ARTICLES

## The Nature of the Intramolecular Charge Transfer Excited State in *p*-Pyrrolocyanobenzene (PBN) and Other Derivatives of Benzene Substituted by Electron Donor and Acceptor Groups

Shmuel Zilberg and Yehuda Haas

Department of Physical Chemistry and the Farkas Center for Light Induced Processes,
The Hebrew University of Jerusalem, Jerusalem, Israel 91904

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The title compound is a representative of a family of molecules known to exhibit dual fluorescence in polar solvents. A theoretical analysis of these compounds, in which benzene is substituted by an electron withdrawing group and an electron donating group para to it is offered. The first excited state is derived from the ^1L_b state of benzene and is of a covalent nature. Light emission from this state is due to local excitation of the benzene moiety (LE fluorescence). The second excited state of benzene (^1L_a) evolves in the presence of these substituents in two highly polar structures. Depending on the substituents, one or two energy minima may form on this surface, both having a charge transfer character. Of these structures, one has a quinoid nature, whose minimum is in the planar form. The other may be termed an anti-quinoid (AQ) structure: the distance between the two bonded central carbon atoms in the benzene ring is longer than in benzene. This structure has a larger dipole moment than the quinoid one, and a minimum at the perpendicular form. The AQ structure minimum is found also on the excited state potential of benzene substituted by an electron donor only, such as pyrrolobenzene, but not for an acceptor only substituted molecule such as benzonitrile. This minimum on the excited state surface is reported here for the first time; it appears to conform with all the experimentally observed characteristics of TICT molecules. The quinoid form is the one predicted by the PICT model. The dual fluorescence of these compounds is due to LE and the CT emissions; the latter arising from either the Q or the AQ structures.

I. Introduction

The dual fluorescence of some substituted benzene derivatives (the typical molecule being *p*-(*N*,*N*′-dimethylamino)benzonitrile (DMABN), Scheme 1), was discovered over 40 years ago.[1] These molecules fluoresce in two different bands when solvated in a polar solvent. The "normal" fluorescence exhibits the familiar mirror image to the absorption spectrum and is only slightly red-shifted upon increasing the polarity of the solvent. The second, so-called "anomalous" emission, is strongly red shifted and appears often as a separate band, whose intensity increases at the cost of the "normal" emission as the solvent's polarity is increased. Intramolecular charge transfer was suggested as the mechanism leading to this phenomenon,[2] as shown in Figure 1. Initial excitation is typically into the locally excited (LE) state, that correlates with the 1^1B_{2u} (L$_b$, Platt's nomenclature[3]) state of benzene. A radiationless intramolecular process leads to the population of the CT state, which correlates with the 1^1B_{1u} (L$_a$) state of benzene. The LE and CT states are often referred to (by their symmetry in C_2 point group) as the B and A states, respectively. Ever since its discovery, the nature of the charge transfer state has been the target of many theoretical studies. Several models were suggested; Bimolecular models,

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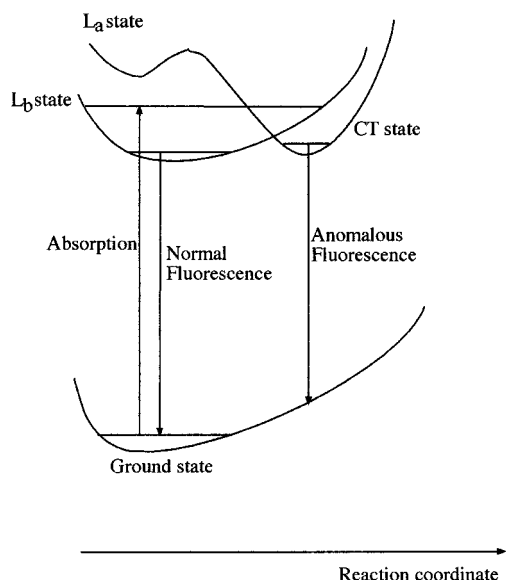
Figure 1. Schematic energy level diagram of molecules exhibiting dual fluorescence. In the TICT model, the reaction coordinate is the twist angle. In the PICT model, it is the planarization of the amino group.

SCHEME 1: Structures of Benzonitrile (BN), *p*-Aminobenzonitrile (ABN), *p*-(Dimethylamino)benzonitrile (DMABN), Pyrrolobenzene (PB), and *p*-Pyrrolobenzonitrile (PBN)
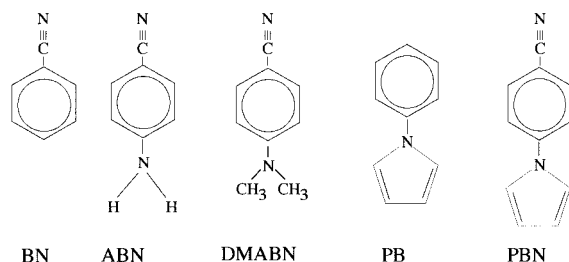
including ones calling for a solute solvent exciplex, have been rejected. Currently, the leading monomolecular models may be divided into four classes: TICT (twisted intramolecular charge transfer[2,4]), WICT (wagged intramolecular charge transfer[5]), in which a pseudo Jahn−Teller coupling to form a planar CT (PICT) state is assumed[6]), and RICT (rehybridization intramolecular charge transfer[7]).

The TICT model appears at this time to be the most widely used model. Evidence for the twisted character of the charge transfer state is extensive, but mostly circumstantial, since direct measurement of its structure is not reported. The main arguments are based on the fact that rigid molecules that cannot twist do not show dual fluorescence.[8,9] In addition, the strongly reduced transition moment for the red-shifted emission, is in accord with the TICT model.[10] Transient absorption spectra of the CT state resembled those of separate A[•−] and D[•+] radical ions, in agreement with the prediction of charge separation to non-interacting species. However, some experimental observations are not easy to reconcile with this model.[11] Evidence has been presented that the amino and benzonitrile moieties are not decoupled in a series of dual fluorescent 4-aminobenzonitriles. It has been argued that the planarization of the amino nitrogen is an important reaction coordinate in the intramolecular CT reaction.[11] In addition, attempts to model the TICT state by quantum mechanical methods (see the Discussion for a brief review) lead to a charge transfer state with a quinoid structure (Scheme 2), which is planar! Such a structure is not compatible

SCHEME 2: Quinoid (Q) and Antiquinoid (AQ) Structures of Donor−Acceptor-Substituted Benzene Derivatives[a]

Quinoid Structure   Anti-quinoid Structure
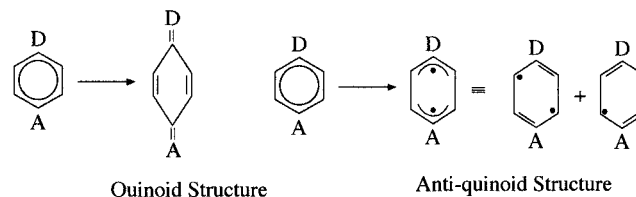
[a] The AQ structure may be viewed as a resonance hybrid of the two allylic structures shown. The charge distribution in the CT state of this structures is discussed in section Va.

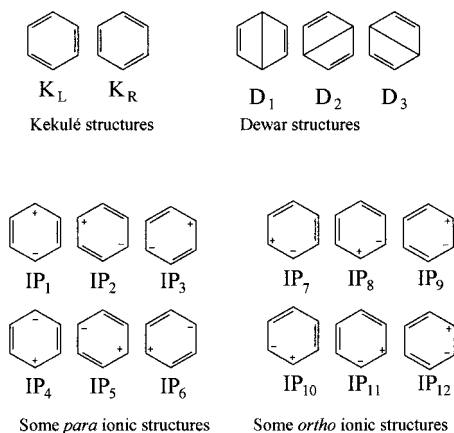with the TICT idea, since in it the phenyl−N-amino bond is of partial double bond character.

