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# Picosecond Transient Infrared Spectrum of 4-(Dimethylamino)benzonitrile in the Fingerprint Region

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The picosecond time-resolved infrared spectrum of 4-(dimethylamino)benzonitrile (DMABN) has been recorded in the fingerprint region in acetonitrile solution. Several induced infrared bands have been obtained. From the temporal behavior of the band intensities, the induced bands have been attributed to the $S_1$ state of DMABN that is believed to be an intramolecular charge-transfer excited state. Vibrational assignments of the observed bands and the molecular structure of the $S_1$ species are discussed. Most of the strong bands have been found in the single bond wavenumber region. From this result, the ring C−NMe$_2$ bond is considered to retain a single bond character in the $S_1$ state. No distinct infrared band that can be assigned to the locally excited state of DMABN has been observed. Measurements are also tried for 4-aminobenzonitrile in acetonitrile, but no induced infrared band has been found.

## 1. Introduction

In many compounds, electronic structures can be altered more easily in electronically excited states than in ground states by various external perturbations. For example, coordination of solvents to an electronically excited solute molecule (and other environmental changes) sometimes induces intramolecular charge-transfer (ICT) reaction. There are numerous studies on ICT reactions in excited states, especially for molecules with donor and acceptor groups linked by aromatic moieties. Among them, 4-aminobenzonitrile (ABN) derivatives, such as 4-(dimethylamino)benzonitrile (DMABN), may be regarded as typical examples.

For nearly four decades the DMABN molecule has been well-known for its dual fluorescence behavior.[1−3] This molecule shows a single ultraviolet spectral component of fluorescence in nonpolar solvents, whereas in polar solvents it shows another spectral component in the longer wavelength (visible) region, in addition to the ultraviolet one. In 1970s Grabowski and coworkers proposed[3−5] that the fluorescence behavior of DMABN can be interpreted by a model of twisted intramolecular charge transfer (TICT).[5−7] They considered that a DMABN molecule is excited by an ultraviolet photon to a locally excited (LE) state, and then it gives an ICT state in polar environments, where charge recombination is hindered by twisting the dimethylamino group perpendicular to the benzene plane. In this model, the dual fluorescence of DMABN in a polar solvent is explained as an overlap of fluorescence bands due to the LE and ICT states. The most essential experimental support for the TICT model has been given by fluorescence spectra of DMABN derivatives with restricted conformations of the dimethylamino group.[3,4,8−11] Although the TICT model has been widely accepted, direct evidence for the molecular structure of DMABN in the $S_1$ state has been very limited.

On the other hand, other models have also been proposed to explain the dual fluorescence behavior of DMABN. For example, some researchers have claimed that the long-wavelength component of the dual fluorescence does not come from an ICT state, but from an exciplex between the solute and solvent molecules.[12−14] According to recent studies, however, the most likely origin of the long-wavelength component is an ICT state which is stabilized in a polar environment. In recent theoretical works, the stability of ICT states with other than the TICT structure (or, in other words, charge-transfer reaction coordinates other than the twisting motion) has been discussed extensively.[15−22] Several possible structures of the ICT state of DMABN are depicted in Figure 1. The TICT structure is given in Figure 1B. The ICT structures shown in Figure 1C,D are called “wagged intramolecular charge transfer” (WICT)[16,21] and “rehybridized intramolecular charge transfer” (RICT),[17] respectively. (According to the most recent calculations, these structures do not seem to be very stable.[16,18−22]) From systematic studies of substituent effects on fluorescence spectra of ABN derivatives, it has been claimed that the ICT state of DMABN has a planar structure, including the carbon atoms of the dimethylamino group.[23−26] In this case, contribution of a zwitterionic structure as shown in Figure 1E may be considered, where the bond between amino N and ring C has a double bond character.

The dynamic behavior of excited DMABN has been extensively studied by time-resolved fluorescence and absorption spectroscopy.[14,27−40] It has been known that the $S_1$ (ICT) state of DMABN is generated on a time scale of 10 ps after photoexcitation in polar solvents, and that this state has a lifetime of hundreds of picoseconds to nanoseconds. Consequently, spectra of the $S_1$ species can be recorded by nanosecond time-resolved spectroscopy under a proper condition.

In the nanosecond infrared spectrum of DMABN in the C≡N triple bond stretching wavenumber region, an induced band by a transient species with a lifetime of the picosecond regime has been found, which is probably assigned to the $S_1$ state.[41] Very recently, a theoretical calculation has shown that the observed infrared wavenumber of the C≡N stretching band cannot be reasonably explained by the RICT structure.[20] However, information is still scanty to discuss other possibilities such as the

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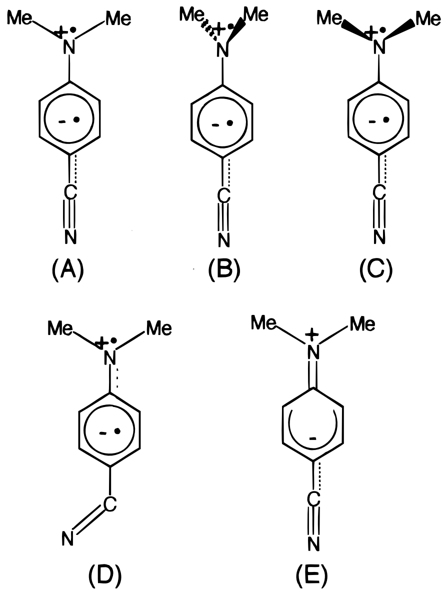

**Figure 1.** Several possible molecular structures for the intramolecular charge-transfer excited state of DMABN: (A) planar intramolecular charge-transfer (PICT) structure; (B) twisted intramolecular charge-transfer (TICT) structure; (C) wagged intramolecular charge-transfer (WICT) structure; (D) rehibridized intramolecular charge-transfer (RICT) structure; (E) another type of PICT structure.

planar structures. It is expected that we gain a deeper insight into the $S_1$-state geometry, if we measure an infrared spectrum of that species in the fingerprint region, which in general contains much structural information.

