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Picosecond Infrared Spectrum of 4-(Pyrrol-1-yl)benzonitrile: Structure of the Excited Charge-Transfer States of Donor−Acceptor Systems[†]

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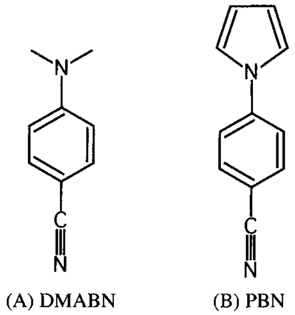
The picosecond transient infrared spectrum of the excited charge-transfer (CT) state of 4-(pyrrol-1-yl)-benzonitrile (PBN) has been recorded in the frequency range of 1700−920 cm^{-1}. The CT state of PBN gives several quite strong infrared bands. The band at 1219 cm^{-1} shifts toward the high-frequency side with increasing delay time between pump and probe pulses. This frequency shift is attributed to vibrational relaxation. Some of the transient bands (1429, ∼1290, 1219, and 964 cm^{-1}) are very close in frequencies to those observed for the benzonitrile moiety of the excited CT state of 4-(dimethylamino)benzonitrile (DMABN). This finding implies that the benzonitrile groups of PBN and DMABN are decoupled from the electron-donating (pyrrole or dimethylamino) groups, and it can be explained by the twisted intramolecular charge-transfer model. To make this point clear, however, further discussion is necessary on the band assignments and on correlation between structure and spectral pattern.

Introduction

Donor−acceptor-substituted aromatic compounds are known for various photochemically and photophysically characteristic features. Some compounds have very high nonlinear optical coefficients, which is a prerequisite for potential applications to optoelectronic devices.[1] Some donor−acceptor compounds are also noted for their dual fluorescent behavior observed particularly in polar solution.[2−4] A number of papers have been devoted to the studies of the dual fluorescence phenomena, especially for 4-(dimethylamino)benzonitrile (hereafter abbreviated as DMABN, Scheme 1A) in which dimethylamino and cyano groups are linked by a *p*-phenylene group. The dual fluorescence of DMABN (and related compounds as well) has an origin in the coexistence of an excited charge-transfer (CT) state and a locally excited (LE) state.[4,5] The ground state of DMABN is optically excited to the S_2 state, which is very rapidly (in a subpicosecond regime) relaxed to the energetically more stable LE state. In a polar environment, the energy of the excited CT state is lowered to a similar level as that of the LE state or sometimes even lower than that. In this case, the excited CT state, as well as the LE state, is populated. Both of these excited states are fluorescent, and consequently, the dual fluorescence is observed.

There has been extensive discussion about molecular structures of the excited CT states of DMABN and related donor−acceptor systems. The idea of the twisted intramolecular charge transfer (TICT)[4−6] was first proposed in the 1970s by Grabowski and co-workers to explain characteristics of fluorescence from the CT state and is still accepted by many researchers. On the other hand, Zachariasse and co-workers have argued that the planar intramolecular charge transfer (PICT) model[7−9] explains experimental data on DMABN and derivatives more consistently. Up to now, it has been still the subject of much controversy which one of TICT or PICT is the reality for excited DMABN. Some other structural models have been also proposed for the CT state, but they seem to be not realistic according to the studies of these several years.[10,11]

SCHEME 1



To discuss structures of molecular species, vibrational spectroscopy or diffraction methods or both sometimes give essential information. Recently, vibrational spectra of the excited CT state of DMABN have been obtained in solution.[12−18] Kwok et al. have recorded the Raman spectrum of the CT excited state of DMABN. They conclude that the observed C−N and C≡N stretching frequencies are reasonably explained by the TICT model,[17] from comparison with the results of CASSCF calculation.[13,16,19] On the other hand, one of the present authors (H.O.) and co-workers have recorded the infrared spectrum of the same species. From the results obtained, they consider that the final conclusion should be made after further careful investigation,[18] because the observed infrared spectrum is not fully consistent with the CASSCF results. Very recently, Techert et al. have performed a picosecond time-resolved X-ray diffraction experiment for solid-state DMABN.[20] They have recorded a powder diffraction pattern after ultraviolet photoexcitation and analyzed the data by adjusting the torsional and wagging angles of the

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dimethylamino group as fitting parameters. They have concluded that the dimethylamino plane is twisted to about 10° from the benzene plane in the excited state in the solid state.

