Excited State Structure of *N*-(4-cyanophenyl)carbazole by Time-Resolved Infrared Absorption Spectroscopy

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Nanosecond time-resolved infrared absorption spectroscopy has been used to study the charge transfer characteristics of the title compound in electronically excited states. The transient infrared bands observed at 2090 cm^{-1} and 2060 cm^{-1} have been attributed to the CN stretch modes in the first excited singlet and triplet states of the molecule. These frequencies are in conformity with enhanced charge separation in the excited states. Comparison of the present result with the existing data for 4-(*N*,*N*-dimethylamino) benzonitrile has indicated that the CN stretch frequency is not a direct measure of the polarity of the excited states of these molecules.

Electron donor-acceptor (EDA) molecules are attractive systems for the study of photoinduced intramolecular charge separation process, distance and orientation dependence of electron transfer, solvation dynamics subsequent to photoexcitation, and nonlinear optical properties due to high electron mobility. They also provide good models for testing the contemporary theories of electron transfer. Quite understandably, these molecular systems have occupied the center stage of photophysical and photochemical research for quite some time.

In this paper, we focus our attention on an EDA molecule, *N*-(4-cyanophenyl)carbazole (**1** in Figure 1), that consists of a cyanophenyl moiety as the acceptor and a carbazoyl moiety as the donor. Electronic excitation of this molecule results in an enhancement of charge separation from the donor to the acceptor moiety.[1,2] While the change in the dipole moment ($\Delta\mu$) on electronic excitation was originally estimated to be as high as 15 D from the solvatochromic absorption and fluorescence data,[1] a significantly lower $\Delta\mu$ value (7.95 D) has recently been obtained from dielectric loss measurement.[2] The resultant value of dipole moment in the excited state is 10.4 D and is much smaller than the value 15.1–16.1 D for 4-(*N*,*N*-dimethylamino)benzonitrile (DMABN),[3] for which the excited-state CT structure is established by a number of physicochemical studies.[3–12] Since a change in the magnitude of the charge separation on electronic excitation is expected to influence the molecular structure in the excited state, we think it pertinent to probe this aspect through time-resolved infrared spectroscopy, a technique ideally suited for obtaining structural information in the excited state.[8] We here concentrate on the CN stretch frequency region of the system in view of the fact that this region is clearly separated from the fingerprint region, which is crowded with many transitions due to the ring and carbazole modes.

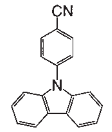

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Figure 1. Molecular structure of *N*-(4-cyanophenyl)carbazole.

The time-resolved infrared measurements were carried out using a setup described elsewhere.[13,14] The time-response of the setup was 60 ns and the wavenumber resolution was 16 cm^{-1}. **1** was prepared following the standard procedure reported in the literature.[1,2] The measurements were performed using a 5×10^{-3} mol dm^{-3} solution of **1** in *n*-butanol. The sample solution was circulated by a roller pump through a CaF$_2$ flow cell (100 μm path length) with continuous bubbling of argon or oxygen in the reservoir.

The time-dependent infrared absorption spectra in the argon bubbled *n*-butanol solution of **1** are depicted in Figure 2. At early times (0–100 ns), a transient band is observed at 2090 cm^{-1}. However, at later times, the absorption shifts to a lower frequency region and the new maximum appears at 2060 cm^{-1}. The decay profiles of the two transients are shown in Figure 3. While the absorption at 2090 cm^{-1} decays rapidly,[15] that at 2060 cm^{-1} decays more slowly. The lifetime of the 2060 cm^{-1} band estimated from the decay profile shown in Figure 3-(b) is 1.1 μs. While oxygen bubbling has negligible influence on the decay behavior of the short-lived transient, the long-lived component disappears completely in the presence of oxygen (Figure 4). Based on these decay behaviors of the absorption bands, the short-lived and long-lived components are assigned to the first excited singlet and triplet state of the molecule, respectively. This assignment is consistent with the photophysics of the system. The lifetime of the first excited singlet state of **1** in polar media is reported to be 8 ns.[2] In the present experiment, such a short lifetime is expected to exhibit a time-profile that is

