Systematics in the Electronic Spectra of Polar Molecules. 1. Para-Disubstituted Benzenes

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Abstract: The absorption and emission properties of para-disubstituted benzenes, one substituent being an electron acceptor and the other an electron donor, are discussed from both computational (CNDO/s) and experimental points of view. It is shown that the energy of the ^1L_a state, $E(^1L_a)$, serves to parametrize the degree of charge transfer (CT) in the ^1L_a state. It is found that $E(^1L_a)$ is more sensitive than $E(^1L_b)$ to the degree of charge transfer, with the result that $E(^1L_b) < E(^1L_a)$ in weakly polar molecules and $E(^1L_a) < E(^1L_b)$ in highly polar molecules. The lowest energy triplet state is found to be ^3L_a in all cases. The consequences of convergence and crossover of the ^1L_a and ^1L_b levels for the luminescence characteristics of these molecules are significant, and this significance is elaborated. Finally, it is shown that the more appropriate zeroth-order description of the charge transfer state is ^1L_a, and not ^{1}CT.

Introduction

1. Prefatory Remarks. Disubstituted benzenes of type D–Ph–A, where D is an electron donor and A an electron acceptor substituent, constitute a broad class of organic molecules with both technological and biological relevance. The electronic spectroscopy of this class of molecules has been discussed from three points of view.

a. The Linear Combination of Configuration Wave Functions (LCCW) Approach.[1,2] The π-electron states of a conjugated D–Ph–A system are supposed to arise from the mixing of electron configurations expressed in terms of π orbitals localized on its fragments (i.e., D, Ph, and A) under the influence of the "exact" π-electron Hamiltonian of the entire D–Ph–A system. The LCCW approach is a modification of the semiempirical LCAO-ASMO-CI method. Applications to D–Ph–A molecules usually involve the introduction of locally excited (LE) and charge-transfer (CT) configurations on an equal footing and, as a result, it is not surprising that the lowest energy excited states are found to contain considerable CT character. For example, in *p*-nitroaniline, the LE/CT mixing (i.e., $^1L_a(Ph)/D^+\text{–}Ph\text{–}A^-$) which yields the lowest energy excited singlet state is found to be so dominated by the CT component that this state is simply referred to as "the ^{1}CT state."

The LCCW approach dominates the literature of D–Ph–A electronic spectroscopy for two reasons: it has been very successful, and it is chemically tactile (presumably, because of its valence-bond connotations).

b. The Perturbation Approach.[3] The zeroth-order electronic states are those of the ring system Ph. When D and A are moderately strong donor and acceptor groups, respectively, it is necessary to introduce perturbations by intersubstituent charge-transfer states. Thus, in the second order of perturbation theory, one may realize the lowest energy electronic state as a ^1L_a state contaminated with some (necessarily slight) amount of CT character.

This approach is of little use since the theory, as it stands, is quite incomplete and since the LCCW results suggest that such a perturbative approach will be inadequate.

c. Whole-Molecule Calculations. These calculations, which may be semiempirical[4] or ab initio[5] in nature, are LCAO-ASMO-CI computations pertinent to the entire D–Ph–A entity. While they have been of considerable help in the assignment of electronic spectra, they provide little help in the way of systematics, either because they are not usually analyzed with such a purpose in mind or because the number of molecules discussed is too small.

2. Intent of This Work. We posit the existence of an index, denoted D/A, which gauges the relative donor/acceptor strengths of the donor and acceptor substituents. Thus, when D and A possess strong electron donor and acceptor characteristics, respectively, the index D/A will approach one extremum (say, large) and when they possess weak electron donor and acceptor properties, respectively, the index D/A will approach the other extremum (say, small). For the moment, we presume only a qualitative knowledge of this index. Thus, as donor strength increases in the series

$$\text{-CH}_3 < \text{-F} < \text{-Cl} < \text{-Br} < \text{-OH} < \text{-OCH}_3 < \text{-NH}_2 < \text{-N(CH}_3)_2$$

and as acceptor strength increases in the series

$$\text{-CH} < \text{-COOH} < \text{-COCH}_3 < \text{-CHO} < \text{-NO}_2$$

we presume a corresponding increase of the D/A index for D–Ph–A.

In terms of such an index, all approaches (a)–(c) above suggest that, when D/A is small, the lowest energy excited state S_1 of *p*-D–Ph–A is ^1L_b and that it possesses little or no CT component. On the other hand, when D/A is large, all approaches (a)–(c) predict that S_1 is either ^1L_a with a large CT component or, simply, ^{1}CT with little or no ring ^1L_a component. Clearly, there must exist an intermediate value of the D/A index at which the ^1L_b and ^1L_a states cross. Furthermore, if, in the vicinity of this crossover point, the ^1L_b state has little or no CT character and the ^1L_a state has considerable CT character, it might be expected that the relative energies of these two states would be very sensitive to solvent effects.

The intent of this work, then, is a discussion of the lowest energy excited electronic states of *p*-D–Ph–A molecules. In this connection, a number of questions arise:

(1) Is ^1L_b the best zeroth-order description of the S_1 state when the index D/A is small?

(2) Which is the better zeroth-order description of S_1, ^1L_a or ^{1}CT, when the index D/A is large?

(3) To what extent does LE/CT mixing occur in states of ^1L_a and ^1L_b parentage and what experimental parameters may be used to gauge the extent of this mixing?

(4) What experimental peculiarities serve as indicators of the crossover region of states of ^1L_a and ^1L_b parentage?

The approach we adopt is correlative and is vested in the study of a large set of D–Ph–A molecules. This study is both computational and experimental. The computations follow along the lines of approach (c) above, the interest focusing on changes from one D–Ph–A entity to another rather than on the details of any one D–Ph–A molecule. In a sense, the computations may be viewed as an investigation of the conclusions

Table I. Calculated and Experimental Values of the Ground State Dipole Moment (D)[a]

molecule	μ_0 (calcd)	μ_0 (exptl)
A	0	0
B	0.864	
C	2.942	4.95
D	3.304	4.48
E ($\perp$)	3.325	
F	3.363	3.10
G	3.487	4.90
H	3.969	5.96
I	4.015	5.94
J ($\perp$)	6.433	
K	6.436	6.31
L	7.634	6.92

[a] The alphabetic molecular designations are given in Figure 1. The experimental values are taken from McClelland (A. L. McClelland, "Tables of Experimental Dipole Moments", W. H. Freeman, San Francisco, 1963) and refer to dielectric constant data in a benzene solvent.

of approach (a) by means of approach (c). The experimental studies are concerned with energies, oscillator strengths, solvent effects, and luminescence properties of D-Ph-A entities. The intent of the experimental work is the provision of a data base which will (1) resolve questions concerning the most appropriate zeroth-order description of a given excited state; (2) pinpoint the crossover region; (3) elicit an experimental parametrization of the D/A index.

We do not imply that this work will provide unambiguous answers to all of the above questions. We merely intend that it indicate a way of providing such answers. Furthermore, since we limit ourselves to the case where Ph is a benzene residue, we have excluded the equally interesting situations which arise when Ph is a condensed-aromatic system, a conjugated polyenic system, or a mixed condensed aromatic-conjugated polyenic system.

Quantum Chemical Correlations

The molecules of interest are shown in Figure 1. All valence-electron, CNDO/s-CI computations, Del Bene-Jaffé formalism,[17,18] were performed on an IBM 360/65 computer.

The charge-transfer nature of an electronic transition is assumed to induce movement of electron density from the donor to the acceptor group. The electron density loss of the donor in an electronic transition, which may be described, in the absence of CI, as an MO promotion 2 ← 1, is given by

$$F_{\mathrm{D}} = \left(\sum_i C_i^2\right)_{\mathrm{D},1} - \left(\sum_i C_i^2\right)_{\mathrm{D},2}$$

where $(C_i)_{\mathrm{D},1}$ is the LCAO coefficient of the ith AO of one of the donor atoms in MO 1, and the sum is over all AOs of all centers of the donor group in MO 1. The concept is readily extended to the CI situation where the states are multiconfigurational in nature. Similarly, the electron-density gain of the acceptor in the MO promotion 2 ← 1 (i.e., absence of CI) is

$$F_{\mathrm{A}} = \left(\sum_i C_i^2\right)_{\mathrm{A},2} - \left(\sum_i C_i^2\right)_{\mathrm{A},1}$$

Again, this concept is readily extended to the CI case. Consequently, the quantity $(F_{\mathrm{A}} + F_{\mathrm{D}})$ constitutes a measure of the CT character of the transition 2 ← 1. This quantity, as defined, is always positive—at least to the extent that A and D behave as bona fide electron acceptors and donors, respectively.

