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Time-Resolved Study of the Triplet State of 4-dimethylaminobenzonitrile (DMABN)

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Nanosecond time-resolved resonance Raman spectra of the triplet states of DMABN, DMABN-d_6, and DMABN−N^{15} have been obtained over the frequency range from 700 to 2300 cm^{-1}. Isotopic shifts identify modes associated with the dimethylaniline subgroup. There is no significant difference between spectra recorded in polar and nonpolar solvents implying that the lowest triplet state ($^3T_1$) state has only one form. Our results characterize it as planar or near planar in structure, with a high negative charge localization on the cyano group and a substantial loosening of the ring skeleton with conjugation extending to the amino group. Nonradiative deactivation of the singlet intramolecular charge transfer state (^{1}ICT) through intersystem crossing is discussed in relation to the transient absorption spectra.

Introduction

Since its discovery in 1951,[1] the solvent dependent dual fluorescence of DMABN (4-dimethylaminobenzonitrile) has been interpreted in terms of an intramolecular charge transfer (ICT) reaction from a Locally Excited (^{1}LE) state to an ^{1}ICT state that occurs only in polar solvents.[2] The ^{1}LE and ^{1}ICT are singlet states emitting the normal and anomalous red fluorescence, respectively. The electronic and geometric properties of these states have been verified by extensive experimental[3−7] and theoretical[8−12] investigations. The ^{1}LE state was found to have conjugated planar character[4,6,8,9,11,12] and a dipole moment of 10 D,[13] and the electronic decoupling TICT (Twisted ICT) model for the highly polar (17 D)[13] ^{1}ICT state was recently confirmed by picosecond Kerr gated time-resolved resonance Raman (ps-K-TR^3) spectroscopy[14] and time-resolved infrared (TRIR) studies performed by several groups.[5−7] We therefore designate the ^{1}ICT state as ^{1}TICT in the text below.

The triplet state has also been extensively studied experimentally[7,15−20] and theoretically.[9,11,21−23] Intersystem crossing (ISC) has been shown to be the principal nonradiative deactivation channel for singlet states, irrespective of solvent polarity.[16,18,20] Most of these studies suggest that the lowest triplet state ($^3T_1$) of DMABN has a planar $\pi\pi^*$ state nature and only this non-ICT triplet state is active in the $^3T_1 \rightarrow S_0$ ISC and phosphorescence processes.[17−19,21−23] However, this view is challenged by TRIR studies performed by Hashimoto and Hamaguchi which identify a ^{3}TICT state in polar solvent.[7] The electronic and structural properties of the $^3T_1$ state and their sensitivity to solvent polarity thus remain unclear. In particular, no vibrational bands of $^3T_1$ have previously been reported, other than the C≡N stretch.[7] Although the frequency of this mode reflects the extent of negative charge localization on the cyano group,[4,7,8] it alone cannot be used to determine the structure of the excited state of DMABN, which is mostly related to the conformation of the dimethylaniline subgroup. Frequencies of the amino nitrogen-phenyl ring stretching mode (ν^s(ph-N)) and ring modes, such as C═C stretching vibrations, are essential in the evaluation of its bonding configuration.[24,25] The lack of structural data has led to some controversy for both the triplet geometry (planar or TICT) and the ISC mechanism. In this paper, we present and discuss resonance Raman and transient absorption data that directly resolve these issues.

Experimental Section

Nanosecond-TR^3 spectra were obtained using a system described previously.[26] The sample was pumped by a 308 nm excimer laser pulse and probed at 532 nm using the second harmonic output of a Nd:YAG laser. Pump and probe energies were between 0.5 and 1 mJ, and the repetition rate was 10 Hz. The laser beam was loosely focused (∼0.5 mm beam diameter) onto a quartz sample tube (3 mm diameter) and light scattered at 90° was imaged onto the spectrograph slit. To reduce fluorescence background (400−600 nm, ∼3 ns lifetime) of DMABN appearing in methanol,[4,27] a gated O−SMA diode array detector was used to obtain the TR^3 spectrum shown in Figure 2(b). The gate width was 50 ns with ∼5 ns rise time and jitter. To enable direct comparison, the same detector and conditions were used for the spectrum of DMABN in hexane in Figure 2(a) although the fluorescence background is small in this case. Figure 3 shows hexane spectra for DMABN and isotopically substituted DMABN recorded with better resolution using a more sensitive nitrogen-cooled CCD detector. Spectra were accumulated over 20−100 min with pump only and probe only spectra being subtracted. The solution was circulated during the experiments, and argon was bubbled through the reservoir to remove oxygen. UV absorption measurements before and after sample use revealed no degradation. Similar spectra were obtained using nitrogen bubbling but oxygen bubbling quenched the Raman signal. Acetonitrile Raman bands were used to calibrate the TR^3 spectra with an estimated accuracy of ±5 cm^{-1} in absolute frequency. The spectra are not corrected for variations in throughput and detector efficiency.

