Isotropic and Anisotropic Magnetic Field Effect on the Exciplex between *all-s-trans*-1,6-Diphenylhexa-1,3,5-triene and 1,4-Dicyanobenzene[†]

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The exciplex between *all-s-trans*-1,6-diphenylhexa-1,3,5-triene and 1,4-dicyanobenzene exhibits both isotropic and anisotropic magnetic field effects (MFEs). The exciplex luminescence increases in the presence of a magnetic field. The maximum MFE occurs at the dielectric constant $\epsilon \approx 10$, which confirms the importance of the charge-transfer characteristics of the exciplex, as observed previously (Aich, S.; Basu, S. *J. Phys. Chem. A* **1998**, *102*, 722). The wavelength dependence of the field effect proves the existence of two types of charge-transfer complexes with different stoichiometries. The MFE is greater when the excitation light is polarized parallel to the field compared to that with the excitation light polarized perpendicular to the field. This observation signifies the presence of an anisotropic MFE with this exciplex system.

1. Introduction

In recent years, considerable interest has grown up for using the magnetic field effect (MFE) as a tool to understand photochemical[1−10] and photobiological[11,12a] processes involving radical pairs (RPs) or radical ion pairs (RIPs). Some thermal enzymatic reactions are also sensitive to a magnetic field.[12] However, from the energy point of view, the photochemical processes have a greater advantage over the thermal reactions in producing RIPs or RPs and exciplex formation is a very special case among them. The physical requirement for an exciplex to show MFE is inherent in the competition between the spin evolution and diffusion dynamics of RIPs. In the absence of any external magnetic field, the singlet (S) and three triplet states ($T_{\pm}$, T_o) are degenerate, if there is negligible exchange interaction, i.e., $J \approx 0$. The electron−nuclear hyperfine interaction (HFI) promotes intersystem crossing (ISC), resulting in mixing of the spin states. An external magnetic field destroys the degeneracy that reduces the S → $T_{\pm}$ conversion, leading to an increase in geminate recombination and exciplex luminescence.

The earlier studies on different exciplexes, viz., pyrene−*N,N*-dimethylaniline (Py−DMA)[8e,f] and 9-cyanophenanthrene−*trans*-anethole (CNP−AN),[8h] confirmed the necessity of medium dielectric constant (ϵ) to maximize the field effect ($14 < \epsilon < 18$) in aprotic solvents. In alcoholic media it is shifted to a much higher value ($\epsilon_{max.} = 28$ for Py−DMA,[8f,i] $\epsilon_{max.} = 38$ for CNP−AN,[8h] and $\epsilon_{max.} = 26$ for Py−diethylaniline[7a]). The medium dielectric constant maximum was also observed for the system Py(CH$_2$)$_n$DMA, in which the donor and acceptor are linked through a polymethylene chain.[3a] However, the linked system (phenanthrene)(CH$_2$)$_n$DMA was found to show a monotonic increase of MFE with the dielectric constant.[6c] For the unlinked donor−acceptor, there is no such controversy. Aich and Basu explored the effect of degree of charge transfer in exciplex on the dielectric maxima.[9a,b] The exciplex between *N*-ethylcarbazole (ECZ) and 1,4-dicyanobenzene (DCB) shows the maximum field effect at the dielectric constant 9. This much lower value is ascribed to a lesser extent of charge transfer in this exciplex. This novel finding made us curious to search out if any other exciplex is present with a comparable $\epsilon_{max.}$ value.

In the present work, we have studied the MFE on the exciplex between *all-s-trans*-1,6-diphenylhexa-1,3,5-triene (DPH) and DCB. The molecule DPH belongs to a group of compounds α,ω-diphenyl polyenes. Polyenes perform important functions in many photobiological processes, e.g., cis−trans isomerization of retinal in the visual cycle,[13] "energy sink activity" of the carotenoid molecules (complexed with electron donor−acceptor) in photosynthesis.[14] Photosynthetic organisms lacking carotenoids suffer from the "photooxidative killing" in the presence of oxygen and light.[15] The fluorophore DPH is well-known for its wide use in biophysical research as a hydrophobic membrane probe.[16] Internal viscosity of the membrane bilayer is estimated by measurement of fluorescence polarization of DPH or its derivative, viz., (trimethylammonio)diphenylhexatriene. Moreover, DPH forms an exciplex with DCB, as reported by Schael, Küster, and Löhmannsröben.[17] Here, we have attempted to find out whether this exciplex can exhibit MFE like other systems, viz., Py−DMA, ECZ−DCB, etc. It was found earlier that DPH can form an exciplex with DMA that is unusual in the sense that it associates two DMA molecules with one molecule of DPH.[18] This type of 1:2 complex is commonly known as a triplex. The DPH−DMA triplex possesses an attractive feature of showing a rare phenomenon, an anisotropic MFE. This phenomenon was first observed for the photosynthetic reaction center.[19] There is still no other example of an anisotropic MFE in solution. In the DPH−DMA system, the DPH acts as an electron acceptor as DMA donates an electron. It is our primary intention to examine whether the DPH−DCB exciplex can exhibit similar properties in which the DPH is the electron donor molecule.

