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binary mixtures including the cmc's. Most needed, however, is clarification of the nature of the various microstructures in water-amphiphile mixtures because many features of the ternary mixtures are apparently already present in the oil-free mixtures and are merely amplified by adding oil.

**Acknowledgment.** M.K. is indebted to Dr. H. Reiss for stimulating discussions during a visit to the UCLA. We, furthermore,

acknowledge valuable contributions by Dr. D. Haase, Dr. R. Schomäcker, and K. V. Schubert. Last, but not least, we are indebted to J. Da Corte, A. Ellroth, B. Faulhaber, T. Lieu, and Th. Sottmann for their assistance with the experiments, and to D. Luckmann for drawing the figures. The work was in part supported by the German Ministry for Research and Technology (BMFT) (Grant No. 0326315 B), and by a NATO travel grant (No. 0425/88).

## ARTICLES

### Intramolecular Charge Transfer in Donor-Acceptor Molecules

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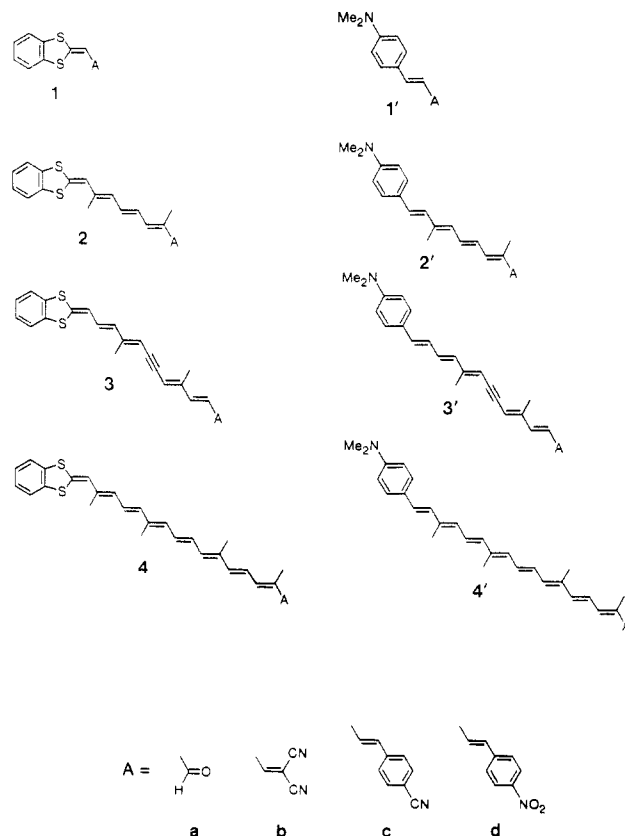
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The photophysical properties of donor-acceptor molecules, "push-pull" polyenes and carotenoids, have been studied by absorption and fluorescence spectroscopy. The compounds bear various acceptor and donor groups, linked together by chains of different length and structure. The position of the absorption and fluorescence maxima and their variation in solvents of increasing polarity are in agreement with long-distance intramolecular charge-transfer processes, the linker acting as a molecular wire. The effects of the linker length and structure and of the nature of acceptor and donor are presented.

#### Introduction

Modification and functionalization of natural carotenoids<sup>1</sup> is an efficient way for molecular engineering of polyenic chains, yielding synthetic molecules of interest in the field of molecular electronics.<sup>2,3</sup> Symmetrically substituted bipyridinium carotenoids, the caroviologens, represent a molecular wire approach to electronic conduction.<sup>3</sup> Unsymmetrical substituted polyene chains bearing an anthryl group at one end and a tetraphenylporphyrin group at the other end display energy transfer between the two terminal units.<sup>4</sup> The anchoring of a carotenoid chain to a porphyrin linked to a quinone group leads to biomimetic systems, of triad type, that undergo long-lived photodriven charge separation, of potential value for photochemical energy storage.<sup>5</sup> On the other hand, very fast charge-transfer processes are of interest as potential molecular devices, for long-distance signal processing and transfer.<sup>6</sup> This may be achieved by "push-pull" carotenoids, obtained by anchoring of the electron donor and acceptor at the opposite terminal ends of the polyenic chain.<sup>7</sup> These compounds should present interesting photophysical properties and undergo (partial) intramolecular charge transfer upon excitation. Such phenomena

CHART I



(1) *Carotenoids*; Isler, O., Ed.; Birkhäuser Verlag: Basel, Switzerland, 1971.

(2) (a) Haddon, R. C.; Lamola, A. A. *Proc. Natl. Acad. Sci. U.S.A.* **1985**, *82*, 1874. (b) Munn, R. W. *Chem. Br.* **1984**, 518.

(3) Arrhenius, T. S.; Blanchard-Desce, M.; Dvornitzky, M.; Lehn, J.-M.; Malthête, J. *Proc. Natl. Acad. Sci. U.S.A.* **1986**, *83*, 5355.

(4) Effenberger, F.; Schlosser, M.; Bäckerle, P.; Maier, S.; Port, H.; Wolf, H. C. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 281.

(5) (a) Moore, T. A.; Gust, D.; Mathis, P.; Mialocq, J. C.; Chachaty, C.; Bensasson, R. V.; Land, E. J.; Doizi, D.; Liddell, P. A.; Nemeth, G. A.; Moore, A. L. *Nature* **1984**, *307*, 630. (b) Seta, P.; Bienvenue, E.; Moore, A. L.; Mathis, P.; Bensasson, R. V.; Liddell, P.; Pessiki, P. J.; Joy, A.; Moore, T. A.; Gust, D. *Nature* **1985**, *316*, 653. (c) Gust, D.; Moore, T. A.; Moore, A. L.; Barrett, A.; Harding, L. O.; Makings, L. R.; Lidell, P. A.; De Schryver, F. C.; Van der Auweraer, M.; Bensasson, R. F.; Rongée, M. *J. Am. Chem. Soc.* **1988**, *110*, 321.