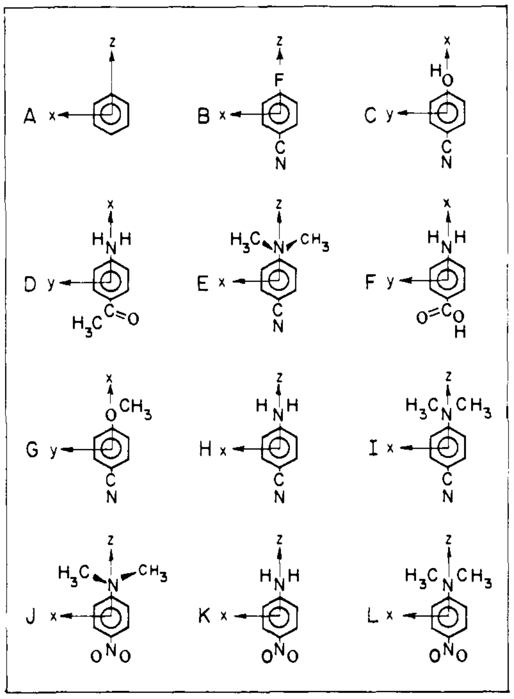

Figure 1. *p*-D-Ph-A molecules, with coordinate systems. The point groups and structural references are as follows: A, D_{6h}, 6; B, C_{2v}, 7; C, C_s, 8; D, C_s, 9; E (perpendicular), C_{2v}, 8; F, C_s, 12; G, C_s, 13; H, C_{2v}, 8; I (planar), C_{2v}, 8; J (perpendicular), C_{2v}, 15; K, C_{2v}, 16; L (planar), C_{2v}, 15. For the perpendicular cases E and J, the (N,C,C) plane of the dimethylamino group is $\perp$ to the benzenoid plane, whereas for the planar cases I and L both of these planes are coplanar.

1. Ground-State Dipole Moments. The ground-state dipole moments, μ_0, were evaluated in the point charge approximation.[19] The results are given in Table I. With the exception of molecules D and F, the order of increasing dipole moment is identical in both the computational and experimental data sets. Hence, we feel free to use the computed value of μ_0 as an ordering parameter. Specifically, since the electron-donor capacity increases along the series F → OH → OCH_3 → NH_2 → $N(CH_3)_2$ and since the electron-acceptor capacity increases along the series CN → COOH → $COCH_3$ → NO_2, it follows that μ_0 constitutes a rough parametrization of the D/A index.

2. Energies and Oscillator Strengths. The computed energies of the $^1L_a \leftarrow {}^1\Gamma_1$ and $^1L_b \leftarrow {}^1\Gamma_1$ transitions of the molecules A to L, arranged in order of increasing μ_0, are shown in Figure 2. The names ^1L_a and ^1L_b are chosen as appropriate designations because of the smooth correlation with the corresponding parental states of benzene or, perhaps better, with those of the weakly polar *p*-fluorobenzonitrile (where the small amounts of CT character permit a unique identification of the parental ring states). As further confirmation of this, the transition labeled $^1L_a \leftarrow {}^1\Gamma_1$ is always polarized along the D-A axis in the C_{2v} entities and is almost entirely polarized along this same axis in the C_s entities. A similar statement applies to $^1L_b \leftarrow {}^1\Gamma_1$ except that polarization is now perpendicular (in plane) to the D-A axis. The regularities evident in Figure 2, the perpendicular cases E and J excluded, follow.

(1) $E(^1L_a)$ decreases as μ_0 increases, whereas $E(^1L_b)$ remains roughly constant. As a result, crossover of the two levels occurs, in this case, at *N*,*N*-dimethyl-*p*-nitroaniline. Consequently, we may take either a decrease of $E(^1L_a)$ or of $E(^1L_a) - E(^1L_b)$ to indicate an increase of either μ_0 or the D/A index.

(2) The oscillator strengths $f(^1L_a)$ remain remarkably constant at $0.2 \leq f \leq 0.3$. Those of ^1L_b remain consistently smaller at $f(^1L_b) \leq 10^{-2}$ but vary by an order of magnitude, $10^{-3} \leq f(^1L_b) \leq 10^{-2}$. Transition polarization directions, as indicated above, also remain remarkably invariant.

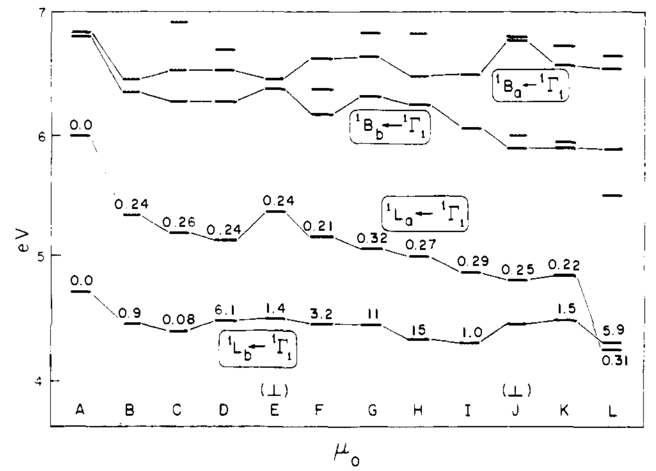

Figure 2. A correlation diagram for ^1L_a and ^1L_b states of *p*-D-Ph-A molecules. Molecules are arranged, left to right, in order of increasing μ_0 (computed). Oscillator strengths are cited above the state energies, those for the ^1L_b states being given as $f(^1L_b) \times 10^3$. Energies of the $^1B_{a,b}$ states are included for completeness.

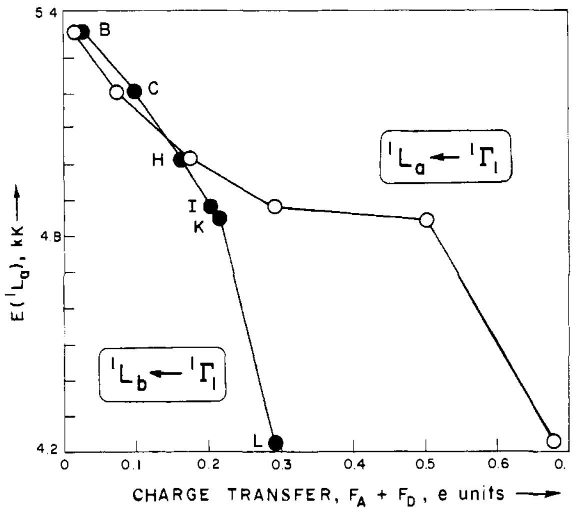

Figure 3. Computed (CNDO/s-CI) total charge transferred from D to A in the $^1L_a \leftarrow {}^1\Gamma_1$ transition (open circles) and in the $^1L_b \leftarrow {}^1\Gamma_1$ transition (closed circles). The quantity $F_A + F_D$ is a measure of total charge transfer and is defined in the text.

(3) Other observations, ones not deemed central to our concerns, are collected in ref 20.

3. The Extent of D → A Charge Transfer. In order to evaluate the degree to which decreasing ^1L_a energy correlates with an increase of charge-transfer character of the ^1L_a and ^1L_b states, we have evaluated the quantity $F_A + F_D$. The results are given in Figure 3 and are quite clear cut: Both states exhibit a massive increase in their CT character, that of ^1L_a becoming rapidly dominant. For example, the ^1L_a state of L is 68% CT and that of K is 50% CT. Indeed, it is not inappropriate to designate these two states as ^{1}CT states. Consequently, we have verified the Murrell-Nagakura attitude[1,2] in the sense that the zeroth-order description most appropriate for the ^1L_a state of L is D^+-Ph-A^-, and there is little doubt that this is the description of choice for the individual whose interests reside in phenomena mediated by the dipolarity of the excited state (e.g., solvent effects). We prefer the name "^1L_a" because (1) it does not preclude a specifiable, large or small, CT character; (2) because it refers to a readily accessible zeroth-order ring state, say that of benzene or of *p*-F-Ph-CN; (3) because the progression from this latter zeroth-order point to the molecule of interest is readily traversed empirically using any of the trends noted in this work. It is also clear that approach (b), based as it is on a perturbative consideration of the parental ring states, is incapable of handling this series of molecules. In sum, we may say that the application of approach (c) is substantiative of approach (a) and that it restricts approach (b) to the class of almost nonpolar D-Ph-A molecules.

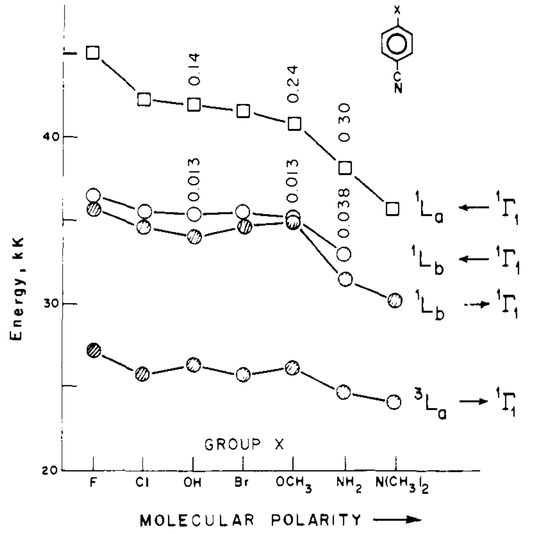

Figure 4. The absorption and emission data for *p*-cyano substituted benzenes. The absorption data refer to nonpolar media such as methylcyclohexane (MCH) or 3-methylpentane (3MP) at room temperature; the emission data refer to glassy ethanol or EPA solutions at 77 K. The squares refer to band maxima; the circles refer to band origins. The molecules are arranged in order of increasing molecular polarity as determined by decreasing $^1L_a \leftarrow {}^1\Gamma_1$ energy. The superimposed numbers are the experimental oscillator strengths of the transitions.

