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Studies on torsional motion in aromatic amines

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Abstract

Results of supersonic jet spectroscopy on various amino aromatic molecules are presented. Contrast is made between 2-phenylindole, where the aromatic rings are coplanar in the excited first singlet state, and twisted by 27° in the ground state, anthryl carbazole, where the aromatic moieties are twisted by 77° in the ground state, 64° in the first excited singlet state, and phenyl carbazole and cyanophenyl carbazole, where both ground and excited states have a twist angle of 90°. In the case of the aminobenzonitriles, the jet spectroscopy is less revealing. Ab initio calculations suggest that in dimethylaminobenzonitrile the ground state is planar, in the locally excited singlet state, the two N–Me bonds are twisted out of the plane of the aromatic ring by 44° and 6° respectively; and in the gas phase, the charge-transfer state with perpendicular structure is actually a transition state between the two equivalent locally excited state geometries. © 1997 Elsevier Science S.A.

Keywords: Torsional motion; Aromatic amines; Supersonic jet spectroscopy

1. Introduction

This paper is concerned with aromatic amines capable of torsional motion of one moiety with respect to another in the molecule. The conformational behaviour of aromatic systems consisting of two rings linked by a single bond has been the subject of considerable experimental and theoretical interest. Such systems can exhibit large-amplitude low frequency motion along the flexible torsional co-ordinate. The equilibrium torsional angle is determined by the conjugative π interactions in the rings and the steric hindrance and/or electrostatic repulsion between non-bonded atoms belonging to different rings. Consequently, the conformation is very much dependent on the electronic state of the system. Examples will be given below of the differing ground and excited state geometrics possible, as revealed by supersonic jet spectroscopy.

The case of an aromatic moiety with an amine, or alkylated amine derivative as subsistuent presents a special case, as molecules typified by dimethylaminobenzonitrile, DMABN, are capable in polar solution of exhibiting charge-transfer fluorescence, and this has been linked by some authors to a twisting of the amine moiety with respect to the aromatic ring. The relevance of jet spectroscopy to this class of molecules and charge-transfer emission will be reviewed below.

2. 2-Phenylindole, 2PI

2PI (structure I Scheme 1) belongs to the class of molecules which can undergo torsional motion of one aromatic moiety with respect to the other. In this class, biphenyl presents the prototypical system studied in this fashion. In biphenyl the two rings are twisted with an interplanar angle of about 44° in the S_0 state, and adopt a coplanar conformation upon excitation to the S_1 state [1,2]. Other notable examples include 1,1′-binaphtyl [3,4], tolane [5], 9-phenylanthracene [6,7], 9,9-bianthryl [8], 2,2′-bithiophene [9] and 9-(*N*-carboxyl) anthracene [10].

2PI is believed to have a significant non-planar conformation in the ground state. Upon electronic excitation to the S_1 state, it is known to undergo a subnanosecond conformational change toward planarity by torsion around the phenyl–heterocycle bond [11].

The results below were obtained using supersonic jet spectroscopic measurements which are fully described elsewhere [12].

Fig. 1 shows the fluorescence excitation spectrum of jet-cooled 2PI for excitation in the $S_1 \leftarrow S_0$ transition, from which a long progression in the torsional mode can be clearly identified. The transition energies and assignments of bonds are shown in Table 1. Single vibronic level fluorescence spectra are shown in Fig. 2, for excitation in a large number of members of the torsional progression.

By fitting these data to torsional potentials of the form, where ϕ is the angle of twist,

$$V(\phi)=\frac{1}{2}\Sigma_n V_n(1-\cos n\phi)$$

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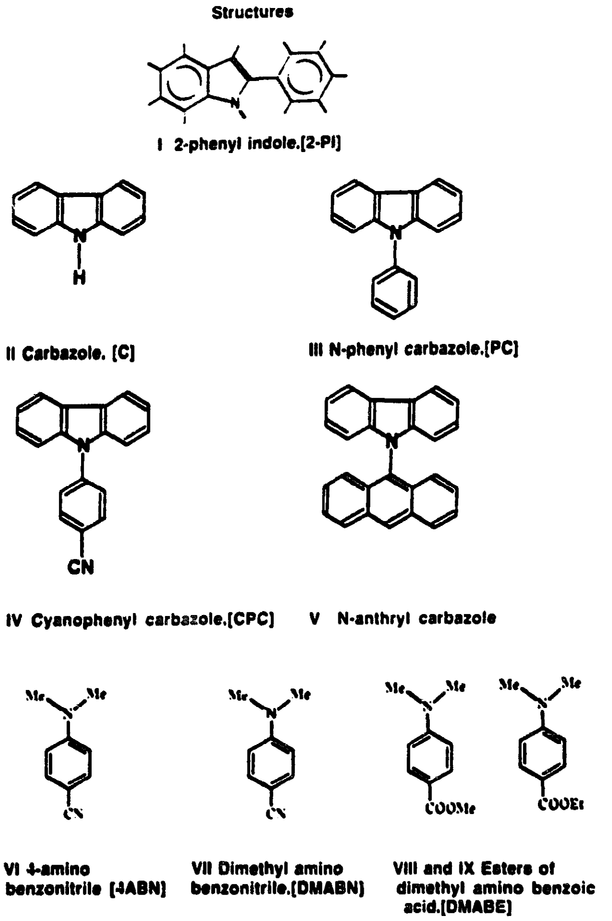

Scheme 1.

ground and excited state potential surfaces, Figs. 3 and 4 can be generated. The best-fit potentials are for the ground state, S_0, $V_2=980\pm50$, $V_4=430\pm20$ cm^{-1}, $V_6=-35\pm5$ and $V_8=-15\pm5$ cm^{-1}, and for the excited state, S_1, the surface is that of a coplanar arrangement of the aromatic rings, with a harmonic potential with $V_2\geq3150$ cm^{-1}. The equilibrium conformation of 2PI is thus shown rigorously to be non-planar in the S_0 ground-state, with a twist angle between the two rings of 27°, and a barrier to planarity of some 130 cm^{-1}. The S_1 state is planar [12].

