphenyl skeleton. For the irradiated 2′-Me- and 2′-F-NBP, however, only one stable triplet species was observed as was described in the previous sections. This may be due to the fact that these derivatives have a fairly small substituent the orientation of which has little influence upon the resonance fields within the present EPR measurement.

On the other hand, the triplet species produced from the *meta*-substituted NBPs are classified into two groups. One group gives detectable their B_{min} signals at 77 K only during UV irradiation and the corresponding D^* values are nearly $0.108\ cm^{-1}$ which is close to the values of the $T_1(\pi\pi^*)$ states of many aromatic molecules. The precursors of these species are 3′-ethoxycarbonyl- and 3′-carboxy-NBPs. These substi-

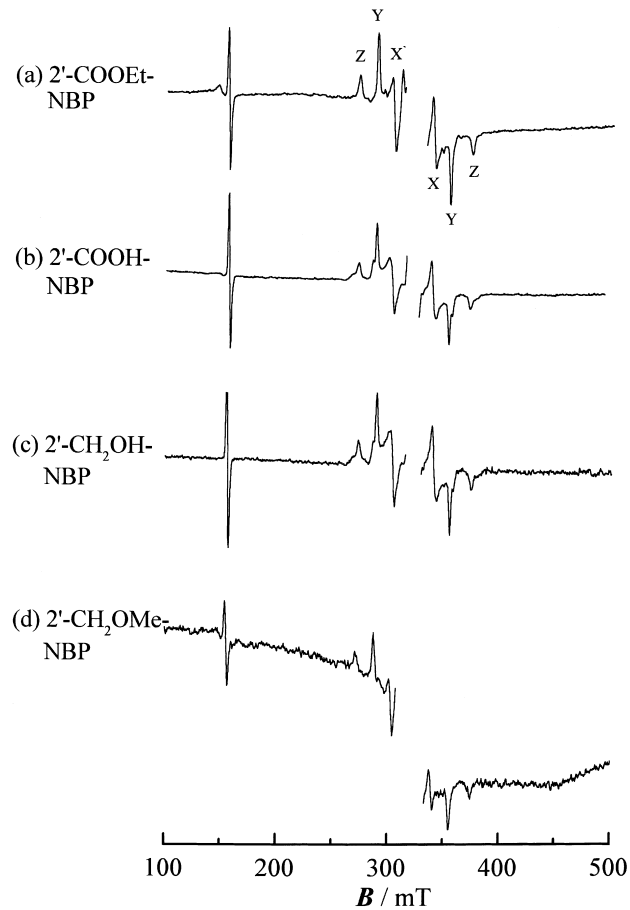


Fig. 6. EPR spectra of the stable triplet species produced from (a) 2′-ethoxycarbonyl-NBP, (b) 2′-carboxy-NBP, (c) 2′-hydroxymethyl-NBP and (d) 2′-methoxymethyl-NBP, observed after UV irradiation. The chemical formulas shown are the precursors.

tuents are electron withdrawing groups that are directly connected with the phenyl ring in each NBP group. Another group is stable at 77 K after UV irradiation and their ZFS parameters are relatively close to those of the irradiated 3′-Me-NBP. Such precursors are 3′-hydroxymethyl- and 3′-methoxymethyl-NBPs. In these molecules, the active group is connected with each phenyl ring through a methylene linkage. Similar experiments were carried out for 2′-, 3′- and 4′-(4-toluenesulfonyloxy)methyl-NBPs at 77 K in MTHF glasses. From the *meta*-substituted derivatives, stable signals of triplet state ($|D| = 0.0501$ and $|E| = 0.047\ cm^{-1}$) were observed after UV irradiation. On the other hand, only a B_{min} signal ($D^* = 0.1012\ cm^{-1}$) was detected from the *ortho*-substituted derivative during UV irradiation, while no signals of the triplet state were observed from the *para*-substituted one. In addition to these signals, the B_{min} signal giving $D^* = 0.1074\ cm^{-1}$ was also observed for 3′-hydroxymethyl-NBP. The EPR spectra of these triplet species are shown in Fig. 7.