As other approaches to the molecular structure of DMABN in the $S_1$ state in a polar solvent, spectroscopic studies of DMABN−solvent complexes in a supersonic jet and those in supercritical fluid have been reported by several researchers.[8,9,39,42−48] However, it is hardly said that much information on the geometrical structure of the excited DMABN molecule itself has been obtained in these studies. Raman spectroscopy would give some information on the $S_1$-state structure, but the transient Raman spectrum of DMABN has not been obtained, probably because of the strong fluorescence.

The technique of ultrafast infrared spectroscopy has been much developed these days.[49−63] Although experimental reports in the fingerprint region are limited, it has become possible recently.[55,56,58−63] I have constructed an experimental setup for the picosecond infrared spectroscopy in the fingerprint region,[56,60] and have succeeded in recording transient infrared spectra of a few compounds in solution.[56,61−63] In the present study, we have tried to measure picosecond transient infrared spectra of DMABN and ABN, to obtain information on the molecular structure of the $S_1$ (ICT) state of DMABN in a polar solvent (acetonitrile). We have found several infrared bands due to the excited DMABN in the fingerprint region. I believe that these bands can serve potentially as a marker of the molecular structure.

## 2. Experimental Section

The experimental apparatus for the transient infrared spectroscopy was basically the same as that already reported elsewhere.[56,60] The transient absorption signal was obtained by a method based on optically heterodyned detection of absorption anisotropy (OHDAA), which I developed recently.[60] By this method we have much higher (factor of about 10) sensitivity in recording transient infrared spectra than by the conventional method. A wire grid infrared polarizer with a $BaF_2$ substrate was used, which was needed in the OHDAA method. The cross-correlation time between the pump and probe pulses was ∼4 ps, which determined the temporal resolution. The second harmonic of an amplified dye laser (ultraviolet) was used to pump the sample. One amplified dye laser was used for generating the infrared probe light as well as the ultraviolet pump radiation. Consequently, the pump wavelength changes as the probe wavenumber is scanned. However, the scanning range of the pump wavelength (276−287 nm), which nearly corresponds to the electronic absorption maximum of the sample, is much narrower than the width of the absorption band. Effects of the pump wavelength change may be hence no more than variation in the pumping efficiency caused principally by a change of the pump pulse energy. The pump energy per pulse was 0.5−3 $\mu$J, depending on the wavelength. Since the pumping efficiency is dependent on the probe wavenumber, the ordinate scale of the transient spectra shown in the following should not be regarded as a quantitative measure. On the transient infrared measurements, the whole spectral wavenumber region was divided into several small regions (typically ∼100 $cm^{-1}$ per small region), and the pieces of the spectrum recorded in small regions were rearranged to give a spectrum of the whole wavenumber region. The ordinate scale of each piece of the spectrum was adjusted by multiplying by a factor so as to connect smoothly to the next pieces in the borders. Other corrections of the intensity data, such as normalization against the pump pulse energy, were not made.

The transient infrared measurements were done in acetonitrile solutions for both DMABN and ABN (sample concentration $\sim(5-8) \times 10^{-2}$ mol $dm^{-3}$). Infrared absorption spectra of the ground electronic ($S_0$) state of DMABN, ABN, and *N*,*N*-dimethylaniline (DMA) in acetonitrile solutions were recorded by a JASCO FT/IR-420 Fourier transform infrared spectrophotometer.

## 3. Results and Discussion

**3.1. Infrared Spectra of the Ground-State Species.** Infrared absorption spectra of the $S_0$ state of DMABN, ABN, and DMA in acetonitrile solutions are shown in Figure 2. Comparison of these three spectra and the result of normal coordinate analysis on ABN[64] allow us to assign the major infrared bands of DMABN as shown in the figure. The C−N single bond stretch of the ring $C-NMe_2$ bond may have a significant contribution to a band observed at ∼1230 $cm^{-1}$. This wavenumber is rather high as a single bond stretching, and may be a result of interaction between lone pair electrons of the amino group and $\pi$ electrons of the benzene ring. A band assignable to the C−C single bond stretch of the ring C−CN bond is found at ∼1170 $cm^{-1}$.

**3.2. Dynamic Characteristics of Transient Infrared Spectra.** In Figure 3, the time-resolved infrared spectrum of DMABN is shown. The direction of the electronic transition moment of the ultraviolet absorption of DMABN (∼280 nm) is considered to be parallel to the longer axis of the molecule.[65] In the OHDAA method, the transient absorption signal depends on the angle ($\theta$) between transition moments of the electronic (for the pumping process) and the vibrational (for the probing process) transitions. A vibrational transition with $0° \le \theta < 54.7°$ (parallel absorption band) gives a signal of sign opposite that with $54.7° < \theta \le 90°$ (perpendicular absorption band).[60] In Figure 3, parallel bands of the excited species and perpendicular bands of the ground state give positive (upward) peaks. All the strong negative peaks can be assigned to the bleached absorption