Rotational coherence spectroscopy on 2PI [13] gives the result shown in Fig. 5, and analysis of the transients, Fig. 6, reveals that the best fit of experimental data to the experimental trace is obtained for an electronic transition moment aligned parallel to, or within 15° of, the long axis of the molecule, Fig. 7.

3. Aryl carbazoles

The case of 2PI above may be contrasted with those of the aryl carbazoles, structures II–V Scheme 1 [14].

The LIF excitation spectra shown in Fig. 8 and the fluorescence emission spectra in Fig. 9 demonstrate that PC and CPC exhibit very similar spectroscopy to the carbazole chromophore with relatively small shifts of −754 and −367 cm^{-1} due to substitution. It can therefore be inferred that the phenyl and cyanophenyl groups have little influence in the carbazole moiety due to the perpendicularity between the two aromatic ring planes caused by steric effects, in the ground state of these molecules. Moreover, the perpendicularity in PC and CPC is preserved on electronic excitation, since the 0–0 transition is of maximum intensity, and there is no evidence of a torsional progression.

By contrast, AC exhibits a completely different pattern, via a large shift of −1820 cm^{-1} from the origin of the anthracene chromophore, and a long torsional progression, as in the case of 2PI. Analysis suggests the twist angle between aromatic moieties in AC in the ground state is 77°, and 64° in the excited state.

CPC, (structure IV Scheme 1), has been reported to show TICT emission in polar solution [15]. An attempt was made to observe anomalous red-shifted emission from CPC when complexed to the polar solvent acetonitrile [14], but although fluorescent complexes were seen, no anomalous emission was observed. Were twisting to be of importance in charge-

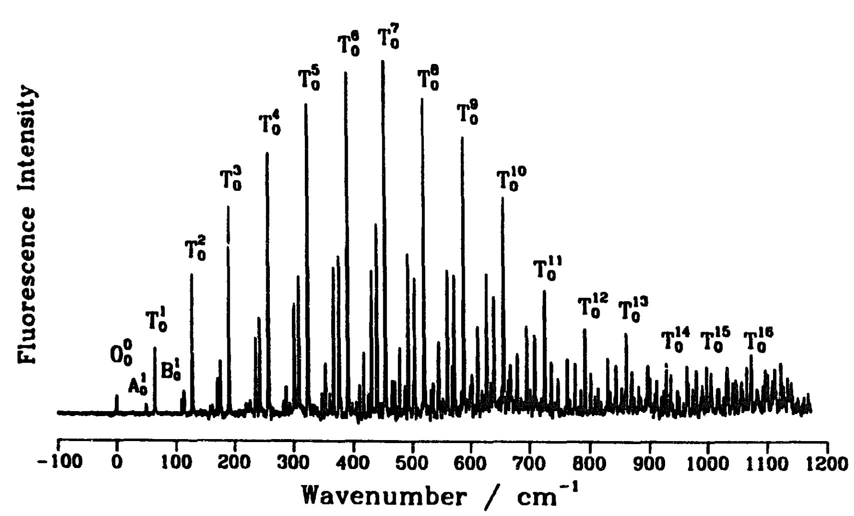

Fig. 1. $S_1 \leftarrow S_0$ fluorescence excitation spectrum of jet-cooled 2-phenyl indole (2-PI). The 0_0^0 band of 2-PI is at 31 315 cm^{-1}. The assignment of the torsional bands are indicated [12].

Table 1
Transition energies and assignments of the vibronic bands in the fluorescence excitation spectrum of 2-PI [12]

ν/cm^{-1}	$\Delta\nu$ [a]/cm^{-1}	Assignment [b]	ν/cm^{-1}	$\Delta\nu$ [a]/cm^{-1}	Assignment [b]
31 355.8	0 [c]	O_0^0	31 746.6	390.8	T_0^6
31 405.1	49.3	A_0^1	31 758.5	402.7	$D_0^1\ T_0^3$
31 419.5	63.7	T_0^1	31 766.3	410.5	$A_0^1\ B_0^1\ T_0^4$
31 454.4	98.6	A_0^2	31 779.0	423.2	$A_0^2\ T_0^5$
31 466.1	110.3	B_0^1	31 786.3	430.5	$B_0^1\ T_0^5$
31 469.3	113.5	$A_0^1\ T_0^1$	31 795.2	439.4	$A_0^1\ T_0^6$
31 483.7	127.9	T_0^2	31 812.9	457.1	T_0^7
31 516.4	160.6	$A_0^1\ B_0^1$	31 824.8	469.0	$C_0^1\ T_0^4$
31 518.1	162.3	$A_0^2\ T_0^1$	31 829.3	473.5	$D_0^1\ T_0^4$
31 529.7	173.9	$B_0^1\ T_0^1$	31 837.2	481.4	$A_0^1\ B_0^1\ T_0^5$
31 534.7	178.9	$A_0^1\ T_0^2$	31 851.6	495.8	$B_0^1\ T_0^6$
31 548.5	192.7	T_0^3	31 862.0	506.2	$A_0^1\ T_0^7$
31 565.3	210.0	C_0^1	31 878.6	522.8	T_0^8
31 577.4	221.6	D_0^1	31 890.2	534.4	$C_0^1\ T_0^5$
31 580.3	224.5	$A_0^1\ B_0^1\ T_0^1$	31 893.9	538.1	$D_0^1\ T_0^5$
31 585.3	229.5	$A_0^2\ T_0^2$	31 902.9	547.1	$A_0^1\ B_0^1\ T_0^6$
31 593.6	237.8	$B_0^1\ T_0^2$	31 917.3	561.5	$B_0^1\ T_0^7$
31 600.1	244.3	$A_0^1\ T_0^3$	31 928.7	572.9	$A_0^1\ T_0^8$
31 614.7	258.9	T_0^4	31 945.6	589.8	T_0^9
31 640.2	284.4	$D_0^1\ T_0^1$	31 958.8	603.0	$D_0^1\ T_0^6$
31 644.0	288.2	$A_0^1\ B_0^1\ T_0^2$	31 968.9	613.1	$A_0^1\ B_0^1\ T_0^7$
31 649.9	294.1	$A_0^2\ T_0^3$	31 995.4	639.6	$A_0^1\ T_0^9$
31 656.5	300.7	$B_0^1\ T_0^3$	32 012.6	656.8	T_0^{10}
31 664.8	309.0	$A_0^1\ T_0^4$	32 034.6	678.8	$D_0^1\ T_0^7$
31 680.4	324.6	T_0^5	32 079.9	724.1	T_0^1
31 703.2	347.4	$D_0^1\ T_0^2$	32 148.0	792.2	T_0^{12}
31 708.4	352.6	$A_0^1\ B_0^1\ T_0^3$	32 215.7	859.9	T_0^{13}
31 715.3	359.5	$A_0^2\ T_0^4$	32 282.7	926.9	T_0^{14}
31 723.0	367.2	$B_0^1\ T_0^4$	32 350.7	994.9	T_0^{15}
31 731.6	375.8	$A_0^1\ T_0^5$	32 419.3	1063.5	T_0^{16}