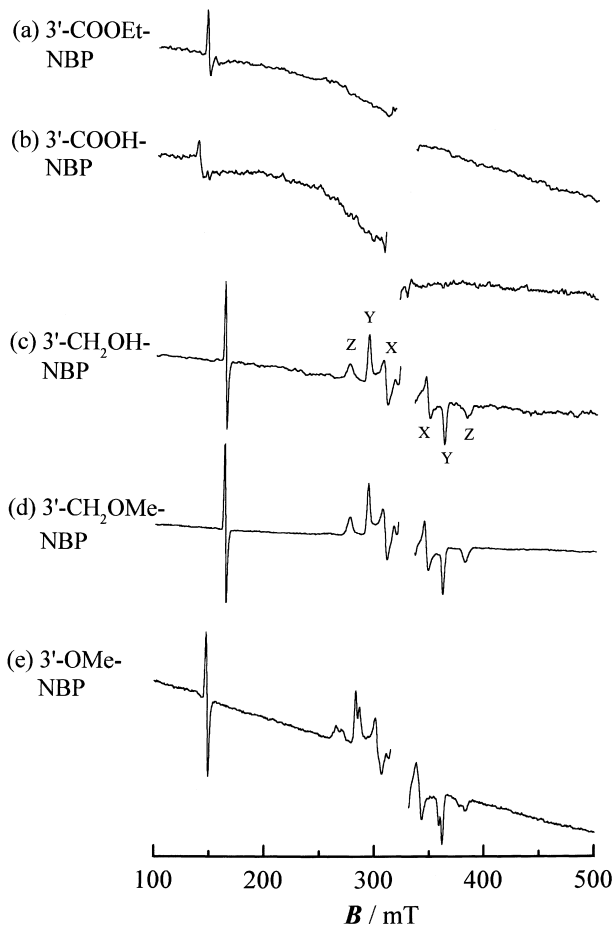


Fig. 7. EPR spectra of the excited triplet states produced from (a) 3′-ethoxycarbonyl-NBP and (b) 3′-carboxy-NBP, observed during UV irradiation, and those for the stable triplet species produced from (c) 3′-hydroxymethyl-NBP, (d) 3′-methoxymethyl-NBP and (e) 3′-methoxy-NBP, observed after UV irradiation. The structural formulas shown are the precursors.

Under these circumstances, a further experiment was undertaken for molecules in which an electron donating substituent is directly connected with the carbon atom at the 3′-position of the NBP skeleton. From 3′-hydroxy-NBP, we could not observe the signals of the triplet state, because it is very unstable and has rapidly changeable color to black under UV irradiation. In the present work, 3′-methoxy-NBP was chosen as such a precursor. In this case, two sets of stable triplet signals were observed in an EtOH glass after its UV irradiation at 77 K, as shown in Fig. 7(e). A set of signals with higher intensity gives a larger $|D|$ value, while another set with lower intensity gives a smaller one. The fact that the larger $|D|$ value of $0.0522\ cm^{-1}$ than that of the irradiated NBP is obviously due to the structure in which the phenyl group is directly connected to a methoxy group with strong electron donating property. The observation of the two sets of signals might be inferred from the reason that there are two conformations for the *meta*-substituted species before UV irradiation, that is, 3′- and 5′-substituted-NBPs. Since only one set of signals was observed for the other *meta*-substituted precursors possessing a relatively large substituent, there remains another possibility that this may be due to the different orientations of the methoxy group.

4. Some remarks

The substituents in most of the molecules treated in the previous section are rather large and it is almost impossible to determine exactly the conformations of these irradiated species in rigid glasses. Further, the D^* value evaluated from the B_{min} signal does not always agree with neither of the two kinds of D^*(calc) values calculated from the two sets of the experimental ZFS parameters for the $\Delta M_S = \pm 1$ transitions. This may be due to the overlapping of these two kinds of B_{min} peaks in addition to signals arising from species having the slightly different twist angles around the central C–C bond. As a result, it is difficult to correspond the $|D|$ values obtained simply to the electronic properties of their active groups.

Here, we choose the irradiated NBP derivatives in which the relatively small active substituents are directly connected with the benzene ring, and their $|D|$ values were plotted against the Hammett substituent constant σ [10,11]. In this case, there are two selections for σ with regard to the 1′-carbon that is connected with the 2-nitrophenyl group before UV irradiation and to the 2′-carbon from which the connected hydrogen atom is abstracted. For the irradiated 4′-substituted species as an example, the substituent is located at a *para*- and a *meta*-position with regard to the 1′- and the 2′-carbon, respectively. Using the former selection, one could not obtain a good correlation between $|D|$ and σ. By adopting the latter selection, however, one can obtain a better linear relation, as shown in Fig. 8. In this case, the 4′-substituted species give a better result as the *meta*-substituted ones, rather than the 2′-substituted species with a