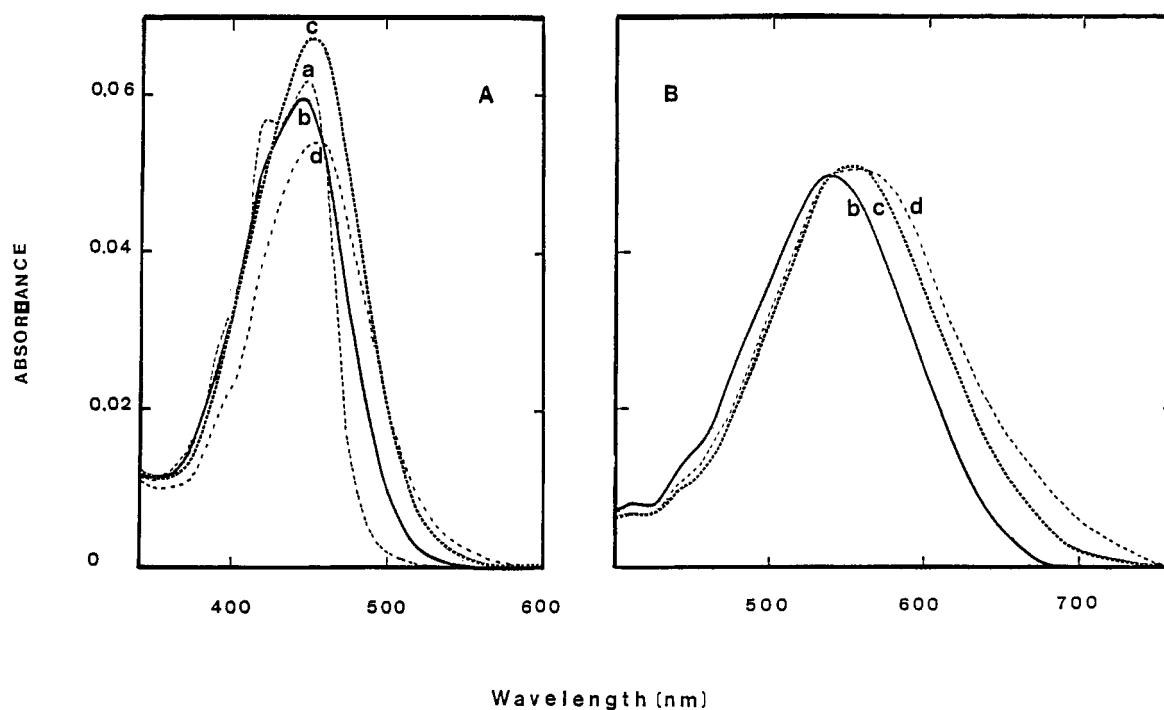
(6) Lehn, J.-M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 107.

(7) Blanchard-Desce, M.; Ledoux, I.; Lehn, J.-M.; Malthête, J.; Zyss, J. *J. Chem. Soc., Chem. Commun.* **1988**, 736.

have been observed in a number of donor-acceptor conjugated molecules like push-pull benzenes (with *p*-nitroaniline as a prototype),<sup>8,9</sup> stilbenes,<sup>9,10</sup> biphenyls,<sup>9,11,12</sup> polyphenyls,<sup>9</sup> and more

TABLE I: Spectroscopic Data for the Aldehyde Series 1a–4a<sup>a</sup>

compound	solvent	$\lambda_{\text{max}}$ , nm absorption	log $\epsilon$	$\lambda_{\text{max}}$ , nm		$\Phi$
				excitation	emission	
1a	cyclohexane	356	4.15	355, 373	(406) 428	$2.7 \times 10^{-4}$
	THF	360	4.22		(409) 436	$1.0 \times 10^{-4}$
	CH <sub>2</sub> Cl <sub>2</sub>	373	4.27	360, 390	438 (455)	$2.1 \times 10^{-4}$
	DMSO	374	4.26	363, 390	437 (457)	$2.5 \times 10^{-4}$
	CHCl <sub>3</sub>	372	4.23			
	ethanol	370	4.25			
2a	cyclohexane	441	4.70	425, 450	598	$1.3 \times 10^{-4}$
	THF	446	4.69		643	$1.6 \times 10^{-4}$
	CH <sub>2</sub> Cl <sub>2</sub>	451	4.79	462	673 (710)	$1.6 \times 10^{-4}$
	DMSO	455	4.64	465	672 (725)	$4.6 \times 10^{-4}$
	CHCl <sub>3</sub>	456	4.66			
	ethanol	450	4.60		671 (720)	$1.7 \times 10^{-3}$
3a	cyclohexane	430			613	$2.4 \times 10^{-3}$
	THF	450	4.76	460	682 (716)	$6.3 \times 10^{-3}$
	CH <sub>2</sub> Cl <sub>2</sub>	459	4.70	467	(684) 747	$8.9 \times 10^{-3}$
	DMSO	462	4.66	470	784	$1.6 \times 10^{-2}$
	CHCl <sub>3</sub>	466	4.67			
	ethanol	452	4.69		(680) 775	$3 \times 10^{-3}$
4a	cyclohexane	483	4.77	478, 515	607 (678)	$4 \times 10^{-5}$
	THF	492	4.94		619 (755)	$5 \times 10^{-5}$
	CH <sub>2</sub> Cl <sub>2</sub>	496	4.85	535	634 (760)	$1 \times 10^{-4}$
	DMSO	506	4.89			
	CHCl <sub>3</sub>	500	4.88			
	ethanol	488				

<sup>a</sup>The numbers in parentheses represent shoulders.**Figure 1.** Absorption spectra of **2a** and **2b** in various solvents: (A) [**2a**] = 1.2  $\mu\text{M}$ , (B) [**2b**] = 0.87  $\mu\text{M}$ ; (a) cyclohexane, (b) THF, (c) CH<sub>2</sub>Cl<sub>2</sub>, (d) DMSO.

recently oligoacetylenes.<sup>13</sup> Moreover, push–pull polyenes should also display electrochromic,<sup>14</sup> semiconducting,<sup>15</sup> or nonlinear optical properties.<sup>7,16</sup> They may be probes for membrane po-

tentials<sup>17</sup> or micropolarity<sup>18</sup> and present analogies with the visual pigment retinal in rhodopsin.<sup>19</sup>

This work reports the photophysical properties of two series of push–pull polyenes of various length 1–4, and 1'–4' bearing different donor and acceptor terminal groups (Chart I). Evidence for long-distance intramolecular charge transfer (ICT) is pres-

(8) Jaffé, H. H.; Orchin, M. *Theory and Applications of Ultraviolet Spectroscopy*; Wiley: New York, 1962; p 260.

