

study the adsorption of aliphatic nitriles at the Hg-aqueous solution interface. They proposed that succinonitrile adsorbed flat on the Hg surface with the two nitrile groups slightly turned toward the solution. Such a configuration necessitated the succinonitrile molecule to assume the thermodynamically unstable *cis* conformation or a conformation slightly different from *cis*.³⁶ The present work on the Cu-aqueous solution interface indicates that succinonitrile adsorbs on the Cu surface in both the *gauche* and *trans* conformations, and that one of the C≡N groups lies close to the metal surface and π -bonding results. Our findings are markedly different from Trasatti's; however, two different metal systems were involved.

In conclusion, two isomeric species of succinonitrile, the *gauche*

and *trans*, have been identified at the copper-succinonitrile solution interface. This is the first report of the observation of two rotational isomers on metal surfaces in surface-enhanced Raman spectroscopy.

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ARTICLES

Dependence of Intramolecular Rotation in *p*-Cyano-*N,N*-dialkylanilines on the Twist Angle. A Fluorescence, UV Absorption, and Photoelectron Spectroscopic Study

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The rate constant \bar{k} for formation of the twisted intramolecular charge transfer (TICT) excited state of several dual fluorescing *p*-cyano-*N,N*-dialkylanilines is measured by using fluorescence decay kinetics and compared to the spectroscopic ground-state twist angle $\langle\varphi\rangle$ derived from photoelectron (PE) spectroscopy. With increasing $\langle\varphi\rangle$, the rate constant \bar{k} also increases considerably, in accordance with a scheme involving an excited-state crossing. PE and UV spectroscopy are used to show that the angular distribution function of flexible compounds is very broad as compared to that of compounds with a rigid carbon skeleton.

Introduction

p-Cyano-*N,N*-dimethylaniline (DMABN) exhibits two fluorescence bands in polar solvents.¹ Many different explanations have been given for this anomalous dual fluorescence (see references cited in ref 2), but in recent years, more and more evidence has been gathered supporting a "twisted intramolecular charge transfer" (TICT) excited state responsible for the red-shifted fluorescence band.² This mechanism involves an adiabatic photoreaction \bar{k} (Figure 1), i.e., a reaction in the excited state proceeding from an initially reached B* state to an A* or TICT state with the dialkylamino group twisted perpendicularly to the benzene ring plane. The reaction coordinate from the more or less planar B* state to the twisted TICT state is thus an intramolecular rotation combined with reorientation effects of the polar solvent molecules around the newly created very high dipole moment of the TICT state.²⁻⁴

For an experimental verification of this twist mechanism, both a static and a dynamic approach are possible. In the static approach, compounds with a rigidly fixed molecular framework with respect to amino group rotation are chosen. Thus, the planar 5-cyano-*N*-methylindoline shows no TICT fluorescence band because the amino group rotation toward the TICT geometry is inhibited.² The counter example with a perpendicularly twisted

amino group is 5-cyanobenzoquinuclidine which shows only the TICT but not the short-wavelength B* band.²

In the dynamic approach, a pair of compounds is chosen with all molecular parameters as similar as possible, except the volume of the rotating moieties. A suitable pair has been shown to be the piperidino and 3,5-dimethylpiperidino analogue of DMABN.⁵ In the latter one with the larger rotational volume the TICT formation is slowed down by a factor of nearly 2 which clearly shows that a rotational motion is separating B* and A* state, and that the measurement of fluorescence kinetics is a powerful tool for studying reaction mechanisms. The study of this very fast intramolecular rotation in the excited state—within some picoseconds in ordinary solvents at room temperature⁶⁻⁹ can give valuable information on the structure of liquids, because two

(1) Lippert, E.; Lüder, W.; Boos, H. In "Advances in Molecular Spectroscopy"; Mangini, A., Ed.; Pergamon Press: Oxford, 1962; p 443.

(2) Grabowski, Z. R.; Rotkiewicz, K.; Siemiarczuk, A.; Cowley, D. J.; Baumann, W. *Nouv. J. Chim.* **1979**, *3*, 443.

(3) Lippert, E.; Ayuk, A. A.; Rettig, W.; Wermuth, G. *J. Photochem.* **1981**, *17*, 237.

(4) Rettig, W. *J. Mol. Struct.* **1982**, *84*, 303.

(5) Rettig, W. *J. Phys. Chem.* **1982**, *86*, 1970.

(6) Rotkiewicz, K.; Grabowski, Z. R.; Króczyński, A.; Kühnle, W. *J. Lumin.* **1970**, *12/13*, 877.