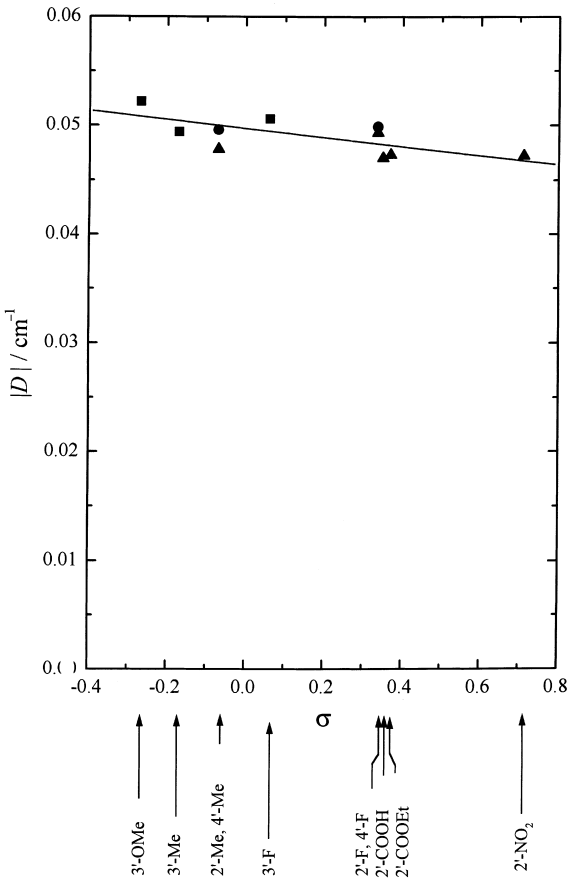


Fig. 8. Plots of the $|D|$ values of the substituted NBPs vs. σ with regard to the 2′-carbons of the NBP group. ▲, ■ and ● indicate the values of the *ortho*-, *meta*- and *para*-substituted NBPs, respectively.

smaller $|D|$ value. The reason for the smaller $|D|$ values for the latter species is that, owing to the steric hindrance arising from the substituents, the conjugation between the two benzene rings is weakened by increasing the twist angle around the central C–C bond. Therefore, the present result may indirectly suggest the existence of the hydrogen-abstracted carbon atom at the 2′-position as an active site for the irradiated NBP derivatives, although there remains some ambiguity on the conformation of the irradiated *meta*-substituted derivatives. On the other hand, Wagner and May pointed out that the $|D|$ values of $T_1(\pi\pi^*)$ states of substituted benzonitriles do not correlate to the Hammett σ values of ground-state parameters [12]. In the stable triplet species treated in the present work, however, one of the singly occupied orbitals is largely localized at the radical-site carbon atom (2′-position of the NBP skeleton) while another one has a π character. As a result, the $|D|$ value is largely dependent upon the spin density at the radical-site carbon atom in the substituted phenyl radical part (2′-position of the NBP derivatives) which is directly influenced on the substituent, and correlated to σ. This situation is generally parallel to the cases of hfs of aromatic radicals due to the spin density at the magnetic nucleus, discussed by Janzen [13].

From these observations, it may be reasonable to infer the following scheme, although the outline of its main part was described in the previous paper [1]. By the UV irradiation, at first the precursor is excited to its $T_1(\pi\pi^*)$ state giving $D^* \approx 0.1\ \mathrm{cm}^{-1}$ through its excited singlet state. The signal of this state is observable if the succeeding reaction does not proceed too rapidly. Afterwards another stable triplet species is produced through the abstraction of a hydrogen atom from the 2′-position of the NBP group by one of the oxygen atoms of the nitro group. It should be noted here that the latter process of hydrogen-transfer can proceed only when the hydrogen is possible to approach rather easily to one of these oxygen atoms. In the molecules treated here, such conformations of the NBP group are possible to be realized depending on the extent of influence of the substituent and of the environment.

From the present experiments in rigid glasses, one can obtain a general trend concerning the dependence of the positions of substituents upon the conformation of the NBP group. That is, the nonplanarity of these intermediates decreases with increasing the interaction between the substituted phenyl and the 2-nitrophenyl groups. The *para*-substituted derivatives are rather planar than NBP itself, because of the relatively strong conjugation of the NBP group with its substituent. As a result, their T_1 states may be more stabilized and need some excess energies to proceed to the above hydrogen-transfer step. Accordingly, the stable triplet species are observable only when such an interaction is relatively weak, as in the cases of the irradiated 4′-Me- and 4′-F-NBP with relatively weak EPR signal intensity.