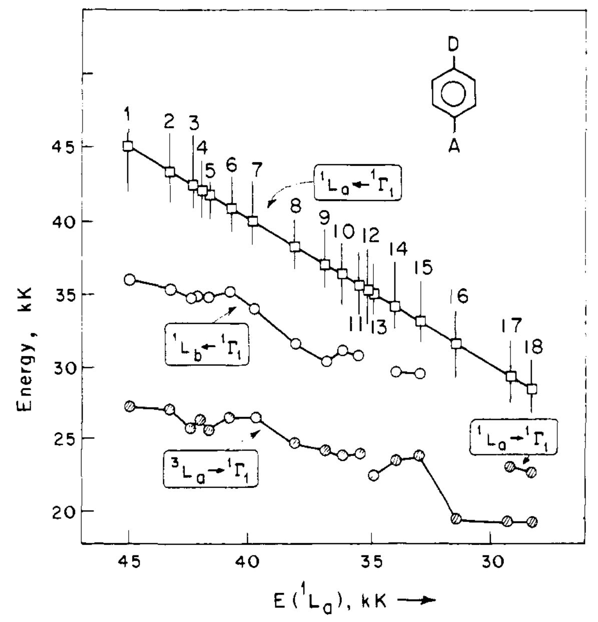

Figure 5. The absorption and emission data for para-disubstituted benzenes, plotted according to increasing molecular polarity as determined by decreasing $^1L_a \leftarrow {}^1\Gamma_1$ energy. The absorption data refer to nonpolar media (methylcyclohexane or 3-methylpentane) at room temperature; the emission data refer to glassy ethanol or EPA media at 77 K. The squares refer to band maxima, the circles to band origins. The molecules are numbered as follows: 1, *p*-fluorobenzonitrile; 2, *p*-toluamide; 3, *p*-chlorobenzonitrile; 4, *p*-cyanophenol; 5, *p*-bromobenzonitrile; 6, *p*-cyanoanisole; 7, *p*-methoxybenzoic acid; 8, *p*-cyanoaniline; 9, methyl *p*-aminobenzoate; 10, *p*-aminobenzoic acid; 11, *N*,*N*-dimethyl-*p*-aminobenzonitrile; 12, *p*-nitrophenol; 13, *p*-aminoacetophenone; 14, *N*-methyl-*p*-aminobenzoic acid; 15, *N*,*N*-dimethyl-*p*-aminobenzoic acid; 16, *p*-nitroaniline; 17, *N*-methyl-*p*-nitroaniline; 18, *N*,*N*-dimethyl-*p*-nitroaniline.

Table II. Absorption Data ($\times 10^3$ cm^{-1}) in Various Solvent Media[a]

molecule	isomer	$^1L_b \leftarrow {}^1\Gamma_1$			$^1L_a \leftarrow {}^1\Gamma_1$		
		ethanol	MCH	3MP	ethanol	MCH	3MP
fluorobenzonitrile, B	*o*	35.97			43.57		
	m	35.52			43.67		
	p	36.54			44.30 (m)		
toluamide	*p*	35.71 (sh)		36.71	42.64 (m)		43.29 (m)
chlorobenzonitrile	*m*	34.78			42.92		
	p	35.56		35.56	42.46 (m)		42.37 (m)
cyanophenol, C	*o*	33.67 (m)	33.46		42.37	42.55	
	m	33.90 (m)	33.83		43.05 (m)	42.79	
	p	35.34	35.30	35.40	42.01 (m)	41.67 (m)	42.07 (m)
bromobenzonitrile	*p*	35.50		35.50	41.04 (m)		41.07 (m)
methylbenzoic acid	*o*	35.97 (m)		34.03			42.37 (m)
	m	37.17 (m)			45.45 (m)		
	p	35.46			42.37 (m)		41.49 (m)
cyanoanisole, G	*o*	33.90 (m)	33.56		42.02	42.20 (m)	
	m	33.60	33.70		43.48 (m)	42.02	
	p	35.34	35.20		40.15 (m)	40.80 (m)	
methoxybenzoic acid	*m*	33.90 (m)			42.92 (m)		
	p	39.68 (m)		36.04	39.06 (m)		39.53 (m)
cyanoaniline, H	*o*	30.75 (m)	31.86 (m)	~30.44	40.30 (m)	41.06 (m)	41.20 (m)
	m	31.20 (m)	32.26 (m)	30.90	39.70 (m)	41.24 (m)	41.20 (m)
	p		33.06	33.00	36.20 (m)		38.20 (m)
methyl aminobenzoate	*o*	29.51 (m)					
	m	31.35 (m)					
	p	33.61 (sh)	33.61 (sh)	33.67 (sh)	34.36 (m)		37.04 (m)
aminobenzoic acid, F	*p*				34.48 (m)		
N,*N*-dimethylcyanoaniline, T	*p*				34.60 (m)		
nitrophenol	*p*				31.95 (m)		
aminoacetophenone, D	*o*	27.40 (m)		28.41 (m)	38.80 (m)		39.53 (m)
	m	29.50 (m)		30.77 (m)	39.00 (m)		40.82 (m)
	p			~29.90 (m)			
N-methylaminobenzoic acid	*p*				33.28 (m)	34.01 (m)	
N,*N*-dimethylaminobenzoic acid	*p*				32.47 (m)	32.51 (m)	32.89 (m)
nitroaniline, K	*o*		26.50 (m)			37.00 (m)	
	m		28.70 (m)		35.41 (sh)	37.20 (m)	
	p				26.90 (m)	31.00 (m)	31.55 (m)
N,*N*-dimethylnitroaniline, L	*p*				25.80 (m)		28.49 (m)

[a] See footnotes to Table III.

4. Triplet States. The lowest energy triplet state is computed, in all instances, to be ^3L_a. This agrees with experiment (vide infra).

Since the exchange energy K of a D^+-Ph-A^- structure is small, it follows that the ^3L_a energy will be less sensitive to molecular polarity than the ^1L_a energy. In other words, since the ^1L_a energy will decrease as either μ_0 or % CT increases and since, in a single configuration basis, $E(^3L_a) = E(^1L_a) - 2K$, it follows that the decrease of the two factors $E(^1L_a)$ and K will tend to cancel and to render $E(^3L_a)$ less sensitive than $E(^1L_a)$ to a change of the D/A index. This expectation is borne out computationally.

The ^1L_a–^3L_a separations follow (in eV): A, 3.096; B, 2.584; C, 2.374; D, 2.310; E, 2.526; F, 2.394; G, 2.207; H, 2.203; I, 2.158; J, 2.061; K, 1.930; L, 1.676. It is clear that they suffer a lesser decrease than ^1L_a but that this decrease is regular and usable as a gauge of increasing D/A index.

5. Planarity and Perpendicularity. The results of computations for planar and perpendicular forms of *N*,*N*-dimethyl-*p*-cyanoaniline and *N*,*N*-dimethyl-*p*-nitroaniline, the perpendicular form being characterized by ∠90° between the (C,N,N) plane of the amine residue and the ring plane, are reported in various places in this text. We find that twisting always increases $E(^1L_a)$ relative to $E(^1L_b)$. We emphasize this result only because it is opposed to recent results obtained by Cowley[21] using Pariser–Parr–Pople methods and because the subject attains some importance in the interpretation of the peculiar luminescence properties of *N*,*N*-dimethyl-*p*-cyanoaniline. We are not absolutely certain of the origin of the discrepancy between the CNDO/s and PPP results, but we can find reasons to suppose that it lies in the exclusive π-electron nature of the latter theory.

Experimental Correlations

The data set is given in Tables II and III. This data set includes, for reasons of economy, the ortho and meta isomers which will be discussed in a following publication.[22]

A selection of these data is plotted in Figure 4 for a fixed acceptor group CN. The molecules are arranged left to right in terms of increasing donor capability (i.e., increasing D/A index). The results are quite clear cut: $E(^1L_a)$ decreases, $E(^1L_a) - E(^1L_b)$ decreases, and $E(^1L_a) - E(^3L_a)$ decreases. These trends conform to the computational predictions of the previous section. Indeed, even the magnitudes of the observed oscillator strengths and energies are in good accord with computation. Since identical conclusions obtain when the donor group is fixed and the acceptor is varied,[23] we can conclude that a decrease of $E(^1L_a)$ serves as a gauge of an increasing D/A index and that this conclusion is justified both experimentally and computationally.

