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ARTICLES

Triplet State Dipole Moments of Aminobenzonitriles

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The triplet state dipole moments μ(T) of a series of 4-amino- and 3-aminobenzonitriles in cyclohexane, benzene, and 1,4-dioxane are recalculated from previously published [*J. Phys. Chem.* **1992**, *96*, 10809] time-resolved microwave conductivity data, on the basis of newly measured intersystem crossing yields. For 4-(dimethylamino)benzonitrile (DMABN), the following values are now determined for μ(T): 8.3 D (cyclohexane), 8.9 D (benzene), and 9.7 D (1,4-dioxane), as compared with the previously reported dipole moment of 12 D for the first and the last solvent. With the other aminobenzonitriles, similar μ(T) data are obtained, between 6.9 D for 4-aminobenzonitrile (ABN) in *n*-hexane and 10.0 D for 4-(di-*n*-decylamino)benzonitrile (DDABN) in 1,4-dioxane. The increase of μ(T) observed for all aminobenzonitriles when going from cyclohexane via benzene to 1,4-dioxane may indicate that their triplet dipole moments become larger with increasing solvent polarity. The present μ(T) of DMABN, between 8.3 and 9.7 D, although larger than the ground state dipole moment μ(0) of 6.6 D, is somewhat smaller than that of the locally excited (LE) state (9.9 D) but considerably smaller than the dipole moment of the intramolecular charge transfer (ICT) state (17 D). By comparing these μ(X) data with the frequency $\tilde{\nu}$(C≡N) of the cyano vibration in each state, it appears that at least for DMABN in the triplet state $\tilde{\nu}$(C≡N) is not a reliable indication of the extent of charge transfer as compared with the other states S_0, LE, and ICT.

Introduction

The triplet state dipole moment μ(T) of 4-(dimethylamino)benzonitrile (DMABN) in cyclohexane and 1,4-dioxane has been determined by employing time-resolved microwave conductivity (TRMC) measurements.[1] From the long-lived component of the TRMC transients, a dipole moment μ(T) of 12 D was estimated for DMABN in these solvents. Despite this relatively large dipole moment, it was nevertheless concluded that intramolecular charge transfer (ICT) does not occur with DMABN in the triplet state; i.e., only a single triplet state is photophysically relevant.[1] The same conclusion has been reached in a number of other experimental[2−4] and theoretical[5] investigations. Different from these studies, the observation of two distinct triplet species, a triplet LE and a triplet twisted ICT (TICT) state, was reported with DMABN in butanol[6] studied by nanosecond time-resolved infrared (TRIR) spectroscopy. This finding was supported by laser-flash photolysis and low-temperature phosphorescence experiments.[7,8] The presence of two different triplet states was, however, not verified for DMABN in *n*-hexane and methanol by a later investigation employing nanosecond time-resolved resonance Raman (TR^3) spectra.[3]

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TABLE 1: Data Used in the Determination of the Triplet Dipole Moment μ(T) of Aminobenzonitriles in the Solvents Cyclohexane, Benzene, and 1,4-Dioxane from the Intersystem Crossing Quantum Yields Φ(ISC), Together with Time-Resolved Microwave Conductivity Results and the Ground State Dipole Moment μ(0) Taken from Ref 1 (See Eq 1)

compound	Φ(ISC)	ΔM(T)Φ(ISC)	ΔM(T)	M(0)	μ(0)	μ(T)
			Cyclohexane			
ABN	0.69 ± 0.03[a]	0.62	0.90	8.48	6.6	6.9 ± 0.1[b]
MABN	0.66 ± 0.04	1.73	2.62	7.41	6.6	7.7 ± 0.1
DMABN	0.70 ± 0.04	3.08	4.40	7.54	6.6	8.3 ± 0.1
DEABN	0.73 ± 0.03	2.90	3.97	5.75	6.7	8.7 ± 0.1
DPrABN	0.75 ± 0.05	2.32	3.09	4.08	6.7	8.9 ± 0.1
DDABN	0.73 ± 0.04	1.48	2.03	2.23	6.7	9.3 ± 0.1
m-ABN	0.77 ± 0.03	4.88	6.34	5.98	5.3	7.6 ± 0.1
m-DEABN	0.79 ± 0.04	6.37	8.06	4.57	5.5	9.1 ± 0.2
			Benzene			
MABN	0.64 ± 0.04	3.20	5.00	9.49	6.6	8.2 ± 0.1
DMABN	0.74 ± 0.03	5.66	7.65	9.26	6.6	8.9 ± 0.1
DEABN	0.79 ± 0.03	4.80	6.08	7.52	6.7	9.0 ± 0.1
DPrABN	0.76 ± 0.05	4.28	5.63	5.35	6.7	9.6 ± 0.2
DDABN	0.74 ± 0.04	2.08	2.81	2.94	6.7	9.4 ± 0.1
m-ABN	0.77 ± 0.04	8.59	11.16	7.42	5.3	8.4 ± 0.1
m-DEABN	0.47 ± 0.04	5.74	12.21	6.58	5.5	9.3 ± 0.3
			1,4-Dioxane			
MABN	0.67 ± 0.04	2.69	4.01	4.73	6.6	9.0 ± 0.1
DMABN	0.80 ± 0.03	4.20	5.25	4.57	6.6	9.7 ± 0.1
DEABN	0.85 ± 0.03	3.29	3.87	3.59	6.7	9.7 ± 0.1
DPrABN	0.85 ± 0.03	2.28	2.68	2.48	6.7	9.7 ± 0.1
DDABN	0.85 ± 0.05	1.38	1.62	1.34	6.7	10.0 ± 0.2
m-ABN	0.64 ± 0.04	3.77	5.89	3.92	5.3	8.4 ± 0.2
m-DEABN	0.46 ± 0.04	3.39	7.37	3.28	5.5	9.9 ± 0.3

