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Intermediates for Photoisomerization of a Butenylnaphthalene in the Presence of Electron Acceptors as Studied by Solvent Dependence of Magnetic Field Effects

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The external magnetic field effect as well as laser flash photolysis was employed to estimate the contribution of ion radical pairs to isomerization of *trans*-2-(3,3-dimethyl-1-butenyl)naphthalene (*t*-BN) in the presence of an electron acceptor in various solvents. The precursor of isomerization, *t*-BN triplet, was produced most efficiently almost through an exciplex in chloroform (ε=4.8) among the employed solvents.

Photoinduced electron transfer reactions have recently been receiving much attention1) and some reports have appeared on the photoisomerization of olefins induced by electron transfer.2–4) Quenching of olefins in excited states by electron acceptors in polar solvents may generate radical pairs which are precursors of geometrical isomerization of the olefins. The excited singlet state of *trans*-2-(3,3-dimethyl-1-butenyl)naphthalene (2-NpCH=CHBu^t, *t*-BN) is efficiently quenched by electron acceptors such as dicyanobenzenes (DCB) and dimethyl 1,4-benzenedicarboxylate to afford the cis isomer (*c*-BN) in various solvents ranging from nonpolar benzene to polar acetonitrile.2,3) In a previous paper we demonstrated that the precursor of *t*-BN isomerization in acetonitrile is the olefin triplet arising from intersystem crossing of a singlet radical pair consisting of a *t*-BN cation radical and an acceptor anion radical.2) In benzene, however, the quenching was accompanied by emissions ascribable to exciplexes between *t*-BN and the acceptors in the longer wavelength regions, suggesting that the isomerization in nonpolar solvents proceeds through the olefin triplet generated from the exciplexes.3) In order to clarify the reaction intermediates and their contribution to the isomerization, we employed laser flash photolyses (LFP) and external magnetic field effects (MFE) on the isomerization quantum yield on steady irradiation in various solvents, since LFP can detect directly the intermediates and MFE can be used as a diagnostic tool for elucidating the role of radical pairs in electron transfer reactions.2)

Irradiation of *t*-BN (0.01 mol dm^{-3}) at 313 nm in various solvents afforded *c*-BN with varying quantum yields ($\phi_{t\rightarrow c}{}^0$), as shown in Table 1. The isomerization was assumed to proceed mainly on the singlet manifold since the quantum yield was not affected by triplet quenchers such as ferrocene.2,3) In the presence of *p*-dicyanobenzene (*p*-DCB) as an electron acceptor, the quantum yield ($\phi_{t\rightarrow c}$) decreased remarkably in propionitrile and acetonitrile, but increased noticeably in benzene, chloroform, and THF, with increasing acceptor concentration to approach the limiting quantum yields ($\phi_{t\rightarrow c}{}^{\infty}$), as summarized in Table 1, where K_{SV} (=$k_q\tau^0$) represents the Stern-Volmer constant for the quenching of the excited singlet *t*-BN by a quencher (Q). Since *t*-BN fluorescence was effectively quenched by *p*-DCB (Table 1) and no ground-state interactions between the reactants were detected by absorption spectroscopy, one can express $\phi_{t \to c}$ as

$$\phi_{t \to c} = \beta + (\alpha - \beta)/(1 + K_{SV}[Q]), \qquad (1)$$

by assuming that the isomerization takes place both without interaction,

$$^1t\text{-BN}^* \longrightarrow \alpha\, c\text{-BN} + (1-\alpha)\, t\text{-BN} \qquad (\text{rate } 1/\tau^0) \qquad (2)$$

and with interaction with the quencher Q.

$$^1t\text{-BN}^* + Q \longrightarrow \beta\, c\text{-BN} + (1-\beta)\, t\text{-BN} + Q \qquad (\text{rate } k_q[Q]) \qquad (3)$$

α and β are equal to $\phi_{t \to c}{}^0$ and $\phi_{t \to c}{}^\infty$, respectively.