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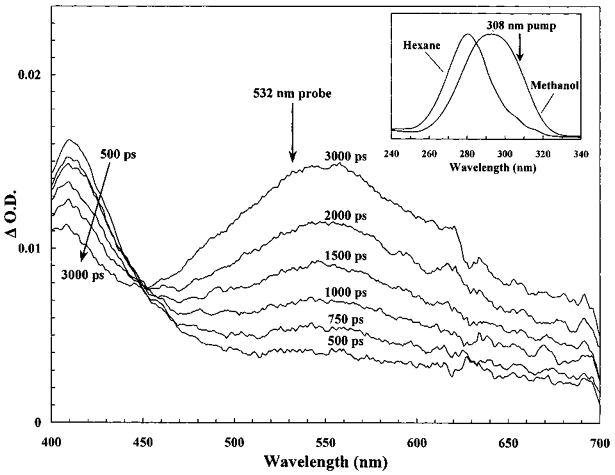

Figure 1. Transient absorption spectra of DMABN in ethanol obtained with 267 nm excitation. The inset displays ground-state absorption spectra of DMABN in hexane and methanol.

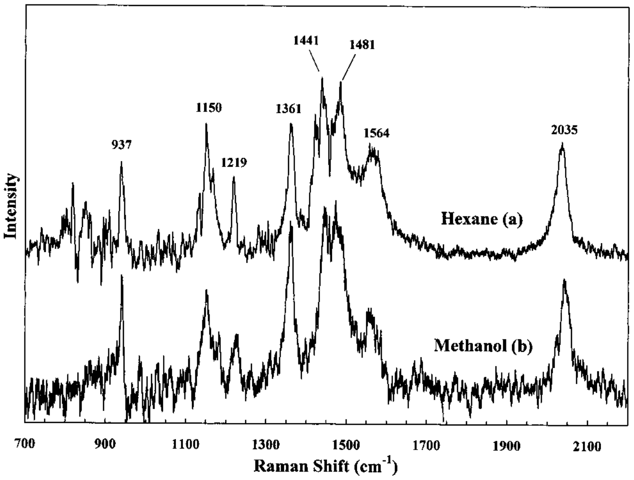

Figure 2. Time-resolved resonance Raman spectra of the lowest triplet state of DMABN in hexane (a) and methanol (b) obtained by using gated O−SMA diode array detector with 308 nm pump and 532 nm probe wavelengths at 100 ns delay time.

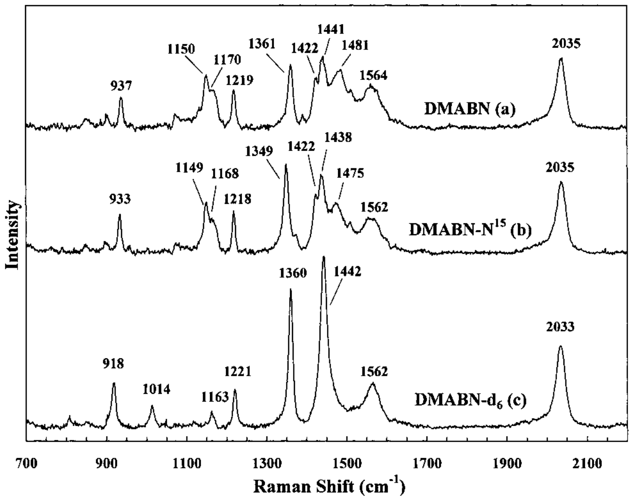

Figure 3. Time-resolved resonance Raman spectra of the lowest triplet state of DMABN (a) and DMABN−N^{15} (b) and DMABN-d$_6$ (c) in hexane obtained by using CCD detector with 308 nm pump and 532 nm probe wavelengths at 50 ns delay time.

