Solvent Dependence of Magnetic Field Effects upon Photoisomerization of 2-(3,3-Dimethyl-1-butenyl)naphthalene in the Presence of Electron Acceptors

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The efficiency of isomerization of *trans*-2-(3,3-dimethyl-1-butenyl)naphthalene (*t*-BN) in the presence of electron acceptors was reduced by an applied magnetic field in polar solvents such as acetonitrile. This effect together with laser flash photolysis studies indicates that the precursor of isomerization is the BN triplet arising from intersystem crossing of a singlet radical pair consisting of a *t*-BN cation and an acceptor anion. The external magnetic field effect as well as laser flash photolysis was employed to estimate the contribution of ion radical pairs to the isomerization of *t*-BN in the presence of *p*-dicyanobenzene in various solvents. The *t*-BN triplet was produced most efficiently almost through an exciplex in chloroform ($\varepsilon=4.8$) among the employed solvents.

Photoinduced electron-transfer reactions have recently been receiving much attention[1—5] and some reports have appeared on the photoisomerization of olefins induced by electron transfer.[6—18] Electron-accepting sensitizers such as cyanoaromatics (singlet), quinones (triplet), and triphenylpyrylium salts (singlet and triplet) are frequently used to generate olefin cation radicals, which undergo isomerization unimolecularly or bimolecularly (through addition and elimination), or give olefin triplets through reverse electron transfer with sensitizer anion radicals; the olefin triplets are well-known intermediates for isomerization.

Direct observation of intermediates by laser flash photolysis (LFP) and measurements of magnetic field effects (MFE) upon reaction efficiency under steady illumination are diagnostic tools for elucidating the mechanisms for electron-transfer induced isomerization of aromatic olefins.[19—23] For example, MFE studies showed that 9,10-dicyanoanthracene (DCA)-sensitized isomerization of stilbene proceeds through the stilbene cation radical[15] and that the key intermediate for pyrene-sensitized isomerization of *trans*-stilbene[21] is the olefin triplets generated by reverse electron transfer between initially produced ion radicals; however, the reports on the magnetic field effect upon photoisomerization are limited.[7,12,21,23,24]

Quenching of olefins in excited states with electron acceptors in polar solvents may generate radical pairs which are precursors of geometrical isomerization of the olefins. We have found that 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 terephthalate (MT) to afford the cis isomer (*c*-BN) in various solvents ranging from nonpolar benzene to polar acetonitrile (Chart 1).[13] We have demonstrated that the precursor of *t*-BN isomerization in acetonitrile is the olefin triplet arising from intersystem crossing of a singlet radical pair.[12] In benzene, however, the quenching was accompanied by emissions ascribable to exciplexes between *t*-BN and the acceptors at the longer wavelength regions, suggesting that the isomerization in nonpolar solvents proceeds through the olefin triplet generated from the exciplexes.[13]

In order to clarify the reaction intermediates and their contribution to the isomerization in various solvents, we employed laser flash photolyses (LFP) and external magnetic field effects (MFE) on the isomerization quantum yield on steady irradiation.[25]

Experimental

A mixture of *c*-BN and *t*-BN was synthesized by the condensation of 2,2-dimethylpropanal with the ylide prepared from 2-naphthylmethyltriphenylphosphonium bromide and butyllithium in ether. Pure *c*-BN and *t*-BN were separated by silica-gel column chromatography. *t*-BN was crystallized from ethanol. Dimethyl terephthalate-d_{10} (MT-d_{10}) was prepared by refluxing terephthalic acid-d_4 in methanol-d_3 in the presence of sulfuric acid. MT and MT-d_{10} were crystallized from ethanol. *o*-, *m*-, and *p*-DCB were also crystallized from ethanol. Tetrahydrofuran and propiononitrile were distilled before use. Benzene, chloroform, dichloromethane (Dotite Luminazol), 1,2-dichloroethane (Dotite Spectrozol), and acetonitrile (Merck) were used as received. All sample solutions were deaerated by several freeze-pump-thaw cycles or bubbling with argon before irradiation.