(7) Huppert, D.; Rand, S. D.; Rentzepis, P. M.; Barbara, P. F.; Struve, W. S.; Grabowski, Z. R. *J. Chem. Phys.* **1981**, *75*, 5714.

(8) Wang, Y.; McAuliffe, M.; Novak, F.; Eisenthal, K. B. *J. Phys. Chem.* **1981**, *85*, 3736.

(9) Wang, Y.; Eisenthal, K. B. *J. Chem. Phys.* **1982**, *77*, 6076.

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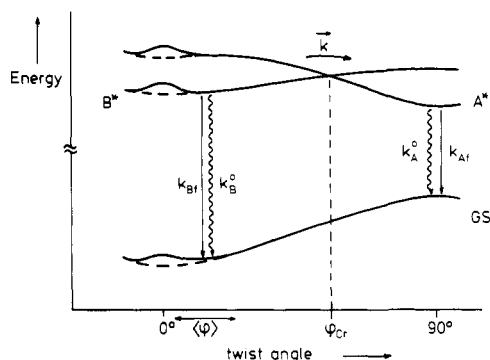


Figure 1. Schematic potential energy diagram for the angular dependence of ground state and of B^* and A^* excited states in *p*-cyano-*N,N*-dialkylanilines for the case of a slight hindrance to planarity. The primary photophysical and photochemical processes are also shown: radiative (k_{Bf} and k_{Af}) and nonradiative (k_{B0} and k_{A0}) decay channels for B^* and A^* , respectively; adiabatic photoreaction $B^* \rightarrow A^*$ (k) (depending on solvent and temperature, the reverse process k may also be significant). See text for the significance of critical twist angle φ_{cr} and spectroscopic mean twist angle $\langle\varphi\rangle$.

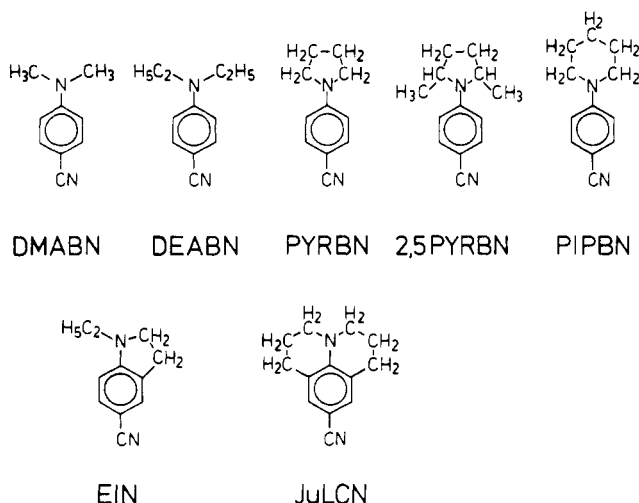


Figure 2. Formulas and abbreviations of the compounds studied.

different types of rotational diffusion are important: diffusion necessitating pushing away the solvent molecules, and diffusion into solvent free volume.^{10,5} A series of especially tailored dual fluorescing *p*-cyano-*N,N*-dialkylanilines thus can serve as fluorescent probes for studying free volume effects.⁵ In this series of compounds, several molecular parameters were changed simultaneously: rotational volume, molecular flexibility, ground-state mean twist angle $\langle\varphi\rangle$, etc. All these factors are in principle important for intramolecular rotation kinetics, and it is the aim of the present study to make a distinction as to the relative importance of these factors.

The ground-state mean twist angle $\langle\varphi\rangle$ represents a weighted average of twist angles φ between the planes of benzene ring and the dialkylamino C-N-C framework—the latter one being close to planar.¹¹ $\langle\varphi\rangle$ determines the angular distance $\Delta\varphi = |\langle\varphi\rangle - \varphi_{cr}|$ from a critical twist angle φ_{cr} where the two excited states 1L_b -type (B^* state, lowest singlet excited state in the near planar region) and 1L_a -type (A^* state, lowest singlet excited state in the perpendicular region, with strong charge-transfer character) cross (Figure 1), i.e., are isoenergetic in the absence of vibronic coupling through a nontotally symmetrical mode.^{5,12} It can be expected that k critically depends on $\Delta\varphi$, increasing for smaller angular distances.