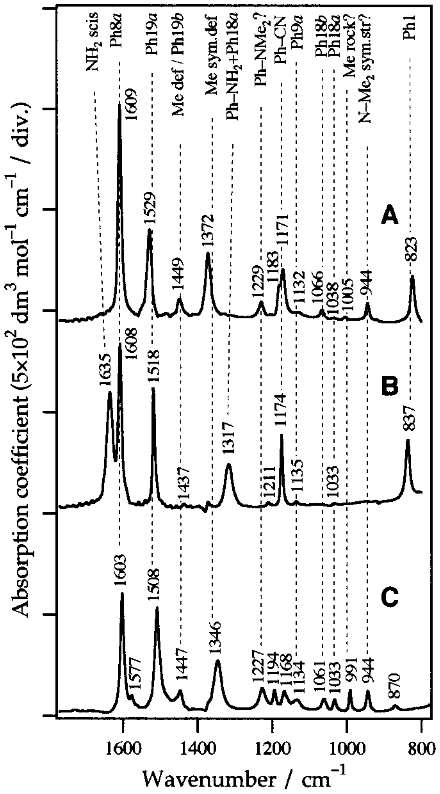

**Figure 2.** Infrared spectra of DMABN (A), ABN (B), and DMA (C) in the $S_0$ state in acetonitrile solutions. The solvent bands are numerically removed. The sample concentration is ~5 × 10$^{-2}$ mol dm$^{-3}$ in each solution. Vibrational assignments are shown at the top: scis, scissoring; Ph, phenyl or phenylene; def, deformation; str, stretch; Ph1 represents, for example, the $\nu_1$ mode (Wilson notation[74]) of the phenyl/phenylene group.

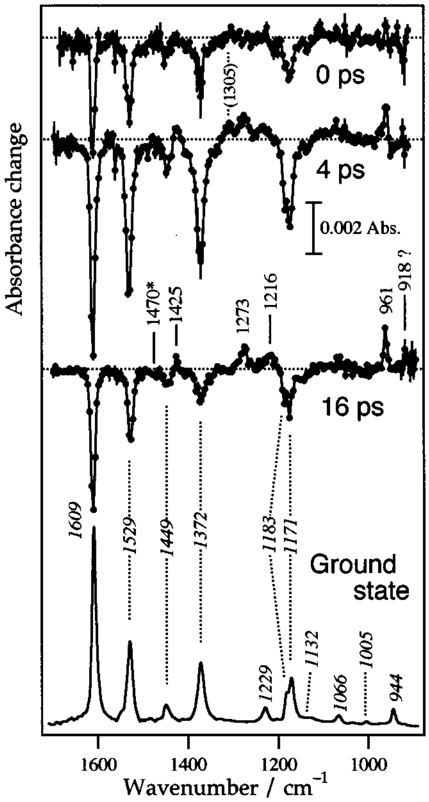

**Figure 3.** Time-resolved infrared spectrum of DMABN in acetonitrile solution. The wavenumbers of bands attributed to the $S_0$ and $S_1$ species are given, respectively, below and above the 16 ps trace. The band marked with an asterisk (1470 cm$^{-1}$) is a negative induced band. See the text for the meaning of the band wavenumber in parentheses (1305 cm$^{-1}$) given above the 4 ps trace. The infrared spectrum of the $S_0$ species (the same one as that in Figure 2A) is shown at the bottom.

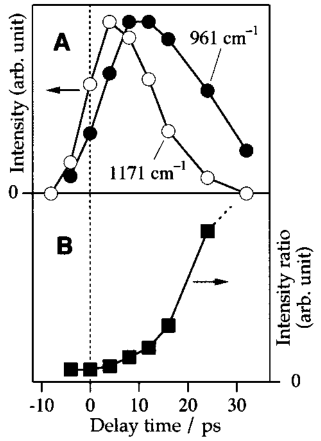

**Figure 4.** (A) Transient infrared absorption intensities (in the OHDAA method) against delay time between pump and probe pulses, at 1171 cm$^{-1}$ (open circles) and at 961 cm$^{-1}$ (closed circles). The intensity scale of each band is normalized to its maximum. (B) The 961 cm$^{-1}$ band intensity divided by that of the 1171 cm$^{-1}$ band.

by the ground-state molecules. These bleached bands rise instantaneously within the temporal resolution, and decay with a lifetime of ~10 ps. The decay observed here is attributed principally to the reorientational relaxation of the $S_0$ molecule.

In addition to the bleached absorption bands, we find several induced bands which can be assigned to transient species. Most of the induced bands are parallel bands. The strongest peak of them is observed at 961 cm$^{-1}$. This band rises in several picoseconds, which is clearly longer than the temporal resolution, and decays with a lifetime of ~20 ps. To examine the dynamic behavior of the excited species observed more in detail, delay-time dependencies of the induced band at 961 cm$^{-1}$ and of the bleached band at 1174 cm$^{-1}$ are roughly recorded. The results are shown in Figure 4A. The difference between the dynamic behavior of the bleached band and that of the induced band is very clear. Assume here that depopulation of the $S_0$ species after the pump pulse remains constant within the time range of the abscissa of Figure 4, and that the decay of the 1174 cm$^{-1}$ band intensity is due solely to reorientational relaxation of the $S_0$ molecules. If we further assume that the reorientational relaxation time of the transient species is the same as that of the $S_0$ state, we can work out the population of the transient species by dividing the intensity at 961 cm$^{-1}$ by that at 1174 cm$^{-1}$. (This treatment corresponds to separation of the effect of reorientational relaxation from the decay curve of the 961 cm$^{-1}$ band.) The result is plotted in Figure 4B. From this plot, the rise time of the transient species giving the 961 cm$^{-1}$ band is estimated to be on the order of 10 ps. Here we have assumed that the reorientational relaxation time of the excited species is the same as that of the ICT state. In the ICT state in reality, however, dipole–dipole interaction between solute and solvent molecules may be stronger than that in the $S_0$ state. Then, the reorientational relaxation time of the ICT state is possibly slower than that of the $S_0$ state. In this case, it should be considered that the rise of the transient is faster than that found in Figure 4B. For example, if we assume the reorientational relaxation time of the transient giving the 961 cm$^{-1}$ band to be twice the observed decay time of the 1174 cm$^{-1}$ band, we obtain a result that the rise of the excited-state population is completed in ~20 ps (i.e., rise time of 10−15 ps). This result shows that the rise time of excited population estimated from the decay of the transient infrared bands is on the order of 10 ps even if the reorientational relaxation of the excited species is slower than that of the $S_0$ species.