(9) Berry, R. W. H.; Brocklehurst, P.; Burawoy, A. *Tetrahedron* **1960**, *10*, 109.

(10) Splitter, J. S.; Calvin, M. *J. Org. Chem.* **1955**, *20*, 1086.

(11) Sherwood, D. W.; Calvin, M. *J. Am. Chem. Soc.* **1942**, *64*, 1350.

(12) Effenberger, F.; Agster, W.; Fischer, P.; Jogun, K. H.; Stezowski, J. J.; Daltrozzi, E.; Kollmansberger-von Nell, G. *J. Org. Chem.* **1983**, *48*, 4649.

(13) Stiegman, A. E.; Miskowski, V. M.; Perry, J. W.; Coulter, D. R. *J. Am. Chem. Soc.* **1987**, *109*, 5884.

(14) Platt, J. R. *J. Chem. Phys.* **1961**, *34*, 862.

(15) Simon, J.; André, J.-J. *Molecular Semiconductors*; Springer-Verlag: Berlin, 1985.

(16) *Non-linear Optical Properties of Organic Molecules and Crystals*; Chems, D. S., Zyss, J., Eds.; Academic Press: Orlando, FL, 1987.

(17) Loew, L. M. *J. Biochem. Biophys. Methods* **1982**, *6*, 243.

(18) Schanze, K. S.; Schin, D. M.; Whitten, D. G. *J. Am. Chem. Soc.* **1985**, *107*, 507.

(19) (a) Honig, B.; Ebrey, T. *Annu. Rev. Biophys. Bioeng.* **1974**, *3*, 151.

(b) Honig, B.; Warshel, A.; Karplus, M. *Acc. Chem. Res.* **1975**, *8*, 92.

(c) Stoekenius, W. *Ibid.* **1980**, *13*, 337. (d) Liu, R. S. H.; Browne, D. T. *Ibid.* **1986**, *19*, 42.

TABLE II: Spectroscopic Data for the Dicyano Series 1b-4b

compound	solvent	$\lambda_{\max}$ , nm absorption	log $\epsilon$	$\lambda_{\max}$ , nm		$\Phi$
				excitation	emission	
1b	THF	442	4.63		500	$1.0 \times 10^{-4}$
	CCl <sub>4</sub>	434	4.66			
	acetone	442	4.63			
	CH <sub>2</sub> Cl <sub>2</sub>	448		450, 478	507	$1.1 \times 10^{-4}$
	DMSO	456	4.61	470	517	$2.5 \times 10^{-4}$
2b	CHCl <sub>3</sub>	446	4.66			
	THF	538	4.70			
	CH <sub>2</sub> Cl <sub>2</sub>	555			800	$1.6 \times 10^{-4}$
	DMSO	558	4.63	560	800	$2.6 \times 10^{-4}$
	dioxane	532	4.61			
3b	THF	520	4.66			
	CH <sub>2</sub> Cl <sub>2</sub>	532		480, 560	640, 800	$7.0 \times 10^{-4}$
	DMSO	526	4.41			
4b	dioxane	522	4.70			
	THF	560	4.73			
	CH <sub>2</sub> Cl <sub>2</sub>	581			625 (673)	$1 \times 10^{-5}$
	DMSO	582	4.79			
	dioxane	568	4.82			

TABLE III: Spectroscopic Data for the Cyano Series 1c-3c

compound	solvent	$\lambda_{\max}$ , nm absorption	log $\epsilon$	$\lambda_{\max}$ , nm		$\Phi$
				excitation	emission	
1c	cyclohexane	401		400	456	$5 \times 10^{-4}$
	THF	404	4.60	397, 418	492	$6 \times 10^{-4}$
	CH <sub>2</sub> Cl <sub>2</sub>	408		408	498	$6 \times 10^{-4}$
	DMSO	409	4.54	410	530	$1.7 \times 10^{-3}$
	CHCl <sub>3</sub>	410	4.58			
2c	cyclohexane			460	622	$5 \times 10^{-4}$
	THF	455	4.80		655	$5 \times 10^{-4}$
	CH <sub>2</sub> Cl <sub>2</sub>	462		465	(678) 761	$1.1 \times 10^{-3}$
	DMSO	466	4.79		(677) 790	$1.3 \times 10^{-3}$
	dioxane	458	4.54			
3c	cyclohexane				610	$1.3 \times 10^{-3}$
	THF	450	4.92	458	650 (702)	$3.7 \times 10^{-3}$
	CH <sub>2</sub> Cl <sub>2</sub>	456		462	665 (718)	$4.6 \times 10^{-3}$
	DMSO	458	4.81	469	(683) 770	$1.2 \times 10^{-2}$
	dioxane	452	4.90			