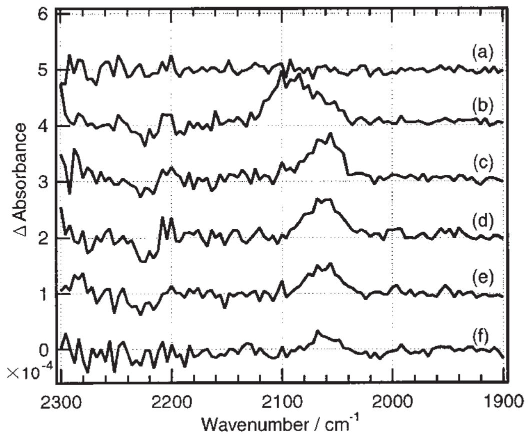

Figure 2. Time-resolved infrared absorption spectra of **1** in *n*-butanol (5×10^{-3} mol dm^{-3}) with argon bubbling: (a) −100–0 ns, (b) 0–100 ns, (c) 100–200 ns, (d) 200–300 ns, (e) 400–500 ns, and (f) 1.5–1.6 μs after photoexcitation.

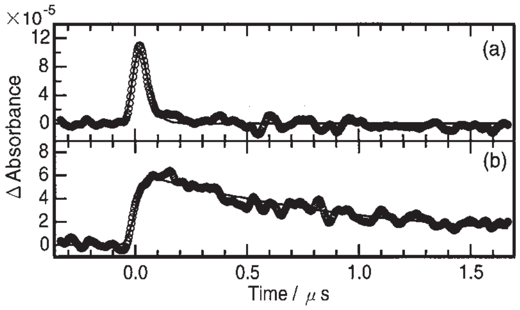

Figure 3. Time-dependance of the transient absorption bands of **1** in *n*-butanol at (a) 2090 cm^{-1} and (b) 2060 cm^{-1}.

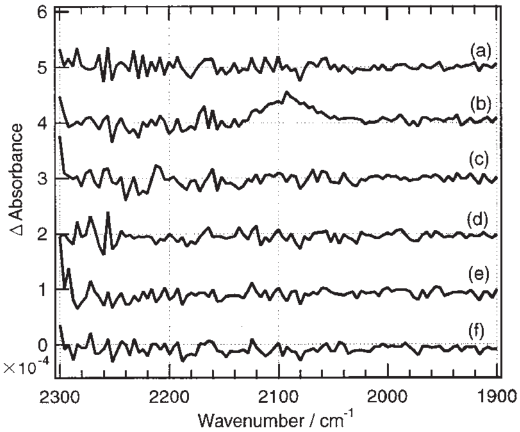

Figure 4. Time-resolved infrared absorption spectra of **1** in *n*-butanol with oxygen bubbling: (a) −100–0 ns, (b) 0–100 ns, (c) 100–200 ns, (d) 200–300 ns, (e) 400–500 ns, and (f) 1.5–1.6 μs after photoexcitation.

identical with the instrumental response function. This is indeed the case. Even though nothing much is known about the triplet state of **1**, the triplet of **1** was observed in the dielectric loss measurement.[2] Assuming an identical dipole moment for the singlet and the triplet state of **1** (which need not be true), the triplet yield of **1** was estimated to be ~ 0.1 in benzene.[2] It is likely that significant number of photoexcited **1** molecules stay in the triplet state after 100 ns from the photoexcitation. The assignment of the two transients to the singlet and triplet state of the molecule is in accordance with the known facts in the literature.

The CN stretch frequency of the molecule appears at 2232 cm^{-1} in the ground state. On the other hand, the absorption in the first excited singlet state appears at 2090 cm^{-1}. A downshift of the CN stretch frequency of the molecule (by 142 cm^{-1}) in the singlet state is indicative of a reduction of the CN bond order in the excited state. The reduction in the bond order of the CN group is in agreement with the enhanced charge separation in the excited state, since the transferred electron is considered to be accommodated partially in the anti-bonding orbital of the CN group.[1,2]

The present molecule **1** is structurally quite similar to DMABN. It is perhaps appropriate to make a comparison of the time-resolved infrared absorption data and the excited state properties such as the dipole moment of the two systems. These data are collected in Table 1. As seen from this Table, the CN stretch frequencies of the two systems are remarkably similar.