Consequently, we no longer feel constrained by any need to maintain either the D or A group constant. Thus, for an indiscriminately chosen group of molecules, we plot absorption/emission energies vs. the $^1L_a \leftarrow {}^1\Gamma_1$ absorption energy, as is done in Figure 5, and we assume that the resulting arrangement constitutes a valid D/A sequencing. The absorption data used in Figure 5 refer to nonpolar solvent media, and the emission data to polar media in order to maximize the ab-

Table III. Emission Data[a-d]

molecule	isomer	solvent	fluorescence energy, cm^{-1}	phosphorescence energy, cm^{-1}	phosphorescence lifetime, s	ϕ_p/ϕ_f
fluorobenzonitrile, B	*o*	ethanol	35 000	26 800	2.43	0.18
	m	ethanol	34 900	26 600	2.60	0.15
	p	ethanol	35 750	27 100	2.05	0.96
toluamide	*o*	EPA	35 590	27 690	0.65	5.3
	m	EPA	34 360	26 870	2.55	6.6
	p	EPA	35 080	27 010	1.25	>100
chlorobenzonitrile	*o*	EPA	34 250	25 970	0.38	10.6
	m	EPA	34 480	26 320	0.47	18.7
	p	EPA	34 250	25 840	0.15	16.8
cyanophenol, C	*o*	EPA	32 050	26 320	2.48	1.31
	m	EPA	32 260	25 320	3.21	0.79
	p	EPA	33 900	26 320	2.63	1.51
bromobenzonitrile	*o*	EPA	34 840 (m)	25 970	1.25×10^{-2}	
	m	EPA	34 970 (m)	26 320	1.05×10^{-2}	
	p	EPA	34 720 (m)	25 770	4.9×10^{-3}	
methylbenzoic acid	*o*	EPA	*e*	27 780	1.2	>100
	m	EPA	*e*	29 710	2.7	>100
	p	EPA	*e*	30 300	1.7	>100
cyanoanisole, G	*o*	ethanol	33 200	26 000	1.4	0.42
	m	ethanol	33 000	25 000	1.82	0.45
	p	ethanol	~35 000–33 900 (m)	26 320	1.59	1.01
methoxybenxoic acid	*o*	EPA	31 250	25 640	0.96	3.9
	m	EPA	31 250	26 320	2.68	1.7
	p	EPA	33 900	26 460	2.03	6.2
cyanoaniline, H	*o*	ethanol	27 600 (m)	24 300 (m)	3.65	0.31
	m	ethanol	27 500 (m)	21 510 (m)	2.65	0.054
	p	ethanol	30 000 (m)	24 500	2.45	0.73
methyl aminobenzoate	*o*	EPA	27 000 (m)	22 570 (m)	2.45	<0.01
	m	EPA	25 500 (m)	23 980 (m)	2.4	0.15
	p	EPA	30 303 (m)	24 380	1.8	0.20
aminobenzoic acid, F	*p*	EPA	31 060	24 040	2.1	0.15
N,*N*-dimethylcyanoaniline, I	*p*	EPA	30 770	24 100	2.13	1.2
N,*N*-diethylcyanoaniline	*p*	EPA	30 488	24 100	2	5.3
aminoacetophenone, D	*o*	ethanol	23 260 (m)	22 000 (m)	5.5×10^{-2}	0.14
	m	ethanol	22 600 (m)	20 000 (m)	0.23	0.13
	p	ethanol	28 300 (m)	22 520 (m)	0.72	1.3
N-methylaminobenzoic acid	*p*	EPA	29 630 (m)	23 530	2.3	0.13
N,*N*-dimethylaminobenzoic acid	*p*	EPA	29 590 (m)	23 810 (m)	1.84	0.18
nitroaniline, K	*o*	EPA	20 000 (m)	*e*	*e*	<0.01
	m	EPA	18 000 (m)	*e*	*e*	<0.01
	p	EPA	*e*	18 100 (m)	0.24	>100
N-methylnitroaniline	*p*	EPA	23 260	19 610	0.23	19.3
N,*N*-dimethylnitroaniline, L	*p*	EPA	22 730	19 230	0.22	2.8

[a] All absorption energies refer to room temperature; all emission energies refer to 77 K. Quoted energies are for 0,0 bands except where marked by (m), which connotes a band maximum, or by (sh), which connotes a shoulder. The experimental error is approximately 50 cm^{-1}. The ratio of phosphorescence to fluorescence intensities is denoted ϕ_p/ϕ_f and has been corrected for instrument parameters. The absence of any symbolism in a given data slot indicates that the quantity in question was not measured. [b] Compounds were purified by standard methods (distillation, crystallization, gas chromatography, volatilization, and/or zone refining) until a constancy of luminescence parameters was achieved. All solvents were "Fluorimetric grade" and were nonemissive at the level of sensitivity needed in this work. Measurement procedures have been described elsewhere.[24] [c] Mesomeric, inductive, and steric effects are undoubtedly operative to some extent in all of these systems. It seems reasonable that the relative importance of these effects in the different isomers varies as follows: *o*, steric, inductive ≥ mesomeric; *m*, inductive only; *p*, mesomeric ≥ inductive. The energies of S_1 and T_1 states will depend on that particular mix of these effects which operates in the given state of a given molecule. For example, in the chloro- and bromobenzonitriles, M is of highest T_1 and S_1 energy, presumably because only the inductive effect operates in this isomer. In a "stronger" DA system, where P possesses the highest T_1 and S_1 energies, we must, it seems, associate this happenstance with a dominant importance of the mesomeric effect in these cases. [d] Arranged roughly in the order of decreasing $E(^1L_a)$. [e] We were unable to measure the quantity in question.

sorption–emission separations. A number of observations are pertinent.

(1) There is a convergence of ^1L_a, ^1L_b, and ^3L_a energies, with crossover of ^1L_a and ^1L_b in the region of *p*-nitroaniline.

(2) Fluorescence disappears prior to level convergence and reappears after convergence. The fluorescence prior to convergence is $^1L_b \rightarrow {}^1\Gamma_1$ and after convergence is $^1L_a \rightarrow {}^1\Gamma_1$.

(3) When the $^1L_a \rightarrow {}^1\Gamma_1$ pathway becomes feasible $^3L_a \rightarrow {}^1\Gamma_1$ phosphorescence tends to disappear. The triplet emission, when observed, is always $^3L_a \rightarrow {}^1\Gamma_1$.

1. Molecule/Solvent Composites. In light of the above we find it useful to view a D–Ph–A molecule and its particular solvent cage as one distinct absorbing and emitting entity. A particular molecule embedded in two different solvent cages becomes, in effect, two different molecules. Because the ^1L_a state is more solvatochromic than the ^1L_b state we can, in effect, adjust the relative energies of these two states by a judicious choice of solvent. If we use the $^1L_a \leftarrow {}^1\Gamma_1$ band to arrange a series of these "molecule–solvent" species, we can arrive at certain generalizations about fluorescence and phosphores-

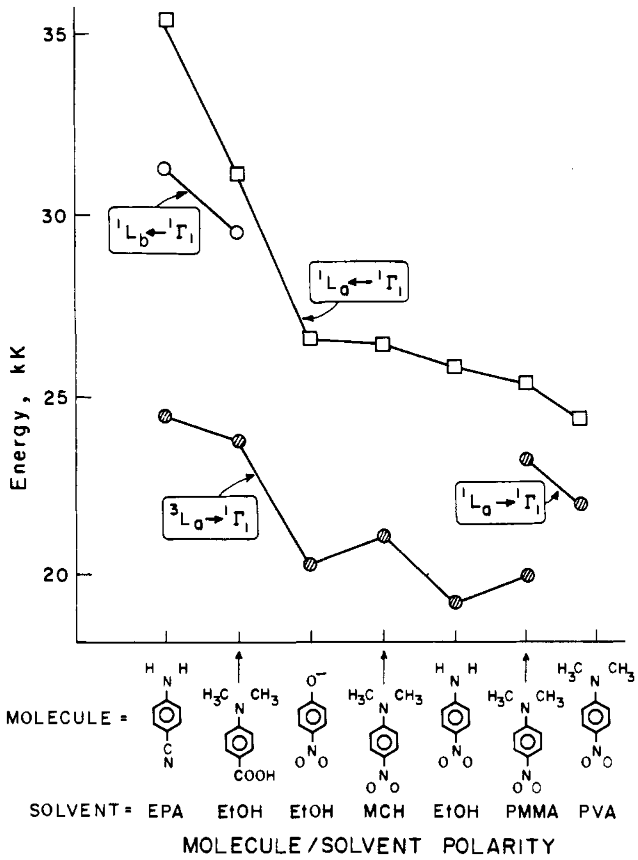

Figure 6. The absorption and emission of a series of "molecule-solvent species", arranged according to decreasing ${}^1L_a \leftarrow {}^1\Gamma_1$ energy. The absorption and emission data were recorded in transparent media at 77 K. The following solvent notations are used: EPA, 5/5/2 by volume mix of ether/isopentane/alcohol; EtOH, ethanol; MCH, methylcyclohexane; PMMA, poly(methyl methacrylate); PVA, polyvinyl alcohol.

