While neither form, P-2 nor M-2, of **3** is preferred,[51] the same may not be true of acyclic disulfides where the substituents directly attached to S are larger than CH_2R. (*S*,*S*)-Bis(1-methylbutyl)disulfide (**4**) exhibits weak positive ($\Delta\epsilon = +0.09$) and negative ($\Delta\epsilon = -0.05$) CD bands at 270 and 238 nm, respectively, in *n*-heptane.[51] The crossover point, 251 nm, coincides with the UV maximum at 252 nm ($\epsilon = 400$). A second crossover point occurs at 234 nm. While **4** undoubtedly exists in several rotameric conformations, the gross characteristics of its CD spectrum resemble the $\phi = 100°$ curve of Figure 6 and therefor are consistent with **4** having preferentially adopted the P conformation with a dihedral angle greater than 90°.

The CD spectrum of D-penicillamine disulfide (**5**) in water has a broad negative band ($\Delta\epsilon = -0.2$) with $\lambda_{max} = 262$ nm.[51] The CD is almost zero at 230 nm but does not change sign. A second negative peak ($\Delta\epsilon = -0.4$) is observed at 220 nm. There is no UV maximum which corresponds to the CD band at 262 nm. The data for **5** are consistent with **5** having a right-handed twist (P chirality) and an S–S twist angle greater than 90°. If, as suggested by molecular machanics calculations on the structurally similar di-*tert*-butyl disulfide,[53] the angle is in excess of 110°, then the lack of UV absorption may be attributable to the predicted low oscillator strength for the $1^1A \rightarrow 2^1A$ transition. The second CD band, which is calculated to be positive and stronger than the first, would be buried under the CD band due to the carboxylate group which occurs at 220 nm.[51]

Acknowledgment. I thank the Natural Sciences and Engineering Research Council of Canada for continuing financial support. The receipt of large amounts of computing time at modest cost from the University of Calgary is gratefully appreciated. The assistance of Scott Collins in the development of the basis sets was of great value.

Registry No. H_2S_2, 13465-07-1; $(CH_3)_2S_2$, 624-92-0.

---

(52) Szantay, C.; Kotick, M. P.; Shefter, E.; Bardos, T. J. *J. Am. Chem. Soc.* **1967**, *89*, 713–714.

(53) Joergensen, F. S.; Snyder, J. P. *Tetrahedron* **1979**, *35*, 1399–1407.

Excited-State Dipole Moment and Solvatochromism of Highly Fluorescent Rod-Shaped Bichromophoric Molecules

Ger F. Mes, Bettina de Jong, Hendrik J. van Ramesdonk, Jan W. Verhoeven,*
John M. Warman,* Matthijs P. de Haas, and Leny E. W. Horsman-van den Dool

Contribution from the Laboratory for Organic Chemistry, University of Amsterdam, Nieuwe Achtergracht 129, 1018 WS Amsterdam, The Netherlands, and Interuniversity Reactor Institute, Mekelweg 15, 2629 JB Delft, The Netherlands. *Received March 5, 1984*

Abstract: Efficient photoinduced charge separation can occur in molecules containing electron donor (D) and acceptor (A) groups separated by an elongated paraffinic spacer. For two molecules of this type the dipole moment of the excited state thus achieved (D^+–A^-) is shown to be as high as 25 ± 2 D via nanosecond time-resolved microwave conductivity measurements. Despite the lack of either direct D/A contact or coupling via a π-electron system the dipolar excited states are found to emit charge-transfer-type fluorescence with a quantum yield exceeding 50% in some solvents. The enormous solvatochromism of this fluorescence makes these molecules attractive as fluorescent polarity probes.

Photoinduced charge separation and migration play a key role in many important photochemical and photophysical processes including photosynthesis.[1] Much information regarding the geometrical requirements for electron-transfer between donor (D) and acceptor (A) species has been acquired from the study of bichromophoric systems incorporating D and A chromophores connected by one or more paraffinic moieties which restrict the D/A separation and orientation. Often the paraffinic moieties allow[2] or even enforce[3,4] close contact of the D and A chromophores (type I in Figure 1), thus mimicing the general situation found in intermolecular complexes and exciplexes.[5] We[6-8] and others[9-11] have shown, however, that (photoinduced) intramolecular electron transfer may also occur if a paraffinic spacer enforces a rod-like molecular shape with D and A located at opposite ends (type II in Figure 1).

In I the D/A interaction occurs essentially via direct through-space overlap, while in II through-bond interaction via the σ framework of the spacer plays an important role.[6,7,12] For both I and II the lowest excited singlet state may acquire extensive charge-transfer (CT) character (i.e., D^+A^-), leading to pronounced solvatochromism of any fluorescence ($\tilde{\nu}_{ct}$) resulting from it. If

---

* J.W.V.: University of Amsterdam. J.M.W.: Interuniversity Reactor Institute.

(1) Jortner, J. *J. Am. Chem. Soc.* **1980**, *102*, 6676–6686.