[a] Standard deviations. [b] Propagated error from the uncertainties in Φ(ISC).

In the calculation of μ(T) from the TRMC data,[1] the intersystem crossing yield Φ(ISC) is needed and the $\mu(T) = 12$ D for DMABN was obtained with data (0.18 in cyclohexane and 0.40 in 1,4-dioxane)[9] taken from the literature. Recently, we reported Φ(ISC) results for DMABN, 4-(methylamino)-benzonitrile (MABN) and 4-aminobenzonitrile (ABN) in alkane solvents such as *n*-hexane, with an average triplet yield of 0.81 for DMABN in four alkanes at 25 °C,[10] in accordance with previous data (Φ(ISC) = 0.80 in *n*-hexane)[2] in the literature. These results made clear that our Φ(ISC) values are considerably larger than those on which the calculation of μ(T) had been based in ref 1. We therefore remeasured the triplet yields Φ(ISC) and present here a recalculation of the triplet state dipole moments of the aminobenzonitriles appearing in ref 1: ABN, MABN, DMABN, 4-(diethylamino)benzonitrile (DEABN), 4-(di-*n*-propylamino)benzonitrile (DPrABN), 4-(di-*n*-decylamino)benzonitrile (DDABN), 3-aminobenzonitrile (mABN), and 3-(diethylamino)benzonitrile (mDEABN). For DMABN, as an example, our recalculation leads to a μ(T) of around 9 D, considerably smaller than the $\mu(T) = 12$ D in our previous publication ref 1. The present investigations were triggered by the recent observation of Ohta et al. that the triplet state of DMABN in a polymer film has the same dipole moment (6.6 D) as the ground state, much smaller than that of the LE (10.0 D) and the ICT state (13.5 D).[11] From laser-induced optoacoustic measurements it was concluded, that the lowest triplet state of DMABN in alkane solvents does not have a pronounced CT character (μ(T) smaller than 10 D).[12]

Experimental Section

The synthesis and purification of the aminobenzonitriles used in the present experiments were described previously.[1] The solvents cyclohexane, benzene, and 1,4-dioxane (Merck, Uvasol) employed in the determination of the intersystem crossing yields Φ(ISC) were purified by column chromatography over alumina. The triplet yields were measured by laser flash photolysis using the energy transfer method with perylene as energy acceptor[13] (except the case of ABN, for which the acceptor was anthracene[14]) at room temperature (23 ± 2 °C). A Lambda Physics EMG 101 exciplex laser provided the pulsed laser light at 308 nm (XeCl), whereas in the case of ABN a frequency-quadrupled Nd:YAG laser (Continuum Surelight) was used for excitation at 266 nm. The Φ(ISC) of the aminobenzonitrile derivatives was determined relative to that of the triplet yield of *N*-methyl-1,8-naphthalimide (Φ(ISC) = 0.96), reported to be independent from the nature of the aprotic solvents.[15] All samples were deaerated by several freeze−pump−thaw cycles and measured in a sealed 1 × 1 × 4 cm quartz cuvette.