For the *meta*-substituted derivatives, the structures of the NBP group are generally close to the unsubstituted NBP. Their photochemical reactions usually proceed to the hydrogen-transfer process, if the interaction between the active substituent and the NBP group is very weak, as in the cases when these groups are separated by a methylene linkage. Similar phenomena are observable if the directly connected substituent is an electron-donating group. However, when the electron-withdrawing substituent is connected to the NBP group directly, only the $T_1(\pi\pi^*)$ state of the precursor is detectable. Taking the nitro group being electron-accepting substituent into consideration, these facts may suggest that the hydrogen-transferred stable triplet species can be produced only when the precursor is somewhat polar.

On the other hand, the *ortho*-substituted derivatives are more twisted around the central C–C bond of the NBP group, owing to the steric hindrance from the substituents. As a result, their hydrogen-transferred intermediates are generally observable, except when a strong steric hindrance occurs owing to a large substituent as in the case of B[2-(2′-NBP)Me]E. It should be noted here that the above discussions are valid only for the molecules with changeable geometries, especially the twisted angle around the central C–C bond of the NBP group. However, the reaction cannot proceed if the spatial restriction from the environment is strong as can be seen for 2,2′-DNBP in its crystal, although

its irradiated species were detected in rigid glasses. In the case of 2,2′-DNBP, the $\Delta M_S = \pm 1$ transitions were observed in EtOH after UV irradiation, while no signals of the triplet state could be detected in the crystalline state. This may show the fact that the hydrogen-transfer process in 2,2′-DNBP occurs only when the molecular structure of the precursor is changeable in the environment.

5. Conclusions

For the NBP derivatives, one may infer the fact that the occurrence of the hydrogen-transfer from the 2′-position of the NBP group is restricted within nonplanar and something flexible molecules in which the above hydrogen atom becomes close to one of the oxygen atoms of the nitro group without any significant hindrance. In this case, it is clear that the structures of such molecules are controlled by the interaction between the substituent and the NBP group.

The molecular structures of the species treated in the present work are rather complicated for discussing the photochemical process in some detail. To eliminate such difficulties, we are taking up the study on the photochemical intermediates of molecules related to the NBP the structures of which are possible to be estimated to some degree.

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Appendix A

A.1. Syntheses of 2-nitrobiphenyl derivatives

In the course of the syntheses, melting points were measured with Yazawa Micro Melting Point BY-2 and were uncorrected. FT-IR spectra were measured using a Shimadzu FTIR-4000 IR spectrometer. ^{1}H NMR spectra were recorded with JEOL JNM-PMX-60 (60 MHz) spectrometer or JEOL JNN-EX-270 (270 MHz) in $CDCl_3$. Signals are expressed as ppm downfield from tetramethylsilane used as an internal standard (δ value). Splitting patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. The mass spectra were taken with a JEOL JMS AX-500 mass spectrometer. Flash column chromatography was done with Merck Kieselgel 60 (230–400 mesh) with a mixture of hexane and ethyl acetate as an elution system. Analytical thin-layer chromatography was done on Merck pre-coated silica gel 60 F-254, 0.25 mm thick TLC plates.

A.2. Methyl-substituted nitrobiphenyls

A.2.1. 2′-Methyl-NBP (2′-Me-NBP)

A mixture of 1-bromo-2-nitrobenzene (2.55 g) and 2-iodotoluene (2.10 g) was heated to 215°C. To it was added copper powder (11 g), and the resulting mixture was stirred at 230°C for 45 min. From the resulting mixture, the materials soluble in acetone were extracted using a Soxhlet apparatus. After the solvent was removed, the extract was purified by a silica gel column chromatography to give 2′-Me-NBP (1.57 g, 76%). ^{1}H NMR δ 2.10 (3H, s), 7.20 (8H, m).

A.2.2. 3′-Methyl-NBP (3′-Me-NBP)

In a similar manner, 3′-Me-NBP (3.16 g, 65%) was obtained from 1-bromo-2-nitrobenzene (5.84 g) and 3-iodotoluene (5.00 g). ^{1}H NMR δ 2.36 (3H, s), 7.20 (8H, m).

A.2.3. 4′-Methyl-NBP (4′-Me-NBP)

In the similar manner, 4′-Me-NBP (3.67 g, 75%) was obtained from 1-bromo-2-nitrobenzene (5.84 g) and 4-iodotoluene (5.00 g). ^{1}H NMR δ 2.40 (3H, s), 7.13 (8H, m).