(2) For a review see: Schryver, F. C. de.; Boens, N.; Put, J. *Adv. Photochem.* **1977**, *10*, 359–465.

(3) Borkent, J. H.; Verhoeven, J. W.; de Boer, Th. J. *Chem. Phys. Lett.* **1976**, *42*, 50–53.

(4) Overfield, R. E.; Scherz, A.; Kaufmann, K. J.; Wasielewski, M. R. *J. Am. Chem. Soc.* **1983**, *105*, 5747–5752.

(5) "The Exciplex"; Gordon, M., Ware, W. R., Eds.; Academic Press: New York, 1975.

(6) Pasman, P.; Verhoeven, J. W.; de Boer, Th. J. *Chem. Phys. Lett.* **1978**, *59*, 381–385.

(7) Pasman, P.; Rob, F.; Verhoeven, J. W. *J. Am. Chem. Soc.* **1982**, *104*, 5127–5133.

(8) Pasman, P.; Koper, N. W.; Verhoeven, J. W. *Recl. Trav. Chim. Pays-Bas* **1982**, *101*, 363–364.

(9) Davidson, R. S.; Bonneau, R.; Joussot-Dubien, J.; Toyne, K. J. *Chem. Phys. Lett.* **1979**, *63*, 269–272.

(10) Calcaterra, L. T.; Closs, G. L.; Miller, J. R. *J. Am. Chem. Soc.* **1983**, *105*, 670–671.

(11) Stein, C. A.; Lewis, N. A.; Seitz, G. *J. Am. Chem. Soc.* **1982**, *104*, 2596–2599.

(12) Baker, A. D.; Scharfman, R.; Stein, C. A. *Tetrahedron Lett.* **1983**, *24*, 2957–2960.

0002-7863/84/1506-6524$01.50/0

Table I. Fluorescence Maximum ($\tilde{\nu}_{ct}$), Quantum Yield (ϕ), and Fluorescence Lifetime (τ_F) of Compounds **1** and **2** in Various Solvents

		compd **1**			compd **2**		
solvent	Δf	$\tilde{\nu}_{ct}$, cm^{-1} × 10^3	ϕ	τ_F, ns^c	$\tilde{\nu}_{ct}$, cm^{-1} × 10^3	ϕ	τ_F, ns
n-hexane	0.092				24.27		
cyclohexane	0.100	27.70	0.32 ± 0.04	3.7 ± 0.1^{a,b}	24.27	0.13 ± 0.02	1.2 ± 0.05^a
benzene	0.116	26.11	0.50 ± 0.05	6 ± 0.5	20.92	0.51 ± 0.05	15 ± 1
1,4-dioxane	0.122	24.63	0.43 ± 0.05	6 ± 0.5	19.38	0.45 ± 0.03	15 ± 1
toluene	0.126				21.01	0.46 ± 0.05	
di-*n*-butyl ether	0.194	27.17	0.43 ± 0.05	9 ± 0.5^b	21.37	0.60 ± 0.05	12 ± 1
diisopropyl ether	0.237				20.75	0.40 ± 0.03	
diethyl ether	0.251	25.45	0.19 ± 0.02	3 ± 0.5	19.76	0.24 ± 0.02	14 ± 1
chloroform	0.251				18.83	0.27 ± 0.02	13 ± 1
ethyl acetate	0.292	22.42	0.45 ± 0.04	10 ± 0.5	17.45	0.11 ± 0.01	6 ± 0.5
tetrahydrofuran	0.308	22.42	0.50 ± 0.04	9 ± 0.5	17.42	0.12 ± 0.01	7 ± 0.5
1,2-dimethoxyethane	0.309				16.81		4 ± 0.5
dichloromethane	0.319	22.12	0.34 ± 0.02	10 ± 0.5	17.27	0.13 ± 0.02	9 ± 0.5
pyridine	0.326				15.95		1 ± 0.5
isopropyl alcohol	0.370	20.83	0.22 ± 0.02	10 ± 0.5			
acetonitrile	0.398	19.12	0.22 ± 0.02	4 ± 0.5	14.39		

[a] Lifetime determined by Luthjens and H. de Leng via the pulse radiolysis methods described in ref 22. [b] An additional slow component (τ_F ~20 ns) is observed. [c] Error limits include those arising from the deconvolution procedures (cf. Experimental Section).