Results and Discussion

Intersystem Crossing Yields Φ(ISC). The intersystem crossing yields Φ(ISC) of ABN in cyclohexane and of MABN, DMABN, DEABN, DPrABN, DDABN, mABN, and mDEABN in cyclohexane, benzene, and 1,4-dioxane are listed in Table 1. They were determined as described in the Experimental Section. Φ(ISC) ranges from 0.46 for mDEABN in 1,4-dioxane to 0.85 for DEABN, DPrABN, and DDABN in this solvent. Except for mABN, the triplet yield generally increases in the series cyclohexane, benzene, and 1,4-dioxane.

From these data, together with the previously published[1] results of the TRMC experiments and the ground state dipole moments μ(0), the triplet state dipole moments μ(T) were calculated by employing eq 1 (see ref 1).

$$\mu(\mathrm{T}) = \mu(0)[1 + (\Delta M_{\mathrm{T}}\Phi(\mathrm{ISC}))/(M_0\Phi(\mathrm{ISC}))]^{0.5} \qquad (1)$$

The difference in the rotational charge mobility of a solute in the triplet state (ΔM_{T}) is given by eq 2.

$$\Delta M_{\mathrm{T}} = M_{\mathrm{T}} - M_0 = (\epsilon' + 2)^2(\mu(\mathrm{T})^2 - \mu(0)^2)F(\omega\tau_{\mathrm{D}})/27ek_{\mathrm{B}}T\tau_{\mathrm{D}} \qquad (2)$$

where ϵ' is the relative dielectric constant of the medium, ω is the radian microwave frequency, τ_D is the dipole relaxation time, e is the elementary charge, k_B is the Boltzmann constant, T is the absolute temperature, and $F(\omega\tau_D)$ is given by eq 3.

$$F(\omega\tau_D) = (\omega\tau_D)^2/[1 + (\omega\tau_D)^2] \qquad (3)$$

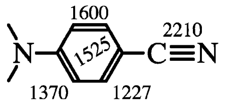
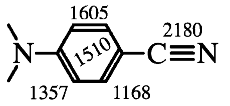
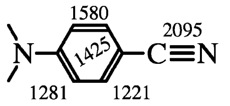
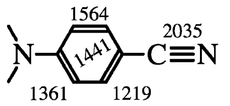
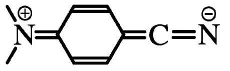
Triplet Dipole Moments μ(T). Possible Solvent Polarity Dependence of μ(T). The calculated triplet dipole moments μ(T) have values between 6.9 D (ABN) and 9.3 D (DDABN) in cyclohexane, between 8.2 D (MABN) and 9.6 D (DPrABN) in benzene, and between 8.4 D (mABN) and 10.0 D (DDABN) in 1,4-dioxane (Table 1). These results may indicate that μ(T) becomes somewhat larger with increasing effective[16] solvent polarity.

For DMABN, the new μ(T) data (8.3 D in cyclohexane, 8.9 D in benzene, and 9.7 D in 1,4-dioxane) are considerably smaller than those of ref 1, where 11.9 D (cyclohexane) and 12.0 D (1,4-dioxane) were reported. From a comparison of μ(T) with the dipole moments[1] of the ground state $\mu(0) = 6.6$ D, the LE state $\mu(\mathrm{LE}) = 9.9$ D (cyclohexane), and the ICT state $\mu(\mathrm{ICT}) = 17$ D, it appears that the triplet dipole moment μ(T) of DMABN is clearly larger than that of the ground state, somewhat smaller than μ(LE), and considerably smaller than μ(ICT). The results support our previous[1] conclusion that with DMABN an ICT state is not formed in the triplet state. This means that, although charge separation has taken place in the triplet state ($\mu(\mathrm{T}) = \sim 9$ D), there is not a second triplet state with a larger dipole moment, in contrast to what is observed in the singlet state with $\mu(\mathrm{LE}) = \sim 10$ D and $\mu(\mathrm{ICT}) = 17$ D.

C≡N Stretch Frequency of DMABN from Time-Resolved Resonance Raman and Infrared Measurements. From time-resolved Resonance Raman (TR^3)[3,4,17] and infrared (TRIR)[18,19] measurements with DMABN in solution, it is found that the stretch frequency of the cyano group (C≡N) is shifted to lower energies upon excitation. Whereas $\tilde{\nu}$(C≡N) occurs at 2210 cm^{-1} for the S$_0$ ground state, this vibration is observed at 2180 cm^{-1} for the LE state (in *n*-hexane) and is strongly downshifted to 2095 cm^{-1} for the ICT state (in MeCN and methanol)[3,17−19] (see Table 2). This shift to lower energies of $\tilde{\nu}$(C≡N) during the S$_0$ → LE → ICT reaction of DMABN has been explained as being a consequence of the decrease in triple bond character of the CN substituent. It was thereby assumed that electric charge was transferred from the C≡N bond to the phenyl ring or to the dimethylaniline moiety of DMABN. The increase of the dipole moment μ(X) taking place during the ICT reaction of DMABN, from 6.6 D for S$_0$, via 9.9 D for LE to 17 D for ICT,[1] was considered to be a direct support for this interpretation. The conclusion was then made[3,4,17] that the frequency $\tilde{\nu}$(C≡N) reflects the extent of negative charge localization on the cyano group.