Absorption spectra were measured on a U-3200 Hitachi

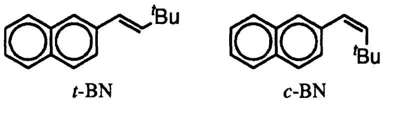

Chart 1.

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or a JASCO 660 spectrophotometer and fluorescence spectra were measured on a Hitachi MPF-2A or a Hitachi F-4000 spectrofluorimeter. Fluorescence lifetimes were measured with a Horiba NAES-1100 time-resolved spectrofluorometer (single photon counting). The excitation light was obtained from a hydrogen-arc lamp through a 330-nm band pass filter and the emission was collected and passed through a monochromator (Horiba SGM-111).

Laser flash photolyses were performed with 308-nm laser pulses from an excimer laser (Lambda Physik EMG-50E) as an exciting light source and a xenon flash lamp (EG&G FX-200) as a probe light source, or with 337-nm laser pulses from a nitrogen laser (Lambda Physik EMG-101) as an exciting light source and a pulsed xenon arc (Wacom KXL-151) as a monitoring light source. The details of the apparatus for laser flash photolysis have been described elsewhere.[23,26)]

Quantum yields for isomerization were measured by irradiating sample solutions with 313-nm light isolated from a 400-W high-pressure mercury lamp through a Toshiba UV-D33S glass filter and a K_2CrO_4–Na_2CO_3 filter solution. Potassium tris(oxalato)ferrate(III) actinometry was used for determining light intensity.

For the measurements of magnetic field effects, sample solutions in quartz cells were placed between the pole pieces of an electromagnet (Tokin SEE-9). The magnetic field strength was controlled by a current-regulated power supply. The residual magnetic field was canceled by a counter current to be lower than 0.3 mT for the measurements at the zero magnetic field strength. Irradiations were made with UV light from an Ushio 500-W xenon lamp filtered by a combination of Toshiba glass filters (UV-25, UV-31, and UV-D33S) or from a 300-W xenon lamp (ILC LX-300F) filtered by a combination of glass filters (Toshiba UV-25, UV-32, UV-D33S, and IRA-25S), which correspond to the excitation of *t*-BN. A high-performance liquid chromatograph (Waters 590 or 600 Multisolvent Delivery System) equipped with an LC spectrophotometer (Waters 481 or 490 Programmable Multiwavelength Detector) was used for analyses of reaction mixtures with a Zorbax-ODS column.

Results and Discussion

Isomerization Quantum Yields. 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. In the presence of electron acceptors such as *p*-DCB and MT, the quantum yield ($\Phi_{t\rightarrow c}$) decreased remarkably in acetonitrile, but increased noticeably in benzene, with increasing acceptor concentration to approach the limiting quantum yields ($\Phi_{t\rightarrow c}{}^{\infty}$), as shown in Fig. 1. The $\Phi_{t\rightarrow c}{}^{\infty}$ values for *t*-BN in the presence of *o*-, *m*-, *p*-DCB, and MT in various solvents are 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), as determined by *t*-BN fluorescence quenching; $\Phi_{t\rightarrow c}$ in the presence of *p*-DCB decreased also in propiononitrile, but increased in chloroform and THF, with increasing *p*-DCB concentration. Since *t*-BN fluorescence (lifetime τ_0=63 ns in acetonitrile) was effectively quenched by the acceptors employed (Table 1; rate constants $k_q=1.4\times10^{10}$ and 1.2×10^{10} mol^{-1} dm^3 s^{-1} for *p*-DCB and MT, respectively, in acetonitrile) and no ground-state interactions between the reactants were detected by absorption spectroscopy, $\Phi_{t\rightarrow c}$ can be expressed as

Table 1. Isomerization Quantum Yields of *t*-BN in the Absence and Presence of Electron Acceptors in Various Solvents