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2. Experimental Section

Apparatus. Fluorescence spectra were recorded in a Hitachi fluorescence spectrophotometer (model F4010). Fluorescence anisopropy was measured by the same instrument with a polarization accessory. The increase in exciplex luminescence ($\Delta\phi$, where ϕ is the exciplex luminescence in the absence of the magnetic field) was studied using a full wave phase-locked detection system described elsewhere.[9b] The signal-to-noise ratio of this system is 1000:1. The value of $\Delta\phi/\phi\%$ is a measure of the MFE on exciplex luminescence. A three-neck Ubbelohde viscometer was used for measuring the flow time of different cellulose acetate solutions.

Materials. DPH and DCB were purchased from Aldrich, and cellulose acetate (acetate content 53.5−54.5%) was from BDH. The solvents used were spectroscopic grade tetrahydrofuran (THF) ($\epsilon = 7.6$), *N*,*N*-dimethylformamide (DMF) ($\epsilon = 36.7$), benzene (Bz) ($\epsilon = 2.28$), and acetonitrile (ACN) ($\epsilon = 37.5$). All the solutions were deaerated by passing through pure argon before the experiment.

Subtraction of Spectra. Subtraction of spectra (A and B) was done using the formula "A − KB" where the factor K was used to make both the maxima of A and B equal. This subtraction was essential to get the exciplex spectrum because DPH is highly fluorescent with a long tail extending up to 650 nm that makes the exciplex spectrum indistinguishable from the DPH spectrum. For a similar reason, the triplex spectrum was also obtained by subtraction, demonstrated later graphically. In this connection, spectrum B refers to that of the exciplex with a very low concentration of DCB (5 mM). A is the exciplex spectrum in which the triplex contribution is to be determined. This subtraction was done by assuming that at a very low concentration of the DCB, triplex contribution is insignificant.

Measurement of Anisotropic Magnetic Field Effect. The sample chamber of the phase-locked detection system was modified for inclusion of polarizers (Hitachi). The MFE was determined with the excitation light polarized either parallel $[(\Delta\phi/\phi\%)_\parallel]$ or perpendicular $[(\Delta\phi/\phi\%)_\perp]$ to the magnetic field. The magnetic field anisotropy was determined using the formula

$$r_b = \frac{(\Delta\phi/\phi\%)_\parallel - (\Delta\phi/\phi\%)_\perp}{(\Delta\phi/\phi\%)_\parallel + 2(\Delta\phi/\phi\%)_\perp} \qquad (1)$$

Measurement of Viscosity. Viscosities of cellulose acetate solutions were determined by the conventional method using the Poiseuille equation.

3. Results

(a) Fluoresence Measurements. Figure 1a shows the fluorescence spectra of DPH and its quenching with varying concentrations of DCB in Bz. The exciplex spectra of DPH−DCB with the maxima at $\lambda_{max.} \approx 500$ nm are shown in Figure 1b. Similarly, parts a and b of Figure 2S and describe the fluorescence quenching and exciplex spectra in a more polar solvent THF. The exciplex emission maxima exhibit a red shift ($\lambda_{max.} \approx 525$ nm) in THF. The formation of exciplex is encouraged with the increasing concentration of DCB. Figure 3 represents the triplex spectrum with the maximum around 560 nm. Both the exciplex and triplex spectra were obtained using the method of subtraction as discussed in the Experimental Section. This method is demonstrated graphically for the triplex (Figure 3). Table 1 depicts the percentage increase in exciplex and triplex with the increasing concentration of DCB. Figure 4
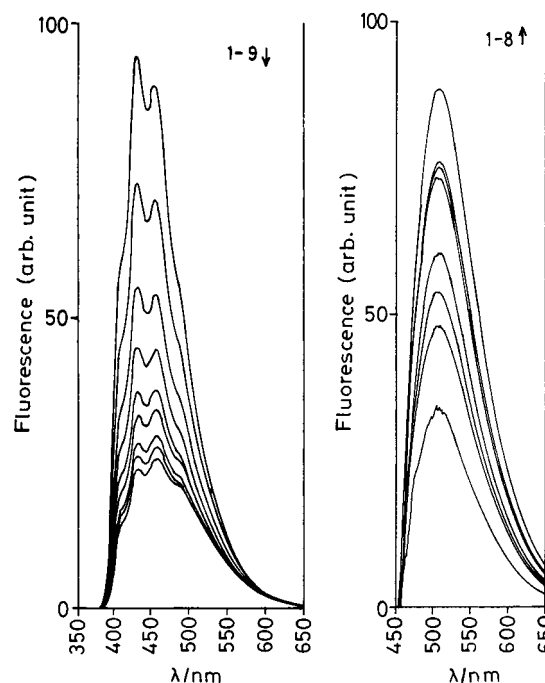