[a] $\Delta\nu = \nu_L - \nu(O_0^0)$ where ν_L is the laser wavenumber.

[b] T denotes the torsional mode. A, B, C and D denote other modes.

[c] O_0^0 at 31 355.8 cm^{-1}.

transfer formation, as the acronym TICT implies, then the absence of any excitable torsional motion in CPC should preclude such emission.

4. Aminobenzenes

In the case of the molecules alluded to above, the aromatic nature of the twisting moiety provides a fluorescent reporter group. In the case of aminobenzenes and aminobenzonitriles, this is not the case. Nevertheless, it was felt that jet spectroscopy might contribute to the understanding of the photophysics of such molecules, particularly with regard to the TICT hypothesis.

Aminobenzonitrile 4-ABN (structure VI Scheme 1) is the simplest aromatic amine model with an electron accepting substituent. Jet excitation spectra for 4-ABN (Figs. 10 and 11) resemble aniline in their spectroscopy, as Table 2 indicates [16]. The amino inversion mode is active in both excitation and dispersed fluorescence spectra. In aniline, the amino group is thought to be pyramidal in the ground state [17], with the angle between ring plane and NH_2 plane 42°, and a barrier to inversion of 550 cm^{-1}. In the S_1 state, the barrier to inversion is greatly reduced, with a quartic potential and zero barrier [17]. AMI calculations for ABN give an out-of-plane angle in the ground state of 19°, compared with 23° calculated for aniline [16]. Four active fundamental modes (6a, 12, 1 and 13) dominate the 4-ABN spectra [16].

The four active fundamentals observed also dominate the excitation spectrum of jet-cooled aniline [18]. The 4-ABN spectrum, however, bears little resemblance to that of jet-cooled benzonitrile [19]. In the latter spectrum only two of these modes, 12 and 1, are prominent. The spectroscopic similarity between 4-ABN and aniline is further revealed in the dispersed fluorescence spectra.

The fluorescence spectrum produced by exciting the O_0^0 transition is shown in Fig. 11. It does not bear a mirror symmetric relationship with the excitation spectrum, the most notable deviation being the appearance of a second band in the 400-cm^{-1} region. This is exactly analogous to the fluorescence behaviour of aniline, where the marked anharmonicity of the inversion potential in the ground state leads to the appearance of the symmetry-allowed I_2^1 inversion transition at 427 cm^{-1} [20], whereas the corresponding transition in

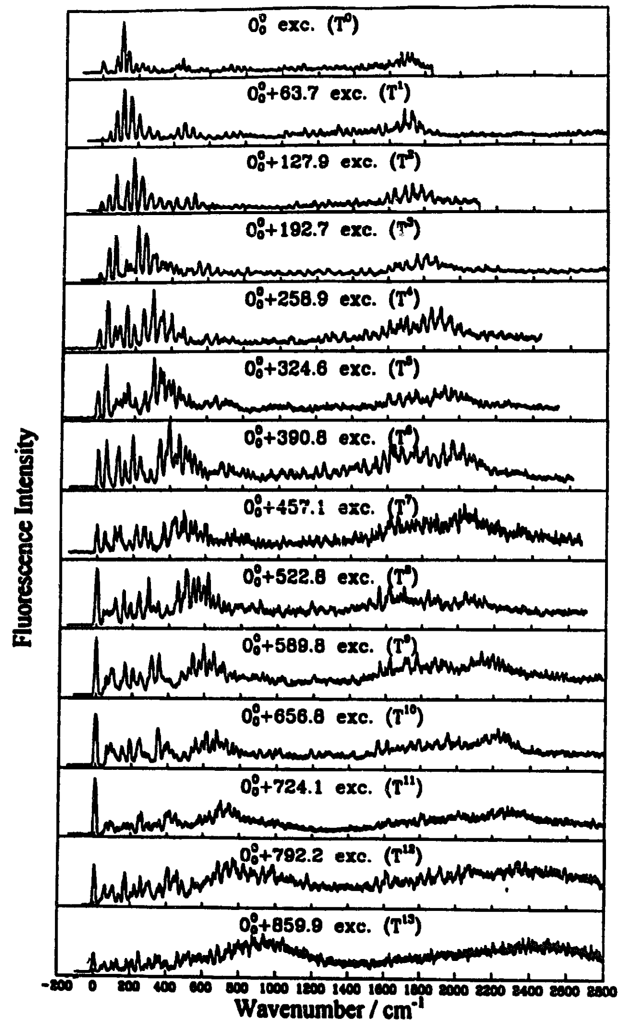

Fig. 2. Single vibronic level spectra of 2-PI following excitation of the torsional modes T_0^0 to T_0^{13} (cf. Fig. 1) [12].