Solvent	Acceptor	ε[a)]	K_{SV}[b)]	$\Phi_{t\rightarrow c}{}^{0}$[c)]	$\Phi_{t\rightarrow c}{}^{\infty}$[d)]
Benzene	MT	2.28	370	0.13	0.17
	o-DCB		470		0.16
	m-DCB		71		0.11
	p-DCB		540		0.23
Chloroform	*p*-DCB	4.81	200	0.14	0.29
Tetrahydrofuran	*p*-DCB	7.58	560	0.13	0.20
Dichloromethane	*p*-DCB	8.93	400	0.19	0.18
1,2-Dichloroethane	*p*-DCB	10.4	230	0.19	0.14
Propiononitrile	*p*-DCB	27.2	690	0.15	0.05
Acetonitrile	MT	37.5	780	0.14	0.02
	o-DCB		830		0.05
	m-DCB		540		0.06
	p-DCB		870		0.04

a) Dielectric constants of the solvents. b) Stern-Volmer constants for quenching of the *t*-BN excited singlet by acceptors. c) Isomerization quantum yields of *t*-BN in the absence of acceptors. d) Isomerization quantum yields of *t*-BN in the presence of an infinitely high concentration of acceptors.

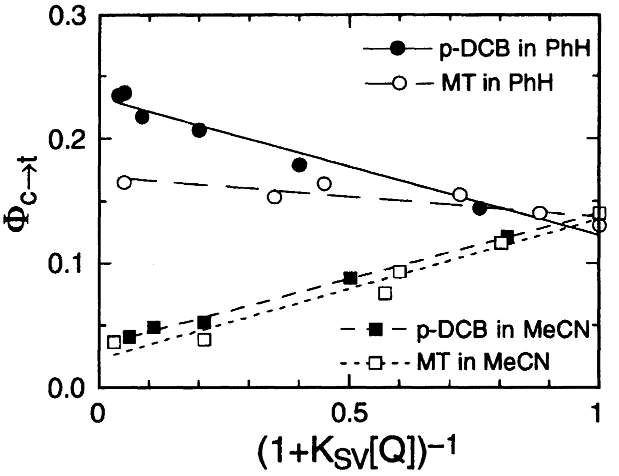


Fig. 1. Acceptor concentration dependence of the isomerization quantum yield.

$$\Phi_{t\rightarrow c}=\beta+(\alpha-\beta)/(1+K_{SV}[Q]), \tag{1}$$

by assuming that the isomerization takes place both without interaction,

$${}^1t\text{-BN}^* \xrightarrow{1/\tau_0} \alpha c\text{-BN}+(1-\alpha)t\text{-BN}, \tag{2}$$

and with interaction,

$${}^1t\text{-BN}^*+\text{Q} \xrightarrow{k_q} \beta c\text{-BN}+(1-\beta)t\text{-BN}+\text{Q}, \tag{3}$$

with the quencher Q. α and β are equal to $\Phi_{t\to c}{}^0$ and $\Phi_{t\to c}{}^{\infty}$, respectively.

The interaction of the excited singlet *t*-BN with the acceptors results in the formation of exciplexes in nonpolar solvents such as benzene and chloroform, as confirmed by emissions in the longer wavelength region. In polar solvents, however, an electron transfer from the *t*-BN singlet to the acceptors is assumed to be a favorable process from energetic considerations based on Rehm–Weller's equation,[27)]

$$\Delta G^\circ = E_{\mathrm{ox}} - E_{\mathrm{red}} - e_0^2/a\varepsilon - E_{0,0}, \qquad (4)$$

where E_{ox} and E_{red} indicate the oxidation potential of *t*-BN (1.55 V vs. SCE) and the reduction potential of the acceptor (−1.64 for MT, −1.62 for *o*-DCB, −1.60 for *p*-DCB, and −1.92 V (peak potential) for *m*-DCB), respectively, as determined in acetonitrile, $E_{0,0}$ is the singlet excitation energy of *t*-BN (3.63 eV, estimated from its fluorescence spectrum), and $e_0^2/a\varepsilon$ is a coulombic term (0.06 eV in acetonitrile).

Transient Absorption Spectra. 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 Fig. 2a—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. 2a) a broad band appeared around 700 nm and decayed in the shorter time range. The decay of this band was accompanied by the 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 is identical with that of the exciplex emission. The latter band can be ascribed to *t*-BN triplets by comparison with the spectrum measured independently.[28)] Similar transient absorption spectra were observed in benzene.