The transient absorption spectra were measured by irradiating *t*-BN (3×10^{-3} mol dm^{-3}) with 337-nm laser pulses in the presence of *p*-DCB (5×10^{-2} mol dm^{-3}) in deaerated solutions, as shown in Figs. 1a-c. The sample concentrations were controlled so that more than 90% of the excited singlet *t*-BN was quenched by the acceptor. In chloroform (Fig. 1a) a broad band appeared around 700 nm and decayed in the shorter time range. The decay of this band was accompanied by build-up of a band around 400 nm. The former absorption is ascribable to the exciplex of *t*-BN with *p*-DCB since its lifetime (31 ns) is in agreement with that of the exciplex emission (30 ns). The latter band can be ascribed to *t*-BN triplets by comparison with the spectrum measured independently.5) Similar transient absorption spectra were observed in benzene.

The transient absorption spectrum of the *t*-BN/*p*-DCB system in acetonitrile was reported previously.2) The bands due to *p*-DCB anion (*p*-DCB$^{-\cdot}$) and *t*-BN cation radicals (*t*-BN$^{+\cdot}$) appear around 340 and 600–750 nm, respectively (Fig. 1c). The bands around 400–500 nm are due to both ionic species.2) The olefin cation radical, *t*-BN$^{+\cdot}$, was similarly detected in dichloromethane (600–750 nm, Fig. 1b) and 1,2-dichloroethane. These observations show unambiguously that photoinduced electron transfer takes place between the excited singlet *t*-BN and the ground-state electron acceptor in polar solvents such as acetonitrile and dichloromethane; however, in nonpolar solvents such as benzene and chloroform no ionic species were generated.

Deaerated solutions (3 ml) of *t*-BN (2×10^{-4} mol dm^{-3}) and *p*-DCB (5×10^{-2} mol dm^{-3}) in various solvents were irradiated for 10–20 min with filtered light ($\lambda \geq 330$ nm) from a 300-W xenon lamp at ambient temperature. The sample solutions were examined after irradiation using an HPLC apparatus to determine the concentrations of

Table 1. Isomerization quantum yields of *t*-BN in the absence ($\phi_{t \to c}{}^0$) and presence of *p*-DCB ($\phi_{t \to c}{}^\infty$) and the asymptotic $\eta(H)/\eta(0)$ values [$\eta(H)^\infty/\eta(0)$] at the high magnetic field in isomerization of *t*-BN in the presence of *p*-DCB in solvents with varying dielectric constants (ε)

Solvent	ε	K_{SV}	$\phi_{t \to c}{}^0$	$\phi_{t \to c}{}^\infty$	$\eta(H)^\infty/\eta(0)$
Benzene	2.28	540	0.13	0.23	≈1
Chloroform	4.81	200	0.14	0.29	≈0.98
Tetrahydrofuran	7.58	560	0.13	0.20	≈0.90
Dichloromethane	8.93	400	0.19	0.18	≈0.87
1,2-Dichloroethane	10.4	230	0.19	0.14	≈0.84
Propionitrile	27.2	690	0.15	0.05	≈0.79
Acetonitrile	37.5	870	0.14	0.04	≈0.67