In this paper we propose a model that differs in some aspects from previous ones. It is based on the properties of the excited states of benzene[12] and is supported by extensive quantum chemical calculations at the CASSCF and CASPT2 levels. Two structures are shown to lie on the 2^1A potential surface: a quinoid one (Q), which was reported before,[4,5,7] and an anti-quinoid one (AQ), in which the distance between the two adjacent central carbon atoms of the benzene ring is longer than that in the ground state (Scheme 2). Both may have a minimum on the A state's surface. The AQ structure has a larger dipole moment (of the order of 15−20 D) than the Q one, in both planar and perpendicular conformations of the donor substituent (for instance, an amino or pyrrolo group) with respect to the benzene plane. The perpendicular conformation, however, is found to be more stable than the planar one for the AQ structure, in contrast with the Q structure, whose minimum energy is at the planar form. In the gas phase, the Q structure minimum is lower than the AQ one. Due to the larger dipole moment, the AQ structure may be lower in energy than the Q structure in polar solvents. The properties of the AQ structure (in which the pyrrolo moiety is twisted to 90° with respect to the benzene ring at its minimum energy) appear to be in good agreement with experiment. The AQ structure is thus a natural candidate for the long sought-after TICT state.

The molecule chosen to demonstrate these properties is PBN, which has been shown experimentally to exhibit dual fluorescence.[13−15] For comparison, calculations were carried out also on three related molecules: benzonitrile (BN), aminobenzonitrile (ABN), and pyrrolobenzene (PB) (their structures are shown in Scheme 1). It is believed that the model applies to other para-substituted benzene derivatives with electron donor and acceptor substituents.

II. Computational Methods

The calculations were performed as follows. First, the ground state of each molecule was calculated by the density functional theory (DFT) method using the B3LYP functional and the cc-pVDZ basis set. Complete optimization was performed until a minimum energy structure was achieved. To compare with excited-state structures, the calculation was repeated using CASSCF with the appropriate active space (see below for individual molecules). The two low-lying excited states were calculated using the CAS method. A C_{2v} symmetry (either planar or perpendicular) was used initially. This led to an approximate structure. For the S_1 state, this constraint was relaxed, and a minimum was obtained with full optimization performed by the standard quadratic approximation. For S_2, it was found that the two minima found were at C_{2v} symmetry (neglecting the small

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SCHEME 3: Some VB Structures of Benzene

Kekulé structures: K_L K_R

Dewar structures: D_1 D_2 D_3

Some *para* ionic structures: IP_1 IP_2 IP_3 IP_4 IP_5 IP_6

Some *ortho* ionic structures: IP_7 IP_8 IP_9 IP_{10} IP_{11} IP_{12}

pyramidal deformation). The stability of the optimized structures was checked by calculating the Hessian matrix.

The active space used for the four molecules included the following orbitals:

Benzonitrile: all π orbitals, and the π orbitals of CN orthogonal (the π_y orbitals) to the benzene π orbitals (8e/8o).

Aminobenzonitrile: all π orbitals, the lone pair of the amino nitrogen atom and the π^*_y orbital of CN (10e/9o).

N-Pyrrolobenzene: all π orbitals of the phenyl and pyrrolo moieties (12e/11o). This active space includes all π orbitals and all π electrons in this system (full π active space).

PBN: There are 13 π orbitals and 14 p electrons in this molecule. For technical reasons, we could not carry out the calculation with the full π active space. We have deleted the lowest lying occupied π MO, and the highest lying unoccupied MO and used 12 electrons in 11 orbitals (12e/12o). The choice of the deleted orbitals was based on the assumption that they have the least interaction with the CN group orbitals.

The double-ζ valence (DZV) basis set of Dunning and Hay[16] was used.

Finally, after stationary points were obtained, single point calculations were performed at the CASPT2 level.

Some additional excited-state calculations were done using the CIS method with the 6-31G basis set.

Most calculations were performed with the GAMESS program suite;[17] some CIS calculations were done with the GAUSSIAN program suite.[18]

III. Properties of the L_b and L_a States of Substituted Benzene, Conical Intersections between Them

The properties of the 1^1B_{2u} (S_1) and 1^1B_{1u} (S_2) electronic excited states of benzene have been extensively discussed. The optical transitions to both from the ground state 1^1A_{1g} are symmetry forbidden but become observable due to vibronic coupling. In substituted benzenes, they evolve into the L_b and L_a states, respectively.[3] Theoretically, both MO and VB methods have been applied to the analysis of these electronic states. For the purposes of this paper, it is convenient to use the VB approach, which lends itself more lucidly to chemical interpretation.

The 1^1B_{2u} state is of an almost purely covalent nature and may be considered as the out-of-phase combination of two Kekulé structures[12,19] (Scheme 3). We have dubbed the 1^1A_{1g} and 1^1B_{2u} states as "twins", since the ground state is primarily an in-phase combination of these two structures.[20] This idea led to a physical interpretation of the well-known exaltation of the Kekulé mode's frequency on promoting the molecule from
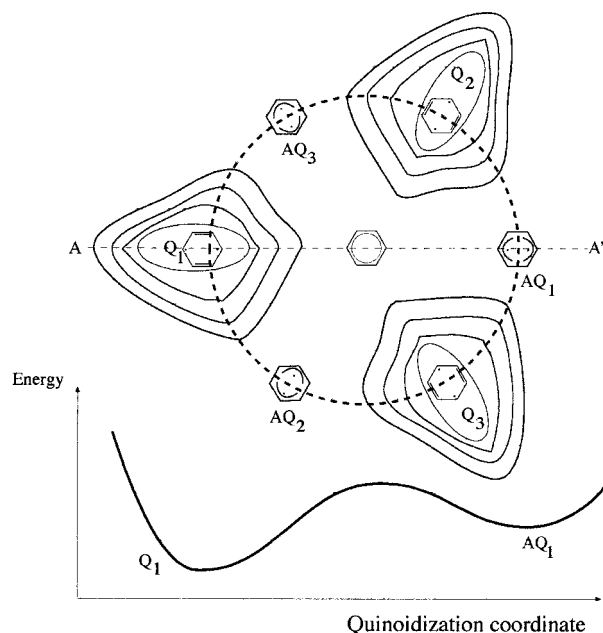
Figure 2. Top: three possible quinoidal distortions that lead from the perfect hexagonal structure of the B_{2u} state of benzene to the quinoidal structure. The contours represent constant energy loci. The heavy circle represents a coordinate that connects any two Q structures. The AQ structures are transition states between the Q structures along this coordinate. Along the AA′ line, the Q and AQ structures are local minima. Bottom: cut across the AA′ line, showing the Q and AQ minima. When a molecule is para-substituted by donor and acceptor moieties, the 3-fold degeneracy is removed, and one of the three quinoid distorted structures becomes more stable than the others.

the ground state to the 1^1B_{2u} state.[12,20] The 1^1B_{1u} state is primarily an ionic state, as realized early on,[21,22] and recently verified by high level quantum chemical calculations.[19] It may be considered as a resonance hybrid of the ionic VB structures, some of which are shown in Scheme 3.