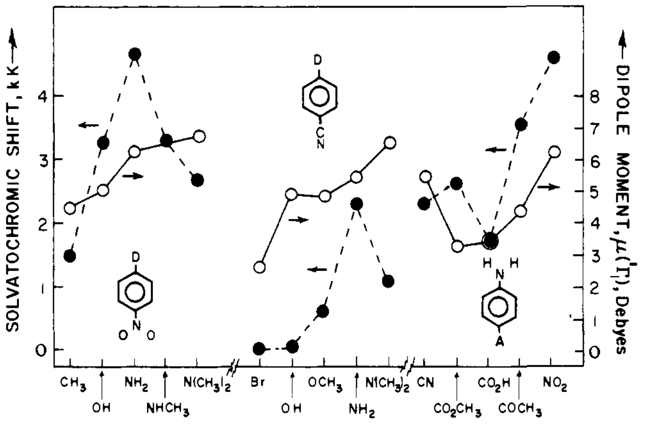

Figure 7. Comparison of solvent shifts and ground-state experimental dipole moments of para-disubstituted benzenes. The solvent shifts are calculated as ($\bar{\nu}$[3MP] − $\bar{\nu}$[ethanol]) for the ${}^1L_a \leftarrow {}^1\Gamma_1$ band maximum at room temperature, except for *p*-methylnitrobenzene. For the latter molecule, the solvents are ethanol and hexane. The dipole moments are from ref 31.

Table IV. Singlet-Triplet Intervals, ${}^1L_a$–${}^3L_a$ ($\times 10^3$ cm^{-1}), of Some *p*-D-Ph-A Molecules[a]

molecule	${}^1L_a$ absorption maximum	${}^3L_a$ phosphorescence origin	${}^1L_a$–${}^3L_a$
p-cyanophenol	40.31	26.37	13.94
p-cyanoaniline	35.71[b]	24.67	11.04
N,N-dimethyl-*p*-aminobenzoic acid	31.25	23.81[b]	7.44
p-nitrophenoxide	26.60	20.26	6.34
p-nitroaniline	25.84	19.58	6.26

[a] All measurements were made in ethanol at 77 K. [b] These measurements refer to an EPA glass at 77 K.

cence. A plot of energies sequenced according to regular variation of the ${}^1L_a \leftarrow {}^1\Gamma_1$ energy is given in Figure 6. The following observations result.

(1) As the polarity of the system increases, fluorescence decreases and phosphorescence dominates.

(2) In the region just prior to the point where ${}^1L_a/{}^1L_b$ crossover occurs, fluorescence disappears entirely. After inversion, fluorescence reappears.

(3) Finally, when $E({}^1L_a)$ has dropped to that of *N,N*-dimethyl-*p*-nitroaniline in PVA, phosphorescence disappears, and ${}^1L_a \rightarrow {}^1\Gamma_1$ fluorescence becomes the dominant emissive path.

2. Dipole Moments and Solvent Effects. $\mu({}^1L_a)$ of *p*-D-Ph-A molecules is parallel to, but larger than, $\mu({}^1\Gamma_1)$. Since neither the solvent nor the solute may rearrange during the course of an electronic transition,[25] solvent stabilization should be larger[26] for ${}^1L_a$ than for ${}^1\Gamma_1$. Thus, a red shift of the ${}^1L_a \leftarrow {}^1\Gamma_1$ band (i.e., a solvatochromism) is expected in polar solvents,[27] and the degree of solvatochromism is expected to be proportional to the static dipole moment change which occurs upon excitation (i.e., to $|\mu({}^1L_a) - \mu({}^1\Gamma_1)|$).[28,29] Indeed, this latter quantity has been adopted by Saidov et al.[30] as a criterion for CT transitions.

Consequently, a correlation between $E({}^1L_a)$ and the degree of solvatochromism is expected. The extent to which such a relationship exists is shown in Figure 7 and is not impressive. Nonetheless, if factors which inhibit the expected relationship are taken into account, most of the deviations may be rationalized. These factors follow.

Solvatochromism is less for alkylamino-substituted aromatics than for amino-substituted aromatics even though the former substituents are known to have the greater electron-donating capacity. This deviation may be ascribed to hydrogen bonding,[28] to methylamino group rotations, and to molecular size.[32,29]

3. The T_1 State. The T_1 state is assigned as ${}^3L_a$. The phosphorescence lifetimes, which usually lie in the range 10^{-1}–10 s, as well as the phosphorescence polarizations, are consistent only with a ${}^3\Gamma_{\pi\pi^*} \rightarrow {}^1\Gamma_1$ transition. The ${}^3L_a$ assignment (as opposed to ${}^3L_b$) follows from the constancy of quantum-chemical predictions on this point (vide supra) and from the smooth correlation with the known ${}^3L_a$ assignments of innocuously substituted benzenes.[33]

The singlet-triplet intervals, $E({}^1L_a) - E({}^3L_a)$, of some para isomers are shown in Table IV. They decrease regularly as the molecules become more polar. There are two primary reasons for this decrease. Firstly, since the more polar substituents tend to be bulkier, the molecular size tends to increase with increasing polarity. Consequently, the pertinent exchange integrals grow smaller and the ${}^1L_a$–${}^3L_a$ interval decreases.[34] Secondly, the extent of charge transfer increases with increasing polarity and this, as is well-known,[34] leads to a drastic reduction in the magnitude of the relevant exchange integrals. In fact, if the ${}^3L_a$ state were 100% CT, the ${}^1L_a$ and ${}^3L_a$ states would be approximately degenerate, and the ${}^3L_a$ state would be biradicaloid.

The ${}^1L_a$ state of *p*-D-Ph-A molecules is quite polar (e.g., for *N,N*-dimethyl-*p*-nitroaniline,[25] $\mu({}^1L_a)$ is ~15 D). The polarity of the T_1 state, however, is less than that of the ${}^1L_a$ state.

(1) If $\mu(T_1)$ and $\mu({}^1\Gamma_1)$ are approximately parallel and comparable in magnitude, then the equilibrium ground-state

solvent cage conformation will approximate the equilibrium conformation appropriate to the T_1 state. In support of this, it is observed that the phosphorescence origin is always prominent, that it is usually the most intense phosphorescence feature, and that considerable vibronic structure accompanies it. Thus the molecule/solvent relative conformations in the T_1 state must be similar to those for the S_0 state.

(2) The solvent shifts[35] experienced by the origin band of the $T_1 \rightarrow S_0$ event are usually very small. For example, in *p*-cyanoaniline the shift $\bar{\nu}_{0,0}$(MCH) − $\bar{\nu}_{0,0}$(ethanol) is only 50 cm^{-1}.

Conclusions

The primary result of this work is that $E(^1L_a)$, the energy of the lowest energy intense band of *p*-D-Ph-A compounds, is a useful and convenient gauge of molecular polarity in the $^1\Gamma_1$, ^3L_a, ^1L_b, and ^1L_a states and that, in particular, it constitutes a good measure of the degree of charge transfer in the ^1L_a state. Both polarity and the degree of charge transfer will increase as $E(^1L_a)$ decreases.

As $E(^1L_a)$ decreases, solvatochromic red shifts of $E(^1L_a)$ become more severe. Consequently, large solvent sensitivities of the $^1L_a \leftarrow {}^1\Gamma_1$ absorption band (and, hence, of color) can be engineered by increasing the D/A index, the size of the conjugating system (e.g., by replacing the benzene residue with a biphenyl residue), or both.

As $E(^1L_a)$ of para D-Ph-A compounds decreases, a crossover of ^1L_b and ^1L_a states occurs. The consequences of this crossover for luminescence characteristics is quite drastic. When the D/A index is small and the energy level order $E(^1L_a) > E(^1L_b) > E(^3L_a) > E(^1\Gamma_1)$ obtains, the fluorescence is $^1L_b \rightarrow {}^1\Gamma_1$ and possesses an intrinsic lifetime of 10^{-7}–10^{-6} s. Since intersystem crossing processes may have comparable cross sections, they can compete with the $^1L_b \rightarrow {}^1\Gamma_1$ fluorescence and the phosphorescence event $^3L_a \rightarrow {}^1\Gamma_1$ may also be observed. In sum, when the index D/A is small one might expect to observe both fluorescence and phosphorescence. When the D/A index is large and the energy level order $E(^1L_b) > E(^1L_a) > E(^3L_a) > E(^1\Gamma_1)$ obtains, the fluorescence is $^1L_a \rightarrow {}^1\Gamma_1$ and possesses an intrinsic lifetime in the nanosecond range. Because of this large cross section and the dearth of intervening states between S_1 and T_1, one can expect the phosphorescence $^3L_a \rightarrow {}^1\Gamma_1$ to be either very weak or absent.