The transient absorption spectra of the *t*-BN/*p*-DCB system in acetonitrile were measured under similar conditions. The bands due to *p*-DCB anion radicals (p-DCB$^{-\bullet}$)[29)] and *t*-BN cation radicals (t-BN$^{+\bullet}$)[30)] appeared around 340 and 600—750 nm, respectively (Fig. 2c). The bands around 400—500 nm were identified as the superposition of absorptions due to both ionic species. The transient absorption spectra of *t*-BN in acetonitrile in the presence of MT, *o*-DCB, and *m*-DCB were ascribed to t-BN$^{+\bullet}$ and the corresponding acceptor anion radicals.[31)] The cation radical t-BN$^{+\bullet}$ was also detected in dichloromethane (600—750 nm, Fig. 2b) and 1,2-dichloroethane in the presence of *p*-DCB.

These observations show unambiguously that photoinduced electron transfer takes place between the excited singlet *t*-BN and the ground-state electron acceptors in polar solvents such as acetonitrile and dichloromethane; however, in nonpolar solvents such as benzene and chloroform no ionic species were detected.

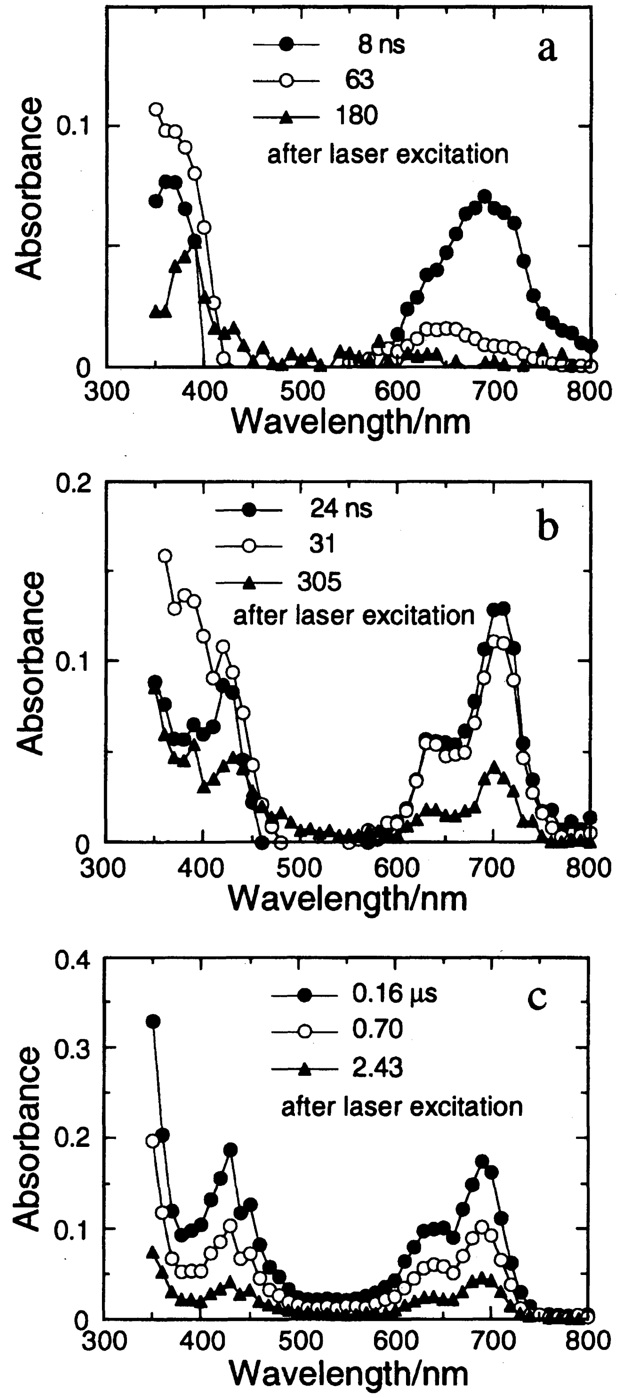


Fig. 2. Transient absorption spectra observed on excitation of *t*-BN in the presence of *p*-DCB in chloroform (a), 1,2-dichloromethane (b), and acetonitrile (c).