Figure 1. (a) Fluorescence spectra of DPH (0.1 mM) in Bz (1) without DCB and (2−9) with DCB of concentrations (2) 5 mM, (3) 10 mM, (4) 15 mM, (5) 20 mM, (6) 25 mM, (7) 30 mM, (8) 35 mM, (9) 40 mM, excitation wavelength $\lambda_{exc} = 337$ nm. (b) Exciplex fluorescence spectra of DPH−DCB in Bz with DPH concentration 0.1 mM and DCB concentrations (1) 5 mM, (2) 10 mM, (3) 15 mM, (4) 20 mM, (5) 25 mM, (6) 30 mM, (7) 35 mM, (8) 40 mM, $\lambda_{exc} = 337$ nm.
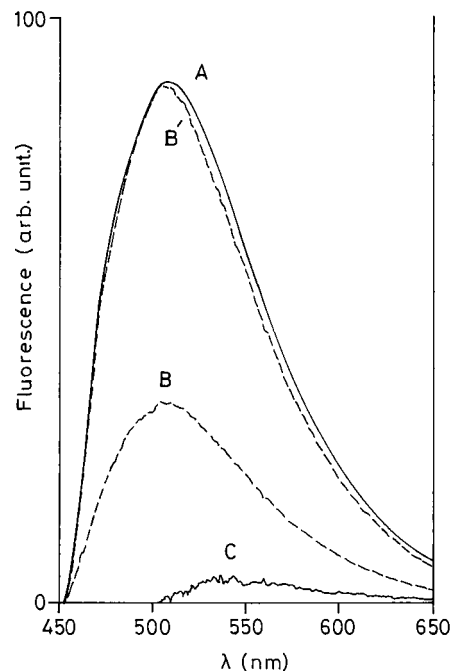

Figure 3. Triplex fluorescence spectrum (C) for DPH−DCB in Bz. The method of subtraction is shown here. The formula is A − KB, where A and B are the exciplex spectra with [DCB] = 40 and 5 mM, respectively. [DPH] = 0.1 mM in both cases, B′ is the exaggerated form of B obtained by multiplying with K, the ratio of the maxima of A and B, and $\lambda_{exc} = 337$ nm.

demonstrates the decrease in exciplex luminescence with the increase in ϵ in binary solvent mixture, viz., THF−DMF and THF−ACN.

(b) Isotropic Magnetic Field Effect. The variation of $\Delta\phi/\phi\%$ of the DPH−DCB system as a function of ϵ is implicated

TABLE 1: Percentage Change in 1:1 and 1:2 Complexes with Concentration of DCB with 0.1 MM DPH in Bz

concn of DCB (mM)	increase[a] in 1:1 and 1:2 complexes (%)	increase[a] in 1:2 complex (%)
30	2.5	17.1
35	3.4	38.8
40	21.2	71.6

[a] % increase is estimated with respect to [DCB] = 25 mM.
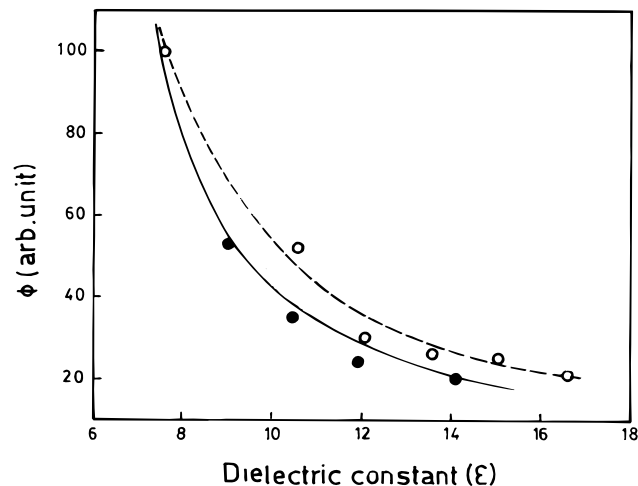

Figure 4. Variation of exciplex luminescence (ϕ) of DPH−DCB with dielectric constant (ϵ) in THF (open circle), THF−DMF (solid line, solid circle), and THF−ACN (dashed line, open circle). [DPH] = 0.1 mM and [DCB] = 40 mM.