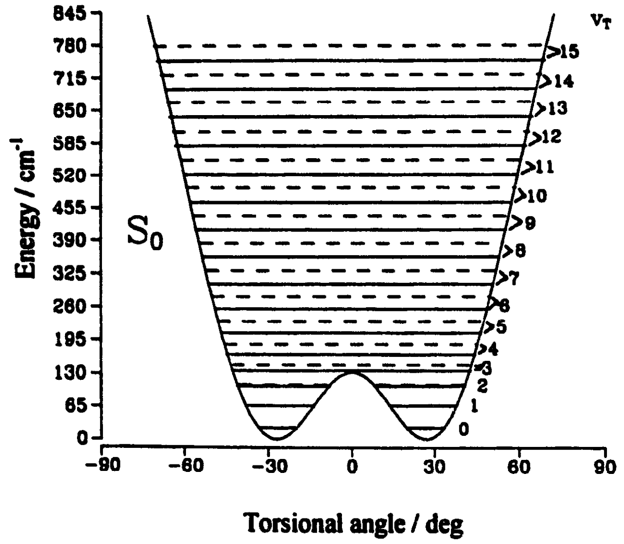

Fig. 3. Potential surface for ground-state of 2-PI. Solid and dashed lines represent levels corresponding to states of symmetric (+) and antisymmetric (−) symmetry species respectively [12].

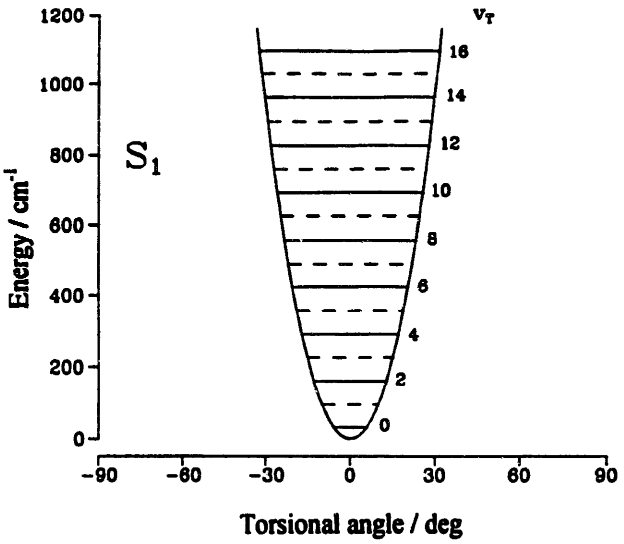

Fig. 4. Potential surface for excited state of 2-PI, as for Fig. 3 [12]. Note change of scale between Fig. 3 and Fig. 4.

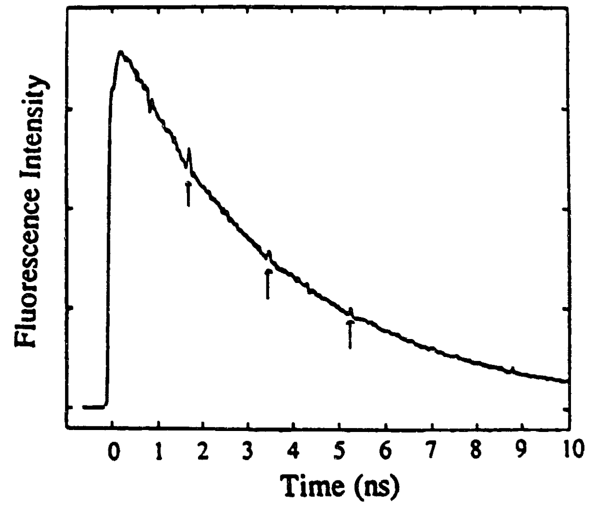

Fig. 5. Experimental trace for rotational coherence spectroscopy on 2-PI. Recurrences are indicated with an arrow.

excitation occurs at 760 cm^{-1}. The 430-cm^{-1} fluorescence transition of 4-ABN is therefore assigned as the $\Delta v = 2$ transition in the amino group inversion mode.

The inversion frequencies observed for 4-ABN are comparable in magnitude to those of aniline (see Table 2), suggesting a similar amino group geometry in the two molecules. Excitation of 4-ABN vibrational levels above 1150 cm^{-1} above the origin results in intramolecular vibrational distribution [21].

5. DMABN (structure VII Scheme 1)

This key molecule has been the subject of several studies under jet conditions. From our own study [16], the origin region of the excitation spectrum of DMABN is shown in Fig. 12(A). It consists of a characteristic pattern of low-

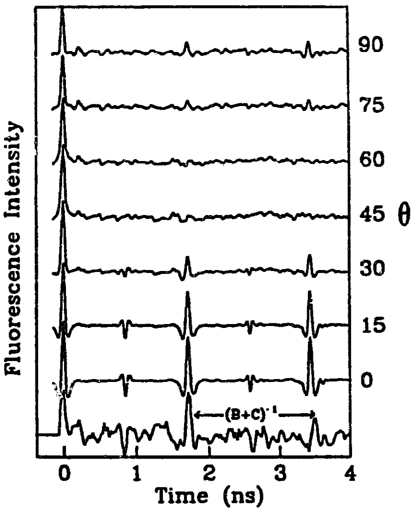

Fig. 6. Observed and calculated residual traces following rotational coherence spectroscopy on 2-PI [13]. Traces are calculated for increasing angles of the transition dipole moment with respect to the ci-inertial axis as indicated in the molecular structure. The recurrence time is indicated on the observed trace.