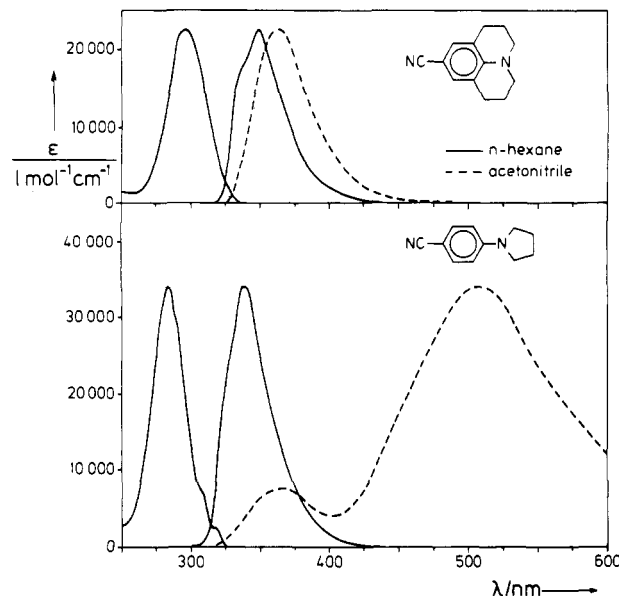


Figure 3. Absorption (—, in *n*-hexane) and fluorescence spectra (---, in acetonitrile) of JULCN and PYRBN.

TABLE I: TICT Formation Rate Constants \bar{k} in *n*-Butyl Chloride at 138 K

compd	DMABN	DEABN	PYRBN	2,5-PYRBN	PIPBN
$\bar{k}/10^7 \text{ s}^{-1}$	101	35	14	24	180

In this study, photoelectron (PE) spectroscopy will be used for conformational analysis and thus the determination of $\langle\varphi\rangle$. These gas-phase $\langle\varphi\rangle$ values will then be compared to k values measured by fluorescence kinetics. The importance of broad angular distribution functions for flexible compounds will be pointed out, and also the effect on the UV absorption spectrum.

Experimental Section

In Figure 2, formulas and abbreviations of the compounds studied are listed. DMABN and DEABN were obtained commercially, and the other compounds were synthesized by nucleophilic aromatic substitution of 4-cyano-1-fluorobenzene with the corresponding secondary amine^{11,13} or by introduction of a cyano substituent using the formylation reaction analogously to ref 6. All compounds were repeatedly recrystallized and finally vacuum sublimed and were identified by mass spectrometry and NMR. Melting points are given in ref 11 and 5 except for the new compound JULCN (mp 108 °C).

n-Butyl chloride (Fluka puriss p.a.) was purified by repeated column chromatography and subsequent fractional distillation. The other solvents were of Merck Uvasol quality. Quantum corrected fluorescence spectra were obtained on a FICA 55 MK II or a Perkin Elmer 650-60 spectrofluorimeter and absorption spectra on a Cary 14 spectrometer. Decay times were measured with a mode-locked frequency-quadrupled Nd-glass laser ($\lambda_{ex} = 265 \text{ nm}$) and the setup described in ref 5.

PE spectra were recorded on a PS 18 photoelectron spectrometer (Perkin-Elmer Ltd. Beaconsfield, England). The calibration was done with Ar and Xe, and a resolution of 20 meV on the $^2P_{3/2}$ Ar line was achieved. The spectra were recorded at 70–90 °C.

Quantum chemical calculations were performed using the MINDO/3 method.¹⁴

Results

Figure 3 shows the UV absorption spectrum of JULCN in a nonpolar hydrocarbon solvent at room temperature, together with

(10) Alwaltar, A. H.; Lumb, M. D.; Birks, J. B. In "Organic Molecular Photophysics"; Birks, J. B., Ed.; Wiley: New York, 1973; Vol. 1, Chapter 8.

(11) Rettig, W. *J. Lumin.* **1981**, 26, 21.

(12) Wermuth, G.; Rettig, W. *J. Phys. Chem.* **1984**, 88, 2729. Rettig, W.; Wermuth, G. *J. Photochem.* **1985**, 28, 351.

(13) Suhr, H.; Grube, H. *Ber. Bunsenges. Phys. Chem.* **1966**, 70, 544.

(14) Bingham, R.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* **1975**, 97, 1285. Bischof, P. *J. Am. Chem. Soc.* **1976**, 98, 6844. We used an extended version of the program QCPE No. 279.