It has been shown, by time-resolved fluorescence and absorption measurements, that it takes on the order of 10 ps for DMABN in polar solvents (6−16 ps in acetonitrile solution at room temperature according to the time-resolved fluorescence data[24,27]) to generate the $S_1$ (ICT) state after photoexcitation to the LE state.[27−35,37,38] The temporal behavior of the 961 $cm^{-1}$ band obtained in Figure 4B approximately agrees with this dynamical characteristic of the $S_1$ state, and consequently this band may be attributed to the $S_1$ state of DMABN. In Figure 3, temporal dependencies of other induced transient bands seem to be the same as that of the band at 961 $cm^{-1}$ within the experimental accuracy. All of these bands may be hence assigned to the $S_1$ state of DMABN. The induced bands are apparently rather weak in Figure 3. However, from Figure 4B, the intrinsic intensities of the induced bands, after completion of the LE → ICT internal conversion, are supposed to be quite strong.

The DMABN molecules should be populated on the LE state immediately after the photoexcitation.[65] In the spectra at 0 and 4 ps in Figure 3, however, we cannot find any distinct induced bands attributable to the LE state within the experimental accuracy. (There is possibly a weak band at 1305 $cm^{-1}$, but a further check is needed.) We may conclude that there is no strong transient absorption band due to the LE state in the wavenumber region under study. It has been believed that the intramolecular charge separation in the LE state is weak (i.e., the dipole moment is small), in contrast to that in the ICT ($S_1$) state.[10,11,66−68] Strong infrared absorption bands are expected for a molecule possessing a large dipole moment, since some of the derivatives of dipole moment against intramolecular nuclear coordinates may be large.[56,62] The present result, that no transient infrared bands due to the LE state are observed, is in accordance with the idea that there is a relatively small extent of charge separation in the LE state.

In Figure 5, the time-resolved infrared absorption spectrum of ABN is shown. We can find no transient bands in this spectrum within the experimental accuracy, except for the bleached absorption bands by the ground state. The dual fluorescence is not observed for ABN even in polar solvents. From this fact it is considered that charge separation does not occur for ABN in solution by ultraviolet photoexcitation.[38] The present observation, that no induced infrared bands are observed, is again in good accordance with the weak charge separation in the excited state of ABN generated by ultraviolet irradiation.

**3.3. Assignments of the Vibrational Bands and Molecular Structure of the $S_1$ State of DMABN.** *Single Bond Stretching Region.* We first discuss the strong transient induced band at 961 $cm^{-1}$. The $S_1$ state of DMABN (in a polar solvent) is considered to have a strong intramolecular charge-transfer character.[10,11,36,66−68] In the ICT state of this molecule, the dimethylamino group may be positively charged, and the negative charge may be delocalized in the benzonitrile moiety. Accordingly, the C−N stretching vibration of the ring C−$NMe_2$ bond may induce a large vibrational transition moment, and is expected to give a strong infrared absorption band. The strong intensity of the 961 $cm^{-1}$ band possibly suggests a significant contribution of the C−N stretch to this band. This band is associated with a parallel vibrational transition moment as mentioned earlier, and this observation is consistent with the assignment of this band to the C−N stretch. If this assignment is correct, the quite low wavenumber of this band may indicate a pure single bond character (i.e., very low $\pi$ bond order) of the ring C−$NMe_2$ bond.

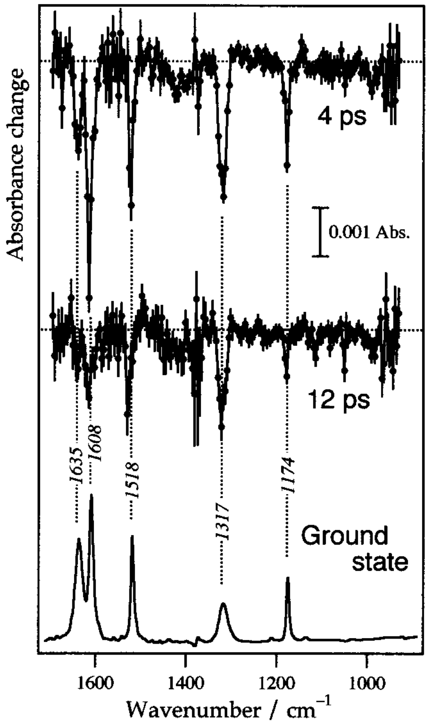

**Figure 5.** Time-resolved infrared spectrum of ABN in acetonitrile solution. The wavenumbers of bands attributed to the $S_0$ species are given below the 12 ps trace. The infrared spectrum of the $S_0$ species (the same one as that in Figure 2B) is shown at the bottom.