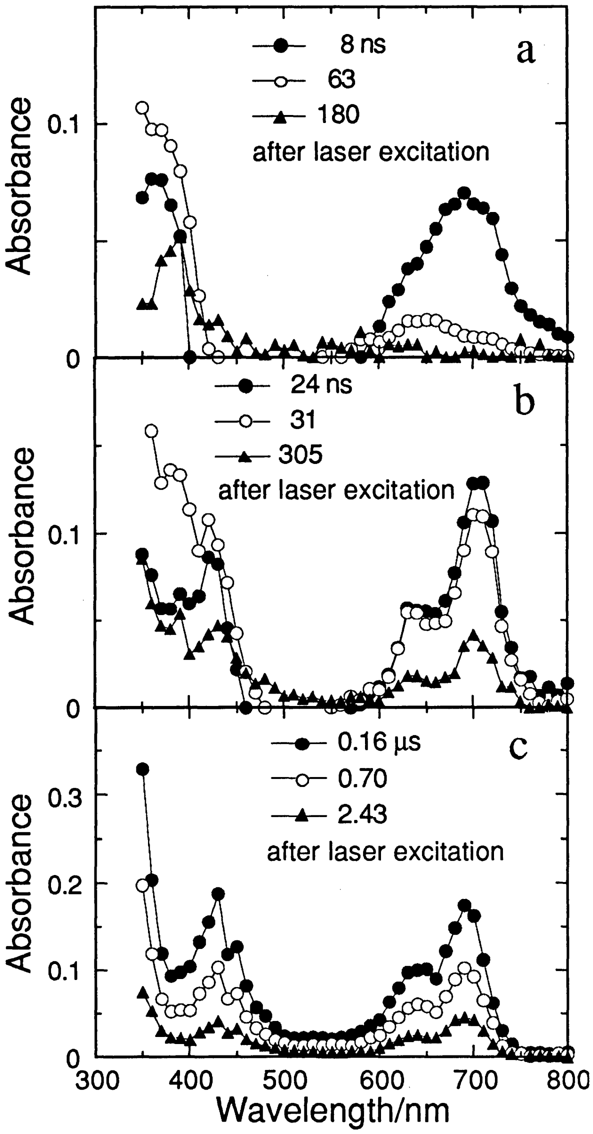


Fig. 1. Transient Absorption spectra observed on excitation of *t*-BN in the presence of *p*-DCB in chloroform (a), 1,2-dichloromethane (b), and acetonitrile (c).

c-BN produced. Under these irradiation conditions the light was absorbed only by *t*-BN; *p*-DCB and *c*-BN formed were not practically excited, and the conversion was controlled at 6–8%. The yields of *c*-BN at various applied magnetic fields [$\eta(H)/\eta(0)$] relative to that at the zero magnetic field strength are plotted in Fig. 2. This figure shows that the relative yields of *c*-BN are reduced, except for benzene as solvent, at the field strengths lower than 1 kG (=0.1 T) and reached nearly constant values in the higher strength region. The effect of magnetic field on isomerization quantum yield arises from the hyperfine interaction in radical pairs.[2] The asymptotic $\eta(H)/\eta(0)$ values [$\eta(H)^{\infty}/\eta(0)$] estimated from Fig. 2 are also summarized in Table 1.

The isomerization mechanism in nonpolar and polar solvents can be described by Scheme 1, where the olefin triplet is the key intermediate.[2] In the *t*-BN/*p*-DCB system the largest magnetic field effect was observed in acetonitrile, and the effect was reduced in the order of acetonitrile, propionitrile, 1,2-dichloroethane, dichloromethane, THF, chloroform, and benzene. In benzene, neither magnetic field effect was observed, nor radical ions were detected in laser flash photolysis, though the *t*-BN fluorescence was effectively quenched and a weak exciplex emission was detected.

It can be reasonably assumed that the isomerization proceeds exclusively through radical ions in acetonitrile;[2] no exciplex emission was detected in this solvent. Accordingly, the asymptotic values, $\eta(H)^{\infty}/\eta(0)$, for various solvents relative to that for acetonitrile correspond to contributions of the ionic intermediates to the isomerization in the respective solvents. Figure 3 shows plots of the total quantum yields for isomerization ($\phi_{t\rightarrow c}{}^{\infty}$) and quantum yields due to ionic intermediates ($\phi_{t\rightarrow c}{}^{ion}$) estimated using the asymptotic values [$\phi_{t\rightarrow c}{}^{ion} = \phi_{t\rightarrow c}{}^{\infty}\cdot(1 - \eta(H)^{\infty}/\eta(0)$ for a solvent$)/(1 - \eta(H)^{\infty}/\eta(0)$ for acetonitrile$)$], and indicates that the isomerization or triplet formation from the interaction of the olefin and acceptor is more efficient through exciplexes than through ion radicals and the maximum efficiency appears at an dielectric constant, ε=4.8 (chloroform). The contribution of radical ions to the total quantum yield decreases with decreasing polarity of solvents but the isomerization due to radical ions reaches a maximum value at a medium ε value of 8.9 (dichloroethane). It can be concluded that the isomerization proceeds through *t*-BN triplets generated from the interactions of *t*-BN singlets with the acceptors,