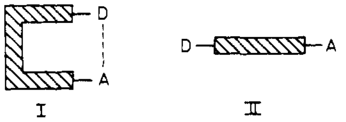

Figure 1. Two types of bichromophoric electron donor (D)/acceptor (A) systems. In I direct D/A contact is enabled or enforced by one or more paraffinic bridges while in II a paraffinic spacer enforces a stretched rod-like structure.

the ground-state dipole moment (p^0) is neglected relative to that of the emissive CT state (p^*), relation 1 can be derived.[13] In

$$\tilde{\nu}_{ct} = \tilde{\nu}_{ct}(o) - (2[p^*]^2/\rho^3hc)\Delta f \qquad (1)$$

(1) $\tilde{\nu}_{ct}(o)$ denotes the wavenumber of the —hypothetical—gas-phase fluorescence maximum and ρ is the radius of a cavity in which the molecule fits. If this cavity has a pronounced ellipsoidal shape, ρ is usually taken to be 40% of its long axis. Δf represents the solvent parameter defined by the dielectric constant (ϵ) and the optical refractive index (n) via (2).

$$\Delta f = (\epsilon - 1)/(2\epsilon + 1) - (n^2 - 1)/(4n^2 + 2) \qquad (2)$$

A measure of the solvatochromic power of a particular D/A system is provided by the slope of a plot of $\tilde{\nu}_{ct}$ vs. Δf, which, according to (1), corresponds to $2[p^*]^2/\rho^3hc$. It should be realized that this only yields an effective value for the $[p^*]^2/\rho^3$ ratio since p^* is treated as a point dipole at the center of a spherical cavity in the derivation of (2).

For intramolecular D/A systems of type I the solvatochromism of their fluorescence parallels that of intermolecular CT complexes and polar exciplexes. The negative slope of $\tilde{\nu}_{ct}$ vs. Δf plots is typically[14] in the range 11 000 ± 5000 cm^{-1}. This implies that upon transfer from a very apolar solvent like *n*-hexane (Δf = 0.093) to a very polar solvent like acetonitrile (Δf = 0.387) the fluorescence undergoes a bathochromic shift of 3200 ± 1500 cm^{-1}, which even in the most favorable case covers less than half of the visible region.

As we have reported earlier[6,7] intramolecular D/A systems of type II may display a much more pronounced solvatochromism as a result of the larger charge separation achievable in such rod-shaped molecules, and slopes up to 20 000 cm^{-1} were reported[15] for some intramolecular D/A systems with a conformation intermediate between I and II. Thus, type II systems seem of potential interest as fluorescent polarity probes. However, the weak electronic coupling between D and A in type II systems in general leads to very low fluorescence quantum yields because of competing radiationless processes.

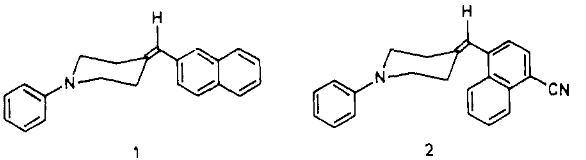

Figure 2. Bichromophoric D/A systems described in the present study.

In the course of our continuing studies on rigid polychromophoric molecules,[16] we have found certain type II systems which combine strong solvatochromism with a very high fluorescence quantum yield, thereby providing an interesting new class of fluorescent polarity probes. The present communication describes the fluorescent properties of two such systems (**1** and **2**; see Figure 2) as well as the determination of the dipole moment of their emissive state from time-resolved microwave conduction measurements.

Results and Discussion

The bichromophoric systems **1** and **2** (Figure 2) were prepared by Wittig condensation of 1-phenyl-4-piperidone with the appropriate triphenylphosphonium ylide (cf. Experimental Section). Both compounds **1** and **2** contain a *N*,*N*-dialkylanilino moiety as an efficient electron donor. The 2-vinylnaphthalene acceptor moiety of **1** is substituted by the more powerful 1-vinyl-4-cyanonaphthalene moiety in **2**. The flattened chair conformation[7] of the interconnecting 4-methylenepiperidine ring gives the molecules a rod shape which fits into an ellipsoidal cavity with a long axis of 15 Å.

The electronic absorption spectra of **1** and **2** are virtually independent of solvent polarity and closely resemble the expected sum spectra of the separate chromophores (cf. Figure 3). The long-wavelength (≥300 nm) parts of the absorption spectra are dominated by the acceptor chromophore since the donor chromophore shows only weak absorption in this region (λ_{max} = 297 nm (ϵ_{max} = 2500 L mol^{-1} cm^{-1}) for *N*,*N*-dimethylaniline in cyclohexane[17]).

In contrast to the absorption spectra the fluorescence spectra of **1** and **2** do not show any emission attributable to the separate D or A chromophores irrespective of the excitation wavelength employed. Instead a single, rather broad emission is observed,

---

(13) Beens, H.; Knibbe, H.; Weller, A. *J. Chem. Phys.* **1967**, *47*, 1183–1184.

(14) Beens, H.; Weller, A. *Acta Phys. Pol.* **1968**, *34*, 593.

(15) Swinnen, A. M.; Auweraer, M. van der; Schryver, F. C. de; Windels, C.; Goedeweeck, R.; Vannerem, A.; Meeus, F. *Chem. Phys. Lett.* **1983**, *95*, 467–470.

(16) Mes, G. F.; Ramesdonk, H. J. van; Verhoeven, J. W. *Recl. Trav. Chim. Pays-Bas* **1983**, *102*, 55–56.