We consider that further investigation is necessary on molecular structures of excited CT states of donor−acceptor systems in solution. In the present paper, we report observation of the picosecond time-resolved infrared spectrum of 4-(pyrrol-1-yl)benzonitrile (*N*-pyrrolobenzonitrile, abbreviated hereafter as PBN, Scheme 1B) in acetonitrile solution. In PBN, the dimethylamino group of DMABN is replaced with a pyrrole ring. Both PBN and DMABN have benzonitrile moieties as the identical partial structure, while the characters of the donor groups (dimethylamino and pyrrole) are quite different. From comparison of vibrational spectra of the CT states of PBN and DMABN, we may expect that some suggestion on detailed band assignments can be obtained. In addition, we may also expect information on interaction between the electron-donating groups (dimethylamino or pyrrole ring) and benzonitrile moieties by comparing benzene-ring vibrational bands. PBN shows fluorescence from the excited CT state in solution,[21−24] as is similar to DMABN. The Stokes shift of the CT fluorescence is especially large in acetonitrile (ca. 14 000 cm^{-1}), and the fluorescence lifetime is moderately long (8.2 ns).[24] We analyze the picosecond infrared data obtained to discuss excited molecular structure as well as dynamical characteristics. Apart from DMABN, the present target compound PBN is up to now the only molecule that has a structure similar to DMABN and gives an excited CT state, of which the transient vibrational spectrum is obtained and discussed.

Experimental Section

The experimental setup for the picosecond transient infrared spectroscopy was basically the same as that already reported elsewhere.[25,26] The essential points are briefly described here. The optical beams for the measurement were obtained from a synchronously pumped dye laser with a dye amplifier excited by the second harmonic output from a Nd:YLF regenerative amplifier. The repetition rate of the laser system was 1 kHz. The infrared probe beam in the wavenumber region between 1700 and 920 cm^{-1} was obtained by two-stage difference frequency mixing of the fundamental output (1053 nm) from the Nd:YLF regenerative amplifier and the output from the amplified dye laser. The ultraviolet pump beam was obtained as the second harmonic of the amplified dye laser (277−289 nm). The pump-pulse energy was in the range between ca. 1 and 4 μJ. The cross correlation time of the pump and probe pulses was about 4 ps. The spectral resolution of the transient infrared spectra was about 8 cm^{-1}. We made use of a method based on optically heterodyned detection of absorption anisotropy (OHDAA)[26] to detect a very small infrared absorbance change.

PBN gives a strong ultraviolet absorption band around 280 nm in solution.[23,24] The pump wavelength of the apparatus used is very close to the peak of the absorption band. The concentration of the sample solution was ca. 2×10^{-2} mol dm^{-3}. The sample solution was circulated through a BaF_2 flow cell with an optical path length of 0.015 mm for the transient infrared measurements. The static infrared spectra of the ground-state molecules were measured by a JASCO FT/IR-420 Fourier transform infrared spectrophotometer.

The sample PBN was purchased from Maybridge Chemical Company Ltd. and used after vacuum sublimation. The solvent (acetonitrile, liquid chromatography grade) was purchased from Wako Pure Chemicals and used as received.

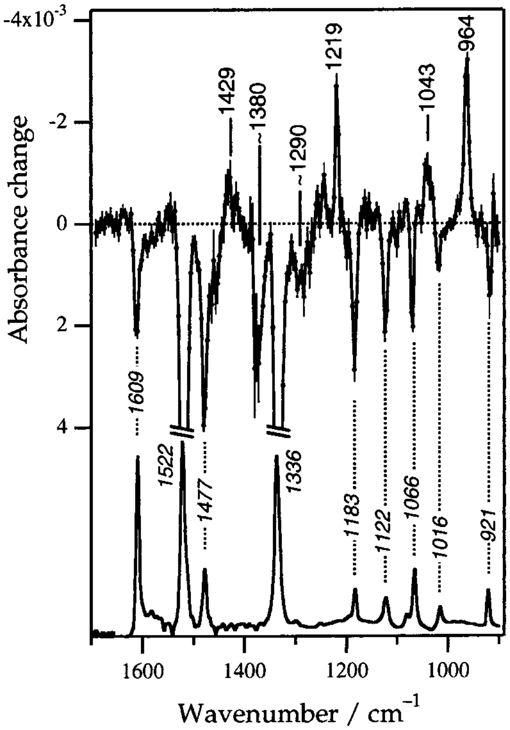

Figure 1. Transient (top) and static (bottom) infrared spectra of PBN in acetonitrile solution. Band frequencies (in cm^{-1}) are given above the top and bottom traces for transient and ground-state species, respectively. The solvent bands have been numerically removed for the bottom trace. The sample concentration is ca. 2×10^{-2} mol dm^{-3}. The delay time between pump and probe pulses (for the top trace) is 8 ps.