TABLE IV: Spectroscopic Data for the Nitro Series 1d-3d

compound	solvent	$\lambda_{\max}$ , nm absorption	log $\epsilon$	$\lambda_{\max}$ , nm		$\Phi$
				excitation	emission	
1d	cyclohexane	436			529	$3.8 \times 10^{-3}$
	THF	442	4.47	428, 451	650	$2.3 \times 10^{-1}$
	CH <sub>2</sub> Cl <sub>2</sub>	450		430, 457	(684) 737	$1.6 \times 10^{-1}$
	DMSO	455	4.40	425, 465	(684) 776	$2.7 \times 10^{-2}$
	CHCl <sub>3</sub>	452	4.40			
2d	cyclohexane	461		465	650 (708)	$1.5 \times 10^{-3}$
	THF	477	4.67		675, 747	$7 \times 10^{-4}$
	CH <sub>2</sub> Cl <sub>2</sub>	476		469	(670) 750	$6 \times 10^{-4}$
	DMSO	494	4.60		800	$4 \times 10^{-4}$
	ethanol	467				
3d	cyclohexane	457		457	620	$1.2 \times 10^{-3}$
	THF	460	4.84	460	787	$1.1 \times 10^{-3}$
	CH <sub>2</sub> Cl <sub>2</sub>	466			a	a
	DMSO	471	4.68		a	a
	CHCl <sub>3</sub>	467	4.88			

<sup>a</sup> No distinct peak.

ented, assessing the "molecular wire" properties of the conjugated chain. The effects of the donor and acceptor character and of the polyenic linker length and structure, as well as of the solvent on the charge transfer, are investigated.

## Results and Discussion

**General Photophysical Features. Absorption Spectra.** The spectral features of the benzodithia 1-4 and dimethylamino 1'-4' compounds are collected in Tables I-VI. Their absorption spectra exhibit a broad and intense band in the visible whose maximum is highly solvent-sensitive. The main absorption bands present bathochromic shifts and broadening of the half bandwidth with increasing solvent polarity. The sensitivity of the absorption to

solvent polarity depends both on the acceptor and on the linker length for a given donor as detailed below. An example is shown in Figure 1 for molecules 2a and 2b.

The variations of the absorption energy of compounds 1-4 and 1'-4' with solvent polarity have been studied with use of mainly aprotic solvents (Tables I-VI). The solvatochromism can be quantitatively measured with polarity scales.<sup>20-22</sup> The data have

(20) Dimroth, K.; Reichart, C.; Siepmann, T.; Bohlmann, F. *Annalen* **1963**, 661, 1.

(21) Kosower, E. M. *J. Am. Chem. Soc.* **1958**, 80, 3253.

(22) Kamlet, M. J.; Abboud, J.-L.; Abraham, M. H.; Taft, R. W. *J. Am. Chem. Soc.* **1977**, 99, 6027.

TABLE V: Spectroscopic Data for the Aldehyde Series 1a'-4a'

compound	solvent	$\lambda_{\max}$ , nm absorption	log $\epsilon$	$\lambda_{\max}$ , nm		$\Phi$
				excitation	emission	
1a'	cyclohexane	356	4.53			
	THF	374	4.51			
	CH <sub>2</sub> Cl <sub>2</sub>	384	4.53			
	CHCl <sub>3</sub>	384	4.48			
	DMSO	387	4.48			
2a'	cyclohexane	430				
	THF	436	4.65	441	670 (700)	$2.7 \times 10^{-3}$
	CH <sub>2</sub> Cl <sub>2</sub>	444	4.67	449, 467	682, 727	$4.6 \times 10^{-3}$
	CHCl <sub>3</sub>	450	4.66			
	DMSO	455	4.69	452, 466	689, 766	$8.7 \times 10^{-3}$
3a'	ethanol	438			(680) 775	$3.3 \times 10^{-3}$
	cyclohexane	448				
	THF	450	4.74			
	CH <sub>2</sub> Cl <sub>2</sub>	456	4.63	468	(691) 788	$1.7 \times 10^{-2}$
	CHCl <sub>3</sub>	461	4.73			
4a'	DMSO	464	4.68			
	cyclohexane	484				
	THF	492	4.99			
	CH <sub>2</sub> Cl <sub>2</sub>	498	4.96		660 (800)	$5 \times 10^{-5}$
	CHCl <sub>3</sub>	498	4.92			
	DMSO	496				

TABLE VI: Spectroscopic Data for the Dicyano Series 2b'-4b'

compound	solvent	$\lambda_{\max}$ , nm absorption	log $\epsilon$	$\lambda_{\max}$ , nm		$\Phi$
				excitation	emission	
2b'	THF	540	4.74			
	CH <sub>2</sub> Cl <sub>2</sub>	548	4.76	550	800	$3 \times 10^{-4}$
	CHCl <sub>3</sub>	560	4.74			
	DMSO	560	4.64			
3b'	THF	520	4.72			
	CH <sub>2</sub> Cl <sub>2</sub>	531	4.70			
	CHCl <sub>3</sub>	538	4.68			
	DMSO	528	4.57			
1b'	THF	564	4.88			
	CH <sub>2</sub> Cl <sub>2</sub>	578	4.86			
	CHCl <sub>3</sub>	588	4.86			
	DMSO	576	4.79			

been successfully fitted to the  $\pi^*$  empirical solvent polarity-polarizability index,<sup>22,23</sup> except for compounds of series b', perhaps due to specific solvent effects (Table VII). An example of the fit to the Taft  $\pi^*$  scale of solvent polarities is shown in Figure 2 for series a. The linearity of the plot of the transition energy  $E$  (absorption or fluorescence) versus  $\pi^*$  allows the determination of  $E_0$  (i.e., extrapolated to cyclohexane) and of the slope  $s$ , which reflects the sensitivity to solvent polarity. All the  $s$  values obtained are negative, which is consistent with a positive solvatochromism.

**Fluorescence Spectra.** The fluorescence spectra of the benzodithia compounds 1-4 are broad and the fluorescence yields are low ( $10^{-2}$ - $10^{-5}$ ). Similar low fluorescence yields have been reported for short benzodithia derivatives.<sup>24</sup> The fluorescence spectra of some of these compounds are wavelength-dependent, as depicted in Figure 3 for 3d in THF. The emission spectrum obtained when the excitation wavelength is set at the maximum of the absorption spectrum, 460 nm, is broad, and contains two peaks at 680 and 780 nm with a distinct shoulder at 570 nm. Therefore, excitation spectra recorded at various emission wavelengths have led to the "decoupling" of two fluorescence bands (Figure 3A), although the two excitation spectra overlap (Figure 3B). The first fluorescence is peaking at 680 and 780 nm; its excitation maximum is found at 470 nm, which fits the main visible absorption peak. This fluorescence will be called *band B*. The other fluorescence maximum lies at higher energy, i.e., 570 nm, and its excitation peak is at 400 nm; it will be called *band A*.