It is well-known that radiationless transitions take place between the two states, since excitation of the 1^1B_{1u} state leads to emission from the 1^1B_{2u} state. Such crossings are most efficiently accomplished through conical intersections, as shown by Meisl and Janoschek[23] and by Palmer et al.[24] It was found that the coordinate along which the crossing takes place is a quinoidization coordinate, in which the molecule distorts such that two opposite CC bonds become shorter and a biradicaloid structure is formed. The physical rational for the relevance of this coordinate in promoting curve crossing between S_1 and S_2 of benzene is as follows. The structure of the 1^1L_b state is a perfect hexagon, while that of the 1^1L_a state is distorted into a D_{2h} (or lower) symmetry. Three such equivalent coordinates are possible in benzene, as shown schematically in Figure 2. The potential surface has three equivalent minima for 1^1B_{1u}, each of which may be reached by using the quinoidization coordinate. In refs 23 and 24 two opposite CC bonds were shortened, as shown in Scheme 2, leading to quinoid (Q) structure. A S_2/S_1 crossing was found upon motion along this coordinate in this direction. However, it is also possible to form a quinoid-type biradicaloid by lengthening these bonds. This will lead to an anti-quinoid (AQ) form that in principle may also lead to curve crossing. In Figure 2, the heavy dashed circle represents the coordinate connecting any two quinoid structures: the anti-quinoid form is a transition state along this coordinate. The energy profile along a coordinate normal to this one (for instance, connecting directly Q_1 with AQ_1 in Figure 2,

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TABLE 1: Computed CASSCF and CASPT2 Excitation Energies (eV) and Dipole Moments (D) of Some Electronic States of Benzene Derivatives[a]

| state	energy (eV)		μ (D)
	CASSCF	CASPT2	
	Benzonitrile		
1^1A	-322.44569 H	-323.035795 H	4.5
1^1B	4.55	4.27	4.4
2^1A	6.60	6.35	4.0
	p-Aminobenzonitrile (ABN)		
1^1A	-377.466234 H	-378.162422 H	6.2
1^1B_2 (planar)	4.49	3.97	6.0
2^1A (planar)	6.07	4.79	13.3
	p-Pyrrolobenzene (PB)[b]		
1^1A (twisted, $\phi = 40, 5°)^c$	-438.355758 H	-439.179869 H	-1.3
1^1B (planar)[d]	4.47	4.13	-0.9
2^1A (Q, planar)	5.59	4.68	0.75
2^1A (AQ, perpendicular)	5.64	5.30	10.8
	p-Pyrrolobenzonitrile (PBN)		
1^1A (twisted, $\phi = 29.5°)^e$	-530.077586 H	-531.068606 H	4.15^f
1^1B (planar)	5.14	3.78	4.0
2^1A (AQ, perpendicular)	5.47	5.07	16.2^g
2^1A (Q, planar)	6.02	3.98	11.0

a Experimental value 4.18 D.[44] *b* In the ground and in the 1^1B states, the pyrrolo group is the electron acceptor. In the 2^1A state, it is the electron acceptor. *c* The twist angle calculated for a minimum energy structure in the ground state. The experimental value is 38.7°.[25] *d* The experimental value is 19.8°. The barrier to rotation is 105 cm^{-1}; therefore the molecule is essentially planar. *e* The twist angle calculated for a minimum energy structure in the ground state. The experimental value is estimated at 30°.[13] *f* Experimental value 3.2 D.[41] *g* Experimental value (in solution) 22.4 D.[15]

line AA′) has two local minima, one at the Q and another at the AQ structures.

When a single electron-withdrawing or -donating substituent is added to the benzene ring, the overall symmetry of the system is reduced from D_{6h} to a lower one (for instance, C_{2v}). Now one of the three quinoidal axes is different from the other two, and motion along it may stabilize a charge-transfer conjugation, with the benzene ring serving as either an electron donor or acceptor. When the benzene molecule is para-substituted by an electron acceptor and an electron donor group, this trend is further enhanced, and one of the three quinoidization coordinates becomes the preferred route. Following common usage, we term the excited state that correlated with the 1^1B_{2u} state of benzene, the 1^1B state, and the state that correlates with the 1^1B_{1u} state of benzene, the 2^1A state.

IV. Computational Results

IVa. Singly Substituted Benzenes: Benzonitrile (BN) and Pyrrolobenzene (PB). We have calculated the properties of benzonitrile and of pyrrolobenzene, as representatives of molecules carrying a single electron-withdrawing or -donating group, respectively. The structures calculated at the CASSCF level were optimized on each electronic potential surface, as described in the section II. Single point CASPT2 calculations were done at the minimum of each structure. The first excited singlet state belongs to the B_1 irreducible representation (irrep) of C_{2v} (B in C_2), and the second, transforms as the A_1 irrep of C_{2v} (A in C_2). We designate them as the 1^1B and 2^1A states, respectively. It was found (Table 1) that for benzonitrile, the dipole moment of S_0, S_1, and S_2 are almost the same, about 4 D. The ground state of PB was found to be twisted (40.50, experimental[25] 300), with a very small dipole moment (1.3 D), which is in the opposite direction to that of BN: the benzene
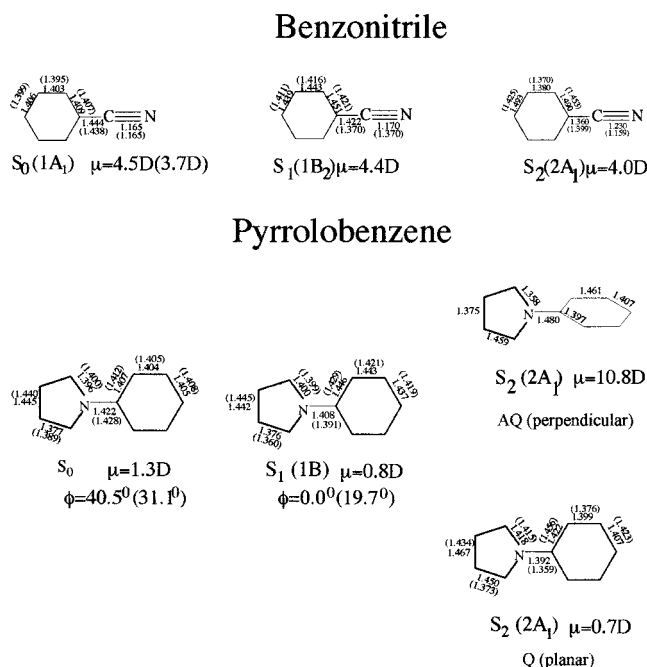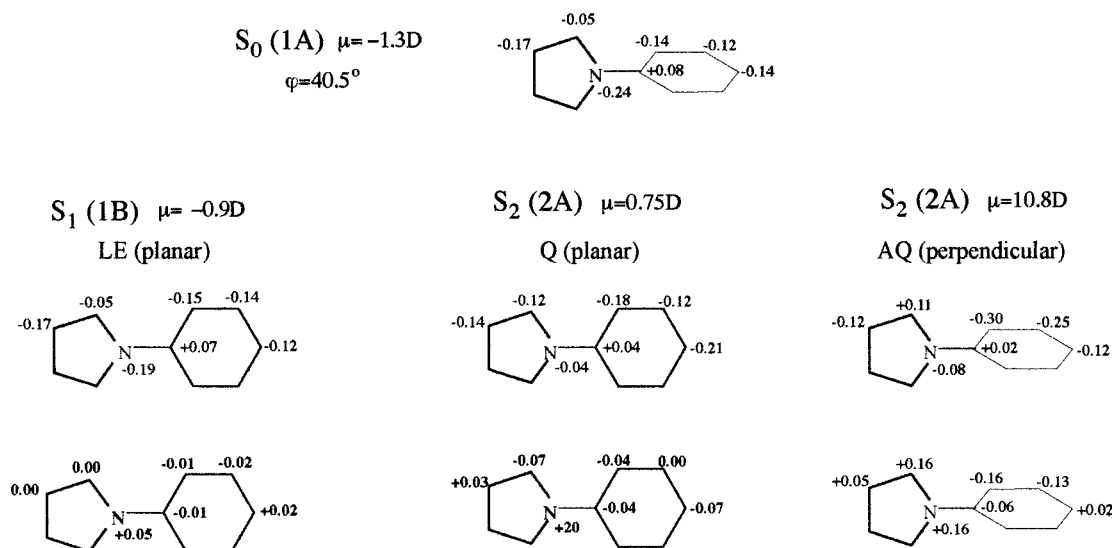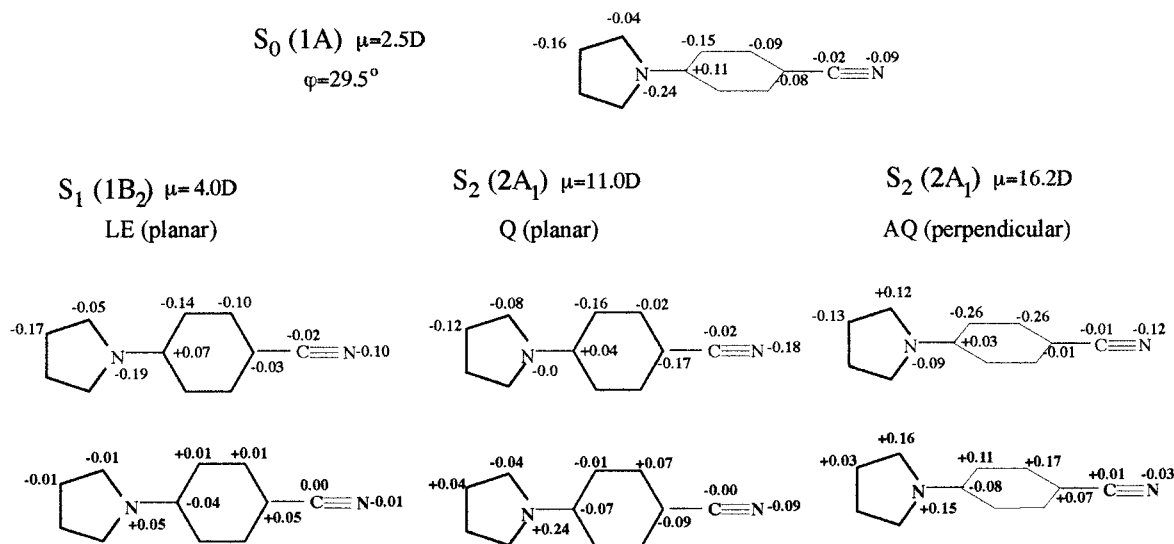