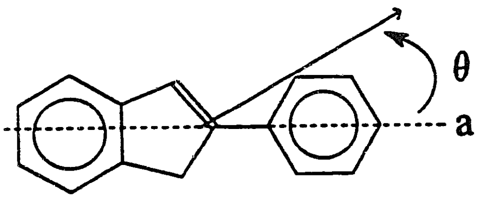

Fig. 7. Inertial axis and direction of transition moment in 2-PI.

frequency transitions; the lowest energy band is very weak, in marked contrast to the intense 0^0_0 transition of 4-ABN. A virtually identical series of low-frequency bands is observed in the excitation spectrum of *N*,*N*-dimethylaniline, as shown in Fig. 12(B). These low-frequency transitions are clearly associated with the dimethylamino group. The similarities in the two spectra suggest that the electron-withdrawing *para* cyano substituent has little effect on the geometry of the dimethylamino group.

Both spectra are dominated by a 60-cm^{-1} transition which appears to be a member of a short progression, as indicated. The same progression occurs again, built on a mode of 37 cm^{-1}. The same pattern of bands recurs at higher energies in the DMABN spectrum, built on vibrations of 373, 494 and 780 cm^{-1}. By analogy with 4-ABN, these can be assigned as $6a^1_0$, $10b^2_0$ and I^1_0, respectively.

A full assignment of the fluorescence spectrum has been published elsewhere [22] and bears a close similarity to that of the corresponding aniline spectrum; the 6a mode is dominant, both in progression and in combination with modes 1 and 12 and with I_2. Dispersed fluorescence spectra following excitation of the $6a^1_0$, 12^1_0, 1^1_0 and 13^1_0 transitions were also measured and provide the ground-state frequencies of these modes, listed in Table 2.

In view of the activity of the inversion mode in fluorescence, a likely assignment for the 807-cm^{-1} absorption is I^2_0, which occurs at 760 cm^{-1} in aniline. This is supported by the corresponding dispersed fluorescence spectrum which is somewhat anomalous in that the most intense transition occurs at 1365 cm^{-1}. This fluorescence behaviour is consistent with the expected anharmonicity of the inversion mode, and the 1365-cm^{-1} transition can be assigned as I^2_4 or $6a^0_1\,I^2_4$.

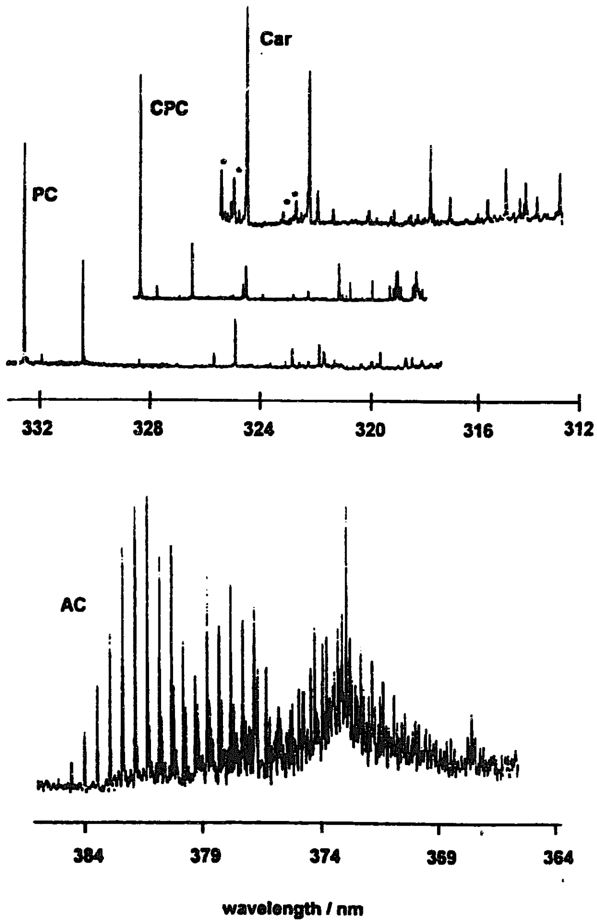

Fig. 8. Fluorescence excitation spectra of carbazole [II], C, *N*-phenyl carbazole III, PC, cyanophenyl carbazole, IVCPC and anthryl carbazole, VAC [14].

The assignment of the above low-frequency modes is difficult in view of the complexity of the dimethylamino group which may undergo *N*-aryl torsion, *N*-methyl torsion, and inversion. Results of a microwave study of DMA [23] show the dimethylamino group to be out-of-plane (with respect of inversion) with $\phi = 27°$; the separation between the 0^+ and 0^- ($v'' = 0$ and $v'' = 1$) inversion states was estimated to be as little as 3 cm^{-1}. Other experiments have provided estimates for ϕ ranging from 29.5° to 0°. The consensus appears to be that ϕ is less in DMA than in aniline. Our AMI calculations support this conclusion, predicting a value of $\phi = 17°$ (cf. $\phi = 23°$ calculated for aniline).