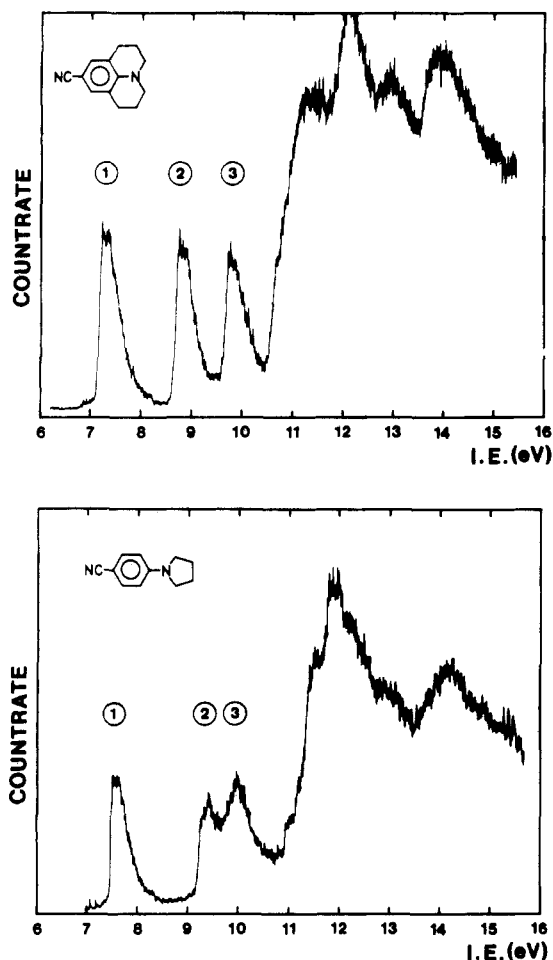


Figure 4. Photoelectron spectra of JULCN and PYRBN.

its fluorescence spectrum in the polar solvent acetonitrile. Only the short wavelength B* band is present. For comparison, the dual fluorescence of PYRBN in the same solvent acetonitrile at room temperature is also shown. The B* band is slightly blue shifted as compared to JULCN. Table I lists the values for the TICT formation rate constant k at 138 K (supercooled liquid), determined in the way described.⁵ For some of the compounds, these values differ by a factor of up to 10.

Figure 4 shows two of the measured PE spectra representative for a nonflexible (JULCN) and a flexible (PYRBN) compound. In all cases, the first three PE bands are clearly separated from the rest of the spectrum. In the case of strongly overlapping bands (for example bands two and three in PIPBN), the band profile was simulated by the addition of two bands possessing the shape of band one of the same compound. Vertical ionization energies I_v and "averaged" ionization energies I_{av} were determined as the maximum of the band profile and as the midpoint at 80% height of the band maximum, respectively. I_{av} is taken in order to make ionization energies determined from bands with strongly different band shapes more comparable. JULCN has an asymmetrical band shape with a steep onset at the low energy side (0-0 band), whereas PIPBN, probably as a consequence of the flexibility of the piperidino ring, has a more Gaussian type band shape. The I_v and I_{av} values are collected in Table II.

The band assignment according to Koopmans' theorem¹⁵ is closely related to that of Maier and Turner for the dialkylanilines,¹⁶ i.e., bands one and three correspond to in-phase and out-of-phase combinations of the amino nitrogen lone pair, and the benzonitrile π orbitals symmetrical to a plane perpendicular to the benzene ring and containing the C-N bond (symmetry b_1 in C_2 point

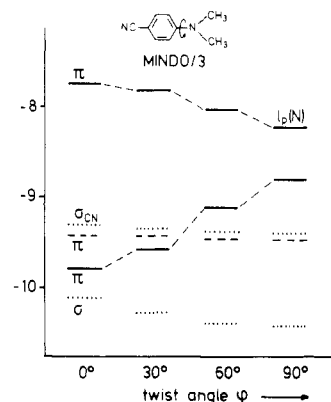


Figure 5. MINDO/3 orbital energies as a function of amino group twist angle in DMABN. The geometry used was the same as in ref 24.

TABLE II: Vertical and Averaged Ionization Potentials I_v and I_{av} (in eV)

compd	band 1	band 2	band 3
DMABN	7.86 (7.87)	9.56 (9.57)	10.19 (10.22)
DEABN	7.65 (7.72)	9.45 (9.52)	10.08 (10.07)
PYRBN	7.56 (7.56)	9.41 (9.41)	10.05 (10.07)
2,5-PYRBN	7.50 (7.54)	9.35 (9.40)	9.98 (9.96)
PIPBN	7.89 (7.90)	9.64 (9.65)	10.10 (10.09)
EIN	7.64 (7.63)	9.27 (9.31)	10.02 (10.05)
JULCN	7.26 (7.30)	8.75 (8.80)	9.75 (9.80)
	7.36		

group). Band two is assigned to the corresponding antisymmetric benzonitrile π orbital (a_2).

For corroboration of this assignment, MINDO/3¹⁴ calculations were performed for DMABN at different twist angles. The results are shown in Figure 5 and illustrate the strong angular dependence for the two interacting orbitals π_1 and π_3 , and a weak dependence for the other orbitals. σ orbitals of the nitrile group seem to be situated above 11 eV; i.e., they do not interfere with the analysis of the first three PE bands.

