Nature of the Fluorescent State of N−Arylcarbazole Derivatives as Derived from Directly Measured Values of the Excited State Dipole Moment

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Laser-induced changes in microwave dielectric loss of benzene solutions of two electron donor−acceptor systems, N−(4-cyanophenyl)carbazole and N−(1-naphthyl)carbazole, have been quantitatively measured with a view to determining the dipole moments and hence the nature of the fluorescent states of these systems. The dipole moments so determined are found to be much lower than that expected for a twisted intramolecular charge transfer state. On the basis of the measured values and the results of AM1 calculations, it is concluded that, contrary to what is commonly believed, these donor−acceptor systems emit from a locally excited state.

Introduction

Intramolecular charge transfer in electron donor−acceptor molecules has been a topic of extensive investigation in recent years. The current activity on this topic can be ascribed to a number of reasons ranging from the importance of the charge-transfer process in photosynthesis, solar energy conversion, chemical transformation, nonlinear optical properties of materials, to testing of contemporary theories of electron transfer. Of late, a number of studies have been directed toward a special type of charge transfer process, commonly termed the twisted intramolecular charge transfer (TICT) phenomenon.[1−16] The TICT phenomenon was introduced by Grabowski and co-workers[1,2] to account for the anomalous fluorescence band of 4-(*N*,*N*-dimethylamino)-benzonitrile (DMABN).[10,11] There occurs a transfer of an electron from the dimethylamino to the cyanophenyl moiety and a decoupling of the donor and the acceptor orbitals through internal twisting of the dimethylamino group in the excited state of the molecule. It was proposed that the normal and anomalous fluorescence bands of DMABN originate respectively from the locally excited (LE) and TICT states of the molecule. Subsequent studies have shown that the photophysical behavior (in particular, the fluorescence properties) of a wide variety of other donor−acceptor systems could also be accounted for in terms of the TICT mechanism.[3−8] It should be noted in this context that the TICT process may not always lead to dual fluorescence as is observed in the case of DMABN and a number of analogous systems. The TICT state has even been proposed for donor−acceptor systems which exhibit a single fluorescence band.[12−16] In these systems, the emission may originate from either an LE state or a TICT state. The nature of the emitting state (whether LE or TICT) in these molecules is usually determined based on the estimated dipole moment of the fluorescent state of the molecule. Because a TICT state is expected to be much more polar than the LE state, the two states can easily be distinguished based on the magnitude of the excited-state dipole moment.

One of the most commonly employed methods for the determination of the change in the dipole moment on electronic excitation is based on the correlation between the difference in the wavenumber of the absorption and fluorescence maxima and a solvent polarity function, ususally defined in terms of the dielectric constant and the refractive index of the medium.[17−22] Among the numerous correlations available,[21] the one suggested by Lippert and Mataga is the most popular.[17−19] However, this method suffers from the disadvantage that the change in the dipole moment of the molecule depends on the third power of the “Onsager cavity radius”, the radius of the spherical cavity in which the molecule (assumed to be a point dipole) is embedded. This quantity is most often chosen somewhat arbitrarily. Quite obviously, the estimated values of the excited-state dipole moments are therefore subject to uncertainty. Hence, the conclusions derived from these values, such as the nature of the fluorescent state, may not be correct.

Taking into consideration the limitation of the solvatochromic methods, we have recently embarked upon measurements of the excited-state dipole moments of various electron donor−acceptor molecules[23,24] employing a technique that involves measurement of the time-resolved changes in the dielectric loss of a solution of the system of interest in a nonpolar solvent.[25−28] This method is more direct and is known to provide more reliable values of the excited-state dipole moment.[26,28] In this particular work, we have focused our attention on two N-aryl carbazoles (Chart 1). The results show that the measured values of the excited state dipole moment of these molecules are far less than those obtained previously from the solvatochromic method.[29]

Experimental Section

Materials. The two systems were prepared according to the published procedure.[30] Compound **I** was prepared as follows and a similar procedure was adopted for **II**. An equimolar (3 mmol) mixture of carbazole and NaH was stirred in dry DMF under nitrogen for 2 h. The sodium carbazole so formed was then heated at 120 °C with 4-fluorobenzonitrile (3 mmol) and NaI (6 mmol) in dry DMF for about 20 h. The product and unreacted starting materials were precipitated by adding water to the reaction mixture. The precipitate was dried and the product