The above microwave investigation also provided an estimate for the frequency of the NMe_2 group torsion about the *N*-aryl bond; the torsional frequency appeared to be < 100 cm^{-1} and possibly as low as 50 cm^{-1}. The *N*-methyl torsion is expected to lie somewhat higher in frequency. The barrier to this motion in *N*-methylaniline [24] has been estimated to

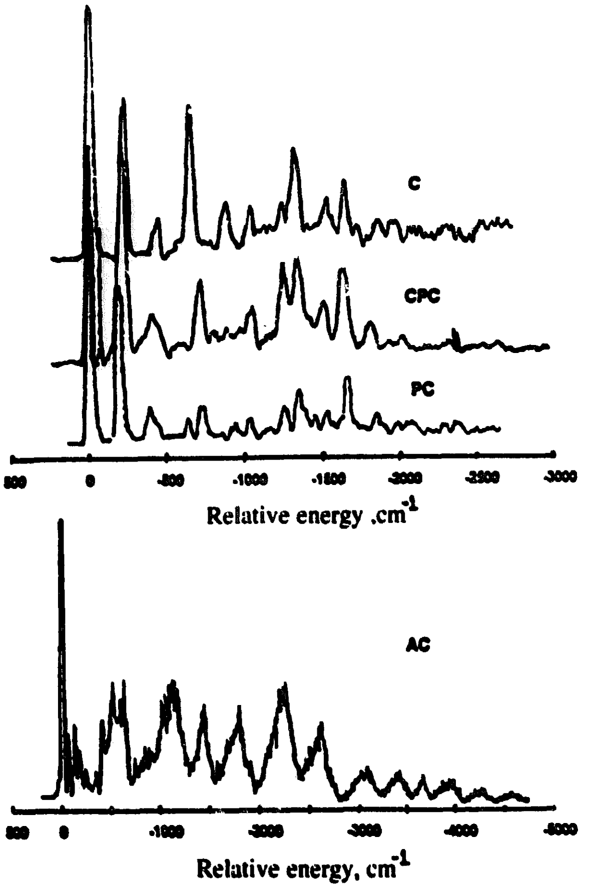

Fig. 9. Dispersed fluorescence spectra of C, PC and CPC following excitation to the zero point level of the excited state, and of AC following excitation of the torsional mode τ_0^{18}.

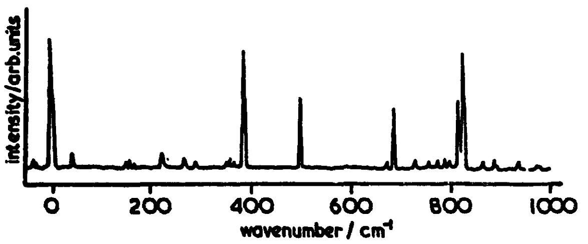

Fig. 10. Fluorescence excitation spectrum of jet-cooled 4-ABN.

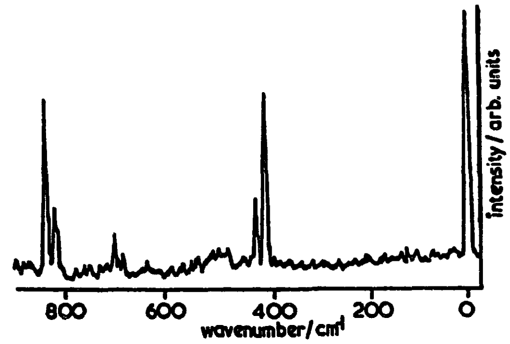

Fig. 11. Dispersed fluorescence spectrum of 4-ABN following excitation of the 0_0^0 transition.

Table 2
Comparison of the frequencies of the active fundamentals and the inversion transition of 4-ABN and aniline [16]

Mode	4-ABN		Aniline	
	ν'/cm^{-1}	ν''/cm^{-1}	ν'/cm^{-1}	ν''/cm^{-1}
6a	382	412	492	533
12	678	728	955	1013
1	815	886	789	824
13	1164	1223	1311	1278
I (ν=2)	807	430	761	427
I (ν=4)		1365/953 [a]	1729	1089

[a] The 1365 cm^{-1} transition observed in the dispersed fluorescence spectrum after excitation of the 807 cm^{-1} (I^2) level may be assigned either as the I_4^2 transition or $6a_1^0\,I_4^2$.

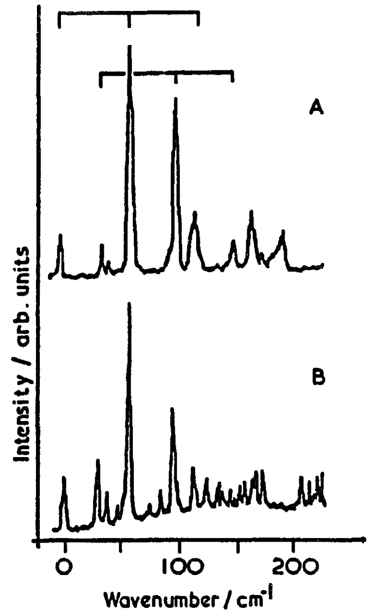

Fig. 12. Fluorescence excitation spectrum under low resolution of jet-cooled DMABN (A) and dimethyl aniline (B). The progressions in the 60 cm^{-1} mode are indicated.

be comparable to that in dimethylamine which has a torsional frequency of ≈257 cm^{-1} [25,26]. The torsional barrier in DMA is expected to be higher than that in *N*-methylaniline.