Magnetic Field Effects in Acetonitrile. Deaerated solutions (5 ml) of *t*-BN (2×10^{-4} mol dm^{-3}) and *p*-DCB (9×10^{-3} mol dm^{-3}) in acetonitrile were irradiated for 15 min with filtered light ($\lambda \geq 310$ nm) from a 500-W xenon lamp at ambient temperature in the applied magnetic field with varying strengths (0—1.1 T). The sample solutions were examined before and after irradiation using a spectrophotometer and an HPLC apparatus to determine the initial and final concentrations of *t*-BN. The disappearance yields of *t*-BN ($\Phi(H)/\Phi(0)$) at various applied magnetic fields relative to that at the zero magnetic field strength are plotted in Fig. 3a. Under these irradiation conditions the light was absorbed only by *t*-BN; *p*-DCB and *c*-BN formed were not practically excited. The reaction was attained to 40—50% *t*-BN conversion, but side products were negligible, providing good reliability in determining the relative disappearance yields. Figure 3a clearly shows that the relative yield is reduced at the field strengths lower than 0.1 T and reached a nearly constant value (ca. 0.86) at the higher strength region.

A similar magnetic field effect was observed on irradiation of deaerated acetonitrile solutions of *t*-BN and MT with the filtered light. The reaction efficiency of *t*-BN decreased similarly with increasing magnetic field strength and was saturated at a nearly constant value ($\Phi(H)/\Phi(0)\approx0.94$, Fig. 3a). In this system, however, the effect is smaller than that observed in the *t*-BN/DCB system. A similar but much smaller magnetic field effect (at most $\Phi(H)/\Phi(0)\approx0.97$, Fig. 3b) was observed when *t*-BN was irradiated with perdeuterated MT (MT-d_{10}) in acetonitrile under similar conditions to those employed for the *t*-BN/MT system.

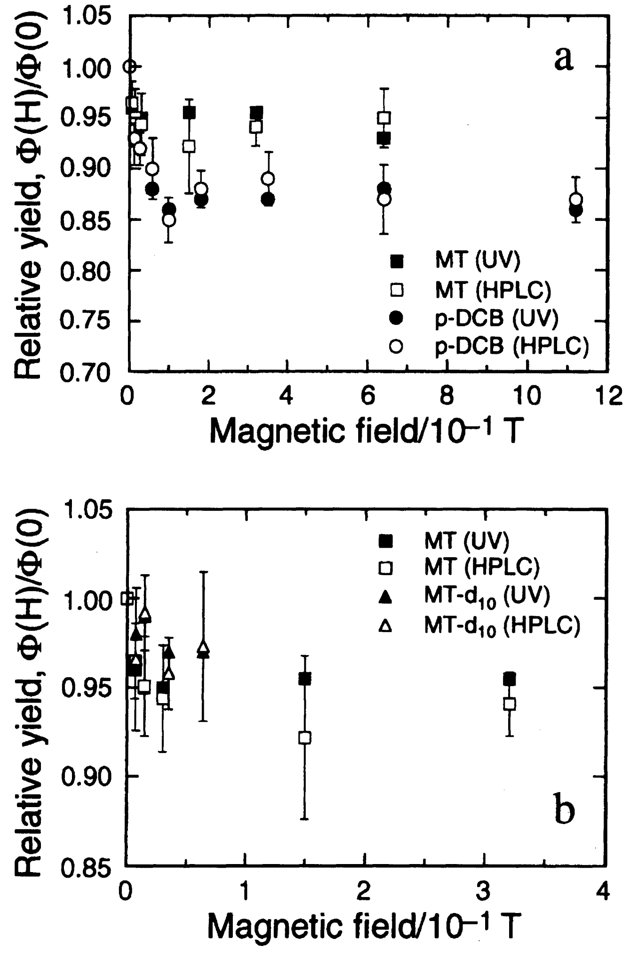


Fig. 3. Relative disappearance yields of *t*-BN in the presence of acceptors at various magnetic field strengths.