Transient absorption (TA) was measured using the arrangement described in ref 4, with a pump wavelength of 267 nm, under “magic angle” conditions.

Spectroscopic grade solvents were used as received. Commercially available DMABN was recrystalized three times before use. DMABN-d$_6$ and DMABN−N^{15} were synthesized according to refs 13, 28, and 29, and the purity was confirmed by NMR and mass spectroscopic analysis. Sample concentrations were 1−5 × 10^{-3} mol dm^{-3} for the TA and TR^3 experiments.

Results

I. Transient Absorption Spectroscopy. TA spectra of DMABN in ethanol from 400 to 700 nm recorded at various delay times are displayed in Figure 1. A broad band peaking at ∼550 nm grows in as the ∼420 nm peak decays on a time scale extending to 3 ns. An isosbestic point at ∼450 nm indicates conversion between two distinct states. Picosecond measurements in polar solvent by Okada et al.[15] and ourselves[4] make it straightforward to attribute the ∼420 nm band to ^1S_n−$^1S_1$ absorption from the ^{1}TICT state. Laser photolysis ^3T_n−$^3T_1$ spectra of DMABN in ethanol presented by Köhler et al.,[18] which show two bands peaking at ∼370 and ∼550 nm, the latter also observed in nonpolar solvent,[18] enable the ∼550 nm band observed here to be attributed to triplet−triplet absorption from the $^3T_1$ state of DMABN. The TR^3 probe wavelength was therefore chosen to be 532 nm. Ground-state absorption spectra of DMABN in hexane and methanol are shown in the inset. Pump and probe wavelengths are indicated by arrows.

The time-dependence of the ^{1}TICT to $^3T_1$ conversion is consistent with the ∼2 × 10^8 s^{-1} ISC rate constant reported before and found to be only slightly dependent on solvent polarity, being 2.15 × 10^8 and 1.36 × 10^8 s^{-1} in heptane and acetonitrile, respectively.[16,20] Because the ∼550 nm ^3T_n − $^3T_1$ absorption band observed here is consistent with the ^3T_n−$^3T_1$ band recorded on ns to ms time scales by Wang[19] and Köhler et al.,[18] it is important to point out the precursor−successor relationship between the ^{1}TICT and $^3T_1$ state in polar solvents. This rules out the possibility of other transient species participating in the ^{1}TICT−$^3T_1$ ISC process and is in good agreement with the results of Okada et al.[15] who measured the temporal evolution of the other ^3T_n−$^3T_1$ absorption band maximum at ∼370 nm. It is also consistent with the proportionality of the intensity of the triplet C≡N TRIR band to the amount of the ^{1}TICT state[7] (although, as discussed below, we find no evidence for the ^{3}TICT structure proposed by these authors).

II. Time-Resolved Resonance Raman Spectroscopy. Figure 2 shows TR^3 spectra of DMABN in hexane (a) and methanol (b), recorded at 100 ns delay time (the spectra obtained at 50 ns delay time were identical). All transient Raman bands decrease and eventually disappear with oxygen bubbling. Considering also the transient absorption results for DMABN in polar solvent, it is clear that only the $^3T_1$ state is populated at 100 ns delay time in both solvents. We therefore attribute the spectra in both solvents to the triplet state.

The resemblance seen in Figure 2 between the spectra in the two solvents is striking evidence that the same state is formed in both. We find that DMABN-d$_6$ spectra are also independent of solvent. Because the ^{1}LE and ^{1}TICT states dominate at early times in hexane and methanol,[4,27] respectively, both are precursors of the same triplet state. The ∼2040 cm^{-1} frequency of the C≡N band coincides with the TRIR C≡N frequency recorded by Hashimoto and Hamaguchi in butanol at ∼100 ns delay time,[7] and we conclude that we are probing the same state here, in both methanol and hexane. However, Hashimoto and Hamaguchi observe only one unusually broad and low intensity