The above conclusions concerning luminescence characteristics are in accord with observation. The experimental work of Lui et al.[36] is fully conformatory of all of the conclusions for the small D/A index range. Little or no experimental work for the large D/A index range appears to be available. Hence, we include an appendix, Appendix 1, which establishes that S_1 of *N,N*-dimethyl-*p*-nitroaniline is indeed ^1L_a. The general run of data, as reported here and elsewhere, is also in accord with the conclusions concerning the partitioning of luminescence intensity into fluorescence and phosphorescence components for the large D/A index regime. Unfortunately, a caveat must be inserted at this point. Our rationalizations concerning fluorescence and phosphorescence intensity ratios were posited on the absence of $^1\Gamma_{n\pi^*}$ excitations. While such excitations are not particularly common to molecules in the low D/A index regime, they are quite ubiquitous for those in the large D/A index regime and, while they have little or no effect on absorption spectra, they may have major import for the luminescence properties. Hence, we include an appendix, Appendix 2, which details the effects introduced by $^1\Gamma_{n\pi^*}$ excited states on the luminescence properties.

The state to which we refer as ^1L_a is normally designated ^{1}CT. This latter designation has had a long[37-40] and useful history. It is predicted, for example, that the $^1\text{CT} \leftarrow {}^1\Gamma_1$ transition should be intense,[37] long-axis polarized,[37] exhibit large solvatochromic effects,[32,40-44] and correlate with Hammett σ constants,[30,45,46] and that it should lead to development of a large static dipole moment in the ^{1}CT state[29,42]—all of which accord with experiment. The question arises, then, as to why we find it expedient to introduce a different nomenclature. The first point to be made is that the name one chooses is defined by one's interests. Our interests lie in modifying benzenoid states so that we can discern the change of excited-state properties as a function of increasing polarity and, for this purpose, there is no doubt concerning the nature of the zeroth-order states. The states of choice are ^1L_a and ^1L_b since they are experimentally accessible in the zeroth order (i.e., low polarity) and since we can trace the evolution of the ^1L_a state, by a more or less continuous parametrization, into a nearly 100% charge transfer state. Had our interests been otherwise, we might have found the ^{1}CT zeroth-order stance to be more appropriate. Hence, our choice of the ^1L_a designation does not imply any criticism of the ^{1}CT zeroth-order stance; it merely indicates that for our purposes the ^1L_a stance is the more convenient. Furthermore, we emphasize that both approaches, prosecuted to similar degrees of quantum-mechanical ultimacy, must yield the same conclusions.

Finally, we note that the present work is quite incomplete. It requires extension to ortho and meta isomers, which will be the subject of a companion paper,[22] and to large aromatic residues, for which prediction is simple but experiment is lacking.

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Appendix 1. Emission Polarization of *N,N*-Dimethyl-*p*-nitroaniline (NNDMPNA or *L*)

The $^1L_a \rightarrow {}^1\Gamma_1$ and $^1L_b \rightarrow {}^1\Gamma_1$ transition moments of NNDMPNA are in plane and mutually perpendicular, the former being directed along the long axis and the latter along the short axis. The $^3L_a \rightarrow {}^1\Gamma_1$ transition moment, on the other hand, will be directed perpendicular[34] to the molecular plane (i.e., "out-of-plane" polarized). Thus, fluorescence, whether $^1L_a \rightarrow {}^1\Gamma_1$ or $^1L_b \rightarrow {}^1\Gamma_1$, should be polarized perpendicular to phosphorescence.[47] This, as shown in Figure 8, is the case.

The majority of intensity in the first absorption band is certainly $^1L_a \leftarrow {}^1\Gamma_1$. Thus, if the fluorescence is $^1L_b \rightarrow {}^1\Gamma_1$, the fluorescence excitation spectrum must exhibit a negative polarization. It is obvious from Figure 8 that this is not so. The interpretation of the fluorescence excitation data requires that the fluorescence be $^1L_a \rightarrow {}^1\Gamma_1$ and that no significant part of the absorption intensity be either $^1L_b \leftarrow {}^1\Gamma_1$ or $^1\Gamma_{n\pi^*} \leftarrow {}^1\Gamma_1$.

If any significant part of the absorption intensity were $^1\Gamma_{n\pi^*} \leftarrow {}^1\Gamma_1$, the phosphorescence excitation spectrum would exhibit a positive polarization. It is obvious from Figure 8 that this is not the case. Nonetheless, it is a fact that the phosphorescence excitation spectrum is least negative at larger λ and that the fluorescence and phosphorescence excitation spectra are not identical. Thus, somewhere in the vicinity of 410 nm, the vibrational deactivation cross section within the singlet manifold become less than the cross section for intersystem crossing to the triplet manifold. The most facile interpretation of this datum suggests the intrusion of $^{1,3}\Gamma_{n\pi^*}$ states in the 410-nm region with the consequent enhancement of intersystem crossing via the processes $^1\Gamma_{n\pi^*} \rightsquigarrow {}^3\Gamma_{\pi\pi^*}$ and $^1\Gamma_{\pi\pi^*} \rightsquigarrow {}^3\Gamma_{n\pi^*} \rightsquigarrow {}^3\Gamma_{\pi\pi^*}$.

Consequently, we may conclude the following.

(1) Phosphorescence is either $^3L_a \rightarrow {}^1\Gamma_1$ or $^3L_b \rightarrow {}^1\Gamma_1$. It is not $^3\Gamma_{n\pi^*} \rightarrow {}^1\Gamma_1$.

(2) Fluorescence is $^1L_a \rightarrow {}^1\Gamma_1$.

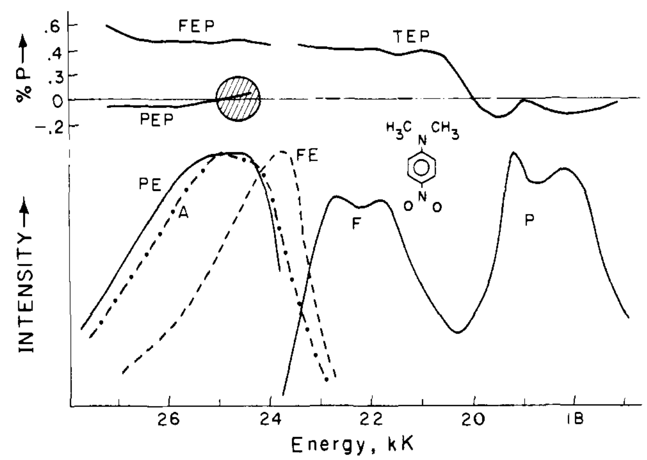

Figure 8. The emission, emission polarization, excitation, and excitation polarization spectra of *N*,*N*-dimethyl-*p*-nitroaniline (L) in EPA at 77 K, ~10^{-5} M. P is the phosphorescence, F is the fluorescence, and TEP is the total emission polarization (λ_{excit} 380 nm). FE is the fluorescence excitation, and FEP is the fluorescence excitation polarization (λ_{emit} 450 nm). PE is the phosphorescence excitation and PEP is the phosphorescence excitation polarization (λ_{emit} 540 nm). A is the absorption spectrum taken in EPA at 77 K. The measurements were performed using the techniques of Azumi and McGlynn.[47] Measurements in the circled region for PEP are unreliable because of scattered light problems and, as a result, they are deemphasized in our discussions.

(3) The majority intensity of the lowest energy absorption band is $^1L_a \leftarrow {}^1\Gamma_1$.

(4) $^{1,3}\Gamma_{n\pi^*}$ states may well intrude in the 410-nm region. (It is appropriate to note that a different interpretation of the disparity between phosphorescence and fluorescence excitation spectra—one which does not invoke the intrusion of $^{1,3}\Gamma_{n\pi^*}$ states and which does not take account of the polarization data—is available in the literature.[48])

Appendix 2. Luminescence of p-D-Ph-NO_2 Compounds

The luminescence properties of the nitroaromatics have long been subject to considerable discussion.[34,44,48-54] Hence, we summarize that which is definitively known about them.

(1) They possess a low-energy $^1\Gamma_{n\pi^*}$ state. This state, for example, is the S_1 state of nitrobenzene[44,51] and 1-nitronaphthalene.[52] As the strength of the donor substituent in D-Ph-NO_2 is increased, the $^1\Gamma_{n\pi^*}$ energy will either increase slightly or remain constant.

(2) The T_1 state of 1-nitronaphthalene,[55,56] possibly that of nitrobenzene,[53] and all D-Ph-NO_2 species where D is at least as strong as -OH are $^3\Gamma_{\pi\pi^*}$. This conclusion is justified by the phosphorescence lifetimes of Table V. The intermediacy of D-Ph-NO_2 phosphorescence lifetimes between that of a typical $^3\Gamma_{\pi\pi^*}$ state (benzene) and a typical $^3\Gamma_{n\pi^*}$ state (benzaldehyde) vindicates[57] the $^3\Gamma_{\pi\pi^*}$ nature of the T_1 states in question and the presence of an adjacent $^1\Gamma_{n\pi^*}$ state. The same conclusion follows by comparison with the substituted benzaldehydes of Table V. As the donor strength of D increases, the energy of this T_1 state (i.e., $^3\Gamma_{\pi\pi^*}$ or ^3L_a) will decrease.