TABLE 1: Infrared Band Frequencies (in cm^{-1}) of Ground-State PBN and DMABN in Acetonitrile Solutions and Assignments

PBN			DMABN[a]	
obsd	calcd[b]	assignment[c,d]	obsd	assignment[d]
1609	1605	8*a*	1609	8*a*
1522	1511	19*a* (18*a*)	1529	19*a* (18*a*)
			1486	Me
1477	1469	P		
			1449	Me
1336	1317	ϕ-N	1372	ϕ-N
1299	1296	3, 14	1328	14
1252	1240	14, 18*b*	1310	3
			1229	N-Me
1217	1209	ϕ-CN, 9*a*		
1183	1172	ϕ-CN, 9*a*	1180	9*a* (ϕ-CN)
			1171	Me, 1
1122	1119	P		
1081	1073	P		
1066	1050	P		
			1066	Me
1016	1001, 993	P, 1, 12	1005	12
921	901	P, 1, 12		
			944	N-Me

[a] Reference 27. [b] Unpublished data, B3LYP/6-31G(d). [c] Tentative assignments based on B3LYP calculation. Notation "P" indicates the vibrational mode of the pyrrole moiety. [d] Benzene-ring vibrational modes are indicated in Wilson notation.[31]

Results

The transient infrared spectrum of PBN in acetonitrile solution at a delay time of 8 ps is shown in Figure 1, together with static infrared spectrum of PBN for the same solution. In Table 1, the observed vibrational frequencies for the ground-state PBN and tentative assignments based on a density functional calculation (B3LYP/6-31G(d) level, unpublished result) are summarized. For comparison, Table 1 also includes the results of a detailed vibrational analysis for DMABN.[27] Some of the ground-state infrared-active modes give strong bleached absorption bands in the transient infrared spectrum. In addition to the bleached bands, several quite strong induced bands due to the transient species are observed. The vibrational frequencies are indicated only for sufficiently reproducible bands in Figure 1. Because of the characteristic of OHDAA method,[26] totally symmetric vibrational modes (a_1 species under C_{2v} symmetry, in-plane) give positive transient absorption peaks, whereas nontotally symmetric modes (b_1 species, out-of-plane; b_2 species, in-plane) give negative peaks. Vibrational modes of a_2 species (out-of-plane) are not infrared active. The PBN molecule in reality is not planar. It has a geometry with a twisted interring C−N single bond, and is approximated as C_2 point-group symmetry.[23,28] Under C_2 symmetry, a_1 and a_2 species of C_{2v} point group are resolved into totally symmetric a species, which give positive transient infrared absorption signals. (Actually, however, out-of-plane vibrational modes of a species, which correlate to a_2 species under C_{2v} symmetry, may have only very low absorption intensities.) Similarly, b_1 and b_2 symmetry species of C_{2v} point group are resolved into nontotally symmetric b species and give negative transient absorption signals.

Figure 2 shows plots of peak intensities of the transient bands as functions of delay time between pump and probe pulses. For comparison, a temporal profile of a bleached band at 1336 cm^{-1} is also shown in Figure 2. Although experimental uncertainty is relatively large for some weak bands, all of the transient bands show approximately the same temporal dependencies. It is clear that the rise of the transient species is a little delayed from that of the ground state. This result indicates that the transient observed rises in a few picoseconds. In the OHDAA method, band intensities of a transient species are affected by the reorientational relaxation, in addition to the population changes of the transient species.[26] We cannot quantitatively discuss the excited-state population of PBN on the basis of the present experimental data because the reorientational relaxation time is not known. So, we analyze here the temporal behavior of the bleached band at 1336 cm^{-1} and of the induced band at 1219 cm^{-1}, assuming that the populations of the ground-state and transient species are not changed in the picosecond time range, after they once rise up. (This means that the decay of the signal is totally due to the reorientational relaxation.)

We assume that the instrumental function is approximated by a Gaussian and that the bleached absorption rises instantaneously after photoexcitation, while the absorption due to the transient rises exponentially. The best-fit results are shown in Figure 2 (first and fifth panels from the top) by solid curves. The obtained decay times (corresponding to reorientational times in this case) for the ground-state and the transient species are 11 and 17 ps, respectively, and the rise time for the transient species is ∼2.5 ps.