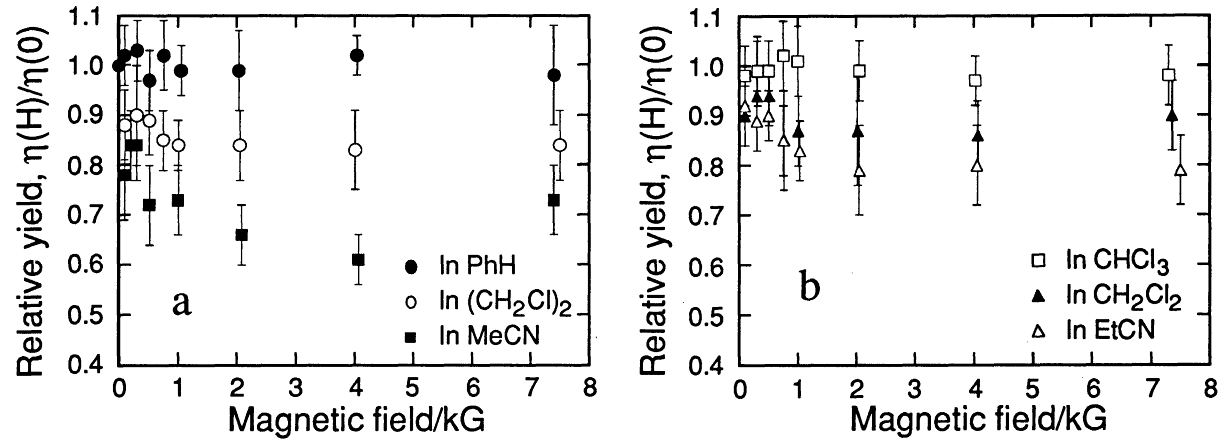
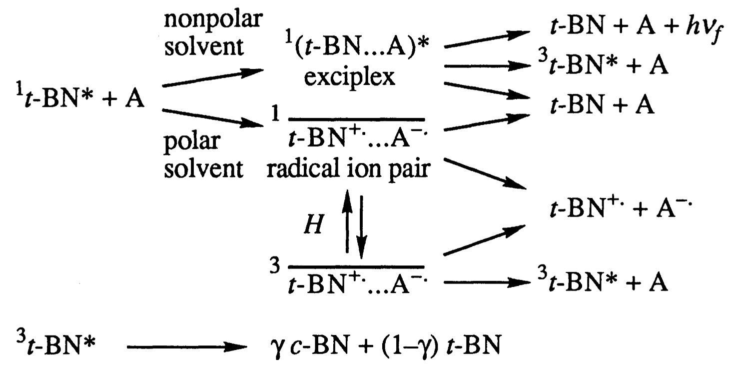


Fig. 2. Plots of relative yields of *c*-BN at magnetic fields of varying intensity.



Scheme 1.

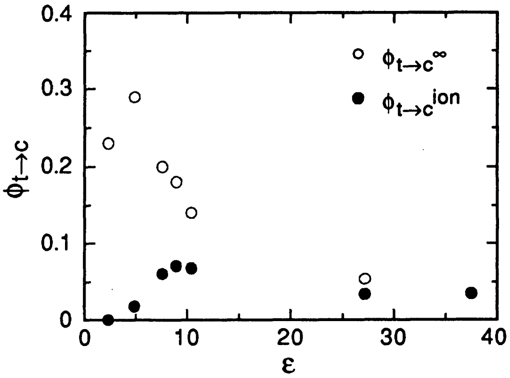


Fig. 3. Contribution of ionic intermediates (•) to the isomerization of *t*-BN in the presence of *p*-DCB (o) in various solvents.

and that the efficiency of triplet formation decreases with increasing polarity of the solvent by switching of the precursors of *t*-BN triplets from exciplexes to radical ion pairs.

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