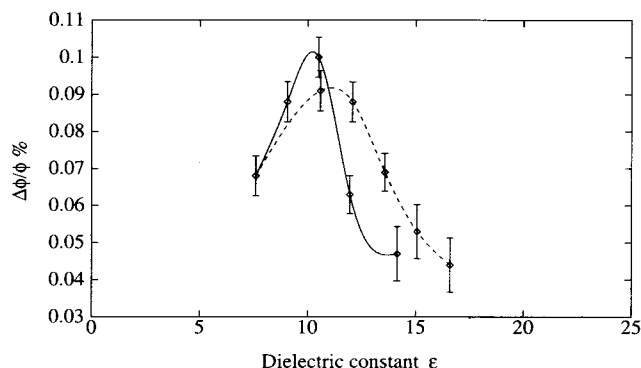**Figure 5.** Dielectric (ϵ) dependence of percentage magnetic field effect ($\Delta\phi/\phi$%) for the DPH−DCB exciplex at the saturating magnetic field (60 G). The solid and dashed lines represent solutions in THF−DMF and in THF−ACN, respectively, with [DPH] = 0.1 mM and [DCB] = 40 mM.

in Figure 5. The maximum MFE is observed at $\epsilon \approx 10$ in THF−DMF and shifts to a slightly higher value ($\epsilon \approx 11$) in THF−ACN. The $B_{1/2}$ value, i.e., the field required for half the saturation of MFE, is obtained around 20 G for different concentrations of DCB (20, 40, and 60 mM) by keeping the concentration of DPH (0.1 mM) constant in THF−DMF ($\epsilon \approx 10.5$). Figure 6 shows the variation of MFE ($\Delta\phi/\phi$%) with wavelength λ.

(c) Anisotropy Measurements. The fluorescence anisotropy of DPH−DCB exciplex changes with the viscosity of the medium (THF−DMF, $\epsilon \approx 10.5$), as shown in Figure 7S where the reciprocal of anisotropy $(1/r)$ is plotted against the reciprocal of viscosity $(1/\eta)$. The medium was made viscous using cellulose acetate.

The anisotropic MFE experiments were carried out in similar viscous media. There is an appreciable enhancement of $\Delta\phi/\phi$
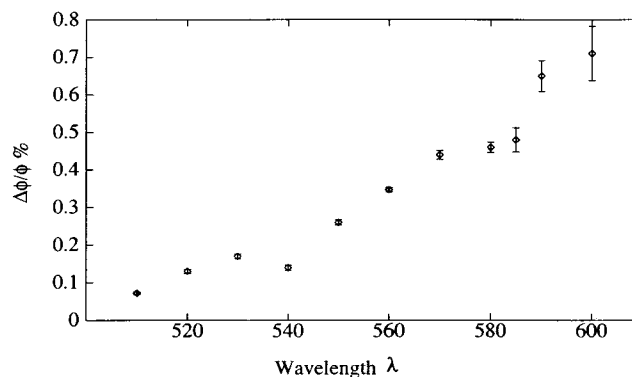

Figure 6. Wavelength (λ in nm) dependence of percentage magnetic field effect ($\Delta\phi/\phi$%) for DPH−DCB exciplex in THF−DMF at $\epsilon \approx$ 10.5, [DPH] = 0.1 mM, and [DCB] = 40mM. The magnetic field applied was 60 G.

TABLE 2: Values of $(\Delta\phi/\phi\%)_\parallel{}^a$ and $(\Delta\phi/\phi\%)_\perp{}^b$ with Different Viscosities of the Medium

viscosity (mP)	$(\Delta\phi/\phi\%)_\parallel$	$(\Delta\phi/\phi\%)_\perp$
18.0	0.106	0.080
36.7	0.100	0.074
63.8	0.109	0.080

[a] MFE with the excitation light polarized parallel to the magnetic field. [b] MFE with the excitation light polarized perpendicular to the magnetic field. Mean values are shown with standard deviations ±0.0054.

(>30%), if the excitation light is polarized parallel to the magnetic field direction (Table 2).

4. Discussion

(a) Fluorescence Measurements. The quenching of DPH fluorescence in the presence of DCB results from the electron transfer and exciplex formation between these two species (Figures 1a and 2Sa). The increase in the concentration of DCB favors the formation of exciplex (Figures 1b and 2Sb). The red-shift in the $\lambda_{max.}$ (Figures 1b and 2Sb) and the decrease in luminescence (Figure 4) with the increase in ϵ are consistent with the properties of an exciplex[20] that motivated us to study the MFE on this DPH−DCB system.