TABLE 1: Frequencies (in cm^{-1}) and Assignments of Raman Bands Observed for the Lowest Triplet State of DMABN and Its Isotopic Substituted Equivalents[a]

tentative assignment	$^3T_1$			$^1S_0$[b]	^{1}TICT[c]
	DMABN	DMABN−N^{15}	DMABN-d$_6$	DMABN	DMABN
C≡N	2035 (1.00)	2035 (1.00)	2033 (1.00)	2210	2095
ring C=C (8a)	1564 (1.10)	1562 (0.90)	1562 (0.87)	1600	1580
ring C=C (8b)	1513 (0.08)	1510 (0.07)	1513 (0.08)	1544	
δ^s_{Me}	1481 (1.13)	1475 (0.86)		1482	
ring C=C (19a)	1441 (0.63)	1438 (0.62)	1442 (1.62)	1525	
δ^s_{Me}	1422 (0.15)	1422 (0.17)	1132[d]	1446, 1417	
ν^s(ph-N)	1361 (0.43)	1349 (0.65)	1360 (0.69)	1370	1281
ν^s(ph-CN) (7a)	1219 (0.17)	1218 (0.15)	1221 (0.16)	1227	1221
ring CH in-plane bending (9a)	1170 (0.23)	1168 (0.21)	1163 (0.07)	1180	1170
ρ^s_{Me}	1150 (0.47)	1149 (0.36)	1014 (0.12)	1162	1116
$'\rho^s_{Me}$	1120[d]	1118[d]	918 (0.24)	1124	
	1086 (0.27)[d]	1080 (0.10)[d]			
ν^s(NC$_2$)	937 (0.15)	933 (0.17)	808 (0.05)[d]	943	907
	902 (0.06)[d]	898 (0.06)[d]			
	852 (0.10)[d]	849 (0.05)[d]	850 (0.04)[d]		

[a] Relative intensities are indicated in parentheses. Frequencies (in cm^{-1}) of Raman bands of the ground and ^{1}TICT state are listed for comparison. [b] Refs 14, 30. [c] Ref 14. [d] Bands are weak features with uncertain assignments.

IR absorption band in hexane, at ~2000 cm^{-1}. As they observe the 2040 cm^{-1} band only in polar solvents (butanol) and find it to be sensitive to the presence of oxygen, they conclude that the band stems from a second distinct triplet species. At this stage, we are unable to comment further on the TRIR observations in hexane as we fail to make similar observations. Our TR^3 results indicate that the same triplet species is present in both polar and nonpolar solvents and this is similar to the one Hashimoto and Hamaguchi observe in butanol.

The Raman bands can be seen in greater detail in Figure 3, where a more sensitive detector was used to obtain spectra of DMABN, DMABN−N^{15} and DMABN-d$_6$ in hexane. These are shown in Figures 3(a), (b) and (c), respectively. Fits to unconstrained Lorentzians gave the band frequencies and relative intensities listed in Table 1. Frequencies of the corresponding bands of the ground (S$_0$) and ^{1}TICT states of DMABN are listed for comparison. On the basis of Figure 2, it is assumed that any solvent dependence is small enough to be neglected. The assignments listed in Table 1 are based on vibrational analyses of the S$_0$ by Okamoto et al.,[30] Schneider et al.,[31] Gate et al.[32] and also on our recent ps-K-TR^3 data for the same isotopically substituted compounds.[14] As vibrational coupling is extensive, the assignments indicate the dominant contributions.

Intense bands at ~2035, ~1564, ~1441, ~1219, ~1170 cm^{-1} (shoulder) and a weak shoulder at ~1513 cm^{-1} are common to all the three compounds and insensitive to N^{15} substitution and amino methyl group deuteration. With the exception of the ~2035 cm^{-1} C≡N vibration, these are therefore attributed to local phenyl ring modes. The strong features are assigned to totally symmetric ring vibrations described consecutively in Wilson notation as 8a, 19a, 7a and 9a, and the weak feature at ~1513 cm^{-1} is assigned to Wilson 8b. Comparing Figures 3(a) and (b), it is clear that only two bands, 1361, 937 cm^{-1}, are sensitive to amino N^{15} substitution, showing ~12 and ~4 cm^{-1} downshift, respectively, on going from DMABN to DMABN−N.[15] Considering also the assignments and isotopic shifts observed in S$_0$,[14,30] they can be confidently attributed to the ν^s(ph-N) and the amino group nitrogen−methyl stretching (ν^s(NC$_2$)) modes, respectively.