The charge-transfer reaction rate of PBN, which may be compared with the rise time obtained above, is so far not measured, and the photophysical process of PBN is not very clear. However, the obtained rise time supports that the transient band is coming from a CT excited state, as mentioned in the following. The vertically photoexcited state of PBN is believed to be, on the basis of density functional calculation,[28] the second A symmetry species (2A) state with a partially charge-transferred character having a relatively small dipole moment. On the other hand, the CT fluorescence of PBN is assigned to a transition from a B symmetry species (1B) state to the ground (1A) state. In the relaxed 1B state, the PBN molecule is considered to have a large dipole moment.[23,24,28] Therefore, the charge-transfer reaction of PBN involves an internal conversion process of the electronic state (from 2A to 1B) or geometric relaxation or both, together with reorientational relaxation of solvent molecules. The solvent reorientational time (solvation time) of acetonitrile is reported to be very rapid (less than 1 ps) from a dynamic Stokes shift experiment on Coumarin 153.[29] Then, the rate of the CT-state formation of PBN may be determined by the internal conversion or geometric relaxation or both and should be very fast, probably in the range of a few picoseconds. The CT-state formation time for DMABN has been found, in fact, to be 4 ps in acetonitrile.[13] The rise time of the induced band (1219 cm^{-1}), 2.5 ps, is comparable to this value and is consistent with the process of the CT-state formation mentioned above.

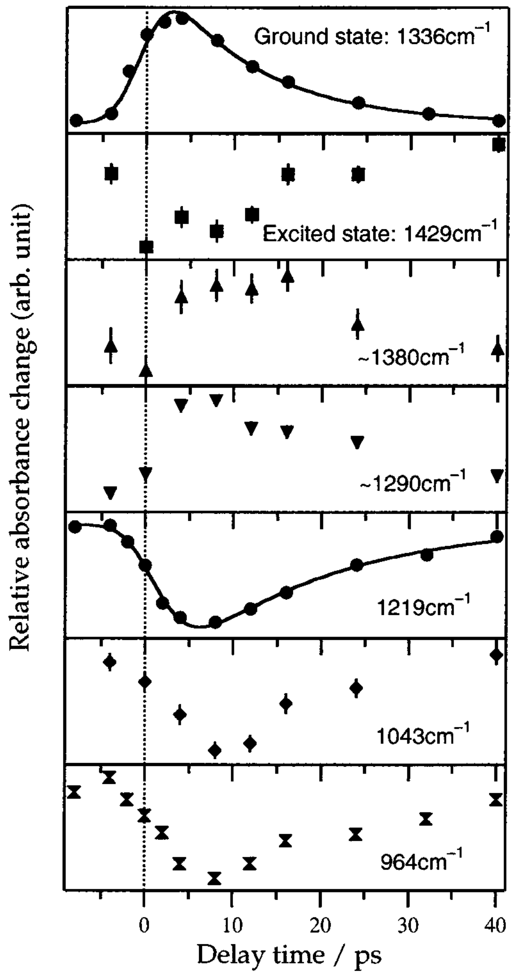

Figure 2. Plots of transient infrared band intensities against delay time: top, bleached band at 1336 cm^{-1} due to the ground state; second from the top to bottom, induced bands due to transient species. The best-fit simulations (see the text) are shown for the bleached band at 1336 cm^{-1} and for the induced band at 1219 cm^{-1} by solid curves.

The population lifetime of the transient species observed is suggested to be very long, as described in the following, and this is consistent with the reported lifetime of the CT fluorescence of PBN in acetonitrile (8.2 ns).[24] Assuming that the Stokes−Einstein relation holds for the PBN molecule in acetonitrile as a rough approximation, we can calculate the molecular volume (V) of PBN from the reorientational relaxation time (τ_{OR}) and viscosity of acetonitrile (η = 0.37 mPa s) at room temperature (T = 298 K). If we further assume that decay

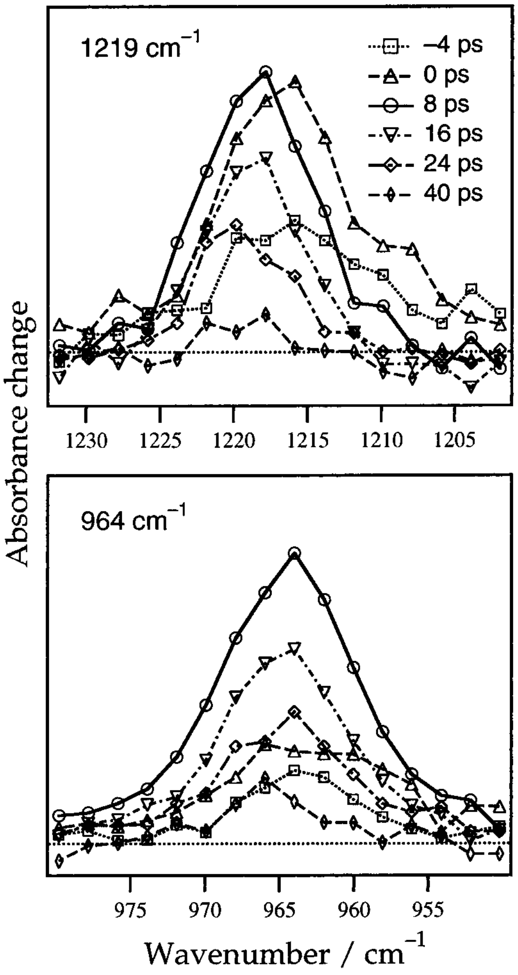

Figure 3. Delay-time dependencies of induced infrared bands.