(b) Isotropic Magnetic Field Effect. *Dielectric Dependence of MFE.* From Figure 5 it is evident that the exciplex DPH−DCB shows a considerable increase in luminescence in the presence of a magnetic field of the order of 60 G around $\epsilon \approx$ 10 in THF−DMF and $\epsilon \approx 11$ in THF−ACN. The dielectric dependence of MFE was explained by a simple model proposed by Chowdhury and co-workers[8] that correlated the MFE with the competition between spin evolution and diffusion dynamics of the RIPs. Though there are other proposals, e.g., preferential solvation in polar−nonpolar binary solvent mixture[7b−e] and changes in the lifetime of RIPs,[3a] we feel this model is quite adequate for the present case. The potential energy diagram (Figure 8) clearly describes how ϵ can have a major influence on the MFE. In this diagram A, C, and D represent a contact ion pair (CIP) or exciplex, solvent-separated ion pair (SSIP), and free ions, respectively, while B is the transition state for the interconversion between CIP and SSIP. With the increase in ϵ, the energy barrier between B and C rises while the barrier between B and A and slope of the path C to D decrease. Therefore, in more polar solvents, free ion formation is favored at the expense of SSIP and SSIP predominates over CIP. At the coordinate E, where $J \approx 0$, S → T transition takes place. The ion pairs existing in the singlet state can either form free

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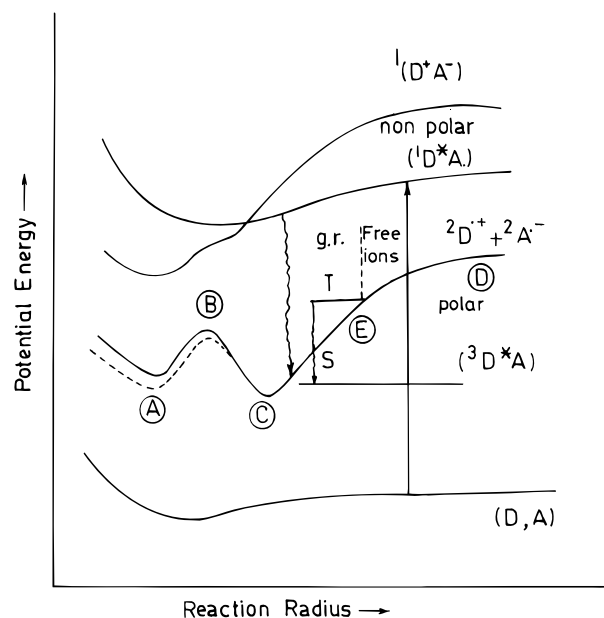*J. Phys. Chem. B, Vol. 103, No. 18, 1999* **3787**

Figure 8. Schematic representation of potential energy profile of electron transfer as a function of reaction radius. CIP (A) is the contact ion pair or exciplex and SSIP (C) is the solvent-shared ion pair. B and D represent the transition state between SSIP and CIP and free ions, respectively. Solid and dashed lines represent respective exciplexes DPH−DCB and DPH−DMA.

ions or return to C (SSIP), a fraction of which crosses the barrier between B and C to produce A (CIP). An external magnetic field lifts the degeneracy between the S and $T_\pm$, resulting in an increasing population of singlet RIPs. In a highly polar medium, most of the singlet ion pairs produce free ions, while in a nonpolar solvent, only a few RIPs can reach E. A medium of intermediate polarity balances all the energy terms, so that the major fractions of RIPs follow the return path (E → C → B → A), appearing as an increase in luminescence.

If the polarity of the solvent is the only parameter to control the dynamics of the RIPs, MFE should maximize at a particular ϵ irrespective of the exciplex system. However, it does not happen for all the exciplex systems, as cited before. Very recently, Aich and Basu proposed that there is another parameter that has an important impact on the diffusion dynamics of RIPs, the extent of charge transfer (δ) in exciplex.[9a,b] Since, in SSIP and free ions, charge transfer is complete, they do not respond to any change in the value of δ. For a lower value of δ, the exciplex experiences less solvent stabilization. As the transition state B has some exciplex character, it also suffers similar experiences but to a lesser extent. This results in an increase in the activation energy between B and C with a simultaneous decrease in barrier height between B and A; i.e., the effect of lowering the value of δ is partly similar to the effect of increasing polarity. Therefore, a relatively lower dielectric medium is required to maximize the MFE. The appearance of a maximum field effect at $\epsilon \approx 10$ for the DPH−DCB is thus consistent with the previous observation that all the exciplexes do not have a similar range of ϵ to give the maximum field effect.[9a,b] Furthermore, we infer DPH−DCB is associated with a lower δ value compared to DPH−DMA ($\epsilon_{max.} = 15$),[18] in which DPH performs the role of an acceptor. The convenient way to understand the extent of charge transfer is by the use of oxidation potentials of electron donor when the acceptors are the same. The higher value of oxidation potential E_{ox} of ECZ (1.12 V)[21] compared to DPH (1.02 V)[21] demands a lower δ value in ECZ−DCB. This effect is manifested in the higher value of $\epsilon_{max.}$ of DPH−DCB.