(3) The lowest $^1\Gamma_{\pi\pi^*}$ state, when D is a weak donor, is ^1L_b, and, when D is a strong donor, is ^1L_a. Both of these states decrease energetically as the donor strength increases, that of ^1L_a being the more sensitive. It follows, as donor strengths increase, that one may sample the energy sequences: $E(^1\Gamma_{n\pi^*}) < E(^1L_b) < E(^1L_a)$, $E(^1L_b) < E(^1\Gamma_{n\pi^*}) < E(^1L_a)$, $E(^1L_b) < E(^1L_a) < E(^1\Gamma_{n\pi^*})$, or $E(^1L_a) < E(^1L_b) < {}^1\Gamma_{n\pi^*}$.

(4) The lowest energy absorption band of D-Ph-NO_2 entities, D being a relatively good donor, encompasses all four transitions: $^1L_a \leftarrow {}^1\Gamma_1$, $^1L_b \leftarrow {}^1\Gamma_1$, $^1\Gamma_{n\pi^*} \leftarrow {}^1\Gamma_1$, and $^3\Gamma_{n\pi^*} \leftarrow {}^1\Gamma_1$. It is this proximity of nearly degenerate states which is responsible for the differences in fluorescence and phosphorescence excitation spectra (see Figure 8) and for the gross effects of solvent polarity and seemingly innocuous chemical substitution (i.e., N-methylation) on the luminescence characteristics.

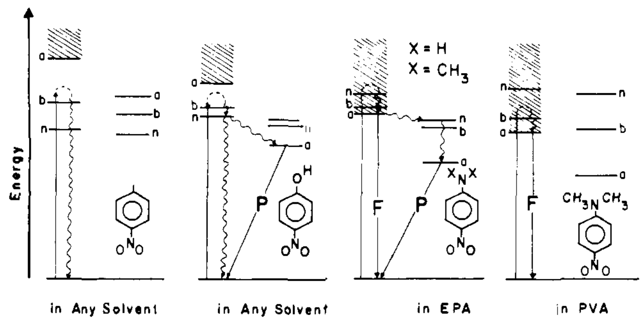

Figure 9. The excited states of para-substituted nitrobenzenes. The molecular polarity increases from left to right. In each of the four systems, the states on the left are singlet states and the states on the right are triplet states. The a refers to L_a, the b refers to L_b, and the n refers to the $\Gamma_{n\pi^*}$ state. Unsubstituted nitrobenzene, or nitrobenzene with weakly polar substituents, exhibits weak or no emission. More polar nitrobenzenes, such as *p*-nitrophenol, phosphoresce but have weak or absent fluorescence. Highly polar nitrobenzenes, such as *p*-nitroaniline and its methylated derivatives, both phosphoresce and fluoresce but the intensities of phosphorescence and fluorescence are substituent and solvent dependent. In the very polar solvent polyvinyl alcohol (PVA), only fluorescence is observed. Radiative events are indicated by straight lines, nonradiative events by wavy lines.

Table V. Phosphorescence Lifetimes, τ, as Indicators of the Nature of the T_1 State

molecule	T_1 type	solvent	τ(s) (obsd)	τ^0(s) (intrinsic)	ref
benzene	$^3\Gamma_{\pi\pi^*}$	MCH	8	33	*a*
PhCHO	$^3\Gamma_{n\pi^*}$	EPA	0.004	0.005	*b*
p-CH_3PhCHO	$^3\Gamma_{\pi\pi^*}$	EPA	0.084	0.14	*b*
p-HOPhCHO	$^3\Gamma_{\pi\pi^*}$	EPA	0.26	0.47	*c*
p-CH_3OPhCHO	$^3\Gamma_{\pi\pi^*}$	EPA	0.10	0.31	*c*
p-H_2NPhNO_2	$^3\Gamma_{\pi\pi^*}$	3MP	0.20		*d*
p-H_2NPhNO_2	$^3\Gamma_{\pi\pi^*}$	EPA	0.24		*d*
p-H_2NPhNO_2	$^3\Gamma_{\pi\pi^*}$	ethanol	0.09		*e*
p-$(CH_3)_2$NPhNO_2	$^3\Gamma_{\pi\pi^*}$	MCH	0.20		*d*
p-$(CH_3)_2$NPhNO_2	$^3\Gamma_{\pi\pi^*}$	EPA	0.22		*d*
p-HOPhNO_2	$^3\Gamma_{\pi\pi^*}$	ethanol	0.08		*e*

[a] C. A. Parker, "Photoluminescence of Solutions", Elsevier, Amsterdam, 1968, p 281. [b] N. C. Yang et al., *J. Am. Chem. Soc.*, **89**, 5466 (1967). [c] R. Lui and E. C. Lim, *J. Chem. Phys.*, **57**, 605 (1972). [d] O. Khalil, C. J. Seliskar, and S. P. McGlynn, *ibid.*, **58**, 1607 (1973). [e] P. P. Dikun, A. A. Petrov, and B. Ya. Sveshnikov, *Zh. Eksp. Theor. Fiz.*, **21**, 150 (1951); *Chem. Abstr.*, **45**, 8347*i* (1951).

(5) The nonradiative intersystem crossing cross sections $^1\Gamma_{n\pi^*} \rightsquigarrow {}^3\Gamma_{\pi\pi^*}$ or $^1\Gamma_{\pi\pi^*} \rightsquigarrow {}^3\Gamma_{n\pi^*}$ are much more efficient than the routes $^1\Gamma_{\pi\pi^*} \rightsquigarrow {}^3\Gamma_{\pi\pi^*}$ or $^1\Gamma_{n\pi^*} \rightsquigarrow {}^3\Gamma_{n\pi^*}$.

(6) The radiative cross sections, as estimated from typical oscillator strength data, are $\sigma(^1\Gamma_{n\pi^*} \rightarrow {}^1\Gamma_1) \simeq (10^{-1}\text{-}10^{-2})\,\sigma(^1L_b \rightarrow {}^1\Gamma_1) \simeq (10^{-4}\text{-}10^{-5})\,\sigma(^1L_a \rightarrow {}^1\Gamma_1)$.

We are now in a position to rationalize the gamut of observed luminescence behavior. Such a rationalization is schematized in Figure 9, where molecular systems which exemplify the expected behavior are specified.

References and Notes

(1) J. N. Murrell, "The Theory of the Electronic Spectra of Organic Molecules", Wiley, New York, 1963, Chapters 8-10.

(2) H. Suzuki, "Electronic Absorption Spectra and Geometry of Molecules", Academic Press, New York, 1967, Chapters 19-23.

(3) See the writings of J. Petruska and P. E. Stevenson in J. R. Platt, "Systematics of the Electronic Spectra of Conjugated Molecules", Wiley, New York, 1964.

(4) O. Khalil, K. Seliskar, and S. P. McGlynn, *J. Mol. Spectrosc.*, **70**, 74

(1978).

(5) G. Bendazzoli, F. Bertinelli, P. Palmieri, and G. Taliani, *Chem. Phys.*, **16**, 319 (1976).

(6) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory", McGraw-Hill, New York, 1970, pp 111–112.

(7) R. T. C. Brownlee and R. W. Taft, *J. Am. Chem. Soc.*, **92**, 7007 (1970).

(8) Standard bond lengths and angles were taken from ref 6.

(9) The structure of the upper half of this molecule was that for *p*-aminobenzoic acid (see ref 10) while that of the lower half was for acetophenone (see ref 11).

(10) T. F. Lai and R. E. Marsh, *Acta Crystallogr.*, **22**, 885 (1967).

(11) Y. Tanimoto, H. Kobayashi, S. Nagakura, and Y. Saito, *Acta Crystallogr., Sect. B*, **29**, 1882 (1973).

(12) M. Alleaume, S. Salas-Ciminago, and J. Decap, *C. R. Acad. Sci., Ser. C.*, **262**, 416 (1966).

(13) The structure of the upper half of this molecule was that of 1,4-dimethoxybenzene (see ref 14, p 146) while that of the lower half was that for *p*-iodobenzonitrile (see ref 14, p 97). Standard bond lengths were used for the CN group (see ref 6).

(14) R. W. G. Wyckoff, "Crystal Structures", Vol. 6, Part 1, 2nd ed., Interscience, New York, 1969.

(15) T. C. Mak and J. Trotter, *Acta Crystallogr.*, **18**, 68 (1965). The CH bond lengths and angles for the $N(CH_3)_2$ grouping were those for $(CH_3)_3N$ as listed in R. C. West, Ed., "CRC Handbook of Chemistry and Physics", 53rd ed., Chemical Rubber Publishing Co., Cleveland, 1972, p F-182.

(16) K. Trueblood, E. Goldish, and J. Donohue, *Acta Crystallogr.*, **14**, 1009 (1961). Bond lengths and angles were averaged to yield a C_{2v} symmetry.

(17) J. Del Bene and H. H. Jaffé, *J. Chem. Phys.*, **48**, 1808, 4050 (1968); **49**, 1221 (1968); **50**, 1126 (1969).