(17) Berlman, I. B. "Handbook of Fluorescence Spectra of Aromatic Molecules"; Academic Press: New York, 1971.

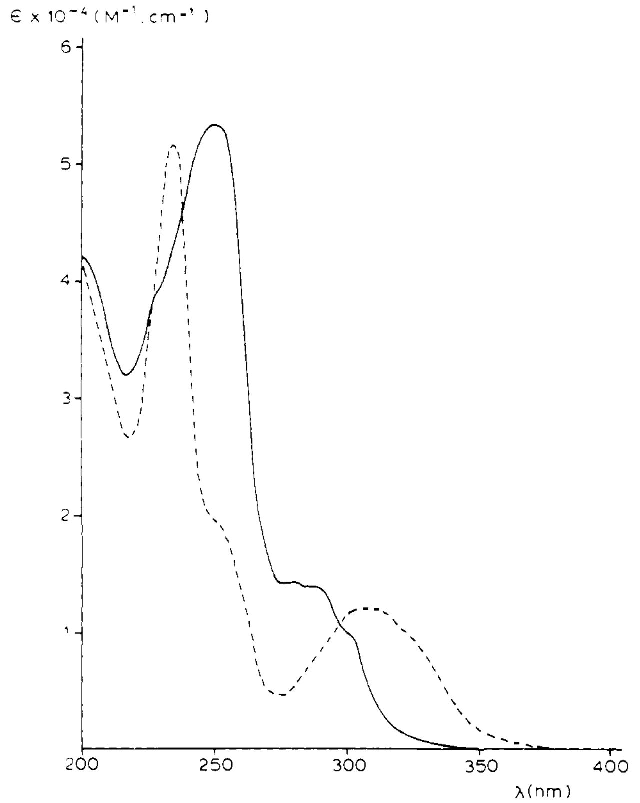

Figure 3. Electronic absorption spectra of **1** (—) and **2** (- - -) in cyclohexane at 20 °C.

the maximum of which undergoes a very large bathochromic shift with increasing solvent polarity. This is typical of a CT-type emission ($\tilde{\nu}_{ct}$) originating from a dipolar excited state ($D^+–A^-$). Relevant emission data for **1** and **2** are compiled in Table I, while plots of $\tilde{\nu}_{ct}$ vs. Δf are shown in Figure 4.

The slope of these plots (−30 500 cm^{-1} for **1** and −34 000 cm^{-1} for **2**) classifies these compounds as extremely sensitive fluorescent polarity probes when compared to type I (Figure 1) systems. The fluorescence quantum yields of **1** and **2** are found to be very high, ϕ reaching values in excess of 50% in solvents of intermediate polarity (cf. Table I). As far as we know such ϕ values even exceed the highest values determined for CT-type fluorescence from type I systems as well as—by extrapolation—for intermolecular CT complexes and polar exciplexes.

The position of $\tilde{\nu}_{ct}$ for **2** covers almost the entire visible region (25 000–13 300 cm^{-1}) if the solvent polarity is varied within the practical available range ($0.1 \leq \Delta f \leq 0.4$). This property enhances the applicability of **2** not only as a spectroscopic probe but also as a visual polarity probe. Such applications will be the subject of future publications, as will be the interesting nonparallel changes of ϕ and τ_F as a function of solvent polarity and structure. It should be mentioned that the strong decrease of ϕ (**2**) in the very polar regime limits the usefulness of **2** as a visual polarity probe in very polar media, where **1** seems to have superior properties despite its slightly lower sensitivity.

As pointed out in the introduction an estimate of the dipole moment (p^*) of the emissive state for molecules like **1** and **2** can be obtained from the slope of the plots shown in Figure 4 by application of eq 1. If $\rho = 6 \pm 0.2$ Å is assumed for both **1** and **2** (i.e., 40% of the long axis (15 ± 0.5 Å) of an ellipsoidal cavity in which the molecules fit) this procedure yields