In another series of experiments deaerated solutions (3 ml) of *t*-BN (2×10^{-4} mol dm^{-3}) and DCB's (5×10^{-2} mol dm^{-3}) in acetonitrile were irradiated for 10—20 min with filtered light ($\lambda\geq330$ nm) from a 300-W xenon lamp at ambient temperature. The concentrations of *c*-BN produced were determined after irradiation using an HPLC apparatus. The conversion was controlled at 6—8%. The asymptotic $\Phi(H)/\Phi(0)$ values $[\Phi(\infty)/\Phi(0)]$ are listed in Table 2.

The hyperfine interaction B_i between the nuclear spins I_k and the unpaired electron spin in each component radical is governed by the isotropic hyperfine coupling constants, a_{ik}, and can be expressed by[32,33]

$$B_i = \left(\sum a_{ik}{}^2 I_k(I_k+1)\right)^{1/2}. \tag{5}$$

The B_i values for the ionic species were computed by using reported a_{ik} for *o*-,[34,35] *m*-,[35] *p*-DCB$^{-\bullet}$,[34] and MT$^{-\bullet}$,[36,37] and a_{ik} estimated for *t*-BN$^{+\bullet}$ according to McConnell's equation ($a_k^{\mathrm{H}}=22.5\times10^{-4}\rho_k$ T)[38,39] where the odd-electron densities, ρ_k, were obtained from LCAO MO calculations for 2-vinylnaphthalene cation radical[40] (a small contribution from the *t*-butyl group was neglected): $B(p\text{-DCB}^{-\bullet})=4.7\times10^{-4}$, $B(o\text{-DCB}^{-\bullet})=6.3\times10^{-4}$, $B(m\text{-DCB}^{-\bullet})=10.4\times10^{-4}$, $B(\mathrm{MT}^{-\bullet})=3.2\times10^{-4}$, $B(\text{MT-}d_{10}^{-\bullet})=0.80\times10^{-4}$, and $B(t\text{-BN}^{+\bullet})=6.9\times10^{-4}$ T.

Comparison of the computed B_i values with the magnitude of the magnetic field effect observed for the above acceptors indicates that the hyperfine interaction plays a major role in the present case. The $B_{1/2}$ values defined by[33]

$$\Phi(B_{1/2}) = \frac{1}{2}[\Phi(0) - \Phi(\infty)] \tag{6}$$

were estimated as 11—18×10^{-4} T by substituting the above B_i values into

$$B_{1/2} = 2(B_1^2 + B_2^2)/(B_1 + B_2). \tag{7}$$

This is consistent with the facts that the isomerization yield was decreased by application of remarkably low

Table 2. Asymptotic $\Phi(H)/\Phi(0)$ Values $[\Phi(\infty)/\Phi(0)]$ at the High Magnetic Field in Isomerization of *t*-BN in the Presence of Electron Acceptors in Various Solvents

Solvent	Acceptor	$\Phi(\infty)/\Phi(0)$
Benzene	*p*-DCB	≈1
Chloroform	*p*-DCB	≈0.98
Tetrahydrofuran	*p*-DCB	≈0.90
Dichloromethane	*p*-DCB	≈0.87
1,2-Dichloroethane	*p*-DCB	≈0.84
Propiononitrile	*p*-DCB	≈0.79
Acetonitrile	*p*-DCB	≈0.67
Acetonitrile	*o*-DCB	≈0.67
Acetonitrile	*m*-DCB	≈0.53

magnetic fields and that the effect was saturated at higher fields.

Magnetic Field Effects in Various Solvents. 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 ($\lambda\geq330$ nm) from a 300-W xenon lamp at ambient temperature. The yields of *c*-BN [$\Phi(H)/\Phi(0)$] at various applied magnetic fields relative to that at the zero magnetic field strength are plotted in Fig. 4. This figure shows that the relative yields of *c*-BN are reduced, except for the case of benzene as solvent, at the field strengths lower than 0.1 T and reach nearly constant values at the higher strength region. The effect of magnetic field on isomerization quantum yield arises from the hyperfine interaction in radical pairs. The $\Phi(\infty)/\Phi(0)$ values estimated from Fig. 4 are summarized in Table 2.