Figure 3. Calculated geometries of BN and PB in the S_0, S_1, and S_2 states. The bond lengths (Å) and twist angles (ϕ) are calculated for all molecules at the CAS/DZV level. In parentheses, values calculated by other methods are shown for comparison: DFT for S_0 and CIS for excited states. See text for details.

ring is the donor in this case, and the pyrrolo one (which contains the strongly electronegative N atom), the acceptor. The dipole moments of PB in the 1^1B state were found to be even smaller (0.8 D), in the same direction as in the ground state. On the 2^1A potential surface, two stationary structures were found. The Q structure (Figure 3) has a minimum in the planar form and a small dipole moment of 0.7 D in the opposite direction (since the N atom becomes a π donor in this structure). The AQ structure (Figure 3), is calculated to have a much larger dipole moment—over 10 D, in both planar (10.3 D) and perpendicular (10.8 D) forms. In this structure, the perpendicular form is more stable than the planar one by 2.4 kcal/mol (CASSCF level). Evidently, this state is a charge transfer state, in which the pyrrole ring is the donor and the benzene ring is the acceptor. This conclusion is supported by the charge redistribution calculated for this molecule, as shown in Figure 4. In the Q structure, the main donor is the pyrrolo nitrogen atom, and the charge is transferred mainly to the benzene ring. In the AQ structure, the donor is the pyrrole ring, mostly the two carbon atoms adjacent to the nitrogen atom (and the nitrogen atom). The charge is transferred mostly to the four central carbon atoms of the benzene ring.

For both BN and PB, the properties of the 1^1B state turn out to be very similar to those of the 1^1B_{2u} state of benzene. The benzene ring remains essentially a perfect hexagon as in S_0, with a small increase in the CC bond length (from about 1.40 to 1.44 Å). Normal-mode analysis indicates a large exaltation of the Kekulé mode frequency, a tell-tale indicator of a 1^1B_{2u}-derived state.[26] This prediction can be checked experimentally using two-photon absorption spectroscopy.[26] In addition, the rotation of the pyrrolo moiety with respect to the phenyl ring in this state is almost free; the barrier is of the order of ~2 kcal/mol. All these properties show that the addition of electron donor or acceptor groups does not change the covalent nature of this state: the electronic structure of the substituent is decoupled from that of the π electron system of the benzene

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Pyrrolobenzene

S$_0$ (1A) $\mu = -1.3$D

$\varphi = 40.5°$

S$_1$ (1B) $\mu = -0.9$D

LE (planar)

S$_2$ (2A) $\mu = 0.75$D

Q (planar)

S$_2$ (2A) $\mu = 10.8$D

AQ (perpendicular)

p-Pyrrolobenzonitrile

S$_0$ (1A) $\mu = 2.5$D

$\varphi = 29.5°$

S$_1$ (1B$_2$) $\mu = 4.0$D

LE (planar)

S$_2$ (2A$_1$) $\mu = 11.0$D

Q (planar)

S$_2$ (2A$_1$) $\mu = 16.2$D

AQ (perpendicular)

Figure 4. The calculated (CAS/DZV) charge distribution for PB and PBN (heavy atoms only). For each molecule, the top row shows the charge distribution in the ground state, the third row, the charge distribution in the three excited structures, and the bottom row, the net charged transferred (in boldface) from or to each atom upon transition from the ground state to the excited state. Note the marked similarity between the distributions of the two molecules in the respective electronic states. The distribution hardly changes in the LE state by comparison to the ground state, while in the Q and AQ structures of the CT states the changes are significant. In the Q structure, most of the charge is transferred from the pyrrolo nitrogen atom to the cyano group. In the AQ structure, the charge is transferred mostly from the C−N−C moiety of the pyrrole ring to the four central carbon atoms in the benzene ring.
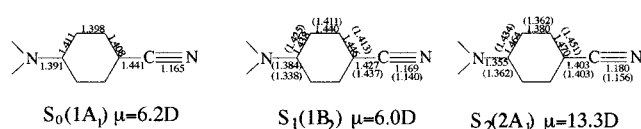
ring. Thus, this state is a truly locally excited (LE) state in which excitation is in the benzene moiety.

For the 2^{1}A state of BN and of PB, an energy minimum was found at the quinoid (Q) structure (Figure 3): the two central CC bonds of the benzene ring are shorter than the other four CC bonds and the bond between the benzene ring and the substituent shortens substantially. For this structure, the calculated dipole moment is relatively small, of the same order as that of the ground state (Table 1). The minimum energy for this structure is obtained at the planar geometry of PB, with the barrier to rotation around the C$_{phenyl}$−N bond quite high (about 19 kcal/mol). These properties suggest stabilization due
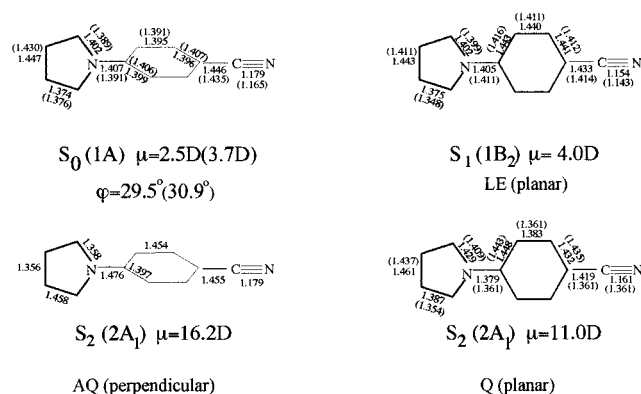
to a conjugated system, in which the C$_{phenyl}$−N bond has a partial double bond character, as depicted in Scheme 2 (see the Discussion).