The bands at 1481, 1422, 1150, 937/1475, 1422, 1149, and 933 cm^{-1} in DMABN/DMABN−N^{15} are replaced by two bands of moderate intensity at 1014 and 918 cm^{-1} in DMABN-d$_6$. The sensitivity to methyl group deuteration associates them with vibrations of the amino methyl group. The 1481 and 1422 cm^{-1} DMABN bands are attributed to the methyl deformation vibration (δ^s_{Me}).[14,30−32] Identification of the 1014 cm^{-1} DMABN-d$_6$ band as the counterpart of the 1150 cm^{-1} DMABN band and attribution to the methyl group rocking mode (ρ^s_{Me}) is straightforward: it appears at 1166/1033 cm^{-1} for DMABN/DMABN-d$_6$ in S$_0$.[14,30] Assignment of the 918 cm^{-1} band in DMABN-d$_6$ is rather tentative. Correlation with the 937 cm^{-1} DMABN band (ν^s(NC$_2$), see above) is hardly reasonable because a downshift of ~110 cm^{-1} is expected in S$_0$, as observed on going from DMABN (943 cm^{-1}) to DMABN-d$_6$ (835 cm^{-1}). This band is assigned provisionally to another methyl rocking mode ($'\rho^s_{Me}$) by analogy with DFT calculated bands 866 (observed at 898 cm^{-1})/1105 cm^{-1} of the S$_0$ of DMABN-d$_6$/DMABN.[30] This assignment is also supported by the Raman bands recorded at 911/1130 cm^{-1} for the closely related compounds DMA-d$_6$/DMA (dimethylaniline).[24] The DMA assignments were confirmed by theoretical calculations.[25] It is probable that the weak shoulders at ~1120 cm^{-1} in DMABN and DMABN−N^{15} (Figure 3(a) and (b)) can be assigned to the same mode. Weak features at ~1087, 902, and 852 cm^{-1} will not be discussed here.

Sensitivity to methyl group deuteration similar to that seen in Figure 3 has been observed in the 800−1200 cm^{-1} region in several dimethylamino aromatic compounds.[3,14,24,25] For example, the ν^s(NC$_2$) mode of DMABN (937 cm^{-1}) is not observed in DMABN-d$_6$. The same behavior was seen in a TR^3 study of the triplet states of 4-(*N*,*N*-dimethylamino)biphenyl (DMAB) and DMAB-d$_6$[33] and was explained in terms of potential energy redistribution of related modes upon deuteration of the methyl group.[24,25]

Discussion

I. Electronic and Geometric Property of the Triplet State of DMABN. The frequencies of the C≡N, ν^s(ph-N) stretches and ring C=C stretch modes such as Wilson 8a, are important in determining the DMABN structure. The first provides direct information on the extent of charge localization,[4,7,8] the second relates to the conformation of the dimethylaniline part (planar or twisted),[8,14,24,25,33] and the third reflects the structure of the ring skeleton.[3,14,24,25,33] The basic electronic and geometric structure of $^3T_1$ can be inferred by comparison of the $^3T_1$ frequencies of these modes with those in states whose structure is known. We take the S$_0$ and ^{1}TICT for reference because frequencies are available[14,30] and the ^{1}TICT is directly related to $^3T_1$ via ISC in polar solvents.[15,18]

The structure of crystalline DMABN has been determined by X-ray analysis to be slightly nonplanar with ~11° wagging angle.[34] However, Gorse et al.[12] have suggested that the effect of solvent polarity on the S_0 dipole moment indicates a planar structure in the solution phase. The frequencies of typical single and double C−N bonds are ~1200 and ~1600 cm^{-1},[35] respectively, so that the ~1370 cm^{-1} ν^s(ph-N) frequency[14,30] in S_0 implies significant double-bond character and a high bond order for ph-N; nπ conjugation is therefore extensive in S_0.[24,25] On the other hand, the ^{1}TICT in methanol was found to be twisted, with full charge transfer from the amino to the benzonitrile subgroup being indicated by the ~90 cm^{-1} downshift of the ν^s(ph-N) on going from the S_0 to ^{1}TICT (1281 cm^{-1}), and by the resemblance of C≡N and phenyl ring local modes frequencies in ^{1}TICT to those found in benzonitrile anion.[3,14] It was proposed that the transferred charge was delocalized over the whole benzonitrile moiety and only partially localized on the cyano group, as reflected by a ~115 cm^{-1} downshift of the C≡N frequency on going from the S_0 (2210 cm^{-1}) to ^{1}TICT (2095 cm^{-1}).[7]