Of course we have to examine possibilities that this band is assigned to other vibrational modes. Then we next discuss vibrational modes of the benzene ring. Let us consider vibrational modes of a hypothetical molecule A−$\phi$−B ($\phi = p$-$C_6H_4$), where A and B are mass points, as a model system of para-disubstituted benzenes such as DMABN (A = $NMe_2$, B = CN). This corresponds to neglect of internal degrees of freedom of groups A and B. Then, 11 vibrational modes of this molecule can be observed in the infrared spectrum as parallel absorption bands. They are two C−H stretches, one C−A stretch and one C−B stretch (the C−N stretch of DMABN discussed above is categorized in this class), three C−C stretches of the benzene ring, two in-plane CH bends, and two CCC deformations of the ring. Among them, C−H stretches should appear around 3000 $cm^{-1}$ and are out of consideration for the assignment of the 961 $cm^{-1}$ band. Vibrational modes with major contributions from CCC deformations may have frequencies lower than 900 $cm^{-1}$. Furthermore, modes with major contributions from CH in-plane bends and one or two modes of ring C−C stretches may appear in the region higher than 1000 $cm^{-1}$. As a result, only three or four vibrational modes of the A−$\phi$−B molecule (including the C−A and C−B stretches) may give parallel absorption bands around 960 $cm^{-1}$.

We further examine this point on the basis of vibrational analyses of related compounds. The electronic structure of the benzene ring part of DMABN is possibly quite different between the $S_0$ state and the $S_1$ state. We therefore compare vibrational modes (those associated with vibrational transition moments parallel to the longer axes of the molecules) of not only substituted benzenes in the ground state but also quinoid molecules and an electronically excited substituted benzene. In

**TABLE 1: Vibrational Wavenumbers of Monosubstituted and Para-Disubstituted Benzenoid and Quinoid Compounds**[a]

| mode[b] | TL[c] | tSB[d] | ABN[e] | BQ[f] | BQM[g] |
|---|---|---|---|---|---|
| $\nu_{8a}$ (C−Cstr) | 1605 | 1533 ($\nu_8$) | 1605 | 1663 ($\nu_2$)[i] | 1621 ($\nu_3$)[k] |
| | | | | 1613 ($\nu_3$) | 1536 ($\nu_4$) |
| $\nu_{19a}$ (C−Cstr/CHbend) | 1494 | 1454 ($\nu_{10}$)[h] | 1510 | 1354 ($\nu_{14}$) | 1344 ($\nu_{20}$) |
| $\nu_{9a}$ (CHbend) | 1175 | 1162 ($\nu_{15}$) | 1140 | 1146 ($\nu_4$) | 1173 ($\nu_6$) |
| | | 1157 ($\nu_{16}$) | | | |
| $\nu_{18a}$ (C−Cstr/CHbend) | 1030 | 993 ($\nu_{19}$) | 1040 | 944 ($\nu_{15}$) | 966 ($\nu_{21}$) |
| $\nu_{12}$ (C−Cstr/CCCdef) | 1003 | 970 ($\nu_{20}$) | 640 | (944) ($\nu_{15}$)[j] | (966) ($\nu_{21}$)[l] |
| | | | 1040 | (728) ($\nu_{16}$) | (779) ($\nu_{22}$) |
| $\nu_1$ (C−Cstr/CCCdef) | 784 | 849 ($\nu_{21}$) | 830 | 770 ($\nu_5$) | 793 ($\nu_7$) |
| $\nu_{6a}$ (CCCdef) | 521 | 588 ($\nu_{23}$) | 440 | 446 ($\nu_6$) | 458 ($\nu_8$) |
| $\nu_{7a}$ (C−A,C−Bstr) | 1208 | 1162 ($\nu_{15}$) | 1280 (C−$NH_2$) | (1663) ($\nu_2$)[i] | (1621) ($\nu_3$)[k] |
| | | 1157 ($\nu_{16}$) | 1170 (C−CN) | (1613) ($\nu_3$) | (1536) ($\nu_4$) |

[a] Only modes of $A_1$ local symmetry species (under $C_{2v}$ local symmetry) are listed. [b] Wilson notation.[74] [c] Toluene, $C_6H_5-CH_3$; mode assignments are given in ref 69. [d] *trans*-Stilbene, $C_6H_5-CH=CH-C_6H_5$; mode assignments and numbering (in parentheses) are given in ref 70. [e] *p*-Aminobenzonitrile, $NC-C_6H_4-NH_2$; mode assignments are given in ref 64. [f] *p*-Benzoquinone, $O=C_6H_4=O$; mode assignments and numbering (in parentheses) are given in ref 71. [g] *p*-Benzoquinodimethane, $CH_2=C_6H_4=CH_2$; mode assignments and numbering (in parentheses) are given in ref 71. [h] Wavenumber in $C_6H_5-CD=CD-C_6H_5$. [i] Modes $\nu_2$ and $\nu_3$ of BQ are hybrid modes of $\nu_{8a}$ and the C=O stretch. [j] Both $\nu_{15}$ and $\nu_{16}$ of BQ seem to include a significant contribution of $\nu_{12}$. [k] Modes $\nu_3$ and $\nu_4$ of BQM are hybrid modes of $\nu_{8a}$ and the $C=CH_2$ stretch. [l] Both $\nu_{21}$ and $\nu_{22}$ of BQM seem to include a significant contribution of $\nu_{12}$.

Table 1, the results of vibrational analyses of substituted benzenes (toluene,[69] $a_g$ modes of *trans*-stilbene in the $S_1$ state,[70] and ABN[64]) and quinoids (*p*-benzoquinone and *p*-benzoquinodimethane)[71] are summarized. Despite serious differences in the electronic structures, the vibrational frequencies of the benzenoid and quinoid molecules listed in the table are quite similar, with a few exceptions such as $\nu_{7a}$. (The dissimilarity in $\nu_{7a}$ is a matter of course considering the difference in the C−A and C−B bond characters of benzenoids and quinoids.) In addition, the similarity seems to apply also to the excited *trans*-stilbene. (We should note, however, that the principally excited part of $S_1$ *trans*-stilbene is the olefinic moiety.[72,73]) Consequently, it is supposed that the vibrational wavenumbers for low-lying excited states of other *para*-disubstituted benzenes are also similar to those in Table 1. Then, within the framework of the discussion here, the only vibrational modes of the benzene ring which can give bands around 960 $cm^{-1}$ are $\nu_{18a}$ and/or $\nu_{12}$.