Intermediates and Their Contribution to Isomerization. In the presence of electron acceptors in polar solvents such as acetonitrile the isomerization quantum yield $\Phi_{t\rightarrow c}$ is lower than that in their absence, but still remains at a finite value even when the excited singlet *t*-BN are completely quenched. The laser flash photolysis indicates that the quenching of the excited singlet *t*-BN by DCB's and MT affords singlet radical pairs consisting of a *t*-BN cation and an acceptor anion (Scheme 1, in polar solvent). These radical pairs undergo either reverse electron transfer to give the starting materials or intersystem crossing into triplet radical pairs. The reverse electron transfer in the triplet pairs generates the triplet state of *t*-BN, a rational precursor of isomerization. The triplet *t*-BN decays to ground-state *c*-BN and *t*-BN in a nearly 1 : 1 ratio ($\gamma\approx0.5$).[28,41] The intersystem crossing between singlet S_0 and triplet T_+, T_- states induced by the hyperfine interaction is appreciably diminished in the presence of high magnetic fields, thereby attenuating the quantum yield of the triplet radical pair. The population of triplet *t*-BN is exothermic since the triplet energy of *t*-BN and the energy of the radical pair can be estimated as 52[28] and 76—78 kcal mol^{-1} (from the difference between the measured electrochemical potentials of *t*-BN ($E(\mathrm{D}^{+\bullet}/\mathrm{D})$) and acceptors ($E(\mathrm{A}/\mathrm{A}^{-\bullet})$), respectively. The possibility of isomerization from *t*-BN$^{+\bullet}$ can be ruled out since *trans*-stilbene cation radicals are reported to be more stable than, and inefficient in isomerization to, the cis cation radicals.[9] Thus, the isomerization mechanism in polar solvents can be described by Scheme 1, where the olefin triplet is the key intermediate.

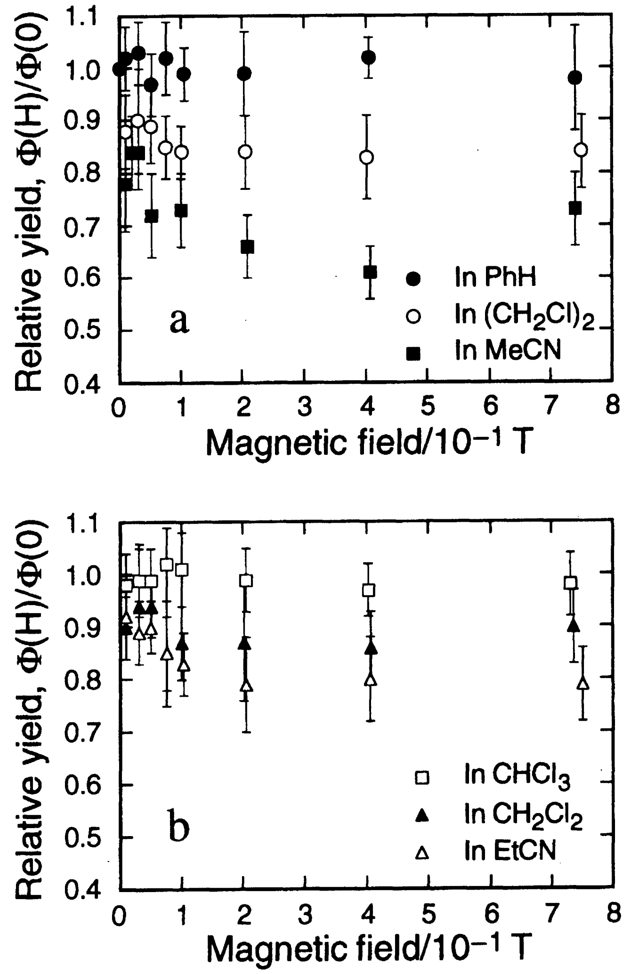
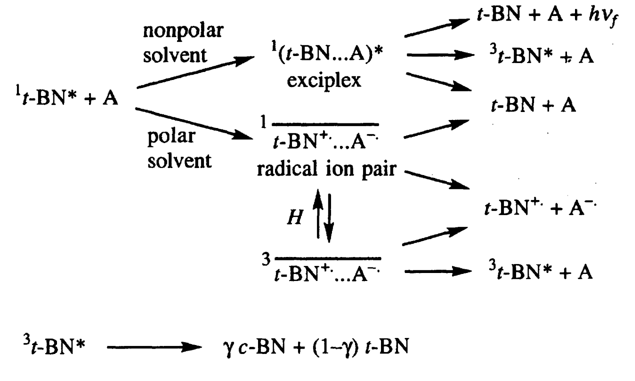