Another minimum was found on the 2^{1}A state potential surface of PB, but not of BN. It is the antiquinoid (AQ) structure shown in Figure 3. The two central CC bonds of the benzene ring are longer than the other four. In addition, the length of the C$_{phenyl}$−N bond in the perpendicular form is (at the CASSCF(12,11)/DZV level) 1.480 Å, almost as long as a single bond, while in the Q structure it is much shorter, 1.392 Å (in the ground state the bond length is 1.422 Å). The pyrrole ring undergoes a reversal of bond lengths with respect to S$_0$: the

p-Aminobenzonitrile

$S_0(1A_1)$ $\mu=6.2D$ $S_1(1B_2)$ $\mu=6.0D$ $S_2(2A_1)$ $\mu=13.3D$

p-Pyrrolobenzonitrile

S_0 (1A) $\mu=2.5D(3.7D)$ S_1 (1B$_2$) $\mu=4.0D$
$\varphi=29.5°(30.9°)$ LE (planar)

S_2 (2A$_1$) $\mu=16.2D$ S_2 (2A$_1$) $\mu=11.0D$

AQ (perpendicular)   Q (planar)

Figure 5. calculated geometries of ABN and PBN in the S_0, S_1, and S_2 states. The bond lengths (Å) and twist angles (ϕ) are calculated for all molecules by the CASSCF method. In parentheses, values calculated by other methods are shown for comparison: DFT (S_0) and CIS (excited states). See text for details.

two N−C bonds are shortened to practically double bonds, as is the central CC bond! The high dipole moment of this structure was mentioned above, as well as the fact that the perpendicular form is more stable than the planar one. Clearly, in the AQ structure, the π electron systems of the two rings are separated, while in the planar form they are conjugated.

The results of the DFT calculations for the ground states of these molecules (section II) are also shown in Figure 3. The CAS results are seen to be in good agreement with these high level calculations. Some calculations were carried out for the excited states using the CIS method[27] using the GAUSSIAN program suite.[18] The resulting geometries were very similar to those obtained by the CAS method, as far as the 1^{1}B state and the Q structure of the 2^{1}A state were concerned. However, no stationary points were found for the AQ structure! Evidently, this structure requires double or higher excitations, implemented in the CAS procedure, to which the CIS method is inapplicable. On the other hand, it appears that the main contributions to the 1^{1}B state and the Q structure of the 2^{1}A state are from singly excited configurations.

IVb. Doubly Substituted Benzenes: Aminobenzonitrile (ABN) and Pyrrolobenzonitrile (PBN). The properties of two doubly substituted molecules were calculated: ABN and PBN. The main results are summarized in Table 1 and in Figure 5. When both electron-donating and electron-attracting groups are added in a para configuration, the 1^{1}B state retains its covalent locally excited character: perfect hexagon structure, CC bond length augmentation, Kekulé mode frequency exaltation, small dipole moment, essentially free rotation around the C$_{phenyl}$−N bond. These results hold for both ABN and PBN.

The 2^{1}A state is polar for these two molecules in both the Q and AQ structures. For ABN, the calculated dipole moment of the Q structure at the minimum energy is 13.3 D. Thus, by comparison with benzonitrile, the introduction of a strong electron donor made this quinoid structure a CT state: a charge

transfer from the amino group to the cyano one took place. A search for the antiquinoid form of ABN did not lead to a stationary point; energy optimization led invariably to the more stable quinoid form.

In the case of PBN, both the Q and the AQ structures were found to have minima on the 2^{1}A potential surface. The AQ structure is found to have a minimum at the perpendicular geometry, and a considerably larger dipole moment (16.2 D) than the planar Q one (11.0 D). The large dipole moment is maintained for the AQ structure when it is forced to a planar geometry, but in this case the energy is 17.6 kcal/mol higher than at the minimum! Thus, the origin of the high dipole moment is in the electronic structure, and not in the fact that the molecule is twisted to a 90° angle between the benzene and the pyrrolo rings.

At the CASSCF level, the energy of the AQ minimum is slightly lower than that of the Q minimum (5.47 vs 6.02 eV above S_0, respectively). Applying CASPT2 to these structures leads to a dramatic change. The Q minimum is significantly reduced to 3.98 eV, while that of the AQ one is only slightly reduced, to 5.07 eV (Table 1) This causes reversal of the order of their stabilization energies. Both are found to be lower than the energy of the Franck−Condon (FC) structure on the 2^{1}A state surface at the CASSCF level (6.41 eV). At the CASPT2 level, the energy of the FC structure on the 2^{1}A surface is 5.3 eV, higher than that of the Q structure, and on par with the AQ structure.
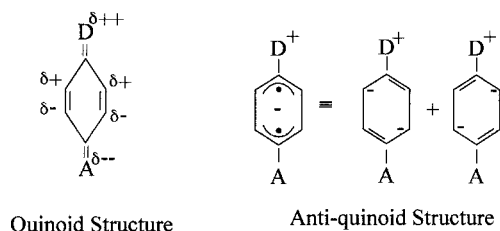
The benzene group of PBN in the AQ structure shows the same bond length alternation as in PB, and the pyrrole ring undergoes a reversal of bond lengths with respect to S_0: the two N−C bonds are practically double bonds, as is the central CC bond. The other two CC bonds are about 1.458 Å long, as compared to 1.374 Å in the ground state.

The geometry of the planar Q structure is similar to that of PB. The large increase of the dipole moment of PBN as compared to PB (from 0.75 to 11.0 D) may be attributed to the cyano group, which is a powerful electron acceptor. It is thus clear that on the 2^{1}A potential surface of PBN two CT minima can in principle be observed, one planar quinoid and the other perpendicular anti-quinoid.

Figure 4 shows the charge distribution (heavy atoms only) calculated for PBN at the four structures. Analysis of the data shows that in the Q structure, the increased dipole moment is due mainly to electron transfer from the pyrrolo nitrogen atom to the benzonitrile moiety. In the AQ structure, the charge redistribution is of completely different character. The main charge donors are the nitrogen atom and the two carbon atoms bonded to it in the pyrrolo ring, and the principal acceptors− the four central carbon atoms in the benzene ring, exactly as in the case of PB! Thus, in this case the benzene ring plays an active role as an electron acceptor, and not merely as a bridge. This situation is sometimes referred to as through-space charge transfer.