Table 1. Excited state dipole moments and CN stretch frequencies of 1 and DMABN

System	State	Dipole moment/D	CN frequency/cm^{-1}
1	S_1(LE)	10.4[a]	2090
	T_1	—	2060
DMABN	CT	15.1–16.1[b]	2096[c]
	T_1	12[b]	2040[c]

[a]From Ref. 2. [b]From Ref. 3. [c]From Ref. 8.

One may get tempted to conclude from this data that the excited state structure or the extent of charge separation in the excited state of the two molecules to be very similar as well. Interestingly, however, the directly measured values of the excited state dipole moment of the two systems are quite different, implying a significant difference in the excited state structure of the two compounds. There seems to be no correlation between the CN stretch frequencies and the dipole moments in the excited states of these two molecules.

An additional point to be noted here is a further downshift of the CN stretch frequency in the triplet state. A similar behavior of the CN stretch frequency has been observed in the case of DMABN, though the reported dipole moment for the triplet state of DMABN is lower than that of the CT state (see Table 1).

In summary, the present study points to a reduction of the CN bond order in the excited state of the molecule **1**, confirming an enhancement of charge separation on photoexcitation. The lack of correlation between the dipole moment and the CN stretch frequency, as observed here, is noteworthy. Further time-resolved infrared and Raman experiments to look at the other vibrational modes, both the ring modes and the carbazole modes, are deemed necessary.

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References and Notes

1 W. Rettig and M. Zander, *Chem. Phys. Lett.*, **87**, 229 (1982).
2 A. Samanta, S. Saha, and R. W. Fessenden, *J. Phys. Chem.*, **105**, 5438 (2001).
3 W. Schuddeboom, S. A. Jonker, J. M. Warman, U. Leinhos, W. Kuehnle, and K. A. Zachariasse, *J. Phys. Chem.*, **96**, 10809 (1992).
4 K. Rotkiewicz, K. H. Grellman, and Z. R. Grabowski, *Chem. Phys. Lett.*, **19**, 315 (1973).
5 Z. R. Grabowski, K. Rotkiewicz, A. Siemiarczuk, D. J. Cowley, and W. Baumann, *Nouv. J. Chim.*, **3**, 443 (1979).
6 W. Rettig, *Angew. Chem., Int. Ed. Engl.*, **25**, 971 (1986).
7 E. Lippert, W. Rettig, V. Bonacickoutecky, F. Heisel, and J. A. Miehe, *Advan. Chem. Phys.*, **68**, 1 (1987).
8 M. Hashimoto and H. Hamaguchi, *J. Phys. Chem.*, **99**, 7875 (1995).
9 H. Okamoto, *J. Phys. Chem.*, **104**, 4182 (2000).
10 H. Okamoto, H. Inishi, Y. Nakamura, S. Kohtani, and R. Nakagaki, *J. Phys. Chem.*, **105**, 4182 (2001).
11 W. M. Kwok, C. Ma, D. Phillips, P. Matousek, A. W. Parker, and M. Towrie, *J. Phys. Chem.*, **104**, 4188 (2000).
12 W. M. Kwok, C. Ma, P. Matousek, A. W. Parker, D. Phillips, W. T. Toner, M. Towrie, and S. Umapathy, *J. Phys. Chem.*, **105**, 984 (2001).
13 K. Iwata and H. Hamaguchi, *Appl. Spectrosc.*, **44**, 1431 (1990).
14 T. Yuzawa, C. Kato, M. W. George, and H. Hamaguchi, *Appl. Spectrosc.*, **48**, 684 (1994).
15 The decay profile is found to be controlled by the time-response of the instrumental setup.