$$p^* \text{ (1)} = 25.5 \pm 1.4 \text{ D}$$

$$p^* \text{ (2)} = 27.0 \pm 1.5 \text{ D}$$

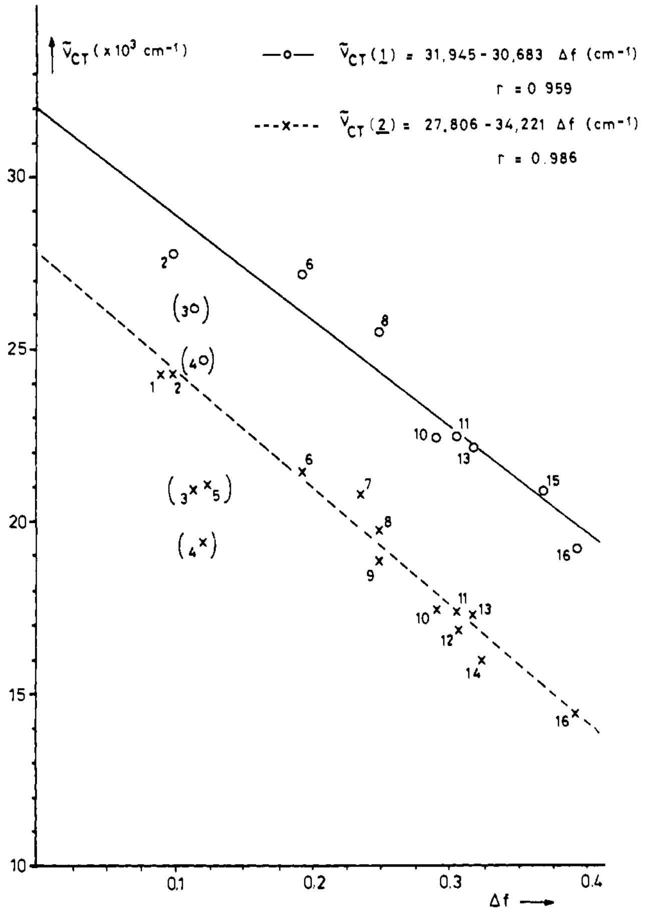

Figure 4. Correlation of $\tilde{\nu}_{ct}$ with Δf for **1** (−o−) and **2** (- - - x - - -). The numbering of the solvents is given in Table I. Data points between parentheses were not used in the calculation of the regression lines.

These very large values testify to the large degree of photoinduced charge separation which occurs in **1** and **2**. In view of the approximations made in the derivation of (1) it seemed highly desirable to verify these large p^* values by another, independent method. Such a method is in principle provided by time-resolved microwave conductivity measurements as recently shown by some of us.[18] The interpretation of these measurements does not rely upon an estimate of molecular solvation energies from macroscopic solvent properties nor does it require the implicit assumption that p^* is solvent independent. A knowledge of the rotational relaxation time of the solute molecules is, however, required for absolute determination of the dipole moment. The transient microwave conductivity changes observed on flash photolysis of solutions of compound **2** in cyclohexane, benzene, and dioxane are shown, plotted semilogarithmically, in Figure 5. (Very similar data were obtained for compound **1** in cyclohexane and dioxane.) For benzene and dioxane the data could be fitted very well with a reaction scheme based on the formation and decay of a single intermediate species with a lifetime of 12 ns in both solvents. This lifetime, which was used to calculate the solid line through the data points in Figure 5, is sufficiently close to the value of 15 ± 1 ns found for the decay of the fluorescence in these solvents (see Table I) to be able to definitely assign the intermediate in the conductivity experiments to the emissive state of the solute.

For the cyclohexane solution, the initial decay of the conductivity transient was too rapid to be able to obtain a definite measure of the lifetime of the intermediate. Only a upper limit of 5 ns could be determined in agreement with the rapid fluorescence decay, $\tau_F = 1.2$ ns, in this solvent. In contrast to the data for benzene and dioxane, the transient in cyclohexane clearly displayed a small, more slowly decaying "tail" as can be seen in Figure 5. The lifetime of this slow component was approximately 20 ns. Since no corresponding delayed decay of the fluorescence is found, it is thought that the slow conductivity component may be due to the formation of a dipolar triplet state with the short lifetime possibly indicating a twisted configuration[19] about the ethylenic

---

[18] Haas, M. P. de; Warman, J. M. *Chem. Phys.* **1982**, *73*, 35–53.

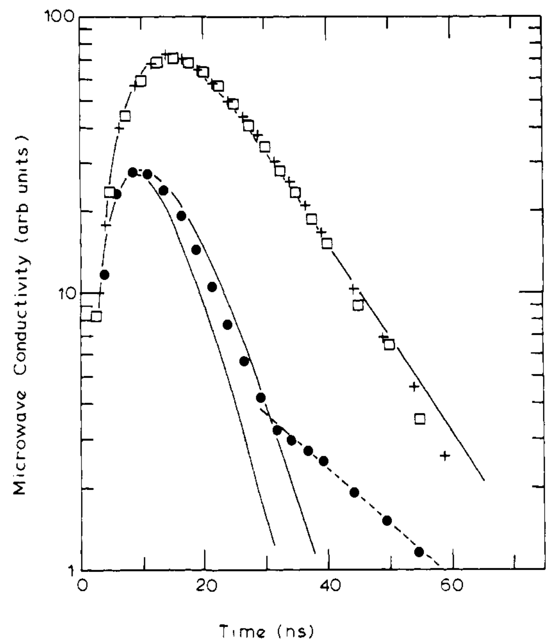

Figure 5. Semilogarithmic plots of the microwave conductivity transients in flash-photolized, degassed solutions of compound **2** in cyclohexane (●), benzene (□), and dioxane (+). The solid lines were calculated for lifetimes of 1, 5, and 12 ns, taking into account the pulse shape and system response function. The dashed line corresponds to a lifetime of 22 ns. In all cases the rise of conductivity follows the instrument response function.

double bond. An additional show component (~20 ns) was also observed during the microwave conductivity measurements for **1** in cyclohexane. In this case, however, the fluorescence decay (cf. Table I) also displays such a slow component. The latter is tentatively attributed to delayed fluorescence via thermal equilibration between a dipolar (twisted) triplet and the emissive CT singlet state.