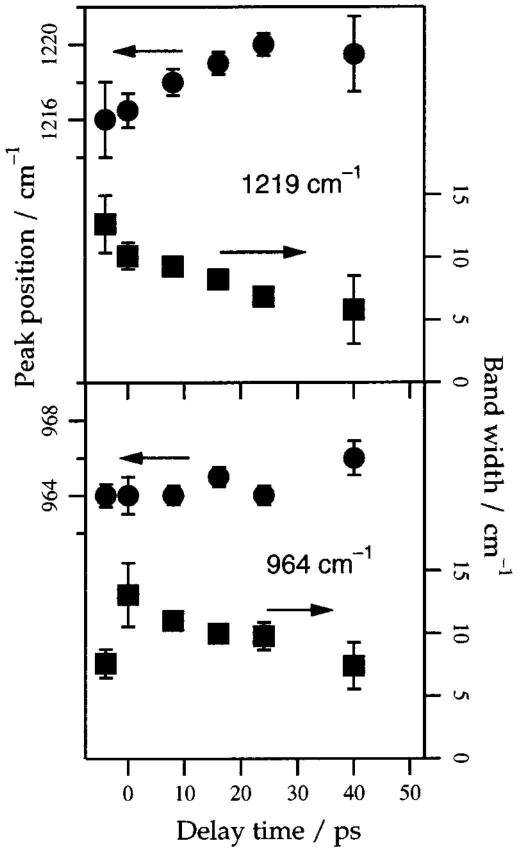

Figure 4. Delay-time dependencies of peak positions (●) and bandwidths (■) for the induced bands at 1219 (top) and 964 cm^{-1} (bottom).

of the induced infrared band (17 ps) is totally determined by reorientational relaxation (i.e., $\tau_{OR} = 17$ ps), V is estimated to be

$$V \equiv 4\pi a^3/3 = \tau_{OR}kT/\eta \approx 190\ \text{Å}^3$$

where a denotes the radius of the molecular sphere and k is the Boltzmann constant. The obtained molecular volume is quite reasonable considering the geometrical size of the molecule (9.3 × 4.3 × 2.3 Å^3, B3LYP/6-31G(d) calculation for the ground state) and diffuseness of valence electron orbitals. This consideration suggests that the decay of the transient infrared bands is indeed determined for the most part by the reorientational relaxation, or in other words, population change of the transient within the reorientational relaxation time, 17 ps, is negligibly small. The lifetime of the transient is consequently estimated to be in the subnanosecond regime or longer. The aforementioned discussion leads to us to a conclusion that all of the transient induced bands in Figure 1 are most probably attributable to the excited CT state of PBN.

Delay-time dependency of the band shape is examined for the strongest two infrared bands (1219 and 964 cm^{-1}) arising from the excited CT state. The results are shown in Figure 3. It is found that the band at 1219 cm^{-1} shifts toward the higher frequency side with increasing delay time, while that at 964 cm^{-1} does not move. At the same time, the bandwidth becomes narrower for the band at 1219 cm^{-1} with increasing delay time, while very small or essentially no change is found for the band at 964 cm^{-1}. The temporal dependencies of the band positions and bandwidths are more clearly seen in Figure 4. The origin of the high-frequency shift of the band at 1219 cm^{-1} may be related to vibrational relaxation of hot molecules generated immediately after excitation to the CT state. Such a high-frequency shift may occur in conjunction with vibrational relaxation, if the equilibrium geometry of the excited CT state is displaced from that of the precursor state along this mode (1219 cm^{-1}) and if there is sizable anharmonicity for this mode. The bandwidth change is also reasonably explained in terms of vibrational relaxation. When the vibrational temperature is high (before vibrational relaxation completes), vibrational populations are distributed broadly to various quantum-number states and this gives a broad spectral width. After cooling, the vibrational populations become concentrated on the ground state, giving a narrower spectral width. The time scale of the changes in position and width of the transient band at 1219 cm^{-1} is on the order of 10 picoseconds, as seen from Figure 4. This time scale is reasonable as that of vibrational relaxation.