The presence of two fluorescence bands is a common feature of the benzodithia-substituted compounds, but the decoupling

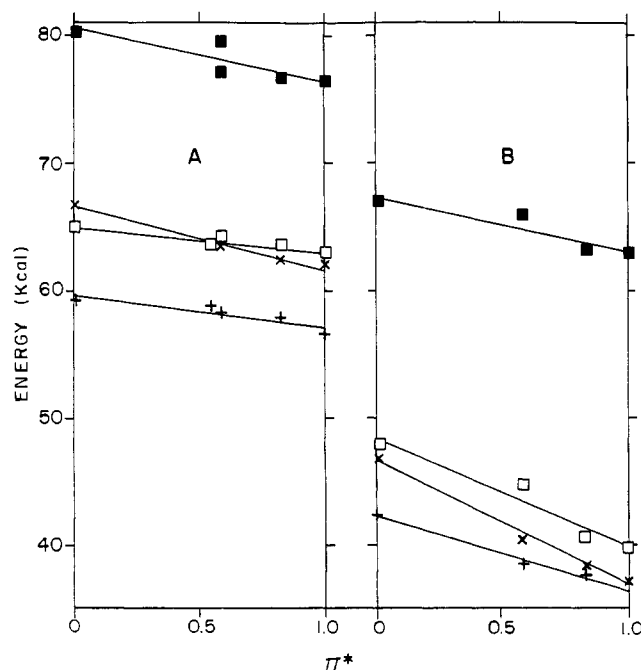
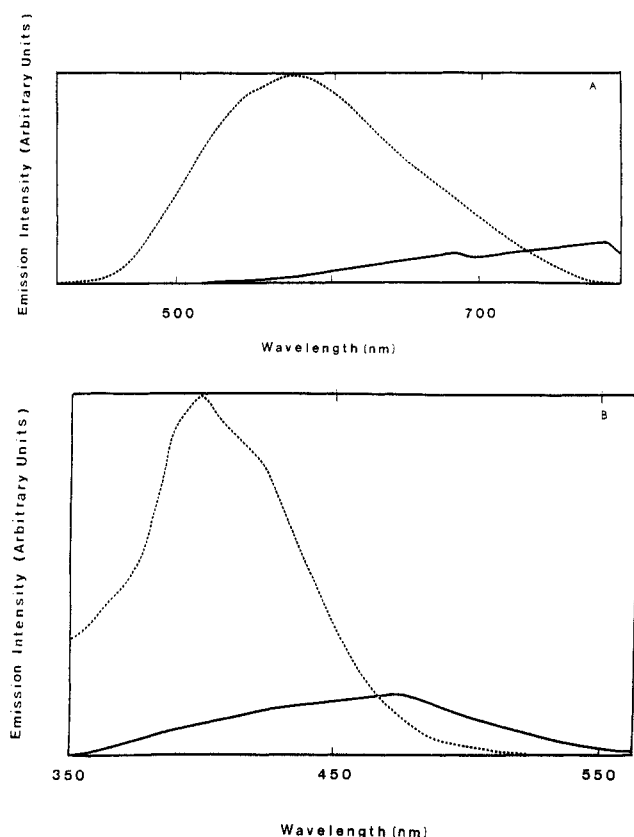


Figure 2. Correlation of absorption (A) and emission energy (B) maxima to Taft  $\pi^*$  values of solvent polarity.<sup>22,23</sup> The energy maxima in different solvents are listed in Table I, and the parameters of the fit to  $\pi^*$  index are in Table VII. Key: 1a (■), 2a (□), 3a (×), 4a (+).

between the two fluorescence bands is generally difficult to achieve at 20 °C. Such phenomenon cannot be accounted for by aggregation, in view of the linearity of both absorption and

(23) Kamlet, M. J.; Abboud, J.-L.; Abraham, R. W.; Taft, R. W. *J. Org. Chem.* **1983**, *48*, 2877.

(24) Le Beuze, A.; Botrel, A.; Samat, A.; Appriou, P.; Guglielmetti, R. *J. Chim. Phys.* **1978**, *75*, 255.



**Figure 3.** (A) Fluorescence spectrum of **3d**. The concentration was 2  $\mu\text{M}$  in THF solution. The fluorescence of band A, peaking at 561 nm, has been obtained by excitation at 400 nm (---). Band B emission (—), peaking at 787 nm, has been observed, when the excitation is monitored at 500 nm. The excitation and emission slits were of 2-nm width. (B) Excitation spectrum of **3d**. The excitation maximum of band A (---), using a 520-nm emission wavelength, is found at 400 nm. The band B excitation (—) obtained by monitoring the emission at 780 nm, is peaking at 470 nm, which corresponds to the absorption maximum in the visible. Same concentration, solvent, and slit conditions as in (A).

fluorescence with concentration in the range used (0.3–5  $\mu\text{M}$ ). NMR and IR data are consistent with an all-trans configuration. Therefore, these fluorescence bands may be attributed to different excited species. Band B fluorescence is highly dependent on solvent polarity (see below). Band A, the higher lying fluorescence, has a distinct excitation maximum, different from the peak of the absorption band. The results presented below will focus on band B fluorescence. It will be shown that the position and yield of this emission is dependent on the end groups and on the linker length and structure. The results, together with the finding that its excitation maximum overlaps with the absorption peak, are in agreement with an intramolecular charge-transfer (ICT) nature of band B, originating mainly from a  $\pi\pi^*$  state.