For the triplet state T$_1$ of DMABN in *n*-hexane and methanol,[3,4] however, $\tilde{\nu}$(C≡N) is even further downshifted with respect to S$_0$ (to 2035 cm^{-1}, independent of solvent polarity) than for the ICT state (2095 cm^{-1}). This was interpreted as indicating that there is a localization of a complete charge separation onto the cyano group in the triplet state of DMABN.[3,4] When the relatively small value for $\tilde{\nu}$(C≡N) of 2035 cm^{-1} for the triplet state T$_1$ of DMABN would be due to a substantial transfer of charge from the CN group to the benzonitrile moiety, i.e., larger than that of the ICT state, this process should result in an increase of the dipole moment μ(T$_1$) as compared with μ(ICT). Exactly the opposite is observed, μ(T$_1$) being with 9 D (Figure 1) much smaller than the μ(ICT) of 17 D and even smaller than the μ(LE) of 9.9 D (Table 2). It can therefore not be maintained that a downshift of $\tilde{\nu}$(C≡N) from its S$_0$ value is an indication that an additional charge transfer from the CN substituent to the benzonitrile moiety of DMABN has occurred. Clearly, the connection between $\tilde{\nu}$(C≡N) and intramolecular charge transfer (μ(X)) is more complex than originally anticipated and depends on the specific state of the molecule.

TABLE 2: Molecular Structures of DMABN with Vibrational Frequencies for Various Bonds of the Ground State S$_0$, the Locally Exited State LE, the Intramolecular Charge Transfer State ICT, the Triplet State T$_1$, and a Quinoidal Canonical Resonance Structure

<table>
<tr><th>DMABN Structure[a]</th><th>State</th><th>μ(X) [D]</th><th>8a - 19a [cm^{-1}][b]</th></tr>
<tr><td>
</td><td>S$_0$</td><td>6.6</td><td>75</td></tr>
<tr><td>
</td><td>LE</td><td>9.9</td><td>95</td></tr>
<tr><td>
</td><td>ICT</td><td>17</td><td>155</td></tr>
<tr><td>
</td><td>T$_1$</td><td>9[c]</td><td>123</td></tr>
<tr><td>
</td><td>canonical structure[d]</td><td>33[e]</td><td>277[f],
309[g]</td></tr>
</table>

[a] With vibrational frequencies (in cm^{-1}) at the different bonds, determined by time-resolved infrared (TRIR) and resonance Raman (TR^3) measurements, selected from refs 3 (TR^3), 17 (TR^3), 18 (TRIR), and 19 (TRIR); see text. [b] Energy difference between the Wilson vibrational modes 8a and 19a: a measure of the phenyl ring quinoidality; see text. [c] Rounded average value of μ(T) in cylohexane (8.3 D), benzene (8.9 D), and 1,4-dioxane (9.7 D); see Table 1. [d] Hypothetical quinoidal resonance structure; see text. [e] Calculated dipole moment; see text and ref 20. [f] For *p*-benzoquinodimethane, see ref 18 and text. [g] For *p*-benzoquinone, see ref 18 and text.

Molecular Structure of the Triplet State of DMABN. In Table 2, five vibrational frequencies for DMABN in the S$_0$, LE, ICT, and T$_1$ states have been listed: for the CN, phenyl−CN, and N−phenyl bonds and two vibrational modes (8a and 19a)[18] of the phenyl ring. These frequencies have been selected from TR^3 and TRIR data.[3,17−19]

On the basis of the quinoidal canonical structure depicted in Table 2, it would be expected that a decrease from triple toward double bond character of the cyano group of DMABN, deduced from the downshift of $\tilde{\nu}$(C≡N) as mentioned above, would be accompanied by a simultaneous transition of the single bond character of the phenyl−CN bond in the direction of a double bond. This increase of the double-bond character should then lead to a larger vibrational frequency $\tilde{\nu}$(phenyl−CN). Such a