Discussion

To estimate the mean angle of twist of the dialkylamino groups with respect to the aromatic plane in the examples listed above we use the PE data presented in Table II. Turner and Maier¹⁶⁻¹⁸ as well as others^{19,20} have demonstrated with a large number of organic molecules that PE spectroscopy can be used as a tool to estimate torsional angles. To analyze our PE data we neglect any π/σ interactions and use first-order perturbation theory to calculate the energy difference between the in-phase and out-of-phase linear combination between the 2p orbital on nitrogen (N) and the symmetric π -orbital of the aromatic fragment (A). This energy difference corresponds to the energy difference $\Delta I_{1,3}$ between bands one and three of the PE spectra of the compounds listed above if Koopmans' approximation¹⁵ is valid.

The basis orbital energies of our two fragments N and A are defined as

$$A_A = \langle \Psi_A | H | \Psi_A \rangle; \quad A_N = \langle \Psi_N | H | \Psi_N \rangle \quad (1)$$

The interaction between both fragments is described by a parameter β :

$$\beta = \langle \Psi_N | H | \Psi_A \rangle \quad (2)$$

If both fragments are twisted by φ , β amounts to

$$\beta = \beta^0 \cos \varphi \quad (3)$$

(17) Maier, J. P.; Turner, D. W. *Faraday Discuss. Chem. Soc.* **1972**, *54*, 149.

(18) Maier, J. P.; Turner, D. W. *J. Chem. Soc., Faraday Trans. 2*, **1973**, *69*, 196.

(19) Kobayashi, T.; Arai, T.; Sakuragi, H.; Tokumaru, K.; Utsunomiya, C. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1658.

(20) Klessinger, M.; Rademacher, P. *Angew. Chem.* **1979**, *91*, 885.

(15) Koopmans, T. *Physica* **1934**, *1*, 104.

(16) Maier, J. P.; Turner, D. W. *J. Chem. Soc., Faraday Trans. 2* **1973**, *69*, 521.

TABLE III: Basis Energy Difference ΔA , IP Difference $\Delta I_{av}(1,3)$ between First and Third PE Band and Derived Mean Spectroscopic Twist Angle $\langle \varphi \rangle$ for TICT State Forming p-Cyano-*N,N*-dialkylanilines, Logarithm of the Preexponential Factor A , and Activation Energy E_A of the TICT Formation Rate Constant in *n*-Butyl Chloride at 138 K

compd	ΔA / eV	$\Delta I_{av}(1,3)$ / eV	$\langle \varphi \rangle^a$	$\log A/s^{-1b}$	E_A / (kJ/mol) ^b
DMABN	0.84	2.35	4^{+14}_{-4}	13.2 ± 0.3	11.4 ± 0.8
DEABN	1.15	2.35	21^{+7}_{-10}	12.6 ± 0.3	10.8 ± 0.8
PYRBN	0.97	2.51	$0 + 17$	11.1 ± 0.1	7.7 ± 0.3
2,5-PYRBN	1.09	2.42	10^{+11}_{-10}	11.8 ± 0.1	9.1 ± 0.4
PIPN	1.19	2.19	33^{+6}_{-6}	12.7 ± 0.4	9.1 ± 1.0

^a Error limits derived by assuming an error of ± 0.1 eV for $\Delta I_{av}(1,3)$.
^b \pm One standard deviation.

With these parameters we are ready to set up the usual secular determinant. The energy difference $\epsilon_1 - \epsilon_3 \equiv I_{1,3}$ amounts to

$$\Delta I = [(A_N - A_A)^2 + 4(\beta^0 \cos \varphi)^2]^{1/2} \quad (4)$$

From (4) it is evident that the energy splitting between bands one and three of the PE spectra of our examples depends on the difference of the basis orbital energies, ΔA , the resonance integral β^0 , and the twist angle φ .

The first two parameters can be taken from experimental data. From benzoquinuclidine we infer a ΔA value for diethylamino-substituents of $\Delta I_{1,3} = \Delta A = 0.70$ eV¹⁶ because the lone pair on N and the π -system are oriented perpendicular to each other. The ΔA value will be increased by introducing a cyano substituent in the para position of the aromatic moiety because the cyano substituent lowers the basis orbital energy of the aromatic part (A). To get an estimate of this increase we compare the ΔA values of *N*-phenylpyrrole and *N*-(4-cyanophenyl)pyrrole (0.36 and 0.81 eV, respectively²¹). Adopting this increase by 0.45 eV for our samples we calculate for DEABN $\Delta A = 1.15$ eV. In the case of DMABN or 2,5-PYRBN we expect different ΔA values due to the different substituents at the nitrogen. For DMABN we expect a smaller value due to the two methyl groups instead of the ethyl groups, and for 2,5-PYRBN a larger one due to the additional methyl groups in the five-membered ring.