If we assume that the 72-cm^{-1} transition observed in DMABN fluorescence corresponds to the 60-cm^{-1} transition in excitation, this mode is too low in frequency to be due to *N*-methyl torsion and too harmonic to be due to inversion. It appears to correspond to torsion about the *N*-aryl bond. Assuming that the NMe_2 group is nonplanar, with respect to inversion, DMABN has C_s symmetry. Under this symmetry, the *N*-aryl torsion is symmetric (a′) and only transitions in even quanta are expected to appear in the electronic spectrum. The *N*-aryl torsion is thus estimated to have a frequency of ≈30 cm^{-1} in the excited state and ≈36 cm^{-1} in the ground state. Photoelectron spectroscopy has shown that the dimethylamino group of DMA is planar with respect to torsion about the *N*-aryl bond; this can be assumed to apply to DMABN also. The presence of a progression in the *N*-aryl torsion (up to $v=6$ if the argument is valid) in the electronic spectra indicates that the S_1 state has a twisted geometry in the free molecules.

6. Solvated aminobenzonitriles

The anomalous a^* fluorescence of DMABN is observed only in polar solution, and this has prompted a number of studies on this molecule in the jet when complexed with a variety of 'solvent' molecules.

Kobayashi et al. [27] reported the absence of any a^* emission in LIF studies of the jet-cooled 'bare' DMABN molecule and of vdW complexes of DMABN with water and with trifluoromethane. The O–O bands in the excitation spectra of the complexes showed blue shifts in contrast to the vdW complexes with rare gas atoms. These facts were interpreted in terms of the structure of the vdW complexes and the authors stressed the importance of the location of the substrate molecule in order for the complex to form a CT state.

Peng et al. [28] presented a fluorescence study of DMABN both in a thermalized vapour and in a supersonic jet. From the jet studies, excited and ground state vibrational spectra of the isolated molecule were resolved, and the spectroscopy of the stoichiometric complexes with water, methanol, ammonia and aceto-nitrile reported. It was concluded that local perturbations in 1 : 1 complexes are not sufficient to cause charge separation. At higher temperatures in the jet, red-shifted emission attributed to DMABN self complexes was reported. Under high pressure and temperature vapour conditions, another fluorescence band with a greater red shift was observed which was assigned to the charge transfer state of DMABN in self-complexes, however this was not observed under jet-cooled conditions.

Bernstein et al. [29] reported two-colour time of flight mass spectra of jet-cooled 3- and 4-dimethylaminobenzonitrile bare molecules and complexes with methane, water, acetone, dichloromethane and acetonitrile. Both 3- and 4-DMABN were said to display significant changes in geometry, associated with rotation-inversion co-ordinates of the dimethylamino group, upon excitation from the ground electronic state S_0 to the first excited singlet state S_1. The mono complexes of 3- and 4-DMABN all showed two distinct types of behaviour: (i) clusters in which the spectra have both red and blue shifts from their respective bare molecule origins that are relatively small (in general less than 200 cm^{-1}), and spectra are sharp, resembling strongly the bare molecule spectra. (ii) Clusters with spectra which have large shifts (500–1000 cm^{-1}) to low energy compared with the bare molecule spectra; these spectra are composed of both sharp and broad features with little resemblance to the bare molecule spectra.

In a subsequent publication [30] the same group presented one-colour time of flight mass resolved excitation spectra of jet-cooled DMABN and some of its chemical analogues, dimethylamiline (DMA), 3-dimenthylaminobenzonitrile (3-DMABN), *N,N*-dimethyl-4-(trifluoromethyl) aniline (4-CF_3DMA), and 4-(d_6-dimethylamino) benzonitrile (4-d_6-DMABN). Near the origin of the S_1–S_0 transition the low frequency transitions were assigned to motions of the dimethylamino group, with the inversion motion and the dimethylamino group torsion about the C_{ipso}–N bond (the twist co-ordinate) in S_1 giving rise to the most prominent features. The potential parameters for the twist co-ordinate were found to be similar for all of the molecules, as was the inversion motion. A Franck-Condon intensity analysis for the dimethylamino twist suggested that the dimethylamino group is displaced in the excited state by ≈ 30 with respect to its assumed planar orientation in the ground state. In both solution and 1:1 complexes of DMABN with polar protic molecules, a low lying CT state was identified in addition to the usual $\pi\pi^*$ excited state of the bare molecule. The relation between the bare molecule twisting displacement upon excitation and the low lying CT state was also discussed.

August et al. [31] recorded LIF excitation spectra for a series of DMABN derivatives, (VII, VIII and IX) the *para* substituted nitrile or ester derivatives of dialkylaminobenzene compounds. LIF excitation spectra of the ester derivatives showed an underlying 'quasi-continuum', and the authors reported observation of red-shifted emission associated with this; however, no emission spectra were presented. These results were claimed as evidence both for torsional motion and TICT state formation in the unsolvated ester, which might be expected to give rise to charge-transfer state emission more readily due to substituent induced level reversal of the ^1L_b and L_a states.

Herbich et al. [32] reported the LIF excitation and fluorescence spectra of jet-cooled 4-(dimethylamino) benzonitriles and 4-(dialkylamino) pyramidines and their complexes with small polar molecules (except TMABN) do not exhibit any distinct long wavelength fluorescence that can be assigned to a TICT state. Microcomplexation of the ground state twisted molecules with methanol and acetonitrile gave rise to the red shifted emission which the authors attributed to the TICT state.

In our own work, we reported excitation and dispersed fluorescence spectra as well as fluorescence lifetimes of jet-cooled DMABN and its vdW complex with methanol. Neither the bare molecule nor mono complex exhibited the anomalous a^* fluorescence seen in polar solution. Multiple complexation resulted in a dramatic reduction in the fluorescence quantum yield, which was interpreted in terms of formation of an a^* state that is non-emissive under jet-cooled conditions. In a further paper Gibson et al. [16] made a comparison of complexes of DMABN and 4-aminobenzonitrile with argon, alkyl cyanides, methanol and water. Spectral shifts are shown in Table 3.