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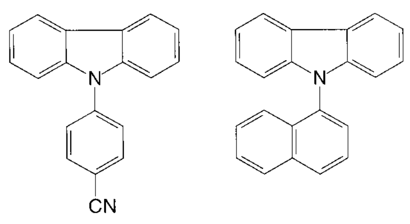
CHART 1



I II

was separated by column chromatography using a silica gel column. A mixture of ethyl acetate and *n*-hexane (50:50) was used as eluent. Colorless crystals were obtained from absolute ethanol upon slow evaporation of the solvent. The structure of the compound was confirmed by NMR spectroscopy.

The reference compound, diphenylcyclopropenone (Aldrich), was recrystallized several times from an ethanol−water mixture before photolysis. Benzene (Fischer Scientific, spectranalyzed) was used without any further purification. The solutions were deoxygenated by bubbling with argon prior to the time-resolved experiments.

Methodology. The present method is based on the principle that addition of a dipolar solute to a nonpolar solvent introduces a dielectric loss (ϵ'') that is proportional to the square of the dipole moment (μ) of the solute and is given by

$$\epsilon'' = A[\mathrm{S}]\mu^2 g(\omega\tau)$$

where [S] is the molar concentration of solute. *A* is a constant that involves the dielectric constant of the media, the absolute temperature and fundamental constants such as Avogadro's number and the Boltzmann constant. The term, $g(\omega\tau)$, takes into account the nature and rate of molecular reorientation (ω is the angular frequency of the microwaves, and τ is the molecular rotational relaxation time). In an ideal case, $g(\omega\tau)$ is given by $\omega\tau/[1 + (\omega\tau)^2]$ but usually $g(\omega)$ is different than this form in view of the fact that there exists a distribution of relaxation times even for a rigid molecule. The unknown values of $g(\omega\tau)$ were determined by measuring the loss at the desired frequency for known concentrations of the ground-state molecules in static experiments as done previously.[26,28]

The transient experiments use a comparison with the change in dielectric loss of a reference compound to eliminate all factors of the experimental setup. The equation employed for the measurement of the excited-state dipole moment is given by[26]

$$\Delta(\mu^2)_\mathrm{s} = (V_\mathrm{s} g_\mathrm{r}/V_\mathrm{r} g_\mathrm{s})\Delta(\mu^2)_\mathrm{r}$$

where the subscripts s and r refer to the unknown sample and reference compounds, respectively, the *g* terms are $g(\omega\tau)$ as defined above, and *V* represents the amplitude of the transient signal. The use of the ground state to measure the loss factor *g* assumes that the direction of the dipole in the ground and excited states is the same. This assumption is strictly valid for compound **I** because of its symmetry. For compound **II**, the small dipole moment makes the direction unclear so the dipole in the excited state may be in a different direction. The effect of the change in axis of the molecular reorientation on the $g(\omega\tau)$ value should not be large however. Thus, the value of the excited state dipole moment determined for this compound should not be greatly in error.

The details of microwave measurements were described in earlier publications.[25,26,28] The microwave signal source was a 40 mW klystron with frequency in the range 9.0−9.2 GHz. The signal amplitudes of the sample were compared with those from the reference compound, diphenylcyclopropenone (DPCP), and necessary corrections were made for adjustments of cavity coupling. Because the response time of the apparatus (36 ns), as determined by the cavity Q, was significantly higher than the fluorescence lifetime of the systems, the cavity Q was lowered by introducing a resistive plate in the cavity. The measured Q factor under these conditions gave a time constant of about 9 ns. The shapes of the decay curves were fitted by integrating a suitable differential equation taking into account the pulse shape of the excitation laser (12 ns full-width, half-maximum Gaussian), the response time of the apparatus from the Q factor, an additional 1 ns time constant for the subsequent amplifier, and the excited-state lifetime of the compound. The equation allowed for a fraction of the singlet to decay into a long-lived (on this time scale) triplet. This calculation was also used to model the rising portion of the data curves observed for DPCP, which gives a step response as a result of the transformation of this compound into nonpolar photoproducts.[26] The response times so measured agreed with the value from the Q factor. Photolysis of the samples was achieved with 355 nm pulses (approximately 10 mJ/pulse over 1 cm^2) from a Quanta-Ray PRO 230−10 Nd:YAG laser. The laser dose was monitored while photolyzing the samples to allow correction for any fluctuation in laser intensity. Considerable care was given to verify, by experiments at several laser pulse energies, that there were no effects such as ground-state bleaching.