Measurement of $B_{1/2}$. The $B_{1/2}$ value can be obtained using the following relation proposed by Weller et al.[22]

$$B_{1/2} = 2(B_1{}^2 + B_2{}^2)/(B_1 + B_2) \qquad (2)$$

The B_i values are related with the hyperfine coupling constant a_{iN} and nuclear spin I_N by the equation

$$B_i = [\sum a_{iN}{}^2 I_N(I_N + 1)]^{1/2} \qquad (3)$$

The B_i of DCB is 4.6 G; since the hyperfine constant of DPH[•+] is not known, we use the B_i value of the anion DPH[•−] (10.4 G).[18] The $B_{1/2}$ obtained using these values is 17.2 G. This somewhat lower value than the experimental one ($B_{1/2} \approx 20$ G) is probably attributed to the approximate use of the B_i value of the anion. The experimental $B_{1/2}$ for DPH−DCB remains almost the same with three different concentrations of DCB. It is well-known that an increase in quencher concentration leads to a higher value of $B_{1/2}$ due to electron hopping.[3e,8e] In the presence of excess quencher concentration the electron hops between neutral and ionic free radicals that interferes with the spin evolution rate. In effect, the fast electron exchange causes uncertainty broadening of the energy of the individual spin state, and the magnetic field has to overcome this broadening in order to suppress the S → $T_\pm$ evolution completely. Thus saturation occurs at a higher field at higher concentrations. In the present exciplex system, the fluorophore, DPH, contributes the maximum to HFI, while the quencher, DCB, has very little hyperfine contribution ($B_i = 4.6$ G). Therefore, the constant value of $B_{1/2}$ for the present case does not imply the absence of electron hopping between DCB[•−] and DCB (as observed for Py-aza-15-crown-5[7c]) but arises due to very little hyperfine contribution of DCB. In contrast, for the DPH−DMA exciplex, the quencher DMA has significant hyperfine contribution ($B_i = 32.5$ G).[18] The much higher $B_{1/2}$ for the exciplex DPH−DMA (104 G)[18] results from the high magnitude of HFI in DMA and electron hopping. In DPH−DCB, both the components have very little HFI to show a very low magnitude of $B_{1/2}$.

Wavelength Dependence of MFE. Figure 6 indicates that the $\Delta\phi/\phi\%$ values are not the same throughout the entire wavelength between 510 and 600 nm where the complex formation between DPH and DCB occurs as obtained earlier from the fluorescence measurements. At a glance, one may be tempted to believe the existence of more than one exciplex because, in the case of single exciplex formation, the $\Delta\phi/\phi\%$ should remain constant.[9a] It certainly raises the question, what causes the different exciplexes to form and in what senses do they differ? One possibility is that the difference of geometry is responsible, as observed for the linked system (anthracene)(CH$_2$)$_n$DMA.[23] The most plausible way in which a difference in geometry may arise for the present case is due to cis−trans isomerization of DPH. It was shown previously that the excitation of parent 1,3,5-hexatriene[24] and phenyl-substituted DPH[25] gave product distribution consistent with the occurrence of cis−trans isomerization. For the DPH, the laser flash photolysis experiment confirmed cis−trans isomerization even in the radical cation DPH[•+].[26] On changing the excitation wavelength from 355 to 380 nm, a significant broadening of the tail part of DPH fluorescence was identified.[27a] This differential was much more enhanced with increasing temperature (30 → 91 °C). The red-shifted component was assigned to *s-cis*-DPH. Interestingly, cis−trans isomerization was found to be solvent sensitive.[27b] In methylcyclohexane, the all-s-trans isomer (s- stands for the intervening single bonds)[28] was observed to be present at almost 90%, while in polar solvent acetonitrile, the major component was cis−trans−
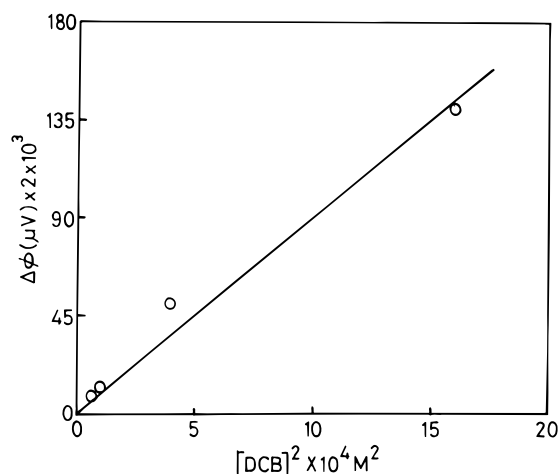
Figure 9. Magnetic field induced change in exciplex luminescence ($\Delta\phi$ in $\mu V \times 2 \times 10^3$) for DPH−DCB as a function of $[DCB]^2$ at $\lambda = 585$ nm in THF−DMF, $\epsilon \approx 10.5$ and $[DPH] = 0.1$ mM. The magnetic field applied was 60 G.