The absolute magnitude of the conductivity signal, $\Delta\sigma$, for the case of a single transient product of photolysis is given by

$$\Delta\sigma(t) = eN^*(t)\Delta M^* \qquad (3)$$

In (3), $N^*(t)$ is the concentration of the product, e is the electronic charge, and ΔM^* is the difference between the rotational charge mobility of the product, M^*, and of a ground-state molecule, M^0, with M being given in general by

$$M = \frac{(\epsilon + 2)^2 p^2}{27ek_BT\,\tau_r} f(\omega\tau_r) \quad \text{m}^2\ \text{V}^{-1}\ \text{s}^{-1} \qquad (4)$$

In (4), ϵ is the relative dielectric constant of the solvent, k_B is the Boltzmann constant, T the absolute temperature, p and τ_r the dipole moment and rotational relaxation time of the species, and ω is the radian frequency of the microwaves. The function $f(\omega\tau_r)$ is equal to $(\omega\tau_r)^2/(1 + (\omega\tau_r)^2)$ for a single, Debye-type relaxation of the dipole and in general tends to unity as the rotational relaxation time increases. If the lifetime of the product and the total light flux are known $N^*(t)$ can be calculated and hence ΔM^* can be derived from the absolute magnitude of $\Delta\sigma(t)$. The values obtained are listed in Table II.

In order to obtain an estimate of the dipole moment of the product a value of the rotational relaxation time is required. In the absence of a direct measurement resort has to be made to an estimate based on a known value of τ_r for a molecule of similar geometry and size. For compounds **1** and **2** (dimethylamino)-nitrostilbene for which $\tau_r = 330\eta$ ps[19] (η = viscosity in cP) provides a reasonable comparison. Taking the rotation time for molecules of similar geometry to be proportional, to a first approximation, to the sum of the atomic volumes[20] one derives values of $\tau_r = 412\eta$ and 432η ps for compounds **1** and **2**, respectively. In the solvents employed (benzene $\eta = 0.65$, cyclohexane $\eta = 1.02$, and dioxane $\eta = 1.45$) the τ_r values thus range between 300 and 600 ps.

Table II. Lifetimes and Dipole Moments of the Relaxed S_1 State of Compounds **1** and **2** As Determined from Time-Resolved Microwave Conductivity Measurements

compd	solvent	τ, ns	$10^9 \times \Delta M^*$, $\text{m}^2\ \text{V}^{-1}\ \text{s}^{-1}$	p^*,[c] D
1	cyclohexane	3.7[a]	11.4	21
	1,4-dioxane	6[b]	14.5	27
2	cyclohexane	1.2[a]	22.8	31
	benzene	12[b]	23.1	24
	1,4-dioxane	12[b]	12.0	25

[a] Fluorescence lifetime (see Table I). [b] From kinetic fits to microwave transients. [c] Based on $\tau_r = 412\eta$ and 432η ps for **1** and **2**, respectively.

For values of τ_r in excess of 70 ps, which is amply satisfied in the present case, the function $f(\omega\tau_r)$ is within 5% of unity and the dipole moment of the product can be derived from

$$[p^*]^2\left\{1 - \frac{[p^0]^2}{[p^*]^2}\right\} = \frac{27ek_BT}{(\epsilon_r + 2)^2}\tau_r\Delta M^* \qquad (5)$$

Since in **1** and **2** the chromophoric groups are uncoupled and in **2** the individual chromophore dipoles are actually opposed, the dipole moment of the ground-state molecules are expected to be approximately equal to or less than that of dimethylaniline (1.6 D[21]). The value of p^0 can therefore be neglected in deriving values of p^* since the square root of the right-hand side of (5) is found to be greater than 500 (D),[2] giving $[p^0]^2/[p^*]^2 < 0.005$. The values of the dipole moment of the upper singlet states of compounds **1** and **2** obtained are listed in Table II.

Taking into account the experimental uncertainties which result from the short excited-state lifetime of **1** and especially **2** in cyclohexane, it would appear reasonable to conclude from the microwave measurements that the dipole moments of the S_1 states of compounds **1** and **2** are independent of solvent and equal to 25 ± 2 D. This is in very good agreement with the dipole moments estimated from the fluorescence solvatochromism. Such a dipole moment corresponds to full charge separation over a distance of approximately 5 Å. This is to be compared with the distance of only approximately 6 Å between the amino nitrogen atom (donor) and the center of the naphthalene (acceptor) moiety, indicating, therefore, almost complete electron transfer on excitation. This also provides evidence that the stretched rod-like shape of the ground-state molecules is retained in the emissive excited state.