The fluorescence lifetime of the systems was measured on a single photon counting spectrofluorimeter equipped with a N$_2$ laser (Photon Technology International, GL 3300) as the excitation source. Spectrophotometric measurements were made using a Shimadzu spectrophotometer (UV 3101PC).

Theoretical Calculation. The ground state dipole moments of the two derivatives were obtained by theoretical calculations for the AM1 optimized geometries of the molecules. The calculations were performed on a Personal Computer using the commercially available Hyperchem package. Unrestricted geometry optimization at the semiempirical level was performed following initial optimization of the geometry by MMX molecular mechanics program. The gradient norms were monitored to test for successful convergence. Moreover, because the crystal structures of the two derivatives are available,[31] the dipole moment values were also calculated for the structures obtained through X-ray crystallography.

Results and Discussion

Time dependent variation of the dielectric loss signals observed upon photolysis of benzene solutions of **I**, **II,** and the reference compound, DPCP, are shown in Figure 1. It should be noted that the curve for DPCP, which represents a decrease in dielectric loss, has been inverted for comparison with the signals for the carbazoles, which show an increase in loss on excitation. That the signals do not arise from any spurious effect, such as heating of the solution or the cavity, has been verified by performing blank experiments on benzene. Further, to be sure that only the dipole moment change of the molecule gives rise to the dielectric loss, we have verified that no signal appears from a benzene solution of anthracene (with a similar absorbance), a molecule for which $\Delta\mu$ is known to be negligible. The best fit to the decay curves, calculated by taking into account the factors described in the Experimental section, are shown as solid curves in Figure 1. The curve for DPCP provides not only the amplitude but also shows that the response time matches the data. The experimental curves in Figure 1, parts a

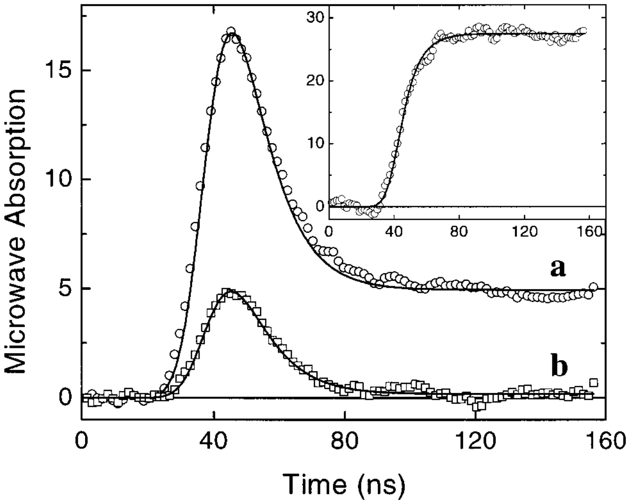


Figure 1. Time-resolved changes in the dielectric loss of argon-bubbled benzene solutions of (a) 10 mM of **I** and (b) 8 mM of **II**. The inset shows the behavior for the reference compound, DPCP, at 3 mM concentration. The latter represents a reduction in dielectric loss so has been inverted for presentation. The solid curves were calculated by the method described in the text. The lack of a return to the baseline (in a and b, particularly in a) is the result of formation of triplet state.

TABLE 1: Excited State Dipole Moments of N-arylcarbazoles along with the Values of Parameters Used in the Calculations

	DPCP	I	II
amplitude[a]	37.07	88.59	57.75
$g(\omega t)$	0.288	0.1774	0.1843
μ_g/D	5.1[b]	2.45[c]	1.57[c]
τ_f/ns		5.6	5.4
$\Delta(\mu^2)$	$(5.1)^2$	102.16	71.50
μ_e	0	10.4	8.6
$\Delta\mu$	−5.1	7.95	7.03
ϕ_T[d]		0.075	0.01

[a] Value from curve fitting corrected for difference in dose, cavity Q, and absorbances. [b] From ref 26. [c] Represents AM1 calculated dipole moment for the structures obtained from X-ray crystallography. For fully optimized geometries μ_g values were 2.86 and 1.64 D for **I** and **II**, respectively. [d] The triplet yield based on the assumption that the triplet state has the same dipole moment as the excited singlet.

and b, show (on this time scale) an approach to a plateau rather than to the baseline. The plateau represents the formation of some longer-lived triplet state. If the dipole moment of the triplet is equal to that of the excited singlet, then the quantum yields are 0.075 and 0.01 for **I** and **II**, respectively.