trans isomer. In our study at room temperature and with medium dielectric constant, we expect the predominance of the all-s-trans isomer. Nevertheless, the question remains whether the s-cis conformer can form an exciplex with DCB with differing MFE. Tanimoto et al.[6c] obtained two different exciplexes for (phenanthrene)$(CH_2)_n$DMA, one resulting from the excitation of phenanthrene and the other from excitation of DMA. The latter complex is absent in the corresponding unlinked system because DMA and phenanthrene should come very close to form the second exciplex that is possible only in the linked system. Therefore, the existence of an exciplex with DCB in the excited state is less likely for the unlinked DPH−DCB. The other possibility remaining, excepting the stereochemical difference, is the formation of exciplexes with different stoichiometry, e.g., naphthalene and DCB are known to form both 1:1 and 1:2 (triplex) complexes.[29] For the exciplex DPH−DMA, only the triplex was found. We feel, for the present case, the exciplex emitting higher wavelength is a triplex in which two DCB molecules are present. This inference is drawn from the fact that $\Delta\phi$ (for a constant value of ϕ) shows almost a linear dependence on the square of the DCB concentration at the wavelength 585 nm (Figure 9). This can only be rationalized by assuming participation of two molecules of DCB. Any other possibility, viz., different exciplexes due to cis−trans isomerization, is thereby ruled out. Triple complex formation is also supported by the steady-state fluorescence measurements in Bz (Figure 3). The λ_{max} of this 1:2 complex is quite red shifted compare to that of the 1:1 complex. It starts forming only at very high concentration of DCB (25 mM). This finding is consistent with the formation of a triplex because one molecule of DPH requires two molecules of DCB and formation of 1:1 complex is always a competing process. For a particular concentration range (25−40 mM DCB), the percentage increase in the triplex is higher than that for the 1:1 complex, as shown in Table 1. This is quite expected because the high concentration of DCB favors the 1:2 complex. We observed a similarity in the dielectric dependence of MFE for both the 1:1 and 1:2 complexes, which is explainable in light of the triplex model. Since, the donor and acceptor groups are the same for both the exciplexes, the relevant energy barriers do not change. Therefore, the conversion between SSIP and CIP maintains the same status, with respect to dielectric variation. However, the extent of the effect is larger in the 1:2 complex ($\Delta\phi/\phi\% \approx 0.46$ at $\epsilon_{max.} \approx 10$, $\lambda = 580$ nm) compared to the 1:1 complex $\Delta\phi/\phi\%$

≈ 0.13 at $\epsilon_{max.} \approx 10$, $\lambda = 520$ nm) since in the former the number of acceptor groups is doubled.

(c) Anisotropic Magnetic Field Effect. The occurrence of anisotropic MFE essentially requires restricted rotational diffusion of the RIPs. The first example of anisotropic MFE was obtained in the study on the photosynthetic reaction center (PRC),[19] where the PRCs are suspended in viscous glycerol to hinder their rotational movements. The only other example of anisotropic field effect known in solution is for the exciplex DPH−DMA,[18] where the rotational motion of the RIPs was restricted by making the medium viscous with polymeric substance. In the present system, prior to carrying out the anisotropy experiment, it is better to be ascertained whether the rotational diffusion of DPH−DCB exciplex is actually hindered or not in the viscous medium. The fluorescence polarization or anisotropy measurements can reveal the hindrance of the rotational diffusion of the fluorophore during the lifetime of its excited state. It is well-known that in a viscous medium DPH shows fluorescence anisotropy.[16] To observe the fluorescence anisotropy of the DPH−DCB exciplex, we have carried out the experiment in THF/DMF with $\epsilon \approx 10.5$ in the presence of cellulose acetate. The purpose of the latter is to increase the viscosity of the medium. In Figure 7S the reciprocal of anisotropy $(1/r)$ at the wavelength 590 nm is plotted against the reciprocal of viscosity $(1/\eta)$ to give the conventional Perrin plot. The linearity is obtained as demanded by the Perrin equation.

$$1/r = 1/r_o + \tau RT/\eta V r_o \qquad (4)$$

where τ, r_o, V, R, and T represent lifetime, anisotropy at infinite viscosity, volume of the rotating unit, gas constant, and temperature, respectively. At the wavelength 530 nm, a similar type of Perrin plot was obtained. From this experiment we chose the proper viscosity of the medium where the rotational diffusion of the DPH−DCB exciplex would be restricted considerably.