The fluorescence spectra of the dimethylamino **1'–4'** compounds present a normal behavior, without any marked excitation wavelength dependence, in the aprotic solvents investigated. The excitation maxima overlap with the absorption peaks. However, in the case of **2a'** in ethanol, a weak but noticeable wavelength dependence is observed. Since the fluorescence yield measured for the dimethylamino derivatives are higher than those observed for the benzodithia analogues bearing the same acceptor (except **4a'**), it cannot be excluded that another weak fluorescence is hidden underneath the observed emission band.

The position of the fluorescence bands, as well as the overlap of excitation and absorption maxima, agree with an ICT nature of this emission, which will be therefore discussed below, together with band B fluorescence of the benzodithia compounds.

The fluorescence maxima of both benzodithia (band B) and dimethylamino compounds are highly solvent-sensitive, which is typical of emissive charge-transfer states. A positive solvatochromism is observed for all the molecules studied as already

**TABLE VII: Correlation of the Solvatochromic Data to the Taft Scale<sup>a</sup>**

compound	absorption			fluorescence		
	$-s$	$E_0$	$r$	$-s$	$E_0$	$r$
<b>1a</b>	4.2	80.4	0.88	4.5	67.1	0.94
<b>2a</b>	2.1	64.8	0.90	8.7	48.2	0.97
<b>3a</b>	5.1	66.2	0.94	10.2	46.4	0.99
<b>4a</b>	2.7	59.5	0.93	6.0	42.0	0.97
<b>1b</b>	4.4	67.3	0.98	4.4	59.8	0.99
<b>2b</b>	5.5	56.4	0.95			
<b>3b</b>						
<b>4b</b>	3.8	52.7	0.88			
<b>1c</b>	1.6	71.3	0.90	8.1	62.9	0.98
<b>2c</b>	2.9	64.3	0.95	10.0	46.8	0.93
<b>3c</b>	2.3	64.7	0.95	9.4	46.8	0.99
<b>1d</b>	2.9	65.8	0.95	17.7	54.0	0.99
<b>2d</b>	3.7	62.4	0.89	4.1	40.6	0.94
<b>3d</b>	1.8	62.6	0.88			
<b>1a'</b>	6.9	80.2	0.99			
<b>2a'</b>	3.6	66.8	0.91	8.3	45.8	0.99
<b>3a'</b>	2.1	64.1	0.86			
<b>4a'</b>	1.8	59.0	0.94			

<sup>a</sup> $-s$  (kcal mol<sup>-1</sup>) is the slope of the plot, transition energy  $E$  vs  $\pi^*$  scale of solvent polarity.  $E_0$  (kcal mol<sup>-1</sup>) is the extrapolated energy to cyclohexane.  $r$  is the correlation coefficient.

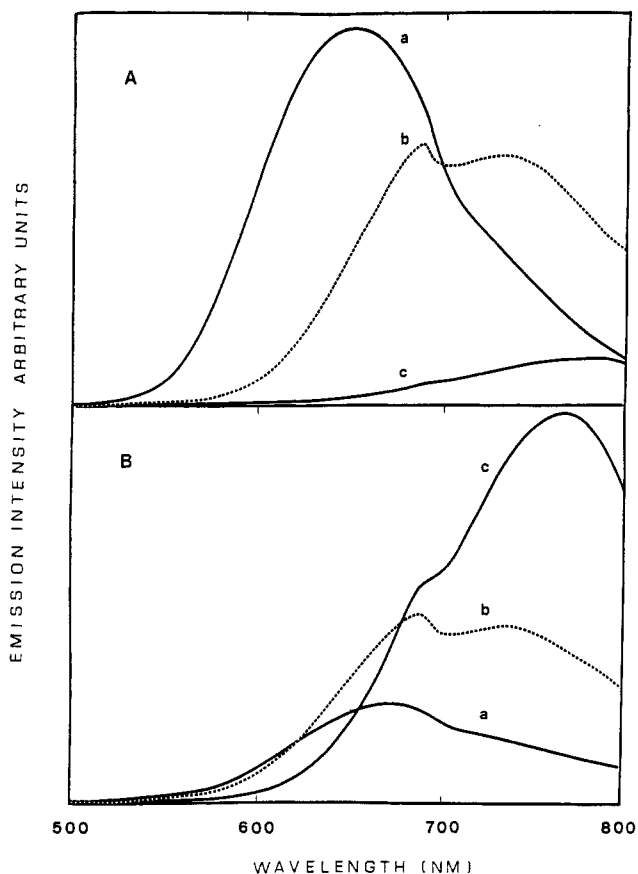
**TABLE VIII: Spectroscopic Data for Band A Fluorescence**

compound	solvent	$\lambda_{\text{max}}$ , nm		$\Phi$
		excitation	emission	
<b>2a</b>	THF		525	
	CH <sub>2</sub> Cl <sub>2</sub>		533	
	DMSO	390, 416	544	
<b>3a</b>	THF	400, 414	513, 550	
	CH <sub>2</sub> Cl <sub>2</sub>	400, 422	518, 556	
<b>4a</b>	cyclohexane	405, 430	523, 573	
<b>2c</b>	cyclohexane	381, 397	517	
	THF		566	
	CH <sub>2</sub> Cl <sub>2</sub>	400, 430	600	
	DMSO		614	
<b>3c</b>	cyclohexane	385	561	
	THF	402	578	
	CH <sub>2</sub> Cl	402	593	
	DMSO	402	643	
<b>2d</b>	CH <sub>2</sub> Cl <sub>2</sub>	395, 418	610	$4 \times 10^{-4}$
<b>3d</b>	THF	400	561	$7.0 \times 10^{-3}$
	CH <sub>2</sub> Cl <sub>2</sub>	403	596	$7.5 \times 10^{-3}$
	DMSO	403 (440)	627	$4.0 \times 10^{-3}$