A.3. Fluorine-substituted nitrobiphenyls

A.3.1. 2′-Fluoro-NBP (2′-F-NBP)

A mixture of 1-bromo-2-nitrobenzene (10.9 g) and 2-fluoroiodobenzene (10.0 g) was heated to 205°C. To it was added copper powder (34.5 g), and the resulting mixture was stirred at 205°C for 3 h. From the resulting mixture, the materials soluble in acetone were extracted using a Soxhlet apparatus. After the solvent was removed, the extract was purified by a silica gel column chromatography followed by recrystallization from 80% ethanol–water to give 2′-F-NBP (5.09 g, 52%). Mp 73.5–74.5°C; IR (KBr) 1525, 1360, 1205 cm^{-1}; MS (70 eV) *m/z* 217 (M^+).

A.3.2. 3′-Fluoro-NBP (3′-F-NBP)

In the similar manner, 3′-F-NBP (6.53 g, 65%) was obtained from 1-bromo-2-nitrobenzene (11.26 g) and 3-fluoro-1-iodobenzene (10.33 g). Mp 49.0–49.5°C; IR (KBr) 1530, 1370, 1190 cm^{-1}; MS (70 eV) *m/z* 217 (M^+).

A.3.3. 4′-Fluoro-NBP (4′-F-NBP)

In the similar manner, 4′-F-NBP (2.88 g, 58%) was obtained from 1-bromo-2-nitrobenzene (5.59 g) and 4-fluoro-1-iodobenzene (5.13 g). Mp 59.5–60°C; IR (KBr) 1520, 1360, 1225 cm^{-1}; MS (70 eV) *m/z* 217 (M^+).

A.3.4. 1-Bromo-2-nitro-4-fluorobenzene

A solution of 4-fluoro-2-nitroaniline (5.0 g) in 24% hydrobromic acid (70 ml) was kept at 0°C. To it was added an aqueous solution of sodium nitrite (2.69 g in

16 ml water) over the time of 30 min. The solution thus formed was then added to the solution of cuprous bromide (prepared from 6.2 g cuprous bromide and 20 ml water) with vigorous stirring at 0°C. The resultant reaction mixture was extracted with ethyl acetate. The organic layer was washed successively with 10% aqueous sodium thiosulfate saturated aqueous sodium hydrogencarbonate, and saturated aqueous sodium chloride, and was dried with anhydrous sodium sulfate. Removal of the solvent followed by silica gel column chromatography gave 1-bromo-2-nitro-4-fluorobenzene (4.42 g, 63%). ^{1}H NMR δ 7.24 (1H, m), 7.61 (1H, dd, $J = 7.92$, 2.97 Hz), 7.75 (1H, dd, $J = 8.91$, 4.95 Hz).

A.3.5. 4-Fluoro-NBP (4-F-NBP)

A mixture of 1-bromo-2-nitro-4-fluorobrnzene (3.89 g) and iodobenzene (7.21 g) was heated to 200°C. To it was added copper powder (16.9 g), and the resulting mixture was stirred at 200°C for 3 h. From the resulting mixture, the materials soluble in acetone were extracted using a Soxhlet apparatus. After the solvent was removed, the extract was purified by a silica gel column chromatography followed by recrystallization from hexane to give 4-F-NBP (1.58 g, 41%). Mp 71–72°C; IR (KBr) 1540, 1360, 1210 cm^{-1}; ^{1}H NMR δ 7.25–7.46 (7H, m), 7.60 (dd, $J = 7.92$, 2.64 Hz); MS (70 eV) *m/z* 217 (M^+).

A.3.6. 1-Bromo-2-nitro-5-fluorobenzene

To a mixture of 3-fluorobromobenzene (99.81 g) and sulfuric acid (200 ml) was added, at 35°C, fuming nitric acid (200 ml) slowly, and the resulting mixture was stirred for 1 h. The reaction mixture was poured onto ice (ca. 500 g), and the mixture was extracted with dichloromethane. The organic layer was washed successively with saturated aqueous sodium hydrogencarbonate and saturated aqueous sodium chloride, and was dried with anhydrous sodium sulfate. Removal of the solvent followed by distillation under the reduced pressure (bp 87–92°C, 1 mm Hg) gave 1-bromo-2-nitro-5-fluorobenzene (92.59 g, 74%). ^{1}H NMR δ 7.18 (1H, m), 7.49 (1H, dd, $J = 7.92$, 2.64 Hz), 7.97 (1H, dd, $J = 8.91$, 5.28 Hz).