Like those of DMABN, the complexes of 4-ABN, with exception of 4-ABN-argon, were found to exhibit hypsochromic spectral shifts relative to the bare molecule; complexes involving interaction with either the cyano or amino group were observed. By contrast, interaction of protic molecules with the dimethylamino group of DMABN was found

Table 3
Microscopic solvent shifts for 4-ABN, DMABN solvent complexes

4-ABN		DMABN	
Ligand	$\Delta\nu$/cm^{-1}	Ligand	$\Delta\nu$/cm^{-1}
CH_3CN	236	CH_3CN	254
CH_3OH	92	CH_3OH	19
H_2O	84, 196, 314	H_2O	18
C_2H_5CN	239		
Iso-C_3H_7CN	238		
		CF_3H	69
		NH_3	21

to result in efficient fluorescence quenching which was attributed to formation of a non-emissive exciplex.

Kajimoto et al. [33], presented evidence for TICT state formation in a supercritical fluid of DMABN in CF_3H and concluded that three polar solvent molecules are required to give rise to an emissive charge-transfer state in DMABN. In the case of the jet expansions, three polar molecules associated with the dimethylamino variety would have produced non-emissive and therefore invisible complexes.

Since red-shifted emission from clusters has been observed under jet conditions, and some evidence of red emission resulting from excitation of a quasi continuum absorption in dimethylaminobenzoic acid esters studies were carried out on large solvent clusters surrounding DMABN [34]. The solvents used, cyclohexane, acetone, methanol, acetonitrile, dichloromethane chloroform and carbon tetrachloride resulted in dual fluorescence spectra best interpreted in terms of a monomeric aromatic amine species complexed with solvent substrate, and a cluster of DMABN complexed with solvent substrate. Only in the case of chloroform and dichloromethane could there be said to be any evidence of emissions which could be attributed to monomeric red-shifted emission.

Thus despite extensive work on aminobenzenes, there is no convincing evidence from supersonic jet spectroscopy of the formation of an emissive charge transfer state which is formed by twisting of the amino moiety with respect to the aromatic ring.

Further high-resolution jet spectroscopy, using REMPI detection as well as fluorescence, may well shed further light on the important class of molecules, but other strategies should also be explored. Time-resolved Raman spectroscopy can in principle give information on shifts in vibrational frequencies in electronically excited states, and hence structural information. Such studies are in train, but results are not sufficient to warrant discussion here.

Alternatively, more sophisticated calculations can be carried out on the geometries of ground and excited states of molecular such as DMABN. Sobolewski et al. [35] have carried out ab initio calculations on benzonitrile, 4-aminobenzonitrile and DMABN. They conclude that geometry optimization on the charge-transfer state in DMABN is reached when the cyano group is bent, suggesting that it is the bending of the cyano group rather than the twisting of the amino group which is responsible for stabilization of the charge-transfer state in aminobenzonitrites.

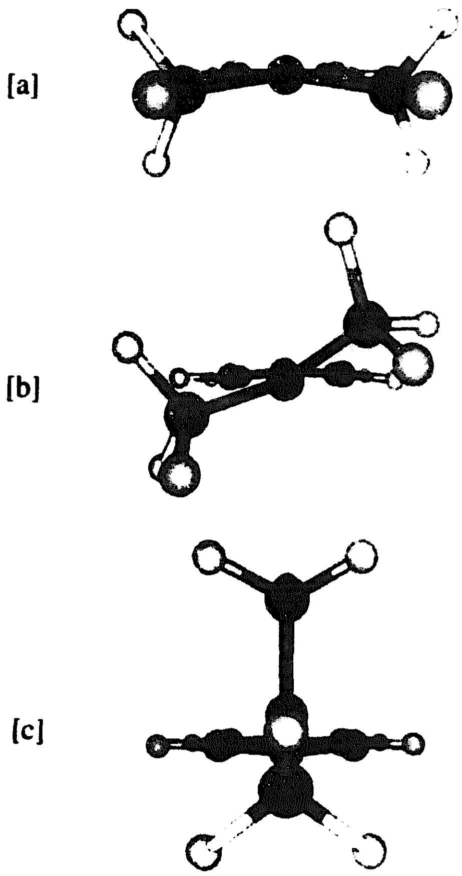

Fig. 13. Structures of DMABN in (a) ground, (b) locally excited state and (c) charge transfer, as revealed by ab initio calculation [36].

The result can be reproduced by us [36], but use of the more extensive 6-31G** basis set, with RHF wave function for the ground state and the CI singles method for excited states, does not produce the same result.

Instead, the structures shown in Fig. 13 are predicted [36] in which the ground state is planar, the locally excited state has the dimethyl amino group twisted somewhat about the N–Ar bond with respective N–Me bonds twisted out of the plane of the aromatic ring by 44° and 6° respectively (i.e. some sp^3 character has been introduced).

Attempts to optimize the charge transfer state in C_{2v} or C_s point groups resulted in a perpendicular structure with TICT character, but corresponding to a double maximum, suggesting that in the isolated molecule the charge transfer state may correspond to a transition state between two equivalent locally excited-state geometries. Further work in this important area of theory is clearly required.

7. Conclusions

Supersonic jet spectroscopy in principle provides a rigorous method for the elucidation of geometries of ground and excited states, but when applied to aminobenzene and aminobenzonitriles, has failed to provide convincing evidence of the geometry of the charge transfer state of such molecules which are seen in emission in polar solution.

Ab initio calculations give differing results for such molecules depending upon the level of sophistication employed, and are thus also unable unequivocally to determine these geometries.

Time-resolved Raman spectroscopy can in principle determine such geometries, but results are so far inconclusive. It seems the structures of these molecules will remain tantalizingly obscure for some time to come.

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