V. Discussion

We have chosen PBN as a prototype TICT molecule, rather than DMABN for two reasons. First, the pyrrolo group is a better electron donor than two methyl groups,[13] as shown by the larger solvent shift. The dipole moment of the CT state of DMABN is about 12 D (gas phase),[14] while that of PBN is calculated as 16 D (Table 1; the experimental value in the liquid state is about 22 D[15]). Second, the free rotation of the two methyls complicates the calculations, without adding physical insight. The main new result of this work is the discovery that the 2^{1}A potential surface

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SCHEME 4: Charge Distribution in the Q and AQ Structures

Quinoid Structure

Anti-quinoid Structure

can support two CT minima. One has a quinoid structure, similar to that reported by previous workers.[7,28,29] Its minimum has a planar geometry, with a gas-phase dipole moment in the range 6−13 D. The other minimum has an anti-quinoid structure, and may be found computationally only if double or higher electron excitations are explicitly introduced. This structure is found to have a minimum when the pyrollo group is strictly perpendicular to the benzene ring. In this geometry, PBN has a larger dipole moment (about 16 D) than in the quinoid structure. Significantly, as the example of PB shows, even substitution by a single strong electron donor makes the AQ structure a local minimum with a large dipole moment (the benzene ring is the acceptor). These properties make the AQ structure a plausible candidate for the long sought after TICT state. In the gas phase, the calculation indicates that the quinoid structure is somewhat more stable than the anti-quinoid one. In polar solvents, the larger dipole moment of the AQ structure is likely to make it the most stable form of the excited state, in agreement with the TICT hypothesis. The dual fluorescence of these molecules is therefore assigned as follows: The "normal" emission is due to the LE state, which is of purely covalent nature (see the next paragraph). The "anomalous" emission is due to a CT state, that has either the Q or the AQ structure. In principle, our results suggest that in less polar solvents the CT emission will be due to the Q structure, while in more polar ones, to the AQ one.

Another important result of this paper is the realization that the 1^1B state is a typically locally excited (LE) state, of covalent nature, even when the benzene ring is substituted by strongly electron donating and electron accepting groups. We propose that the properties of both CT and LE states are intimately related to the properties of the excited states of benzene, briefly summarized in section III. In particular, we argue that the benzene ring is not an inert spacer between the donor and acceptor moieties, but an important component that strongly influences the properties of both LE and CT states. This section is therefore structured as follows: First we analyze the properties of the two CT states (section Va), then those of the LE state (section Vb). Next, the results are compared with experimental data (section Vc); a comparison with previous theoretical analysis follows (section Vd). Finally, a brief of the implications of the model presented in this paper on the dynamics and photophysics of TICT molecules is given (section Ve).

Va. Properties of the CT States. The quinoid structure (Q), which was reported by several groups[4,6,7,28] is found to have a minimum on the 2^1A surface at planar geometry for all four molecules surveyed. Its dipole moment is usually larger than that of the ground state and of the LE (1^1B) state. Analysis of the computed charge distribution shows that the electron transfer is across the whole length of the molecule, from the amino nitrogen atom to the cyano group. A conjugated bond chain is formed across the whole molecular frame, as shown in Scheme 4. Stabilization due to the double bond conjugation tends to distribute the charge more evenly than for the AQ structure and thus leads to a smaller dipole moment. Calculation shows that

twisting around the C_{phenyl}−N bond to 90° does not change the dipole moment but increases the energy of the Q structure considerably. This result means that the Q structure is planar, in contradiction with the TICT model. Rather, it is agreement with Zachariasse's PICT model.

The antiquinoid (AQ) structure is characterized by long bonds between the central carbon atoms of the six-membered ring (about 1.455 Å), almost as long as a single bond. In PBN, the pyrrolo group also undergoes a large geometric change: the former double bond lengths increase to approximately the same value (1.458 Å). In addition, the C_{phenyl}−PP bond increases from 1.422 Å in the ground state to 1.480 Å. The origin of the large dipole moment (as compared to the Q structure) is revealed by considering the calculated charge redistribution upon electronic excitation (Figure 4). It is found that the charge is not transferred from the nitrogen atom to the CN group but rather from the whole pyrrolo moiety to the benzonitrile one. The negative charge is found to reside mainly on the four middle carbon atoms in the benzene ring (Figure 4). This result may be understood when the diallylic character of the AQ structure is considered (Scheme 2). Adding negative charge to the allyl moiety partially converts it from an allyl radical to an allyl anion, which is also resonance stabilized. Thus, on average, the amount of charge in the AQ structure is larger than that in the Q structure, leading to a larger dipole moment.

The energy stabilization of the perpendicular form of the AQ structure as compared to the planar one, may be explained as follows. In this structure, the electron density is shifted from being approximately uniform across the hexagonal ring to being more concentrated near the four central carbon atoms of the benzene ring. As shown in Scheme 2, the resulting structure may be viewed as two allyl moieties fused together. Allyl structures are known to be exceptionally stable, due to stabilization of the two resonance forms shown also in Scheme 2. The resonance energy has been estimated by various methods to be 12−15 kcal/mol.[30] The energy difference between the planar and perpendicular forms of PB and PBN was found to be 3 and 14.5 kcal/mol at the CASSCF(12,11)/DZV level, respectively. The twisting is due to the "gauche effect"[31]—in the absence of resonance stabilization, the lone pair nitrogen atom electrons and the electrons of the benzene π-system tend to repel each other and acquire a perpendicular conformation. This structure has the properties predicted by the TICT model of Grabowski et al.[2] and agrees with their minimum overlap rule[32] and also with a VB rationalization given by Rettig.[14] At the risk of repetition we note that the charge distribution in both the Q and the AQ structures is almost independent of the twist angle, although the energy is strongly changed. The Q structure prefers a planar form, while the AQ, a perpendicular one.

Since two minima can exist on the 2^1A surface, the question which of them is populated under given experimental conditions must be addressed. The calculations presented in this paper relate to gas-phase systems; solvation by a polar solvent is expected to lower the energy of a CT state much more than that of a nonpolar one such as the 1^1B state. In the gas phase, the energy of the ionic states is too high for effective crossing, while in polar solvents the ionic states are stabilized so that crossing becomes feasible. As shown in this paper, motion along the quinoidization coordinate is of key importance in achieving this crossing. Moving toward the anti-quinoid geometry will lead to the TICT state, while motion in the opposite direction will lead to the PICT state. The actual dynamics may require other coordinates, for instance if conical intersections are involved. This topic is qualitatively discussed in section Ve.

As seen from Table 1, the MP2 correction of the CASSCF calculations, as implemented by the CASPT2 method, changes the energy of the CT states considerably. For both PB and PBN, it is seen to lower the energy of the Q structure much more than of the AQ one. For PBN, the energy ordering of the states is inverting on applying this correction! It is not clear at this time whether this change reflects a physical reality, or is an artifact of the method.

Vb. Properties of the LE State. The computational results show, in agreement with the well-known character of the L_b state, that no matter what substituents are present on the benzene ring, the following attributes characterize the 1^1B state:

—Its dipole moment does not increase with respect to that of the ground state.

—The main geometry change with respect to the ground state is a uniform increase of the benzene ring C—C bond lengths from about 1.40 to 1.44 Å.

—The frequency of a single vibrational mode, the Kekulé mode, is significantly increased, from about 1350 cm^{-1} to about 1570 cm^{-1}.[12,26]

—Facile rotation around the C_{phenyl}—N bond is possible.

—The oscillator strength of the transition from the ground state is small ($\sim$0.02). It increases by comparison with benzene itself, upon substitution by electron donating or accepting groups.

—A small decrease in the bond length of the donor atom ring with respect to the ground state.

All these properties can be traced to the fact that the 1^1B state is a twin state of the ground state:[20] it may be viewed as an out-of-phase combination of the two Kekulé structures, while the ground state is the in-phase combination. The origin of the frequency exaltation and the small oscillator strength have been discussed in detail using a VB approach.[12] The facile rotation around the C_{phenyl}—N bond is due to the fact that this bond is strictly a single bond, in contrast with the case of the Q structure on the 2^1A surface. The small dipole moment indicates that the state is covalent in nature, as in the parent molecule, benzene. Thus, there is very little interaction between the electron-donating and the electron-accepting moieties—the benzene ring in this state acts as an almost perfect insulator. Interestingly, recent studies on phenol and hydroxybenzonitriles shows that the 1^1B state in these molecules has similar properties.[33] As will be shown in a separate publication, the increases acidity of phenols in the excited state may be explained using a model very similar to the present one.