Experimental Section

Measurements. Electronic absorption and corrected emission spectra were recorded on Cary 17D and Spex-Fluorolog instruments, respectively. The samples were contained in 1-cm rectangular-fused silica cells. Samples for emission spectroscopy were diluted to A (1 cm) ≤0.2 at the wavelength of excitation (290 nm for **1** and 310 nm for **2**) and were deoxygenated by purging with argon. Quantum yields were determined relative to 9,10-diphenylanthracene (ϕ = 1 in cyclohexane[17]), using the same excitation wavelengths. All emission spectra were corrected to represent relative intensities in a quanta per wavelength interval on a linear wavelength scale, followed by electronic integration of the total emission intensity. For measurement of fluoroescence lifetimes excitation by a nitrogen laser (337 nm) was employed (Lambda Physik EMG101 filled with N_2, fwhm 8 ns). The fluorescence was detected at right angles to the laser beam with a RCA C-31025C GaAs photomultiplier via a Zeiss M4QIII monochromator. The transients were digitized by a Biomation 6500 transient digitizer and fed to a Tandy TRS-80 Model III microcomputer. The lifetimes were obtained by comparing the decays with convoluted decays with known lifetimes. The very short fluorescence lifetimes of **1** and especially **2** in cyclohexane were measured more ac-

---

(19) Kawski, A.; Kaminski, J.; Kukielski, J. *Z. Naturforsch.* **1979**, *349*, 702-707.

(20) Gavezzotti, A. *J. Am. Chem. Soc.* **1983**, *105*, 5220-5225.

(21) McClellan, A. L. "Tables of Experimental Dipole Moments"; Rahara Enterprises: El Cerrito, CA, 1974; Vol. 2.

curately via a pulse radiolysis technique.[22]

The time-resolved microwave conductivity measurements were carried out by using the same cell design and microwave circuitry reported previously.[18] The solutions, of absorbance at approximately unity, were flash photolyzed at 308 nm by using 10-ns fwhm pulses from a Lambda Physik EMG100 excimer laser with a total incident energy flux per pulse of 6.9 mJ/cm^2 (determined by using (dimethylamino)nitrostilbene[18] as a secondary actinometer). The response time of detection, controlled mainly by the microwave cavity, was 4 ns. The transient changes in detector output were recorded by using a Tektronix-7912 transient digitizer. Calculated fits to the conductivity transients included corrections for the system response function, the shape of the laser pulse, and the geometrical distribution of products in the cell as described previously.[18]

Materials. Spectrograde solvents were obtained from Merck and used without further purification. Compounds **1** and **2** were both synthesized by a Wittig-type condensation from 1-phenyl-4-piperidone (**3**), which was prepared as described previously.[23,24]

1-Phenyl-4-(2-naphthylmethylene)piperidine (1). A solution of triphenyl-2-naphthylphosphonium bromide (41 mmol, prepared from reaction of triphenylphosphine and 2-(bromomethyl)naphthalene (Aldrich)) in 200 mL of tetrahydrofuran was stirred under dry nitrogen and cooled to −60 °C. Of *n*-Butyllithium, 1 equiv (16.3 mL of a 1.6-M solution in *n*-hexane) was slowly added. After 15 min the reaction mixture was warmed to room temperature and **3** (27 mmol) was added. Stirring at room temperature was continued for 60 h, followed by removal of the solvent in vacuo. To the residue 150 mL of HCl (20%) and 300 mL of ether were added. The acid layer were separated and extracted 8 times with ether, made alkaline (pH 13) with NaOH, and again extracted with ether. The latter extracts were dried on $MgSO_4$ and concentrated in vacuo. The residue was purified by chromatography over a short silica column by using ethyl acetate/p.a. 60–80 (1:10 v/v) as eluent, followed by recrystallization from a *n*-pentane/ether mixture: yield, 7.4%, white crystals; mp 87–89 °C; UV (cyclohexane) 249 nm (ϵ 53 000 M^{-1} cm^{-1}), 279 (14 000 M^{-1} cm^{-1}), 288 (13 800 M^{-1} cm^{-1}); ^1H NMR (250 MHz, $CDCl_3$) δ 6.8–7.8 (m, 12 H), 6.5 (s, 1 H), 3.4 (t, 2 H), 3.3 (t, 2 H), 2.7 (t, 2 H), 2.55 (t, 2 H); high-resolution mass spectrum, *m/z* 299.16738. Anal. Calcd for $C_{22}H_{21}N$: 299.1674.