A.3.7. 5-Fluoro-NBP (5-F-NBP)

A mixture of 1-bromo-2-nitro-5-fluorobenzene (5.00 g) and iodobenzene (9.27 g) was heated to 200°C. To it was added copper powder (21.6 g), and the resulting mixture was stirred at 200°C for 2 h. From the resulting mixture, the materials soluble in acetone were extracted using a Soxhlet apparatus. After the solvent was removed, the extract was purified by a silica gel column chromatography followed by distillation under the reduced pressure (bp 131–137°C, 3 mm Hg) to give 5-F-NBP (2.35 g, 48%). Mp 71–72°C; IR (KBr) 1530, 1360, 1195 cm^{-1}; ^{1}H NMR δ 7.1–7.2 (2H, m), 7.2–7.3 (2H, m), 7.4–7.5 (3H, m), 7.92 (1H, dd, $J = 4.46$, 8.22 Hz); MS (70 eV) *m/z* 217 (M^+).

A.3.8. 2,6-Dinitro-1-chlorobenzene

A mixture of 2,6-dinitrophenol (10.14 g), 4-toluenesulfonyl chloride (14.5 g), and N,N-diethylaniline was stirred at 90–93°C for 25 h. The resultant reaction mixture was extracted with ethyl acetate. The organic layer was washed successively with 10% hydrochloric acid, 10% aqueous sodium hydroxide, and saturated aqueous sodium chloride, and was dried with anhydrous sodium sulfate. Removal of the solvent followed by silica gel column chromatography gave 2,6-dinitro-1-chlorobenzene (8.79 g, 80%). ^{1}H NMR δ 7.63 (1H, t, $J = 8.25$ Hz), 8.01 (2H, d, $J = 8.25$ Hz).

A.3.9. 2,6-Dinitrobiphenyl (2,6-DNBP)

A solution of 2,6-dinitro-1-chlorobenzene (17.3 g) and iodobenzene (34.8 g) in nitrobenzene (50 ml) was heated to 220°C. To it was added copper powder (54.3 g), and the resulting mixture was stirred at 220°C for 1.5 h. After the solid material was removed by filtration, nitrobenzene and the unreacted 2,6-dinitro-1-chlorobenzene and iodobenzene were removed by distillation under the reduced pressure. The residue was recrystallized from ethyl acetate to afford 2,6-DNBP (15.82 , 76%). ^{1}H NMR δ 7.27 (2H, m), 7.45 (3H, m), 7.68 (2H, t, $J = 8.24$ Hz), 8.00 (2H, d, $J = 8.25$ Hz).

A.3.10. 3-Nitro-2-phenylaniline

To a refluxing mixture of 2,6-dinitrobiphenyl (15.0 g) in ethanol (220 ml) was added a mixture of sodium sulfide (17.5 g), sulfur (4.3 g), and water (85 ml), and the resulting mixture was refluxed for 3 h. Ethanol was removed under reduced pressure, and the residue was extracted with dichloromethane. The organic layer was washed with saturated aqueous sodium chloride, and was dried with anhydrous sodium sulfate. Removal of the solvent followed by silica gel column chromatography gave 3-nitro-2-phenylaniline (12.81 g, 97%).

A.3.11. 6-Fluoro-NBP (6-F-NBP)

To a mixture of 3-nitro-2-phenylaniline (6.0 g), concentrated hydrochloric acid (60 ml), and water (60 ml) at 0°C was added a solution of sodium nitrite (5 g) in water (25 ml), and the resulting mixture was stirred for 3 h. After the unreacted material was filtered off, fluoroboric acid (60 ml) was added and the resulting precipitate was collected by filtration. After the solid was washed by a mixture of methanol and ether and dried, it was heated to 150°C. The product was extracted by ethyl acetate. The organic layer was washed successively with 10% aqueous sodium hydroxide and saturated aqueous sodium chloride, and was dried with anhydrous sodium sulfate. Removal of the solvent followed by silica gel column chromatography and recrystallization from hexane twice gave 6-F-NBP (0.16 g, 3%). Mp 68–69°C; IR (KBr) 1535, 1370, 1250 cm^{-1}; ^{1}H NMR δ 7.30–7.53 (7H, m), 7.68 (1H, d, $J = 7.91$ Hz); MS (70 eV) *m/z* 217 (M^+).