From Table 1, it can be seen that the C≡N and C═C (Wilson 8a) stretching frequencies decrease progressively on going from S_0 to ^{1}ICT to $^3T_1$, with successive downshifts of the C≡N frequency of ~115 and ~60 cm^{-1}, respectively. This implies a significant decrease of the C≡N bond order, which can be interpreted as being due to intensive localization of the transferred charge on the C≡N antibonding orbital in the $^3T_1$ state. On the other hand, the 8a mode shows ~36 and ~16 cm^{-1} downshifts on going to $^3T_1$ from S_0 and ^{1}TICT, respectively, indicating reduced ring π bonding density and substantial enlargement of the ring skeleton upon formation of $^3T_1$. However, contrary to the trend of the C≡N and 8a modes, the frequency of ν^s(ph-N) changes little between $^3T_1$ and S_0 (1361 and 1370 cm^{-1}), but is much lower in ^{1}TICT (1281 cm^{-1}). Two other modes associated to amino group vibrations, $\nu^s(NC_2)$ and ρ^s_{Me}, also have frequencies in $^3T_1$ comparable to those in S_0 but significantly different from the ^{1}TICT state, suggesting that the conformation of the amino group in $^3T_1$ resembles that in S_0. We therefore propose a conjugated planar or near planar structure of the $^3T_1$ state. Electronic conjugation does not extend beyond the ring and dimethylamino subgroups. The ~9 cm^{-1} downshift of the ν^s(ph-N) frequency on going from S_0 to $^3T_1$ implies a slight lengthening of the ph-N bond and therefore somewhat less nπ conjugation in $^3T_1$ than that in S_0 but not enough to affect the planar or near planar character of the $^3T_1$.[36] Because the amino group is similar in $^3T_1$ and S_0, it is reasonable to infer that it is the ring that acts as the donor from which charge is transferred onto the cyano group in the $^3T_1$. This charge separation leads to substantial weakening of the ring π bonding strength and the amino group remains almost intact.

In summary, our data provides direct and detailed evidence that the $^3T_1$ state of DMABN is a charge-separated state of planar or near planar structure in both polar and nonpolar solvents, with high negative charge localized on the cyano group, and having electronic conjugation between the ring and dimethylamino group. We find no evidence for the ^{3}TICT state proposed in ref 7.

The proposed structure is in good agreement with previous work. For example, Köhler et al.[18] and Günther et al.[17] suggest the same structure for the triplet based on the similarity of phosphorescence and $^3T_n-^3T_1$ transient spectra from DMABN and forced planar DMABN derivatives. It is also supported by results of several recent theoretical investigations.[9,11,21,22] In structural studies of the $^3T_1$ states of *para*-disubstituted and monosubstituted benzenes, Malar et al. found that the $^3T_1$ states have appreciable quinoidal character and less aromatic nature than the corresponding S_0 states.[37,38] The indication for this is the pronounced enlargement and quinoidal deformation of the ring. Our result is consistent with this. We also note that Poizat et al. have reported similar resonance Raman frequencies of bands related to the amino group, such as the ν^s(ph-N), $\nu^s(NC_2)$ and ρ^s_{Me} modes observed here and also downshifts of the ring C═C stretching frequency for the $^3T_1$ states of DMAB[33] and N,N,N′,N′-Tetramethylbenzidine (TMB).[39] A planar or near planar structure with quinoidal character was suggested. For the $^3T_1$ state of DMABN, the ring quinoidal character is possibly indicated by the observation of a substantially larger downshift of the Wilson 19a (~84 cm^{-1}) than 8a (~36 cm^{-1}) on going from the S_0 to $^3T_1$, because they are dominated by C_{ipso}═C_{ortho} and C_{ortho}═C_{meta} stretching vibrations, respectively.[30,35]

The charge-separated character of the $^3T_1$ proposed here is also consistent with previous results. It accounts for the substantially higher dipole moment of the triplet state (12 D) than of S_0 (6.7 D).[13] It is also in full agreement with the ESR measurements of Köhler et al.[18] and Wagner et al.[40] who found a charge-separated 1,4-biradicaloid structure for the $^3T_1$ of DMABN with high spin density on the cyano group, the amino group acting as π-delocalizer conjugated with the ring.