In the ICT state of DMABN, the negative charge may be delocalized in the benzonitrile moiety, and the charge distribution may be easily changed by small perturbations. It may then be possible that either one of $\nu_{18a}$ or $\nu_{12}$ of the benzene ring or the C−C stretch of the ring C−CN bond is associated with a large vibrational transition moment. In that case these vibrational motions may give rise to the infrared band at 961 $cm^{-1}$.

We should consider at the same time some possibilities that the C−$NMe_2$ stretching coordinate contributes to modes other than that giving the 961 $cm^{-1}$ band. We have observed relatively strong transient infrared bands at 1273 and 1216 $cm^{-1}$. It may be possible that $\nu_{18a}$, $\nu_{12}$, and $\nu_{9a}$ of the benzene ring and the C−CN and C−$NMe_2$ stretching coordinates are hybridized, and that the large vibrational oscillator strength of the C−$NMe_2$ stretch is distributed among the three strong infrared bands (1273, 1216, and 961 $cm^{-1}$).

In any case, all the strong transient infrared bands due to the $S_1$ state are observed in the region between 1300 and 900 $cm^{-1}$ (this point will be mentioned again later). It is reasonable to consider that the C−$NMe_2$ stretching vibration contributes to one (or more) of these strong bands as mentioned in the first part of this subsection. This wavenumber range corresponds to the single bond stretching region, and it may be safely concluded that the C−$NMe_2$ bond of the $S_1$ (ICT) state has a single bond character.

Some internal vibrational modes of the dimethylamino group, which is treated as being fixed in the discussion above, can give parallel infrared absorption bands. One or two modes among them (i.e., symmetric N−Me stretch and symmetric Me rock) may have vibrational wavenumbers around 960 $cm^{-1}$. However, it is not very conceivable that these vibrational motions of the dimethylamino group are directly coupled to dipole moment changes. These modes perhaps do not give strong transient infrared bands like that at 961 $cm^{-1}$.

*Double and Triple Bond Stretching Region.* If the ring C−$NMe_2$ bond is more like a double bond than a single bond, then a band due to stretching of this double bond should appear in the transient infrared spectrum. The band must be quite strong as far as charge separation occurs between the dimethylamino and benzonitrile moieties in the $S_1$ state. However, no induced infrared band of the $S_1$ state is observed in the double bond stretching region in Figure 3. This leads to a conclusion that the C−$NMe_2$ bond does not have a double bond character and is rather described as a single bond in the $S_1$ state.

Hashimoto and Hamaguchi recorded the nanosecond transient infrared spectrum of the $S_1$ state of DMABN in butanol in the triple bond stretching region,[41] and found a band attributed to the C≡N triple bond stretch at ∼2100 $cm^{-1}$. This wavenumber region is outside our present measuring range, but the excited species they observed may be the same as that observed in the present study. If the $S_1$ state has a RICT structure (Figure 1D), the C−N bond of the cyano moiety is supposed to become more like a double bond.[17,20] Then, a transient infrared band due to the C−N stretch of the cyano group should appear in the double bond stretching region. In fact, Sobolewski et al. have tried normal coordinate calculation for the $S_1$ state of DMABN with the RICT structure, and have obtained a result that agrees with this expectation.[20] The experimental observations, that the C≡N triple bond stretch is observed at ∼2100 $cm^{-1}$ in the previous study[41] and that no infrared band is observed in the double bond region in the present study, indicate that the structure of the $S_1$ state of DMABN in a polar solvent is not a RICT-type one.

## 4. Concluding Remarks

In the present study, on the basis of picosecond transient infrared spectroscopy in the fingerprint region, it has been concluded that the structures shown in Figure 1D,E are not likely for the $S_1$ state of DMABN in acetonitrile. The ring C−$NMe_2$ bond has a single bond character, and the C−N bond of the cyano group is regarded as a triple bond (or a cumulative double bond). On the other hand, assignments of the observed infrared bands are still not clear, and measurements of isotope-substituted compounds are highly desired. If the directions of the vibrational transition moments are determined in a reasonably high precision from a polarization dependence measurement,[56] further detailed information on the $S_1$-state structure is expected. We can discuss clearly, in principle, the possibility of the WICT-type structure by this method. That is, if the molecule has a WICT structure, then $\theta$ (the angle between electronic and vibrational transition moments) of neither 0° nor 90° is possible, while it should give only 0° or 90° in the case of a TICT or a planar structure. Further discussion of vibrational assignments and the excited molecular structure may also be possible, through analyses of the presently obtained infrared spectrum based on theoretical calculations.

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**Note Added in Proof.** After submission of the original manuscript of this paper, I was informed by Drs. Zachariasse and Nibbering that they and their co-workers had recently measured a picosecond infrared spectrum of DMABN in the wavenumber region above 1270 cm$^{-1}$, and a manuscript dealing with the data was already submitted. The paper has been published in ref 75 very recently. The data they have obtained are consistent with those in the present study at least as far as the ICT state is concerned.