The actual changes of ΔA can be estimated by comparing the ionization energies of the corresponding alkylamines.^{11,22} The values thus obtained for ΔA are given in Table III.

To estimate β_{AN}^0 we use EIN and JULCN, two compounds in which the twist angle between N and the aromatic part should be 0°. The energy difference for both compounds is $\Delta I_{1,3} = 2.5$ eV. With this value and $\Delta A = 1.15$ eV we obtain $\beta_{AN}^0 = 1.1$ eV from eq 4. This value is somewhat less than that determined from julolidine and benzoquinuclidine¹⁶ ($\beta_{AN}^0 = 1.23$ eV) and reflects the polarization of the π -orbitals of the aromatic part due to the cyano substituent. With the data derived for ΔA and $\Delta I_{1,3}$ we can calculate the mean of the twist angle φ using (4). The values obtained are collected in Table III.

The deviations from planarity found for PIPBN and 2,5-PYRBN can be anticipated, while the twist found for DEABN is unexpected. We can explain these results by the existence of sterically hindered conformations possible for DEABN by the rotation of the ethyl chains^{11,25} and, for all flexible compounds, by taking into account a broad angular distribution function which also allows the population of twisted conformations. As a consequence we encounter smaller $\Delta I_{1,3}$ values leading to nonzero $\langle \varphi \rangle$ values even in the case of DMABN. A similar observation could be made with *N*-phenylpyrroles.²¹

Concluding Remarks

Comparison between the rate data of Table I and the values for the mean twist angle in Table III allows us to rationalize several observations.

(i) 2,5-PYRBN reacts faster toward the TICT state than PYRBN by a factor of ~ 1.7 although the rotational volume of the former is larger due to the two additional methyl groups. This observation of the higher rate of the more bulky compound is just opposite to our expectation since two additional methyl groups are expected to slow down rotation by a factor of 1.8.⁵ This apparent contradiction can be solved by taking into account the fact that 2,5-PYRBN is twisted in the ground state by 10° while PYRBN is near coplanar. The average twist angle of 10° thus increases the TICT formation rate by a factor of ~ 3 .

(ii) The comparison between DMABN and 2,5-PYRBN shows that also the size of the rotator is important. Although both compounds show about the same mean twist angle, the rate constant for DMABN is larger than for 2,5-PYRBN.

(iii) A third point which deserves interest is the preexponential Arrhenius factor, A . By comparing the different Arrhenius activation energies for rotators of similar size (7.7 kJ/mol for PYRBN and 9.1 kJ/mol for PIPBN, see Table III) we find no correlation between the activation energies E_A and $\langle \varphi \rangle$. The main source of the difference in rate constant for the compounds DEABN, PYRBN, 2,5-PYRBN, and PIPBN with comparable rotational volume is thus due to different A values (see Table III). This correlation of solution-phase rate constants (Table I) and A values with $\langle \varphi \rangle$ values determined in the gas phase also suggests that the order of mean twist angles $\langle \varphi \rangle$ does not change in going from gas phase to solution phase. The differences in E_A can be rationalized by using the microviscosity theory.⁵ In our case the factor A could be interpreted as being proportional to the probability that the rotator moves from $\langle \varphi \rangle$ to φ_{cr} (see Figure 1). Only at φ_{cr} a crossing from the B to the A surface is possible thus leading directly to the TICT state. This movement along the shallow B energy surface closely corresponds to free angular diffusion, thus following Einstein's law of squared diffusion time for doubled diffusion gap. When the molecule crosses to the A surface, it is suddenly accelerated toward the TICT state because on the A surface the perpendicular geometry ($\varphi = 90^\circ$) has an energy minimum (see Figure 1)^{2,23} with a maximum for the dipole moment.³

Further points to note are connected with JULCN, a new planar reference compound for DMABN. It does not show the long-wavelength TICT fluorescence band (Figure 3) in close agreement with the substituted indolines.^{21,24} This is a further experimental verification that the possibility for a twisted conformation is necessary in order to obtain TICT state formation.