mentioned for absorption. These data are consistent with a large increase in dipole moment in the excited state. The main difference between absorption and fluorescence data is the much larger sensitivity of the latter to solvent polarity. An increase of the Stokes shifts with solvent polarity, ranging between 4000 and 9000 cm<sup>-1</sup>, is generally observed. A parallel increase of the emission half bandwidth is found (4500–8000 cm<sup>-1</sup>). An example is depicted in parts A and B of Figure 4 for **1d** and **2a'**, respectively. The spectra present a distinct shoulder in a less polar solvent like THF, which becomes the major peak, substantially red-shifted in DMSO. The spectral shapes suggest the existence of species, whose fluorescence maximum and relative quantum yield depend on solvent polarity. This change in band shape is compatible with a cis-trans isomerization in the excited state as reported for 4-(dicyanomethylene)-2-methyl-6-[*p*-(dimethylamino)styryl]-4*H*-pyran (DCM), which undergoes cis-trans isomerization mainly in nonpolar solvents.<sup>25</sup>

The variations of the fluorescence energy of compounds **1–4** (band B) and **1'–4'** with solvent polarity have also been fitted to the  $\pi^*$  polarity scale (Table VII). An example is shown in Figure

(25) (a) Drake, J. M.; Lesiecki, M. L.; Camaioni, D. M.; *Chem. Phys. Lett.* **1985**, *113*, 530. (b) Preliminary results show that, subsequent to steady-state illumination with visible light in nonpolar solvents, a cis-trans isomerization is observed, indicated by the formation of the "cis band" in the absorption spectrum.



**Figure 4.** Fluorescence spectra in various solvents: (A) compound 1d, with excitation at 440 nm, (B) compound 2a' excitation at 450 nm; (a) THF, (b) dichloromethane, (c) DMSO. Slit width: 2 nm.

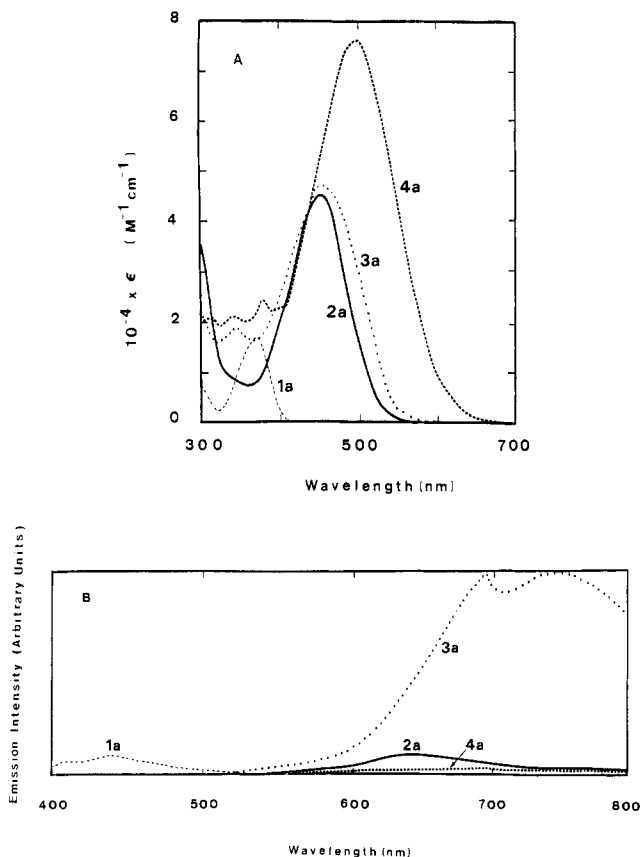
2 for series **a**. It should be emphasized that the fluorescence data used in the correlation include only the lowest lying peak or shoulder, which should correspond to the trans isomer.<sup>25a</sup> This  $-s$  values obtained for fluorescence are higher than for absorption as expected for the larger sensitivity of fluorescence to solvent polarity.

The data available on solvatochromism of band A fluorescence in the nitro, cyano, and aldehyde benzodithia derivatives (Table VIII), indicates a positive solvatochromism. Reasonable fits to the Taft  $\pi^*$  scale for compounds 2a, 2c, and 3c lead to the following  $E_0$  and  $-s$  values: 57.1, 4.5, 55.3 and 9.0, and 51.7 and 5.7 kcal mol<sup>-1</sup> for 2a, 2c, and 3c, respectively. Comparison of  $E_0$  and  $-s$  values for bands A and B shows that band A lies 5 kcal (3c) to 9 kcal (2c and 2a) above band B and is less polar than band B.

**Effect of Temperature.** The effect of the temperature on the fluorescence spectra has been investigated from -10 to +20 °C. A decrease in temperature causes an increase of the fluorescence yield by a factor of about 2 in this range, and the emission and excitation spectra are slightly red-shifted. The increase of the fluorescence yield is expected upon lowering the temperature, due to a decrease in the internal conversion rate. A very large increase of the fluorescence yield upon decreasing the temperature to 77 K has been reported for 1a' and attributed to a decrease of nonradiative emission, via a "free-rotor" mechanism and cis-trans isomerization.<sup>26</sup>

**Effect of Linker Length and Structure.** Since both the nature of the end groups and the length of the linker affect band B fluorescence, the effect of the linker size will be analyzed in a family of molecules possessing the same donor and acceptor.