## References and Notes

(1) Lippert, E. *Angew. Chem.* **1961**, *73*, 695.
(2) Nakashima, N.; Mataga, N. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 3016.
(3) Rotkiewicz, K.; Grellmann, K. H.; Grabowski, Z. R. *Chem. Phys. Lett.* **1973**, *19*, 315.
(4) Siemiarczuk, A.; Grabowski, Z. R.; Krówczyński, A.; Asher, M.; Ottolenghi, M. *Chem. Phys. Lett.* **1977**, *51*, 315.
(5) Grabowski, Z. R.; Rotkiewicz, K.; Siemiarczuk, A.; Cowley, D. J.; Baumann, W. *Nouv. J. Chim.* **1979**, *3*, 443.
(6) Rettig, W. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 971.
(7) Lippert, E.; Rettig, W.; Bonačić-Koutecký, V.; Heisel, F.; Miehé, J. A. *Adv. Chem. Phys.* **1987**, *68*, 1.
(8) Kobayashi, T.; Futakami, M.; Kajimoto, O. *Chem. Phys. Lett.* **1987**, *141*, 450.
(9) August, J.; Palmer, T. F.; Simons, J. P.; Jouvet, C.; Rettig, W. *Chem. Phys. Lett.* **1988**, *145*, 273.
(10) Sinha, H. K.; Muralidharan, S.; Yates, K. *Can. J. Chem.* **1992**, *70*, 1932.
(11) Rettig, W.; Braun, D.; Suppan, P.; Vauthey, E.; Rotkiewicz, K.; Luboradzki, R.; Suwińska, K. *J. Phys. Chem.* **1993**, *97*, 13500.
(12) Visser, R. J.; Varma, C. A. G. O. *J. Chem. Soc., Faraday Trans. 2* **1980**, *76*, 453.
(13) Visser, R. J.; Varma, C. A. G. O.; Konijnenberg, J.; Bergwerf, P. *J. Chem. Soc., Faraday Trans. 2* **1983**, *79*, 347.
(14) Weisenborn, P. C. M.; Huizer, A. H.; Varma, C. A. G. O. *Chem. Phys.* **1989**, *133*, 437.
(15) Kato, S.; Amatatsu, Y. *J. Chem. Phys.* **1990**, *92*, 7241.
(16) Serrano-Andrés, L.; Merchán, M.; Roos, B. O.; Lindh, R. *J. Am. Chem. Soc.* **1995**, *117*, 3189.
(17) Sobolewski, A. L.; Domcke, W. *Chem. Phys. Lett.* **1996**, *250*, 428.
(18) Sobolewski, A. L.; Domcke, W. *Chem. Phys. Lett.* **1996**, *259*, 119.
(19) Gedeck, P.; Schneider, S. *J. Photochem. Photobiol., A* **1997**, *105*, 165.
(20) Sobolewski, A. L.; Sudholt, W.; Domcke, W. *J. Phys. Chem. A* **1998**, *102*, 2716.
(21) Parusel, A. B. J.; Köhler, G.; Grimme, S. *J. Phys. Chem. A* **1998**, *102*, 6297.
(22) Sudholt, W.; Sobolewski, A. L.; Domcke, W. *Chem. Phys.* **1999**, *240*, 9.
(23) von der Haar, T.; Hebecker, A.; Il'ichev, Y.; Jiang, Y.-B.; Kühnle, W.; Zachariasse, K. A. *Recl. Trav. Chim. Pays-Bas* **1995**, *114*, 430.
(24) Zachariasse, K. A.; Grobys, M.; von der Haar, T.; Hebecker, A.; Il'ichev, Y. V.; Jiang, Y.-B.; Morawski, O.; Kühnle, W. *J. Photochem. Photobiol., A* **1996**, *102*, 59.
(25) Zachariasse, K. A.; Grobys, M.; von der Haar, T.; Hebecker, A.; Il'ichev, Y. V.; Morawski, O.; Rückert, I.; Kühnle, W. *J. Photochem. Photobiol., A* **1997**, *105*, 373.
(26) Il'ichev, Y. V.; Kühnle, W.; Zachariasse, K. A. *J. Phys. Chem. A* **1998**, *102*, 5670.
(27) Huppert, D.; Rand, S. D.; Rentzepis, P. M.; Barbara, P. F.; Struve, W. S.; Grabowski, Z. R. *J. Chem. Phys.* **1981**, *75*, 5714.
(28) Wang, Y.; McAuliffe, M.; Novak, F.; Eisenthal, K. B. *J. Phys. Chem.* **1981**, *85*, 3736.
(29) Wang, Y.; Eisenthal, K. B. *J. Chem. Phys.* **1982**, *77*, 6076.
(30) Hicks, J.; Vandersall, M.; Babarogic, Z.; Eisenthal, K. B. *Chem. Phys. Lett.* **1985**, *116*, 18.
(31) Heisel, F.; Miehé, J. A. *Chem. Phys.* **1985**, *98*, 233.
(32) Meech, S. R.; Phillips, D. *Chem. Phys. Lett.* **1985**, *116*, 262.
(33) Heisel, F.; Miehé, J. A. *Chem. Phys. Lett.* **1986**, *128*, 323.
(34) Meech, S. R.; Phillips, D. *J. Chem. Soc., Faraday Trans. 2* **1987**, *83*, 1941.
(35) Okada, T.; Mataga, N.; Baumann, W. *J. Phys. Chem.* **1987**, *91*, 760.
(36) Su, S.-G.; Simon, J. D. *J. Chem. Phys.* **1988**, *89*, 908.