1-Phenyl-4-(4-cyano-1-naphthylmethylene)piperidine (2). Triphenyl-1-(4-cyano)naphthylphosphonium bromide (**4**) was prepared from triphenylphosphine and 4-(bromomethyl)-1-naphthonitrile[25] in refluxing toluene (yield ~90%). A solution of **4** (4.3 mmol) in 3 mL of methanol was poured in 10 mL of aqueous 1 N NaOH. The yellow ylide which precipitated from the solution was separated by immediate extraction with 75 mL of benzene. The benzene extract was washed twice with ice–water, dried on magnesium sulfate, and concentrated in vacuo to about 30 mL. The ketone **3** (4.29 mmol) was then added, and the reaction mixture was refluxed under a nitrogen atmosphere for 28 h. The reaction mixture was transferred into a separating funnel, diluted with benzene (50 mL), washed with water (3 × 20 mL), dried on magnesium sulfate, and concentrated in vacuo. The residue was dissolved in warm ethanol/water (10:1 v/v) from which, after treatment with activated carbon and filtration, **2** crystallized in light yellow needles. The product was purified by repeated crystallization from ethanol: yield, 5%; mp 124–125 °C; UV (cyclohexane) 234 nm (ϵ 52 000 M^{-1} cm^{-1}), 308 (12 000 M^{-1} cm^{-1}); ^1H NMR (250 MHz, $CDCl_3$) δ 6.8–8.3 (m, 11 H), 6.7 (s, 1 H), 3.4 (t, 2 H), 3.2 (t, 2 H), 2.7 (t, 2 H), 2.4 (t, 2 H); high-resolution mass spectrum, *m/z* 324.1627. Anal. Calcd for $C_{23}H_{20}N_2O$: 324.1627.

Acknowledgment. The microwave conductivity experiments were carried out by using the laser facilities of the group of Dr. C. A. G. O. Varma at the University of Leiden with the help of Petra Weisenborn and Robert-Jan Visser for which we are very grateful. We thank L. H. Luthjens and H. C. de Leng for the measurement of the fluorescence lifetimes of 1 and 2 in cyclohexane. The asistance of Frank M. Niele in preparation and identification of compound 1 was of great help. The present investigation was supported, in part, by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).

Registry No. 1, 91759-51-2; **2**, 91759-52-3.

---

(22) Luthjens, L. H.; Haas, M. P. de; Leng, H. C. de; Hummel, A.; Beck, G. *Radiat. Phys. Chem.* **1982**, *19*, 121–123.

(23) Baty, J. D.; Jones, G.; Moore, C. *J. Chem. Soc. C* **1967**, 2645–2647.

(24) Gallagher, M. J.; Mann, F. G. *J. Chem. Soc.* **1962**, 5110–5120.

(25) McCullough, J. J.; MacInnis, W. K.; Lock, C. J. L.; Faggiani, R. *J. Am. Chem. Soc.* **1982**, *104*, 4644–4658.

Intramolecular Proton Exchange in 9-Hydroxyphenalen-1-one and Methyl-9-hydroxyphenalen-1-one

Kathryn L. Kunze and Jose R. de la Vega*

Contribution of the Chemistry Department, Villanova University, Villanova, Pennsylvania 19085.
Received April 10, 1984

Abstract: A recent ^{13}C NMR study indicates that the fast proton exchange in 9-hydroxyphenalen-1-one is not eliminated when the symmetry of the potential energy profile for the exchange is destroyed by adding a methyl group to form methyl-9-hydroxyphenalen-1-one. Ab initio SCF calculations on 9-hydroxyphenalen-1-one confirm the existence of two equivalent minimum-energy structures with an asymmetric hydrogen bridge. The interconversion between these two structures occurs through a symmetric (C_{2v}) intermediate which is 5.20 kcal/mol above the minimum-energy C_s structures. A 0.64-Å interminimal distance for the resulting double-minimum potential produces a gerade–ungerade splitting of 105.5 cm^{-1} for the hydrogen and 15.8 cm^{-1} for the deuterated species, in good agreement with the experimental results of a laser-excited fluorescence and fluorescence-excitation study. Calculations for methyl-9-hydroxyphenalen-1-one gave a 0.46-kcal/mol energy difference between the two tautomers, in agreement with fluorescence results. The change of the probability density of the proton as a function of time is used to calculate the maximum fraction of the proton that leaks through the barrier. We found that only one-third of the proton will leak to the other well, and this with the frequency increased to 165 cm^{-1}.

In an intramolecular proton exchange, if the initial and final structures are identical, the double-minimum potential for the exchange is symmetric and tunneling will occur whenever barrier and distance between minima are finite.[1-4] When a change in structure destroys the symmetry of the double-minimum potential, the proton will tunnel only if the barrier is low and the interminimal distance is small, or if the energy difference between the minima is very small.[5] This approach has been used to explain

---

(1) J. H. Busch and J. R. de la Vega, *J. Am. Chem. Soc.*, **99**, 2397 (1977).

(2) J. D. Swalen and J. A. Ibers, *J. Chem. Phys.*, **36**, 1914 (1962).

(3) M. C. Flanigan and J. R. de la Vega, *Chem. Phys. Lett.*, **21**, 521 (1973).

(4) J. R. de la Vega, *Acc. Chem. Res.*, **15**, 185 (1982).