The fluorescence lifetimes of the carbazoles were measured because those values are required for the calculation of the true amplitudes (those corresponding to the absence of distortion by a finite pulse width and restricted response time). The values obtained for **I** and **II** are 5.6 and 5.4 ns, respectively. The calculation also requires the knowledge of the ground state dipole moments of the systems. These values have been evaluated by two different procedures. First, the structures of the molecules have been obtained through X-ray crystallography, and then the dipole moments corresponding to these structures have been obtained through AM1 calculations. Second, the geometries of the molecules were fully optimized theoretically and the ground-state dipole moments evaluated by AM1 method. The values so obtained are 2.45 and 1.57 D for **I** and **II** by the first method and 2.86 and 1.64 D by the second method. Even though the dipole moment values obtained for a given system by the two methods are very close, the former set using the experimental geometries has been used in the calculation of the excited-state dipole moments.

The excited-state dipole moments of **I** and **II**, as obtained by the analysis of the dielectric loss data in benzene (Table 1), are 10.4 (±0.5) and 8.6 (±0.5) D, respectively. The changes in the dipole moment of the molecules on electronic excitation ($\Delta\mu$) lie between 7 and 8.0 D. (The much smaller amplitude of the curve for **II** in Figure 1b is mainly because of a smaller absorbance for that compound.) These directly measured values of the change in the dipole moment of the molecules are almost one-half of the previously estimated values based on a range of polar solvents.[29,32] Therefore, a reinterpretation of the nature of the fluorescent state of the two systems may be required. It must also be noted that our calculation of the dipole moments has assumed that only a single excited-state species is present. The discussion below addresses these points together.

Of the two molecules studied here, **I** resembles the prototype TICT system, DMABN, rather closely in the sense that only the electron donor moiety is different between the two systems. According to the TICT mechanism, an electron is transferred from the amino nitrogen to the cyanophenyl moiety, and the distance between the center of the positive and the center of the negative charges is almost the same for the two systems. Therefore, one should expect the dipole moment of the TICT state of **I** to be similar in magnitude to that for DMABN. However, the measured excited-state dipole moment of **I** is far lower than that for the TICT state of DMABN (ca. 17 D).[33] Interestingly, the dipole moment of the LE state of DMABN (ca. 10 D)[33] is almost identical to the measured dipole moment for the excited state of **I**. In view of this, we conclude that it is the LE state from which the fluorescence of the systems originates.

Because the dielectric loss measurements have been made in the relatively nonpolar solvent, benzene, one might argue that in polar solvents such as acetonitrile, the emitting state could be a more polar TICT state. However, the following observations clearly argue against this idea. First, had there been a change in the nature of the emitting state while going from the relatively nonpolar solvent benzene to the more polar solvent acetonitrile, one would have expected the plot of the emission energy against the microscopic solvent polarity parameter, $E_T(30)$[34] to be nonlinear with a change of slope in between. However, such measurements (in benzene, 1,4-dioxane, tetrahydrofuran, and acetonitrile) have been found to be linear (see Figure 2) with correlation coefficients of 0.994 for **I** and 0.999 for **II**. Quite obviously, it is the same state that is the origin of fluorescence in benzene and acetonitrile.

Second, the fluorescence yields of the present systems are quite high as shown in Table 2 (ϕ_f of 0.38−0.52 for **I** and 0.19−0.29 for **II**) despite the fact that the fluorescence from a TICT state is expected to be forbidden.[2,3] In addition, the TICT fluorescence yield is expected to be quite sensitive to the polarity of the medium. Bhattacharyya et al.[8] and others have demonstrated that the TICT fluorescence yield of DMABN increases with an increase in the polarity of the medium until it reaches a maximum. Subsequent increases in the polarity of the medium have been found to decrease the TICT fluorescence yield. The fluorescence yield of the two systems studied here is reported to be very much the same in nonpolar *n*-hexane (0.34 for **I** and 0.12 for **II**) and polar acetonitrile (0.38 for **I** and 0.19 for **II**).[29] The near constancy of the fluorescence yield of the present systems also goes against the TICT hypothesis.