Conformational change in the excited state, which would be coupled to the CT reaction, can also be an origin of the shift of the band position. In this case, however, the magnitude of the band shift may be much larger than that presently observed. In addition, the time scale of the conformational change should be essentially the same as that of the CT reaction, which is ~3 ps or less as described earlier, but the observed band shift is obviously slower. Consequently, the observed frequency shift and the change of width for the band at 1219 cm^{-1} is probably not due primarily to conformational changes.

This observation for the band at 1219 cm^{-1}, together with the vibrational frequency and the strong band intensity, implies that this band is (at least partly) due to a mode with significant contribution from the interring C−N stretch, as mentioned in

TABLE 2: Infrared Band Frequencies (in cm^{-1}) of CT Excited-State PBN and DMABN in Acetonitrile Solutions and Assignments

PBN		DMABN[a]	
obsd[b]	assignment[c,d]	obsd[b]	assignment[d]
1429	BN (19*a*)	1425	19*a*
~1380*	P		
~1290*	BN (3, 14)	1276*	3, 14
		1276	*ϕ*-N
1219	*ϕ*-N, BN (*ϕ*-CN, 9*a*)	1220	*ϕ*-CN (9*a*)
1043	P		
964	BN (12)	959	12

[a] Reference 18. [b] Negative peaks are indicated by asterisks. [c] Tentative assignments. Notations "P" and "BN" indicate vibrational modes of the pyrrole moiety and the benzonitrile moiety, respectively. [d] Benzene-ring vibrational modes are indicated in Wilson notation.[31]

the following. In the CT state, charge separation is considered to take place between the pyrrole and benzonitrile moieties. We may then expect that the stretching vibration of the interring C−N single bond induces a large dipole moment change and hence gives a strong band. In addition, the C−N bond length of PBN in the CT excited state may be substantially different from that in other electronic states (ground state, LE state, etc.). As for anharmonicity, it may be sufficiently possible that curvature of the potential energy surface changes with the C−N bond length. This means that the C−N stretching mode is accompanied by a significant magnitude of third-order anharmonicity. The frequency of the band, 1219 cm^{-1}, is a little lower than the C−N single-bond stretching frequency of the excited CT state of DMABN (1276 cm^{-1}, see Table 2) and is reasonable as an interring C−N stretch. The aforementioned discussion may show that the observed characteristics of the band at 1219 cm^{-1} are in good accordance with what are expected for the interring C−N stretching vibration.

Infrared band frequencies and tentative assignments for the excited CT state of PBN are summarized in Table 2. The table also includes frequencies and assignments for the excited CT state of DMABN.[18]

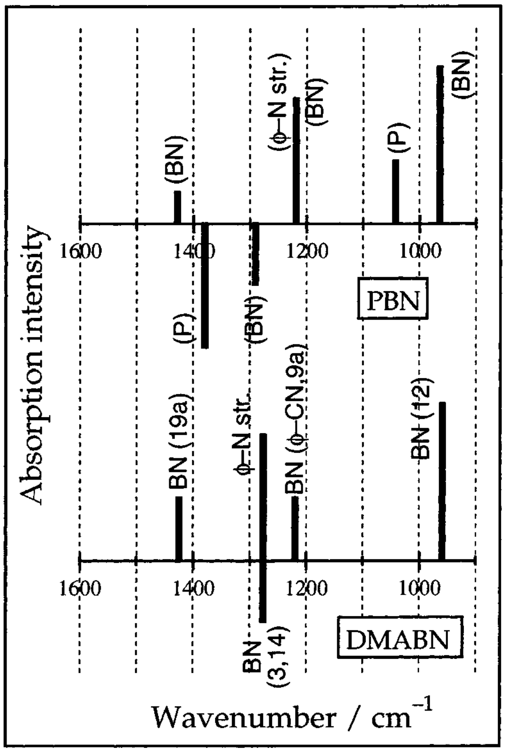

Figure 5. Transient infrared spectral patterns for the excited CT states of PBN (top) and DMABN (bottom). Tentative band assignments are given in parentheses for PBN. Assignments are based on ref 18 for DMABN. BN refers to the benzonitrile moiety; P refers to the pyrrole moiety.