Fig. 4. Relative yields of *c*-BN formation in various solvents in the presence of *p*-DCB at varying magnetic field strengths.

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, propiononitrile, 1,2-dichloroethane, dichloromethane, 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. Thus, in nonpolar solvents the isomerization is assumed to proceed through *t*-BN triplets generated from collapse of the exciplex between *t*-BN and the acceptor (Scheme 1, in nonpolar solvent).

It can be reasonably assumed that the isomerization proceeds exclusively through radical ions in acetonitrile. Accordingly, the asymptotic $\Phi(H)/\Phi(0)$



Scheme 1.

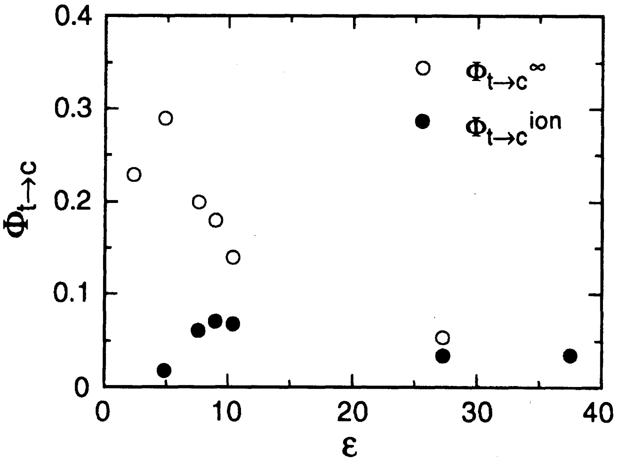


Fig. 5. Contribution of ionic intermediates (●) to the isomerization of *t*-BN in the presence of *p*-DCB (○) in various solvents.

values at the high magnetic field in various solvents, $[\Phi(\infty)/\Phi(0)]_{\text{solv}}$, relative to that in acetonitrile, $[\Phi(\infty)/\Phi(0)]_{\text{MeCN}}$, correspond to contributions of the ionic intermediates to the isomerization in the respective solvents. Figure 5 shows plots of the total quantum yields for isomerization ($\Phi_{t\to c}{}^{\infty}$) and quantum yields due to ionic intermediates ($\Phi_{t\to c}{}^{\text{ion}}$) estimated using the asymptotic values, i.e., $\Phi_{t\to c}{}^{\text{ion}} = \Phi_{t\to c}{}^{\infty} \times [\Phi(\infty)/\Phi(0)]_{\text{solv}}/[\Phi(\infty)/\Phi(0)]_{\text{MeCN}}$, as a function of solvent polarity (ε). These results show that the contribution of radical ions decreases with decreasing polarity of solvents, but that $\Phi_{t\to c}{}^{\text{ion}}$ reaches a maximum value at a medium dielectric constant (ε 8.9) of dichloromethane. Taking into account the fact that the isomerization quantum yield of *t*-BN in the presence of electron acceptors decreases, after the maximum in chloroform (ε 4.8), with increasing solvent polarity (Table 1 and Fig. 5), it can be concluded that the isomerization proceeds through *t*-BN triplets generated from the interactions of *t*-BN singlets with the acceptors, 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 ion radical pairs.

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