Third, a more reliable indicator of the nature of the emitting state may be[29] the radiative rate constant which is also shown in Table 2. These values are seen to decrease only moderately

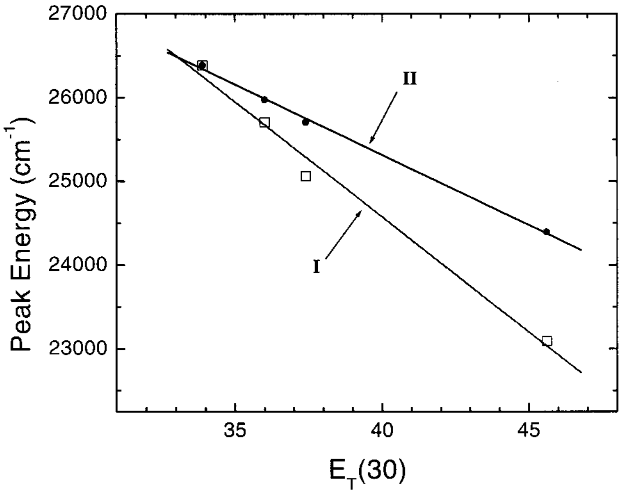


Figure 2. Plot of the energy of the fluorescence maximum against the solvent parameter $E_T(30)$ for the two compounds studied here (data in Table 2). The solvents are (left to right) toluene, 1,4-dioxane, tetrahydrofuran, and acetonitrile. The straight lines are least-squares fits.

TABLE 2: Fluorescence Decay Properties of Compounds I and II in Some Solvents

Cyanophenyl carbazole (**I**)

solvent	$E_T(30)$	peak energy (cm^{-1})	ϕ_f^a	τ_f^b	k_f^c
toluene	33.9	26 385	0.48	3.60	13.3
1,4-dioxane	36.0	25 707	0.52	5.29	9.8
tetrahydrofuran	37.4	25 063	0.48	6.20	6.8
acetonitrile	45.6	23 095	0.38	8.00	4.8

Naphthyl carbazole (**II**)

solvent	$E_T(30)$	peak energy (cm^{-1})	ϕ_f^a	τ_f^b	k_f^c
toluene	33.9	26 385	0.27	4.47	6.0
1,4-dioxane	36.0	25 974	0.29	5.87	4.9
tetrahydrofuran	37.4	25 707	0.23	5.93	3.9
acetonitrile	45.6	24 390	0.19	7.04	2.7

[a] Fluorescence quantum yield, measured relative to the value in acetonitrile which has been reported previouly[29] and corrected for refractive index. [b] Fluorescence lifetime in ns. [c] Radiative rate constant (s^{-1}), k × 10^{-7}.

from toluene (presumed to be similar to benzene) to acetonitrile solvent, and the value is very similar in toluene and dioxane. The very big decrease of 5−10-fold in the case of 4-(*N*,*N*-dialkylamino)-benzonitriles[1,35] is not seen for the present compounds. This, again, suggests that there is no reversal of the LE and TICT states while the solvent is changed in this series. The presence of a single excited state seems evident for the carbazoles in these solvents.

On the basis of the results of the time-resolved microwave experiments and the above arguments, we are led to conclude that the emitting state of the present systems is not as polar as previously thought. The fluorescence of **I** and **II** originates from a state in which the molecular geometry is not very different from that in the ground state. The reason for a smaller dipole moment than that found in the previous work[29] is not clear, but may involve the selection of the radius parameter in the Lippert−Mataga treatment.

Conclusion

Time-resolved microwave dielectric loss measurements of two N-arylcarbazole derivatives suggests that the dipole moments of the fluorescent states of the two systems in benzene and 1,4-dioxane are significantly lower than previously determined from the solvatochromic fluorescence data in a range of solvents. From the present measurement, it is concluded that the present systems fluoresce from a state that has predominantly an LE character. On the basis of the available photophysical data of the systems, it is argued that no TICT state could be seen to be contributing to the fluorescence even in polar media.

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