Discussion

Several reports have been published on quantum chemical calculation of electronically excited states of PBN.[21,28,30] It has been revealed that molecular orbitals of PBN are different from those of DMABN in the following points. (1) In PBN, the highest occupied molecular orbital (HOMO) has a node at the nitrogen atom of the pyrrole moiety. On the other hand, DMABN does not have any orbital that corresponds to the HOMO of PBN. For this reason, PBN gives an excited CT state belonging to a B symmetry species, which is absent in DMABN (the lowest excited CT state of DMABN belongs to an A symmetry species). The experimentally observed CT fluorescence of PBN has been assigned to emission from the excited CT state of the B symmetry species.[28] (2) The lowest unoccupied molecular orbital (LUMO) of PBN is of nonbonding character along the interring C−N bond, but that of DMABN is of antibonding character along the C−NMe$_2$ bond. Very recently, Parusel reported calculation of electronic excitation energies and their C−N torsional angle dependencies for PBN and DMABN by the DFT/MRCI method.[28] In that study, solvent effects are taken into consideration by the Onsager model. The result shows that the LUMO energy is strongly dependent on the C−N torsional angle for DMABN, while only weak dependence is found for PBN in a vacuum. Consequently, the excited CT state may be generated at any torsional angle for PBN. Under the highly polar condition of the Onsager model, on the other hand, the calculated CT states (especially that of the B symmetry species mentioned above) are stabilized at a large torsional angle.

Now, we compare the observed infrared spectral patterns of the excited CT states of DMABN and PBN in Figure 5 and Table 2. It has been established for DMABN, by the isotope substitution experiment, that the C−N single-bond stretch contributes principally to the band at 1276 cm^{-1}.[18] Assignments for the other four infrared bands[18] are also quite convincing. It is clear at least that the four bands are due to vibrational modes of the benzonitrile moiety. For the excited CT state of PBN, we have so far no isotopic data, and clear band assignments are not available, except for the tentative assignment of 1219 cm^{-1} (interring C−N stretch) mentioned earlier. However, the following spectral characteristics are worth being noted. That is, some of infrared bands observed for the CT-state of PBN [1429, ~1290 (negative band), 1219, and 964 cm^{-1}] are very close in frequencies to the infrared bands due to the benzonitrile moiety of the excited CT state of DMABN [1425, 1276 (negative band), 1220, and 959 cm^{-1}]. If assignments of these bands of PBN are essentially the same as those of DMABN, this observation suggests similarity of the structure of the benzonitrile moiety of PBN to that of DMABN in the excited CT states. If so, it further implies that interaction between the benzonitrile moiety and the NMe$_2$ (for DMABN) or the pyrrole ring (for PBN) is small in the CT state. This result is apparently explained by the TICT model more easily than by the PICT model (or other structure models) for DMABN. In the TICT model, the electronic (and consequently geometric) structure of the benzonitrile moiety of the CT-state PBN is approximately the same as that of the CT state of DMABN. As mentioned above, the excited CT state of PBN is considered to belong to a B symmetry species.[28] However, the electronic character of the benzonitrile moiety of PBN is not affected very much by the symmetry species to which the CT state belongs, under the twisted structure. It has been claimed that the benzonitrile moiety of PBN in the CT state is decoupled from the pyrrole part even in a planar geometry and that CT-state stability is not much affected by the twist angle.[21−24] On the other hand, it has been concluded from the theoretical calculations that the twisted geometry is more stable in the lowest excited CT state.[28] In any case, the similarity of the CT-state infrared spectra of DMABN and PBN suggests that the benzonitrile moieties are decoupled from the electron-donating groups in these compounds. This is consistent with, at least for DMABN, the excited CT state with a twisted geometry. To summarize, the comparison of the CT-state spectral patterns of DMABN and PBN in Figure 5 rather supports that the CT state of DMABN has a twisted structure (TICT model).

It has been presumed in the discussion above that band assignments for the benzonitrile moiety of DMABN similarly apply to PBN. In addition, it has been implicitly assumed that infrared spectral patterns are substantially affected by minor change in electronic and geometric structures of molecules. We can never reach the final conclusion unless these points are carefully examined. Band assignments for PBN are, in principle, possible by isotope-substitution experiments. For the effects of structural changes on spectral patterns, comparison of the ground-state PBN and DMABN may give some suggestions. In Table 1, we find a frequency difference of ca. 7 cm^{-1} for mode 19*a* (Wilson notation[31]) between PBN and DMABN. Mode 12 also seems to be quite different in these two compounds. On the other hand, mode 9*a* and the ϕ-CN stretch seem to be almost unchanged. For the excited CT states of PBN and DMABN, the bands around 1425 cm^{-1} (due to mode 19*a* for DMABN) agree well with each other, and the bands around 960 cm^{-1} (due to mode 12 for DMABN) do as well. We should note, however, that the benzonitrile moiety exists as an anion in the CT state, which is a very different situation to the ground state. We think that it is too early in the present stage to conclude similarity of the benzene-ring structures for the CT states of PBN and DMABN and that we need further discussion of spectral patterns for various related compounds.