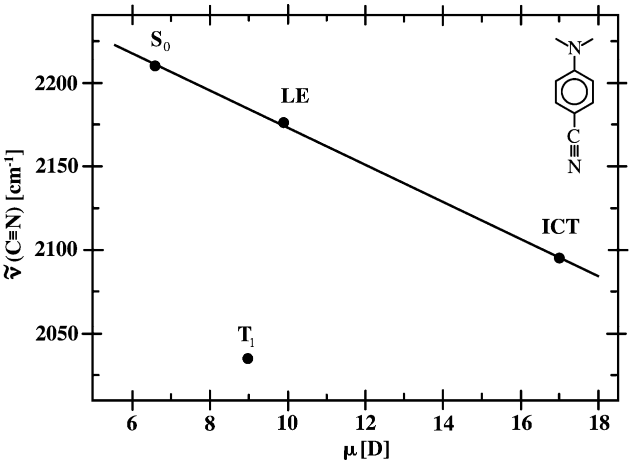


Figure 1. Plot of the cyano stretch frequency $\tilde{\nu}$(C≡N) vs the dipole moments of DMABN in the ground state S_0, the locally excited state LE, the intramolecular charge transfer state ICT, and the triplet state T_1 (Tables 1 and 2). For the hypothetical quinoidal resonance structure from Table 2 with a dipole moment of 33 D, the following vibrational frequency is obtained for the cyano group by extrapolation from the S_0, LE, and ICT data: $\tilde{\nu}$(C≡N) = 1917 cm^{-1}.

correlation is not observed for S_0, ICT and T_1, however, as $\tilde{\nu}$(phenyl−CN) is practically the same for these states (see Table 2).

Likewise, the changes in the *N*-phenyl frequency do not go parallel with the downshift of $\tilde{\nu}$ (C≡N), $\tilde{\nu}$(N−phenyl) being the same for the S_0, LE, and T_1 states. The quinoidality of the phenyl ring of DMABN, determined from the difference between the two ring frequencies 8a and 19a (Table 2), increases in the order S_0, LE, T_1, ICT (Table 2). This increase does not show a correlation with $\tilde{\nu}$(C≡N). Note that the largest values found for (8a−19a), 155 cm^{-1} (ICT) and 123 cm^{-1} (T_1), are still much smaller than those for the molecules *p*-benzoquinodimethane (277 cm^{-1}) and *p*-benzoquinone (309 cm^{-1}), having a quinoidal phenyl ring structure (Table 2).

In conclusion, it is seen that the vibrational frequencies of the various bonds for DMABN in the S_0, LE, ICT, and T_1 states cannot easily be reconciled with a classical resonance structure. It appears that the relationship between a vibrational frequency and a bond length is complex and not uniform for the different states of DMABN.

Conclusions

By measuring the triplet yields Φ(ISC) of a series of aminobenzonitriles, the triplet dipole moment μ(T) could be determined from previously published TRMC data (ref 1) for ABN in cyclohexane and for MABN, DMABN, DEABN, DPrABN, DDABN, mABN, and mDEABN in cyclohexane, benzene, and 1,4-dioxane. For DMABN, the recalculated μ(T) is with 8.3 D in cyclohexane and 9.7 D in 1,4-dioxane considerably smaller than the previous values of 11.9 and 12.0 D. This decrease is due to the fact that the present yields Φ(ISC) are with 0.71 in cyclohexane and 0.80 in 1,4-dioxane much larger than those of DMABN (0.18 and 0.40) employed in ref 1. For the other aminobenzonitriles, dipole moments μ(T) between 6.9 D (ABN in cyclohexane) and 10.0 D (DDABN) in 1,4-dioxane are obtained. It is found that for DMABN μ(T) becomes larger when going from cyclohexane (8.3 D) via benzene (8.9 D) to 1,4-dioxane (9.7 D). A similar increase is also observed for the other aminobenzonitriles and may indicate that the triplet dipole moment becomes larger with increasing effective solvent polarity. From a comparison of the dipole moments μ(X) of the S_0, LE, ICT, and T_1 states of DMABN with the vibrational frequency $\tilde{\nu}$(C≡N) of the cyano substituent, it follows that the downshift of $\tilde{\nu}$(C≡N) for T_1 (2035 cm^{-1}) as compared with S_0 (2210 cm^{-1}) cannot uniformly be explained by a transfer of charge from the cyano group to the benzonitrile moiety in a manner similar to that for the other molecular states. A further comparison between several bond frequencies of DMABN in the S_0, LE, ICT, and T_1 states reveals that the molecular structure of these states cannot easily be described in term of classical resonance structures, indicating a possibly complex relationship between vibrational frequencies and bond lengths. It may also be concluded that for DMABN the molecular structure of T_1 is different from that of the LE, ICT, and S_0 states.

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