A.4. Nitrobiphenyls possessing an ether linkage

A.4.1. 2′-Ethoxycarbonyl-NBP

A mixture of 1-bromo-2-nitrobenzene (4.6 g) and 2-iodotoluene (5.0 g) was heated to 215°C. To it was added copper powder (8.6 g), and the resulting mixture was stirred at 230°C for 45 min. From the resulting mixture, the materials soluble in acetone were extracted using a Soxhlet apparatus. After the solvent was removed, the extract was purified by a silica gel column chromatography to give 2′-ethoxycarbonyl-NBP (2.02 g, 43%). ^{1}H NMR δ 1.05 (3H, t), 4.15 (2H, q), 7.55 (8H, m).

A.4.2. 3′-Ethoxycarbonyl-NBP

In the similar manner, 3′-ethoxycarbonyl-NBP (4.01 g, 86%) was obtained from 1-bromo-2-nitrobenzene (4.6 g), ethyl 2-iodobenzoate (5.0 g), and copper powder (8.6 g). ^{1}H NMR δ 1.40 (3H, t), 4.40 (2H, q), 7.80 (8H, m).

A.4.3. 2′-Carboxy-NBP

A mixture of 2′-ethoxycarbonyl-NBP (1.0 g), ethanol (6.5 ml), and 10% aqueous solution of sodium hydroxide (2 ml) was refluxed for 2 h. After the solution was acidified by dilute hydrochloric acid, the mixture was extracted with ethyl acetate. To the organic layer was added saturated aqueous sodium hydrogencarbonate, and the aqueous layer was separated. It was again acidified by dilute hydrochloric acid, and the resulting aqueous solution was extracted with ether. After the solvent was partially removed under the reduced pressure, the crystals of 2′-carboxy-NBP were obtained (0.54 g, 57%).

A.4.4. 3′-Carboxy-NBP

In the similar manner, 3′-carboxy-NBP (0.84 g, 89%) was obtained from 3′-ethoxycarbonyl-NBP (1.0 g).

A.4.5. 2′-Hydroxymethyl-NBP

To a solution of 2′-carboxy-NBP (0.50 g) in 3 ml THF was added a 2.0 M THF solution of BH_3-Me_2S complex (1.23 ml), and the resulting solution was stirred for 2 h at room temperature. To it was added water (2 ml), and the resulting mixture was extracted with ethyl acetate. The organic layer was washed with saturated aqueous sodium chloride, and was dried with anhydrous sodium sulfate. Removal of the solvent followed by the purification with a silica gel column chromatography afforded 2′-hydroxymethyl-NBP (0.25 g, 76%). ^{1}H NMR δ 2.10 (1H, s), 4.46 (2H, s), 7.56 (8H, m).

A.4.6. 3′-Hydroxymethyl-NBP

In the similar manner, 3′-hydroxymethyl-NBP (0.44 g, 94%) was obtained from 3′-carboxy-NBP (0.50 g). ^{1}H NMR δ 2.10 (1H, s), 4.80 (2H, s), 7.60 (8H, m).

A.4.7. 2′-Methoxymethyl-NBP

To a suspension of sodium hydride (ca. 60% in mineral oil, 0.15 g) and THF (3 ml) was added a solution of 2′-hydroxymethyl-NBP (0.49 g) in THF (5 ml) slowly, and the resulting mixture was stirred for 15 min at room temperature. To the solution was added methyl iodide (2 ml), and stirring was continued for 3 h. After the addition of ethanol (2 ml) and water, the organic layer was washed with saturated aqueous sodium chloride, and was dried with anhydrous sodium sulfate. Removal of the solvent followed by the purification with a silica gel column chromatography afforded 2′-methoxymethyl-NBP (0.44 g, 86%). ^{1}H NMR δ 3.15 (3H, s), 4.15 (2H, s), 7.40 (8H, m).

A.4.8. 3′-Methoxymethyl-NBP

In the similar manner, 3′-methoxymethyl-NBP (0.20 g, 54%) was obtained from 3′-hydroxymethyl-NBP (0.35 g). ^{1}H NMR δ 3.40 (3H, s), 4.46 (2H, s), 7.23 (8H, m).

A.4.9. 2′-(4-Toluenesulfonyloxy)methyl-NBP

To a suspension of sodium hydride (ca. 60% in mineral oil, 0.24 g) and THF (3 ml) was added a solution of 2′-hydoxymethyl-NBP (0.91 g) in THF (2 ml) slowly, and the resulting mixture was stirred for 15 min at room temperature. To the solution was added a solution of 4-toluenesulfonyl chloride (1.52 g in 4 ml THF), and stirring was continued for 20 h. After the addition of methanol (2 ml) and water, the organic layer was washed with saturated aqueous sodium chloride, and was dried with anhydrous sodium sulfate. Removal of the solvent followed by the purification with a silica gel column chromatography afforded 2′-(4-toluenesulfonyloxy)methyl-NBP (0.43 g, 29%). ^{1}H NMR δ 2.45 (3H, s), 4.85 (2H, s), 7.30 (12H, m).