Vc. Comparison with Experiment. This work deals with the gas-phase molecules only. Nonetheless, the results are in agreement with the main experimental features obtained in liquid solution. A charge transfer state is predicted, with a large dipole moment in the gas phase. The measured solution dipole moment is expected to be even larger, due to polarizability effects. The results are in agreement with the large solvent shift observed in polar solvents for the "anomalous" emission. They also explain naturally the TICT idea: the twisted geometry is the preferred one for the AQ structure. At the same time, the results show that a planar CT state also has a minimum on the excited-state potential surface, in agreement with the PICT model. Which of these will be the lower (and thus the emitting) state depends on the system. It turns out that the large dipole moment of the AQ structure is due to charge transfer from the substituents on the amino (or pyrrolo) nitrogen atom. A hydrogen atom, or even a single methyl group, is not a strong enough electron donor, explaining the lack of dual fluorescence

from aminobenzonitrile and from mono(methylamino)benzonitrile.[10]

Our calculations predict a gas-phase minimum for the TICT state for several molecules. However, experimental observation of dual fluorescence requires that the molecule will reach that minimum after optical excitation. Studies on BN[34] and PB[25] in a supersonic jet revealed only LE emission. This indicates that if a CT minimum exists, the crossing point of the LE and CT states in the gas phase was higher that the highest excitation energy used in those experiments. Gas-phase data for PBN are not available at this time. In solution, and particularly in polar solvents, the CT state is further stabilized and is thus observed experimentally.[15]

In solution,[10] and also in solvated CH_3CN clusters,[35] ABN does not show dual fluorescence, while DMABN and PBN do. Our calculations are in line with the ABN results since the computed energy of the CT state is much higher than that of the LE state The electron-donating power of the donor group is increased relative to ABN in DMABN and PBN. Calculations on DMABN,[7,36] as well as those presented here for PBN, indicate that the LE-CT gap is much smaller than in ABN. In polar solvents, this smaller gap is further reduced, allowing the crossing between the 1^1B and 2^1A states. As shown by ref 35, a minimum of five acetonitrile molecules is required to lower the energy of the CT state enough to allow its population by a radiationless process from the LE state.

The calculated energies of the excited states can be compared with experiment mostly for the LE state. The values for BN and PB are 4.52[34] and 4.40 eV,[25] respectively. They are a bit lower than the CASSCF values (4.55 and 4.47 eV, respectively) and higher than the CASPT2 values (4.27 and 4.13 eV, respectively). It thus appears that the MP2 correction, as implemented in the GAMESS program, overcompensates the energy for this state. For PBN, only a liquid-phase value is available (in hexane, 4.13 eV[15]), as compared with 5.14 eV (CASSCF) and 3.78 eV (CASPT2). Again it appears that the MP2 correction overestimates the stabilization of the 1^1B state.

The large dipole moment change we calculated on excitation of PBN from the ground state to the AQ structure is in agreement with experiment, and the fact that the AQ structure obtains a minimum at the perpendicular geometry is in line with the TICT idea that is supported by indirect evidence.

The frequencies of DMABN in the A state have been recently measured using time-resolved resonance Raman (TR^3) spectroscopy[37] and transient infrared absorption spectra.[38] It was found by TR3 that many stretch frequencies were reduced by comparison with ground-state frequencies. For instance, the phenyl—N stretch frequency by 96 cm^{-1}, the CN stretch by 114 cm^{-1}, the ring C=C stretch (Wilson mode 8a) by 29 cm^{-1}, and the ring breathing (Wilson mode 1) by 38 cm^{-1}. These results were interpreted as indicating support of the TICT model, in predicting a charge transfer from the amino group to the CN group. In particular, the phenyl—N stretch mode frequency decrease indicates lengthening of the C_{phenyl}—N bond, a result supported by our computations for the AQ state of PBN, but not for the Q state. The change in the Wilson mode 8a is also in line with our prediction of lengthening the middle CC bonds of the benzene ring. Our computations predict an increase in the cyano CN bond length from 1.165 to 1.179 Å, again in agreement with experiment.

In the IR study, only one band of the A state was reported, at 2112 cm^{-1}, which was assigned to the cyano CN stretch. This represents a 103 cm^{-1} downshift from the ground-state

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value, in reasonable agreement with the Raman data cited above, and with our model.

Rettig et al.[10] recently compared the photophysical properties of some para-substituted DMABN derivatives with the corresponding meta-substituted ones. It was found that the radiative rate constant is strongly reduced when the "anomalous" (i.e., strongly red-shifted) CT fluorescence is observed. This was the case for the para compounds, and not for the meta ones. In the latter, the solvent shift was much smaller and it was concluded that only para-substituted molecules exhibit dual fluorescence. Our model predicts that only para-substituted benzenes can have the AQ electronic structure and is thus in accord with these results. The AQ structure requires diallyl stabilization, which is possible only for the para-substituted molecules.

Vd. Comparison with Previous Theoretical Work. In recent years, several ab initio calculations of TICT systems were published. The following survey does not aim at a comprehensive coverage but tries to highlight some of the prevailing theoretical efforts. Sobolewski and Domcke used the configuration interaction singles CIS and MC-SCF (CAS) methods to probe the LE and CT potential surfaces.[7] They concluded initially that the bending of the CN group is more important than the twisting in stabilizing the CT state. Later, they proposed that rehybridization of the cyano group may be an important factor (The RICT mechanism). More recently, they excluded the amino group wagging as an important coordinate and proposed that twisting is in fact important, but the twist angle is closer to 60° rather than to 90°. Dreyer and Kummrow[28] used the CAS method with six electrons in five orbitals. The electronic wave function of the TICT state in their work is characterized by a single excitation from the localized amino nitrogen lone pair to a π^* orbital located entirely in the benzonitrile moiety. They excluded the RICT mechanism, favored the TICT one, but could not exclude the PICT mechanism. Note that their suggested TICT geometry (cf. Figure 2 in ref 28) corresponds to our Q structure. Roos, Serrano-Andrés, and co-workers[36] used CAS and CASPT2 with 10 electrons in 9 orbitals to calculate the properties of ABN and DMABN. The results fully confirmed the TICT mechanism. However, the structures of the optimized excited states were not reported, neither were their frequencies. Mennucci et al.,[39] used a multireference perturbed CI method to calculate the DMABN states, including solvent effects. Their results support the TICT model, but structural data were not reported.

More recently, Proppe et al. reported a high level study of PB and concluded that the TICT mechanism holds.[40] Their calculations, performed at the CASSCF and CASPT2 levels, may be compared directly with ours. In this work, no frequency calculations were reported, making it difficult to certify whether the structures are real minima, or other stationary points. This paper proposed that the TICT state is the perpendicular 2^1B_1 state, which lies 5.35 eV (CASPT2) above the ground state and has a dipole moment of 11.0 D. The benzene ring has a quinoid structure, the $C_{phenyl}-N$ distance is 1.444 Å, and the pyrrolo ring has a structure similar to our AQ 2^1A perpendicular state. The only difference from our suggestion for the TICT state is that we propose an anti-quinoid structure for the benzene ring and that our structure has A_1 symmetry. Vibrational analysis was not reported; The optimized structure of the 2^1B state may be a stationary point, perhaps a transition state between two quinoid 2^1A structures. Unfortunately, optimized structures for the 2^1A state were not reported.

Parousel et al.[41] used a combination of density functional theory and configuration interaction approaches to study the

excited states of DMABN and some derivatives. Only single excitation CI was used. He concluded that the TICT mechanism is the most likely mechanism for dual fluorescence. In a more recent paper[29] PB and PBN were also studied using a DFT/MRCI for the excited states. The results for the ground states of PB and PBN (twist angle, dipole moment) are very similar to ours. In the excited state, the paper focused on the twist angle. One-dimensional DFT/MRCI calculations were made with the ground state optimized geometries, in which the twist angle was varied. However, since no optimization of the excited state is possible in this method, we cannot compare these results directly with ours.