(18) QCPE Program CNDO 174 was used in conjunction with the Mataga–Nishimoto approximation for two-center integrals [N. Mataga and K. Nishimoto, *Z. Phys. Chem.* (*Frankfurt am Main*), **13**, 140 (1957)]. The convergence criteria and iteration procedures were those of King and Van Putten [G. W. King and A. A. G. Van Putten, *J. Mol. Spectrosc.*, **42**, 514 (1972)]. Convergence occurred after 11 iterations in all cases except *p*-fluorobenzonitrile and *p*-aminobenzoic acid, which required 15 and 25 iterations, respectively. The C, H, N, and O parametrizations were those of Del Bene and Jaffé (see ref 17); that for F was taken from Kuehnlenz and Jaffé [G. Kuehnlenz and H. H. Jaffé, *J. Chem. Phys.*, **58**, 2238 (1973)]. Only the first 30 monoexcited configurations were included in the CI procedure.

(19) S. P. McGlynn, L. G. Vanquickenborne, M. Kinoshita, and D. G. Carroll, "Introduction to Applied Quantum Chemistry", Holt, Rinehart and Winston, New York, 1972, pp 324–325.

(20) Other observations evolving from the quantum-chemical processing follow.

(1) In molecules containing a cyano group, two other states normally lie between the ^1L_a and ^1L_b levels. These are of σ(CN)$\rightarrow\pi^*$ and $\pi\rightarrow\sigma^*$(CN) type. The σ(CN) orbital is an MO with $\geq$50% of its electron density localized on the CN group. For example, in *p*-fluorobenzonitrile, σ(CN) has 25% electron density of $2p_x$ carbon and 48% of $2p_x$ nitrogen AO types (see Figure 1 for axes and molecule).

(2) In molecules of low polarity, the third and fourth $^1\Gamma_{\pi\pi^*}$ states correlate with the ^1B states of benzene. However, as μ_0 increases, a number of higher lying $^1\Gamma_{\pi\pi^*}$ states intrude into the energy range of the ^1L_b, ^1L_a, ^1B_a, and ^1B_b states.

(3) The computed lowest energy excited states of *p*-aminobenzoic acid and all nitroanilines are of $^1\Gamma_{n\pi^*}$ type. This erroneous result is typical of CNDO procedures and is disregarded.

(21) D. J. Cowley and A. H. Peoples, *J. Chem. Soc., Chem. Commun.*, 352 (1977). The controversy which Cowley seeks to resolve is concerned with the nature of multiple luminescences in *N,N*-dimethyl-*p*-cyanoaniline. Concerning this subject see E. Lippert, W. Lüder, and H. Boos, *Adv. Mol. Spectrosc.*, 443 (1962); K. Rotkiewicz, K. H. Grellmann, and Z. R. Grabowski, *Chem. Phys. Lett.*, **19**, 315 (1973); O. S. Khalil, R. H. Hofeldt, and S. P. McGlynn, *ibid.*, **17**, 479 (1972); N. Nakashima and N. Mataga, *Bull. Chem. Soc. Jpn.*, **46**, 3016 (1973); W. S. Struve, P. M. Rentzepis, and J. Jortner, *J. Chem. Phys.*, **59**, 5014 (1973); E. M. Kosower and H. Dodiuk, *J. Am. Chem. Soc.*, **98**, 924 (1976).

(22) G. L. Findley, T. P. Carsey, and S. P. McGlynn, *J. Am. Chem. Soc.*, following paper in this issue.

(23) For the example D = NH_2 and A variable see T. P. Carsey, Ph.D. Dissertation, Louisiana State University, Baton Rouge, 1977.

(24) See, for example, Y. H. Lui and S. P. McGlynn, *J. Lumin.*, **9**, 449 (1975); O. S. Khalil, R. H. Hofeldt, and S. P. McGlynn, *Chem. Phys. Lett.*, **6**, 147 (1973).

(25) N. S. Bayliss and E. G. McRae, *J. Phys. Chem.*, **58**, 1002 (1954).

(26) W. M. Schubert, H. Steadly, and J. M. Craven, *J. Am. Chem. Soc.*, **82**, 1353 (1960).

(27) W. Liptay, *Angew. Chem., Int. Ed. Engl.*, **8**, 177 (1969).

(28) P. Suppan, *Spectrochim. Acta, Part A*, **30**, 1939 (1974).

(29) M. B. Ledger and P. Suppan, *Spectrochim. Acta, Part A*, **23**, 641 (1967).

(30) G. V. Saidov and N. G. Bakshiev, *Dokl. Akad. Nauk SSSR*, **175**, 1090 (1967); G. V. Saidov, O. V. Sverdlova, and N. G. Bakshiev, *ibid.*, **81**, 638 (1968).

(31) A. L. McClelland, "Tables of Experimental Dipole Moments", W. H. Freeman, San Francisco, 1963.

(32) N. G. Bakshiev, M. I. Kyazhanskii, V. I. Minkin, O. A. Osipov, and G. V. Saidov, *Russ. Chem. Rev.* (*Engl. Transl.*), **38**, 740 (1969).

(33) R. B. Cundall and S. M. Ogilvie in "Organic Molecular Photophysics", Vol. 2, J. B. Birks, Ed., Wiley-Interscience, New York, 1975, p 35.

(34) S. P. McGlynn, T. Azumi, and M. Kinoshita, "Molecular Spectroscopy of the Triplet State", Prentice-Hall, Englewood Cliffs, N.J., 1969.

(35) This discussion assumes the existence of a rigid matrix in which no solvent–solute reorganization occurs. Reorganization can be a very important factor. For example, Yamaguchi et al. [G. Yamaguchi, K. Kakinoki, and H. Tsubomura, *Bull. Chem. Soc. Jpn.*, **40**, 526 (1967)] have shown that the phosphorescence of *p*-aminoacetophenone in a rigid matrix (ethanol, 77 K) exhibits a prominent origin band which, when warmed to 150 K in order to permit solvent reorganization, experiences a red shift of ~1700 cm^{-1} but remains equally prominent. This shift reflects the increased solvent sensitivity of the T_1 state and suggests that $\mu(T_2) > \mu(S_0)$.

(36) Y. H. Lui and S. P. McGlynn, *J. Lumin.* **9**, 449 (1975); *J. Mol. Spectrosc.*, **55**, 163 (1975); *J. Lumin.*, **10**, 113 (1975); *Spectrosc. Lett.*, **11**, 47 (1978).

(37) M. Godfrey and J. N. Murrell, *Proc. R. Soc. London, Ser. A*, **278**, 57, 64 (1964).

(38) N. Mataga, *Bull. Chem. Soc. Jpn.*, **36**, 1607 (1963).

(39) S. Nagakura and J. Tanaka, *J. Chem. Phys.*, **22**, 236 (1954).

(40) S. Nagakura, *J. Chem. Phys.*, **23**, 1411 (1955).

(41) K. Semba, *Bull. Chem. Soc. Jpn.*, **34**, 722 (1961).

(42) T. Abe, *Bull. Chem. Soc. Jpn.*, **40**, 1571 (1967).

(43) W. M. Schubert, J. M. Craven, and H. Steadly, *J. Am. Chem. Soc.*, **81**, 2695 (1959).

(44) A. I. Kiss and G. Horvath, *Acta Chim. Acad. Sci. Hung.*, **42**, 15 (1964).

(45) A. V. Finkelshtein, E. Y. Belyaev, and Z. M. Kuzmina, *Russ. J. Phys. Chem.* (*Engl. Transl.*), **41**, 1044 (1967).

(46) R. T. C. Brownlee and R. D. Topsom, *Spectrochim. Acta, Part A*, **29**, 385 (1973).

(47) T. Azumi and S. P. McGlynn, *J. Chem. Phys.*, **37**, 2413 (1962).

(48) O. S. Khalil and S. P. McGlynn, *J. Lumin.* **11**, 185 (1975–1976).

(49) R. Foster, D. L. Hammick, G. M. Hood, and A. C. E. Sanders, *J. Chem. Soc.*, 4865 (1956).

(50) M. Kasha, *Radiat. Res., Suppl. 2*, 243 (1960).

(51) J. M. Corkill and I. J. Graham-Bryce, *J. Chem. Soc.*, 3893 (1961).

(52) O. S. Khalil, H. G. Bach, and S. P. McGlynn, *J. Mol. Spectrosc.*, **35**, 455 (1970).

(53) R. Hurley and A. C. Testa, *J. Am. Chem. Soc.*, **90**, 1949 (1968).

(54) V. G. Plotnikov and V. M. Komarov, *Spectrosc. Lett.*, **9**, 265 (1976).

(55) R. Rusakowicz and A. C. Testa, *Spectrochim. Acta, Part A*, **27**, 787 (1971).

(56) E. C. Lim and J. Stanislaus, *Chem. Phys. Lett.*, **6**, 195 (1970).

(57) L. Vanquickenborne and S. P. McGlynn, *J. Chem. Phys.*, **45**, 4755 (1966).