The maximum extinction coefficient ϵ_{max} of the first UV absorption band of JULCN ($\epsilon_{max} = 22\,500$ L/(mol cm), see Figure 3) is anomalously low as compared to PYRBN ($\epsilon_{max} = 34\,000$ L/(mol cm)) or other dialkylaminobenzonitriles.¹¹ This is also in close agreement with the corresponding indolines²⁴ and can be traced back (i) to the occurrence of broad angular distribution functions for the nonrigid compounds and (ii) to the breakdown of the often applied cosine-square law (eq 5) for the angular dependence of ϵ for this class of compounds with very low lying charge-transfer states.²⁴

Although both PYRBN and JULCN may possess a ground-state minimum for the planar conformation with respect to rotation around the C-N amino bond, the corresponding angular distribution function for PYRBN may be very broad, leading to a reduced effective overlap between N lone pair and benzene π -orbitals. This is witnessed by the increased electron delocalization and donor capabilities of juloidines and indolines as compared with dialkylanilines.^{25,26} For the UV spectrum, increased planarity is expected to result in an increased extinction coefficient of the

(23) Rettig, W.; Zander, M. *Chem. Phys. Lett.* **1982**, *87*, 229.

(24) Rettig, W.; Rotkiewicz, K.; Rubaszewska, W. *Spectrochim. Acta* **1984**, *40A*, 241.

(25) Bent, R. L.; Dessloch, J. C.; Dünnebier, F. C.; Fasset, D. W.; Glass, D. B.; James, T. H.; Julian, D. B.; Ruby, W. R.; Schell, J. M.; Sterner, J. H.; Thirtle, J. R.; Vittum, P. M.; Weissberger, A. J. *Am. Chem. Soc.* **1951**, *73*, 3100.

(26) Ahmad, M. *Bangladesh J. Sci. Ind. Res.* **1978**, *13*, 74.

(27) Wepster, B. M. In "Progress in Stereochemistry"; Klyne, W., De la Mare, P. B. O., Eds.; Butterworths: London, 1958; Vol. II.

(21) Rettig, W.; Marschner, F. *Nouv. J. Chem.* **1983**, *7*, 425.

(22) Aue, D. H.; Webb, H. M.; Bowers, M. T. *J. Am. Chem. Soc.* **1976**, *98*, 311.

¹L_a-type band, if the cosine-square law (eq 5) is valid.^{27,28}

$$\epsilon(\varphi) = \epsilon(0^\circ) \cos^2 \varphi \quad (5)$$

Its validity seems, however, to be confined to an angular range of $\sim 30^\circ < \varphi < 90^\circ$ for substituted anilines with strong donor-acceptor character.²⁴ For smaller twist angles, ϵ is diminished with regard to the expected value. Thus, the combined effects i and ii lead to the anomalously low extinction coefficients for substituted indolines and julolidines.

Broad angular distribution functions and the specific angle dependence of the energy of the ¹L_a-type state²⁴ may also be

(28) Braude, E. A.; Sondheimer, J. *J. Chem. Soc.* **1955**, 3754.

responsible for the significant red shift of the absorption maximum of JULCN (33 700 cm⁻¹) as compared to PYRBN (35 300 cm⁻¹)²⁴ (compare also Figure 3 for the corresponding shift of the fluorescence spectrum).

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Registry No. DMABN, 1197-19-9; DEABN, 2873-90-7; PYRBN, 10282-30-1; 2,5-PYRBN, 80887-45-2; PIPBN, 1204-85-9; EIN, 89937-22-4; JULCN, 97315-60-1.

Enhancement of Molecular Fluorescence and Photochemistry by Small Metal Particles

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We examine a quantum mechanical model for the enhancement of fluorescence yield and photochemical rates by the presence of a small particle capable to sustain electromagnetic resonances. The sphere lowers the absorption and emission efficiency by taking energy from the molecule and storing it into nonradiative modes, enhances the absorption by increasing the local field, and enhances the fluorescence by emitting efficiently the energy transferred from the emitting state to a radiative electromagnetic resonance of the particle. The present paper studies how the interplay of these effects modifies fluorescence intensity and the rate of photochemical reactions.

I. Introduction

The spectroscopy and the relaxation dynamics of vibrational and electronic excitations of molecules and atoms adsorbed on metal surfaces have received a great deal of attention lately since they are involved in many surface processes such as surface photochemistry,¹⁻⁴ surface photoemission,⁵ surface-enhanced Raman scattering (SERS),^{6,7} and photoluminescence.⁸⁻¹⁰ In the present article we examine molecular fluorescence and photochemistry in the presence of a surface.

Qualitatively these phenomena are fairly well understood.^{7a} In all surface-enhanced processes the local field acting on the molecule is increased by reflection of the incident radiation. This increase is substantial if surface curvature is large,¹¹ if the incident light excites surface electromagnetic resonances,¹¹⁻¹⁶ or if solid

particles are used to polarize each other.¹⁷ This local field enhancement increases the rate of photochemical processes and the intensity of adsorbate fluorescence. The presence of the surface, however, causes energy transfer from the molecule to surface excitations, such as plasmons,^{18,19} electron-hole pairs, or phonons.^{20,21} This results in a decrease of the excited population which causes a decrease of the photochemical rate. The total rate is established through the competition of these opposing effects.