In all the aforementioned extensive calculations, the AQ structure was not reported. A method considering only single electron excitation (such as CIS), cannot be used to find this structure, since it is primarily a doubly excited state. CAS should reveal it, but the minimum energy point is obtained only by moving along the correct direction of the quinoidization coordinate. In addition, one has to use a minimum of 10 electrons, and in fact 12 provide a more realistic description for PBN, since all π electrons are important, as well as the nitrogen atom lone pair.

Ve. Photophysical Properties: Role of Conical Intersections. The results of this paper apply strictly to the isolated molecule. When a molecule is dissolved in a polar solvent, CT states tend to stabilize more strongly than LE ones. In view of the large dipole moment calculated for ABN, PB, and PBN, it is likely that the energy of the CT state's minima (one or both) will be lowered to below that of the LE state. Therefore, a curve crossing can take place, and even if light absorption to the LE state is preferred in the Franck−Condon region, emission may ensue from the CT state. In this section we argue, that such a crossing is very likely to occur rapidly and efficiently, since it may take place via (or around) a conical intersection.

Figure 6 shows a schematic representation for several possibilities. The 1^1B state was found to be the first excited state at the FC geometry for all molecules considered. It may cross the 2^1A state by moving along the quinoidization coordinate (Scheme 2) either toward the Q structure or toward the AQ one. The left-hand part of Figure 6a shows a situation in which a crossing occurs for both structures. The Q structure is expected to be preferred, being of lower energy. Therefore, if CT emission can be observed, it will be from the Q structure. The right-hand part shows a case where crossing occurs only for the AQ structure, leading to AQ-type emission. It is well-known that the crossing between the two electronic states is most efficient at the conical intersection. A conical intersection is a locus on the potential surface, in which the two electronic states are degenerate. It has been shown[42,43,45] that a conical intersection is found along two coordinates that differ in terms of the behavior of the total electronic wave function of the system. Motion along one preserves the phase of the total electronic wave function (a phase-preserving coordinate), while motion along the other coordinate inverts the phase (a phase-inverting coordinate). The quinoidization coordinate is a totally symmetric one in C_{2v} and therefore phase preserving. A phase-inverting coordinate that is available in this system is the Kekulé mode of the benzene ring, the one that exchanges the two Kekulé structures of the 1^1B state (Scheme 5). This coordinate ensures the phase change of the total electronic wave function when transported in a closed loop around the conical intersection (a necessary condition for the existence of a conical intersection).[42] In Figure 6b we show schematically the conical intersections formed for the cases shown in Figure 6a.
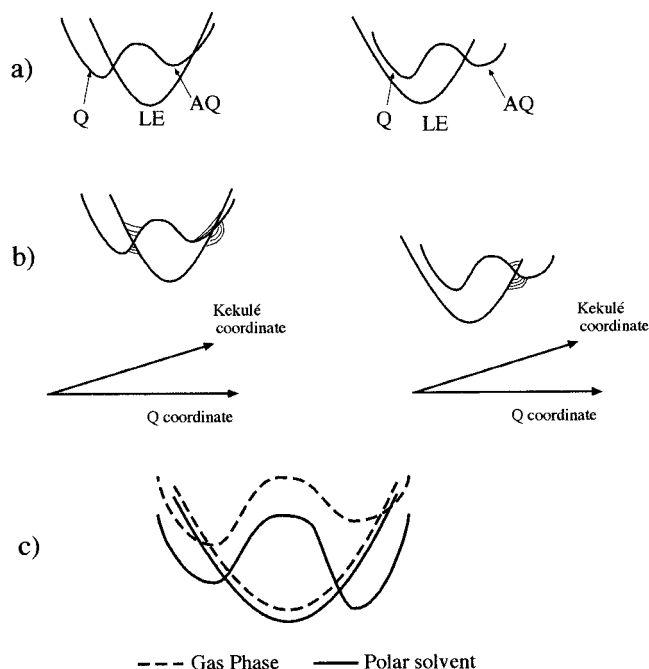
Figure 6. (a) Schematic representation of the potential surface of the LE state and CT states along the quinoidization coordinate. The left-hand diagram shows the case where the LE state crosses the CT state near the Q and AQ structures. The right-hand diagram depicts the situation where a crossing takes place on the AQ side. (b) Same diagram, showing the two coordinates spanning the conical intersection: the Q (quinoidization) coordinate, which is phase preserving, and the phase-inverting coordinate—the Kekulé coordinate. (c) Effect of a polar solvent on the system. In the gas phase, the Q structure is lower in energy than the AQ one (dashed lines). In the polar solvent, the larger dipole moment of the AQ structure leads to its preferential stabilization (solid lines).

SCHEME 5: Schematic Representation of the Two Coordinates Spanning the Conical Intersection Connecting the S_1 and S_2 States of Benzene[a]
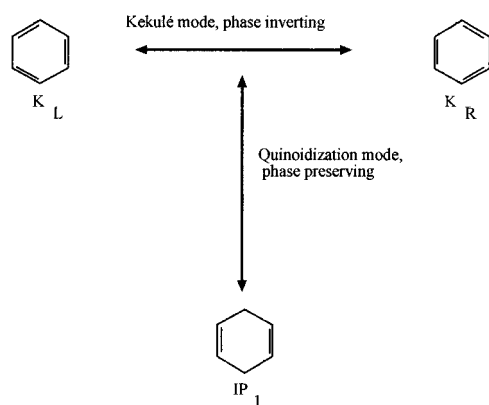
[a] The S_1 state is an out-of-phase combination of the two Kekulé structures shown at the top, which are connected by the phase-inverting Kekulé mode. This state lies at the midpoint of the line connecting the two structures. The quinoidization coordinate (leading from the S_1 equilibrium structure to the IP1 para ionic structure of Scheme 3) is a phase-preserving one.

The crucial role of the solvent is reiterated. In the gas phase the CT states are typically too high in energy to be reached after LE excitation. Solvation in a polar solvent lowers the energy of both CT structures more than that of the LE state, making curve crossing possible. The somewhat less polar Q structure is usually lower in energy in the gas phase than the AQ one, and in the presence of a polar solvent may become

the emitting CT state. That is the PICT mechanism. Due to the higher dipole moment of the AQ structure, in a strongly polar environment it may become lower in energy than the Q one and yield the observed TICT emission, as depicted in Figure 6c.

VI. Summary

The calculations presented in this paper show that the L_a-based potential surface can support two distinct electronically excited structures of a charge transfer nature. One has a quinoid structure and a planar geometry at the energy minimum. It corresponds to the proposed PICT model. The other, which has not been reported before, is an anti-quinoid one, has a larger dipole moment than the quinoid one, and has an energy minimum with the amino group twisted by 90° with respect to the benzene ring. This structure agrees with the TICT model of Grabowski et al.[2] The benzene moiety distorts to a diallylic form in this structure, and this is the physical cause for the extra stability of the twisted form. In addition, it is shown that the 1^1B state is of purely covalent nature, even when the molecule is substituted by strong electron donor and acceptor moieties. It is the locally excited (LE) state referred to in the TICT state literature. This state's properties are accounted for by assuming that it is formed by an out-of-phase combination of the two Kekulé structures. The "anomalous" fluorescence observed in these molecules is due to a radiationless transition from the initially excited LE state to one of the CT states through a conical intersection. The conical intersection is found along two coordinates: the phase-inverting Kekulé mode and the phase-preserving quinoidization mode.

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