To summarize, we have measured the infrared spectrum of the excited CT state of PBN in acetonitrile solution. The CT-state of PBN gives infrared bands very similar to those due to the benzonitrile moiety of the excited CT state of DMABN. To correlate this result with the structural similarity of the CT states of DMABN and PBN, we need clear band assignments by isotope substitutions and detailed discussion on structure dependence of the infrared bands.

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References and Notes

(1) Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 690.
(2) Lippert, E.; Lüder, W.; Moll, F.; Nägele, W.; Boos, H.; Prigge, H.; Seibold-Blankenstein, I. *Angew. Chem.* **1961**, *73*, 685.
(3) Nakashima, N.; Mataga, N. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 3016.
(4) Rotkiewicz, K.; Grellmann, K. H.; Grabowski, Z. R. *Chem. Phys. Lett.* **1973**, *19*, 315.
(5) Grabowski, Z. R.; Rotkiewicz, K.; Siemiarczuk, A.; Cowley, D. J.; Baumann, W. *Nouv. J. Chim.* **1979**, *3*, 443.
(6) Rettig, W.; Bliss, B.; Dirnberger, K. *Chem. Phys. Lett.* **1999**, *305*, 8.
(7) Leinhos, U.; Kühnle, W.; Zachariasse, K. A. *J. Phys. Chem.* **1991**, *95*, 2013.
(8) Zachariasse, K. A.; von der Haar, T.; Hebecker, A.; Leinhos, U.; Kühnle, W. *Pure Appl. Chem.* **1993**, *65*, 1745.
(9) Zachariasse, K. A. *Chem. Phys. Lett.* **2000**, *320*, 8.
(10) Sobolewski, A. L.; Sudholt, W.; Domcke, W. *J. Phys. Chem. A* **1998**, *102*, 2716.
(11) Parusel, A. B. J.; Köhler, G.; Grimme, S. *J. Phys. Chem. A* **1998**, *102*, 6297.
(12) Hashimoto, M.; Hamaguchi, H. *J. Phys. Chem.* **1995**, *99*, 7875.
(13) Chudoba, C.; Kummrow, A.; Dreyer, J.; Stenger, J.; Nibbering, E. T. J.; Elsaesser, T.; Zachariasse, K. A. *Chem. Phys. Lett.* **1999**, *309*, 357.
(14) Okamoto, H. *J. Phys. Chem. A* **2000**, *104*, 4182.
(15) Kwok, W. M.; Ma, C.; Phillips, D.; Matousek, P.; Parker, A. W.; Towrie, M. *J. Phys. Chem. A* **2000**, *104*, 4188.
(16) Kummrow, A.; Dreyer, J.; Chudoba, C.; Stenger, J.; Nibbering, E. T. J.; Elsaesser, T. *J. Chin. Chem. Soc.* **2000**, *47*, 721.
(17) Kwok, W. M.; Ma, C.; Matousek, P.; Parker, A. W.; Phillips, D.; Toner, W. T.; Towrie, M.; Umapathy, S. *J. Phys. Chem. A* **2001**, *105*, 984.
(18) Okamoto, H.; Inishi, H.; Nakamura, Y.; Kohtani, S.; Nakagaki, R. *J. Phys. Chem. A* **2001**, *105*, 4182.
(19) Dreyer, J.; Kummrow, A. *J. Am. Chem. Soc.* **2000**, *122*, 2577.
(20) Techert, S.; Schotte, F.; Wulff, M. *Phys. Rev. Lett.* **2001**, *86*, 2030.
(21) Rettig, W.; Marschner, F. *Nouv. J. Chim.* **1983**, *7*, 425.
(22) Rettig, W. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 971.
(23) Rettig, W.; Marschner, F. *New J. Chem.* **1990**, *14*, 819.
(24) Cornelissen-Gude, C.; Rettig, W. *J. Phys. Chem. A* **1998**, *102*, 7754.
(25) Okamoto, H.; Tasumi, M. *Chem. Phys. Lett.* **1996**, *256*, 502.
(26) Okamoto, H. *Chem. Phys. Lett.* **1998**, *283*, 33.
(27) Okamoto, H.; Inishi, H.; Nakamura, Y.; Kohtani, S.; Nakagaki, R. *Chem. Phys.* **2000**, *260*, 193.
(28) Parusel, A. B. J. *Phys. Chem. Chem. Phys.* **2000**, *2*, 5545.
(29) Horng, M. L.; Gardecki, J. A.; Papazyan, A.; Maroncelli, M. *J. Phys. Chem.* **1995**, *99*, 17311.
(30) Rettig, W. *J. Mol. Struct.* **1982**, *84*, 303.
(31) Wilson, E. B., Jr. *Phys. Rev.* **1934**, *45*, 706.