Taking the amino and cyano group as donor (D) and acceptor (A) substituents, respectively, DMABN is a typical *para*-disubstituted benzene of type D-ph-A. Systematic studies by McGlynn et al.[41] show that the $^3T_1$ of this type of molecule is generally of $\pi\pi^*$ nature, described as $^3A_1$, with 1,4-biradicaloid character derived from the ^1L_a singlet state and unrelated to the donor and acceptor abilities of the substituents. Our results taken together with previous studies suggest that this is also valid for the $^3T_1$ state of DMABN. The $\pi\pi^*$ nature of the $^3T_1$ state of DMABN is confirmed by our observation that its TR^3 spectrum is independent of solvent polarity. The DFT/SCI study of Bulliard et al.[22] found that the $^3T_1$ of DMABN is related, in terms of orbital occupation, to the ^1L_a state, the second excited state in the FC region with transition moment along the long axis of DMABN molecule. This and the similarity of the amino group in the $^3T_1$ and S_0 imply that the $^3T_1$ state of DMABN does not have strong CT character, which is consistent with the $^3T_1$ having a lower dipole moment than the ^{1}TICT state.

II. ISC Processes of DMABN. The temporal evolution of the transient absorption spectra presented by us (above) and Okada et al.,[15] the ns to ms time scale $^3T_n-^3T_1$ spectra presented by Wang[19] and Köhler et al.,[18] and the phosphorescence measurements[17,18] are all consistent with the $^3T_1$ state being the only intermediate involved in the nonradiative deactivation channels of the singlet excited states of DMABN, independent of solvent polarity. Therefore, ISC deactivation of excited-state DMABN in the solution phase channels can be described as: $^1LE \rightarrow {}^3T_1 \rightarrow S_0$ and $^1TICT \rightarrow {}^3T_1 \rightarrow S_0$.

The ^{1}TICT → $^3T_1$ ISC process can be viewed as back charge transfer from the phenyl ring to the amino group accompanied by back twist of the amino group with more negative charge localizing on the cyano group. Considering the conjugated character of the S_0 state,[8,12,14,30] the $^3T_1$ → S_0 ISC phosphorescence process is seen as charge recombination occurring mainly between the ring and cyano group. As to the deactivation of ^{1}LE because ^{1}LE,[4,6,8,12] $^3T_1$ and S_0 are all planar or near planar, ISC takes place without significant structural change, consistent with the conclusion of the LIOAS study.[20]

Conclusion

Nanosecond time-resolved resonance Raman spectra of the $^3T_1$ of DMABN, DMABN-d_6 and DMABN$-$N^{15} have been obtained. Similar spectra were recorded in polar solvent methanol and nonpolar solvent hexane. Bands associated with vibrations of the amino, ring and cyano groups were observed and assigned with reference to isotopic shifts. The 2035 cm^{-1} C$\equiv$N stretch frequency, 1361 cm^{-1} ν^s(ph-N) frequency and substantial downshift of the ring C$=$C mode of the $^3T_1$ relative to S_0 indicate that the triplet state is planar or near planar with high negative charge localization on the cyano group and conjugation of the ring with the amino group. Taking previous studies into account, it is concluded that the $^3T_1$ state of DMABN is a $^3A_1$ state of the kind typical of D-ph-A compounds and can be described as a $\pi\pi^*$ state with 1,4-diradicaloid character and quinoidal ring conformation. Combined with transient absorption measurements, our results suggest that, the ^{1}TICT $\rightarrow$ $^3T_1$ ISC is dominated by a mechanism of back charge transfer from the ring to the amino group accompanied by back twisting of the amino group, whereas the $^3T_1 \rightarrow S_0$ ISC is a charge recombination process occurring mainly between the ring and cyano group.

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