The fascinating feature of the DPH−DCB exciplex is in its manifestation of anisotropic MFE. It was observed that the $\Delta\phi/\phi\%$ is dependent on the direction of polarization of exciting light with respect to the axis of the magnetic field. Table 2 summarizes the $\Delta\phi/\phi$ values when light was polarized parallel $(\Delta\phi/\phi\%)_{\parallel}$ or perpendicular $(\Delta\phi/\phi\%)_{\perp}$ to the field. The anisotropy vanishes in the nonviscous medium. Boxer et al.[19] showed in their study on PRC that the quantum yield of triplet (ϕ_T) in quinone-depleted PRC is dependent on their orientation in the magnetic field. In the high-field region, quantum yield anisotropy is mainly caused by the anisotropy of the **g** tensors in the RIP. For the field strength $0 < H < 1$ kG the dominating terms are anisotropic electron dipole−electron dipole or nuclear hyperfine interactions. Tang and Norris[30] pointed out the importance of anisotropic dipolar interaction at low field in the solid state. For our study on DPH−DCB, at low field, it is quite reasonable to invoke anisotropic dipolar interaction and HFI. It was reported previously for the DPH−DMA exciplex that the determining factor for this effect is the anisotropic dipolar interaction rather than HFI.[18] In a rigid environment the anisotropic dipolar interaction between the RIPs changes the energy splitting between the singlet and triplet sublevels.[19b] Since dipolar coupling is anisotropic, the spin evolution of the RIPs is strongly dependent upon their orientations in the magnetic field. This interferes with the spin evolution and diffusion dynamics interplay of RIPs to a significant extent. For a particular orientation of the RIPs, the singlet spin state is favored, while in the other orientation, RIPs may prefer triplet spin states.[19e] For the present system, the RIPs are initially

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formed in singlet spin states and triplet RIPs are formed due to HFI present in the system. In the presence of a magnetic field, singlet to triplet transitions are reduced. Hence, the magnetic field induced increase in luminescence actually measures the increase in singlet population. If the excitation light is polarized in a particular direction, it would generate an anisotropic distribution of RIPs in the magnetic field. If such an orientation prefers to reside in the singlet state, the geminate recombination enhances, leading to an increase in the MFE. The fundamental difference of anisotropic MFE between PRC and DPH–DCB is that in PRC the excitation anisotropy is negligible.[19a] For PRC the excitation was almost isotropic. Due to the anisotropic magnetic interactions, a particular orientation of PRCs prefers to evolve to the triplet. In the other orientation, ground state products are preferentially formed. This results in optically polarized ground state absorption.

Since a more viscous medium restricts the rotational motions more, it is expected that the anisotropic MFE should increase with the viscosity of the medium. From Table 2, calculation using eq 1 shows that though the mean value of the anisotropic MFE increases (0.097 at 18.0 mP, 0.104 at 36.7 mP, and 0.107 at 63.8 mP), the change is too small to come beyond the limit of the errors. This apparent anomaly results from the quenching of MFE in the presence of cellulose acetate. This quenching is similar to that which occurs in alcoholic solvent[8f,h,i] for exciplex systems as the alcoholic OH groups present in cellulose acetate can make a hydrogen-bonded cage to restrict the diffusion of the ion pairs.

The extent of anisotropy is somewhat higher for the DPH–DCB than that for DPH–DMA (18–25%).[18] Since the extent of charge transfer is less for DPH–DCB, MFE maximizes at a lower dielectric constant ($\epsilon_{max} \approx 10$ in THF–DMF) compared to that for DPH–DMA ($\epsilon_{max} \approx 15$ in THF–DMF). The anisotropy experiments were carried out near the dielectric maxima. For DPH–DMA the more polar medium would stabilize the individual radical ions, dissipating their charges, and consequently reduce the anisotropic dipole–dipole interactions. Thus the anisotropic MFE would be less in DPH–DMA compared to the DPH–DCB exciplex.

5. Conclusion

We have attempted to compare the donor–acceptor characteristics of DPH in forming exciplexes. The exciplexes DPH–DMA and DPH–DCB bear similarities, viz., the triplex formation and anisotropic MFE. In the DPH–DCB system both 1:1 and 1:2 complexes are formed while for DPH–DMA only the 1:2 complex is feasible. The anisotropic MFE in DPH–DCB is somewhat higher due to greater anisotropic dipolar interaction.

Supporting Information Available: Figures of fluorescence and exciplex spectra and a plot of $1/r$ vs $1/\eta$ (mP^{-1}). This information is available free of charge via the Internet at http://pubs.acs.org.

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