A.4.10. 3′-(4-Toluenesulfonyloxy)methyl-NBP

In the similar manner, 3′-(4-toluenesulfonyloxy)methyl-NBP (0.36 g, 69%) was obtained from 3′-hydroxymethyl-NBP (0.31 g). ^{1}H NMR δ 2.45 (3H, s), 5.03 (2H, s), 7.20 (12H, m).

A.4.11. Bis[2-(2′-nitrobiphenyl)methyl]ether (B[2-(2′-NBP)Me]E)

To a suspension of sodium hydride (ca. 60% in mineral oil, 56 mg) and THF (3 ml) was added a solution of 2′-hydroxymethyl-NBP (0.24 g) in THF (5 ml) slowly, and the resulting mixture was stirred for 15 min at room temperature. To the solution was added a solution of 2′-(4-toluemesulfonyloxy)-methyl-NBP (0.27 g in 5 ml THF), and the resulting mixture was refluxed for 1 h. After the addition of methanol (2 ml) and water, the organic layer was washed with saturated aqueous sodium chloride, and was dried with anhydrous sodium sulfate. Removal of the solvent followed by purification with silica gel column chromatography afforded B[2-(2′-NBP)Me]E (26 mg, 17%). ^{1}H NMR δ 4.43 (4H, s), 7.20 (16H, m).

A.4.12. Bis[3-(2′-nitrobiphenyl)methyl]ether (B[3-(2′-NBP)Me]E)

In the similar manner, B[3-(2′-NBP)Me]E (0.28 g, 74%) was obtained from 3′-hydroxymethyl-NBP (0.20 g) and 3′-

(4-toluenesulfonyloxy)methyl-NBP (0.29 g). ^{1}H NMR δ 2.45 (3H, s), 5.03 (2H, s), 7.20 (12H, m).

A.4.13. 3′-Methoxy-NBP

A mixture of 1-bromo-2-nitrobenzene (21.6 g) and 3-iodoanisole (25.0 g) was heated to 190°C. To it was added copper powder (34.0 g), and the resulting mixture was stirred for 3 h. From the resulting mixture, the materials soluble in acetone were extracted using a Soxhlet apparatus. After the solvent was removed, the extract was purified by a silica gel column chromatography followed by recrystallization from ethanol to give 3′-methoxy-NBP (13.92 g, 57%).

A.5. A nitrobiphenyl possessing a methylene linkage

A.5.1. 3,3′-Diiododiphenylmethane

To the dilute sulfuric acid (6.75 ml conc sulfuric acid and 125 ml water) was added 3,3′-diaminodiphenylmethane (5 g), and the resulting mixture was refluxed for a while. The resulting solution was cooled to 0°C, and to it was added an aqueous solution of sodium nitrite (10.44 g in 160 ml water) and an aqueous solution of potassium iodide (21.0 g in 41 ml water) successively, and the resulting mixture was stirred overnight. Extraction with ethyl acetate followed by the washings of the organic layer with 10% aqueous sodium thiosulfate, aqueous saturated sodium hydrogencarbonate, and aqueous saturated sodium chloride, successively. The organic layer was dried with anhydrous sodium sulfate. Removal of the solvent followed by the purification with a silica gel column chromatography afforded 3,3′-diiododiphenylmethane.

A.5.2. 3,3′-Bis(2-nitrophenyl)diphenylmethane (3,3′-B(2-NBP)DPM)

The mixture of 3,3′-diiododiphenylmethane (0.5 g) and 2-bromonitrobenzene (0.48 g) was heated up to 205°C. To it was added copper powder (1.52 g), and the resulting mixture was stirred at that temperature for 3 h. From the resulting mixture, the materials soluble in acetone were extracted using a Soxhlet apparatus. After the solvent was removed, the extract was purified by a silica gel column chromatography to give 3,3′-B(2-NBP)DPM (0.2 g, 41%). IR (KBr), 1600, 1570, 1520, 1472, 1445, 1435, 1420, 1355 cm^{-1}; MS (70 eV) *m/z* 410 (M^+), Calculated for $C_{25}H_{18}O_4N_2$: (M) 410.1267. Found: 410.1240.

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