(37) Su, S.-G.; Simon, J. D. *J. Phys. Chem.* **1989**, *93*, 753.
(38) Leinhos, U.; Kühnle, W.; Zachariasse, K. A. *J. Phys. Chem.* **1991**, *95*, 2013.
(39) Kajimoto, O.; Nayuki, T.; Kobayashi, T. *Chem. Phys. Lett.* **1993**, *209*, 357.
(40) Fisz, J. J.; van Hoek, A. *Chem. Phys. Lett.* **1997**, *270*, 432.
(41) Hashimoto, M.; Hamaguchi, H. *J. Phys. Chem.* **1995**, *99*, 7875.
(42) Kobayashi, T.; Futakami, M.; Kajimoto, O. *Chem. Phys. Lett.* **1986**, *130*, 63.
(43) Peng, L. W.; Dantus, M.; Zewail, A. H.; Kemnitz, K.; Hicks, J. M.; Eisenthal, K. B. *J. Phys. Chem.* **1987**, *91*, 6162.
(44) Gibson, E. M.; Jones, A. C.; Phillips, D. *Chem. Phys. Lett.* **1987**, *136*, 454.
(45) Kajimoto, O.; Futakami, M.; Kobayashi, T.; Yamasaki, K. *J. Phys. Chem.* **1988**, *92*, 1347.
(46) Warren, J. A.; Bernstein, E. R.; Seeman, J. I. *J. Chem. Phys.* **1988**, *88*, 871.
(47) Grassian, V. H.; Warren, J. A.; Bernstein, E. R.; Secor, H. V. *J. Chem. Phys.* **1989**, *90*, 3994.
(48) Howell, R.; Phillips, D.; Petek, H.; Yoshihara, K. *Chem. Phys.* **1994**, *188*, 303.
(49) Spanner, K.; Laubereau, A.; Kaiser, W. *Chem. Phys. Lett.* **1976**, *44*, 88.
(50) Moore, J. N.; Hansen, P. A.; Hochstrasser, R. M. *Chem. Phys. Lett.* **1987**, *138*, 110.
(51) Graener, H.; Ye, T.-Q.; Laubereau, A. *Chem. Phys. Lett.* **1989**, *164*, 12.
(52) Hübner, H.-J.; Wörner, M.; Kaiser, W.; Seilmeier, A. *Chem. Phys. Lett.* **1991**, *182*, 315.
(53) Beckerle, J. D.; Cavanagh, R. R.; Casassa, M. P.; Heilweil, E. J.; Stephenson, J. C. *J. Chem. Phys.* **1991**, *95*, 5403.
(54) Stoutland, P. O.; Dyer, R. B.; Woodruff, W. H. *Science* **1992**, *257*, 1913.
(55) Hamm, P.; Zurek, M.; Mäntele, W.; Meyer, M.; Scheer H.; Zinth, W. *Proc. Natl. Acad. Sci. U.S.A.* **1995**, *92*, 1826.
(56) Okamoto, H.; Tasumi, M. *Chem. Phys. Lett.* **1996**, *256*, 502.
(57) Akhremitchev, B.; Wang, C.; Walker, G. C. *Rev. Sci. Instrum.* **1996**, *67*, 3799.
(58) Hamm, P.; Zurek, M.; Röschinger, T.; Patzelt, H.; Oesterhelt D.; Zinth, W. *Chem. Phys. Lett.* **1997**, *268*, 180.
(59) Hamm, P.; Ohline, S. M.; Zinth, W. *J. Chem. Phys.* **1997**, *106*, 519.
(60) Okamoto, H. *Chem. Phys. Lett.* **1998**, *283*, 33.
(61) Okamoto, H. *Chem. Lett.* **1998**, 1141.
(62) Okamoto, H.; Tasumi, M. *Laser Chem.* **1999**, *19*, 363.
(63) Okamoto, H. *J. Phys. Chem. A* **1999**, *30*, 5852.
(64) Kumar, A. P.; Rao, G. R. *Spectrochim. Acta A* **1997**, *53*, 2049.
(65) Herbich, J.; Rotkiewicz, K.; Waluk, J.; Andresen, B.; Thulstrup, E. W. *Chem. Phys.* **1989**, *138*, 105.
(66) Jonker, S. A.; Warman, J. M. *Chem. Phys. Lett.* **1991**, *185*, 36.
(67) Schuddeboom, W.; Jonker, S. A.; Warman, J. M.; Leinhos, U.; Kühnle, W.; Zachariasse, K. A. *J. Phys. Chem.* **1992**, *96*, 10809.
(68) Baumann, W.; Bischof, H.; Fröhling, J.-C.; Brittinger, C.; Rettig, W.; Rotkiewicz, K. *J. Photochem. Photobiol., A* **1992**, *64*, 49.
(69) Tasumi, M.; Urano, T.; Nakata, M. *J. Mol. Struct.* **1986**, *146*, 383.
(70) Urano, T.; Hamaguchi, H.; Tasumi, M.; Yamanouchi, K.; Tsuchiya, S.; Gustafson, T. *J. Chem. Phys.* **1989**, *91*, 3884.
(71) Yamakita, Y.; Tasumi, M. *J. Phys. Chem.* **1995**, *99*, 8524.
(72) Dyck, R. H.; McClure, D. S. *J. Chem. Phys.* **1962**, *36*, 2326.
(73) Myers, A. B.; Trulson, M. O.; Mathies, R. A. *J. Chem. Phys.* **1985**, *83*, 5000.
(74) Wilson, E. B., Jr. *Phys. Rev.* **1934**, *45*, 706.
(75) Chudoba, C.; Kummrow, A.; Dreyer, J.; Stenger, J.; Nibbering, E. T. J.; Elsaesser, T.; Zachariasse, K. A. *Chem. Phys. Lett.* **1999**, *309*, 357.