In the case of fluorescence an additional complication arises because the excited molecule polarizes the surface^{7a,8,9,18,19} and this emits at the molecular frequency, thus enhancing the emission intensity. This enhancement is particularly strong if the emission frequency matches that of a radiative surface resonance.

Recently several theoretical models^{2,14-16,22,23} predicting and/or explaining observed fluorescence⁸⁻¹⁰ and photochemistry²⁴ of adsorbates have appeared in the literature.

Our purpose in this article is twofold: to provide a more systematic derivation of the quantum mechanical behavior of the molecule-sphere system, and to carry out a more extensive numerical study of fluorescence and photochemical rates. Previous work included surface effects in an intuitive manner by replacing the oscillator strength and width appearing in the quantum theory for an isolated molecule with surface-dependent expressions

- (1) C. J. Chen and R. M. Osgood, *Appl. Phys.*, **A31**, 171 (1983).
- (2) A. Nitzan and L. E. Brus, *J. Chem. Phys.*, **75**, 2205 (1981).
- (3) G. M. Goncher and C. B. Harris, *J. Chem. Phys.*, **77**, 3767 (1982).
- (4) G. M. Goncher, C. A. Parsons, and C. B. Harris, *J. Phys. Chem.*, submitted for publication.
- (5) A. Schmidt-Ott, P. Scharfberger, and H. C. Siegmann, *Phys. Rev. Lett.*, **45**, 1284 (1980).
- (6) "Surface Enhanced Raman Scattering", R. K. Chan and T. E. Furtak, Ed., Plenum, New York, 1982.
- (7) (a) H. Metiu, *Prog. Surf. Sci.*, **17**, 153 (1984); (b) H. Metiu and P. Das, *Annu. Rev. Phys. Chem.*, **35**, 507 (1984).
- (8) (a) G. Ritchie and E. Burstein, *Phys. Rev. B*, **24**, 4843 (1981); (b) J. F. Owen, P. W. Barber, P. B. Dorain, and R. K. Chang, *Phys. Rev. Lett.*, **47**, 1075 (1981).
- (9) D. A. Weitz, S. Garoff, C. D. Hanson, T. J. Gramila, and J. I. Gersten, *Opt. Lett.*, **7**, 89 (1982); *J. Lumin.*, **24/25**, 83 (1981).
- (10) A. M. Glass, P. F. Liao, J. G. Bergmann, and D. H. Olson, *Opt. Lett.*, **5**, 368 (1980).
- (11) J. I. Gersten and A. Nitzan, *J. Chem. Phys.*, **75**, 1139 (1981); **73**, 3023 (1980).
- (12) D. S. Wang, M. Kerker, and H. Chew, *Appl. Opt.*, **19**, 2256, 4159 (1980).
- (13) D. S. Wang and M. Kerker, *Phys. Rev. B*, **24**, 1777 (1981).
- (14) S. Efrima and H. Metiu, *J. Chem. Phys.*, **70**, 1602, 1939, 2297 (1979).

- (15) P. K. Aravind and H. Metiu, *Chem. Phys. Lett.*, **74**, 301 (1980).
- (16) J. Arias, P. K. Aravind, and H. Metiu, *Chem. Phys. Lett.*, **85**, 396 (1982).
- (17) P. K. Aravind, A. Nitzan, and H. Metiu, *Surf. Sci.*, **110**, 189 (1981).
- (18) R. R. Chance, A. Prock, and R. Silbey, *Adv. Chem. Phys.*, **37** (1978).
- (19) H. Morawitz and M. R. Philpott, *Phys. Rev. B*, **10**, 4863 (1974).
- (20) P. Avouris and B. N. J. Persson, *J. Phys. Chem.*, **88**, 837 (1984), and references therein.
- (21) (a) H. Metiu, *Isr. J. Chem.*, **22**, 329 (1983); (b) K. M. Leung, G. Schon, P. Rudolf, and H. Metiu, *J. Chem. Phys.*, **81**, 3307 (1984).
- (22) D. A. Weitz, S. Garoff, J. I. Gersten, and A. Nitzan, *J. Chem. Phys.*, **78**, 5324 (1983).
- (23) X. Y. Huang, J. Lin, and T. F. George, *J. Chem. Phys.*, **80**, 893 (1984).
- (24) S. Garoff, D. A. Weitz, and M. S. Alvarez, *Chem. Phys. Lett.*, **93**, 283 (1982).