**Effect of Linker Length. Absorption Spectra.** Each series presents a general bathochromic and hyperchromic shift of the absorption with increasing linker length. Additional conjugated



**Figure 5.** (A) Comparison of the absorption spectra of the aldehyde series compounds 1a, 2a, 3a, and 4a. Sample concentration used was 2.8 μM in chloroform. (B) Comparison of the fluorescence spectra of aldehyde series compounds 1a, 2a, 3a, and 4a. The absorbances were OD = 0.06 in dichloromethane at the excitation wavelength, which was set at 380, 440, 459, and 540 nm for 1a, 2a, 3a, and 4a, respectively. Excitation and emission slits: 2-nm width.

bonds induce smaller red shifts, as the length of the polyenic chain increases. These trends are shown in Figure 5A for the aldehyde series **a** in chloroform. The relative red shift observed between 1a and 2a and between 2a and 4a are 84 and 44 nm (4952 and 1930 cm<sup>-1</sup>). These bathochromic displacements are in agreement with an increased delocalization, due to a more extended conjugated  $\pi$  system. The relative red shift levels off at large molecular size as can be observed in Table VII from the comparison of the absorption energies  $E_0$ . Similar trends have been already reported for polyenes,<sup>27,28</sup> merocyanines,<sup>29,30</sup> and carotenoids.<sup>31</sup>

In the case of the benzodithia compounds (series **a-d**), no regular behavior is observed for the variation of  $-s$  with the linker length. Nevertheless a decrease of  $-s$  with increasing linker length can be noticed in the dimethylamino series **a'** (Table VII). A similar behavior has been reported for *p*-(dimethylamino)phenyl, *p*'-nitrophenyl substituted compounds, from zero to three double bonds.<sup>32</sup>

**Fluorescence Spectra.** The fluorescence spectra show, with increasing number of conjugated double bonds, a bathochromic displacement that is even more pronounced than in absorption (see Figure 5A,B for the aldehyde series **a**). The position of the fluorescence maxima exhibits a small leveling off with polyenic size; it parallels the behavior of the absorption band (see text above).

(27) Dahne, S.; Radeaglia, R. *Tetrahedron* **1971**, *27*, 3673.

(28) Fabian, J.; Hartmann, H. *Light Absorption of Organic Colorants*; Springer-Verlag: Berlin, 1980; p 25.

(29) Malhotra, S. S.; Whiting, M. C. *J. Chem. Soc.* **1960**, 3812.

(30) Fabian, J.; Hartmann, H. *Light Absorption of Organic Colorants*; Springer-Verlag: Berlin, 1980; p 193.

(31) (a) Vetter, W.; Englert, C.; Rigassi, N.; Schwieter, U. In ref 1, p 192.

(b) Reference 31b, p 193.

(32) Schin, D. M.; Whitten, D. G. *J. Phys. Chem.* **1988**, *92*, 2945.

(26) Abdel-Mottaleb, M. S. S.; El-Zawawi, F. M.; Antonious, M. S.; Abo-Aly, M. M.; El-Feky, M. *J. Photochem. Photobiol. A* **1989**, *46*, 99.

Similarly the Stokes shift extrapolated to cyclohexane increases with the number of conjugated bonds for the shorter compounds and only slightly for the longest one. It is 16.6 kcal for **2a**, 3.3 kcal larger than for **1a** (13.3 kcal), whereas it is 17.5 kcal for **4a**.

This leveling off may be rationalized as the combined effect of two different parameters: the charge delocalization and the charge separation. The extension of the conjugated polyenic system causes a larger charge delocalization in the excited state and therefore a decrease of the net charges on the acceptor and the donor. However, the charge separation in the molecule is larger when the distance between donor and acceptor is increased. These antagonistic effects of charge separation and charge delocalization has been suggested to explain the influence of the chromophore length.<sup>22</sup>

The variation of the fluorescence quantum yield with increasing number of conjugating bonds for the shorter compounds (size **1** and **2**) is dependent on the donor and on the acceptor. The yields of the shorter compounds in the benzodithia aldehyde compounds (**1a** and **2a**) are comparable, whereas they decrease for the dimethylamino molecules **1a'**<sup>26</sup> and **2a'**.

In the cyano and dicyano series, the fluorescence yield increases somewhat between sizes **1** and **2**. For **1d** and **2d**, it is respectively 0.16 and  $6 \times 10^{-4}$  in dichloromethane. A large decrease of the fluorescence yield with increasing linker length has been reported for short push-pull acetylenic and ethylenic compounds, which bear a nitro group as acceptor and whose linker size ranges from one to three conjugated bonds.<sup>13,32</sup> The corresponding products in this study are **1d** and **2d**, possessing respectively two and five ethylenic bonds; they also show a decrease with increasing linker length.

The smallest fluorescence yields are observed for the compounds of longest size, i.e., **4a**, **4a'**, and **4b**, due probably to fast internal conversion rates. The increase of the fluorescence yield with lowering the temperature, as shown above, is in agreement with this assumption. It should be noted that C<sub>40</sub> carotenoids are nonfluorescent, ( $\phi < 10^{-5}$ ), and rapid deactivation is the main process.<sup>33</sup>

**Effect of Linker Structure. Absorption Spectra.** An hypsochromic effect is observed for the triple bond with respect to the double bond. Thus, the red shift in dichloromethane between **2a** and **3a**, (8 nm, 387 cm<sup>-1</sup>) is much smaller than that between **3a-4a** (37 nm, 1624 cm<sup>-1</sup>). In the dicyano compounds, the pattern is even more pronounced: a blue shift of 23 nm (779 cm<sup>-1</sup>) being obtained between **2b** and **3b**. Similar hypsochromic effects of the triple bond have been observed in carotenoids.<sup>31</sup> The replacement of an ethylenic by an acetylenic bond in *p*-amino-*p*'-nitrostilbene induces also an hypsochromic displacement.<sup>9</sup> These data indicate a reduction in the electronic transmission between D and A groups, for a linker containing a triple bond instead of a double bond. For ICT in donor-acceptor oligoacetylenes, the linker length does not affect greatly the energy of the ICT electronic transition (absorption and fluorescence).<sup>13</sup> This behavior is consistent with the weaker conjugating effect of the triple bond mentioned above.

Examination of the difference between the  $E_0$  values for analogous compounds **2** and **3** (Table VII) evidences that the magnitude of the hypsochromic effect of the triple bond depends on the nature of the acceptor and follows the reverse order of the acceptor strength. Thus, the weakest acceptors (series **a** and **c**) lead to the largest effects. The poorer electronic transmission of the triple bond is more pronounced when the acceptor group is weaker.

In parallel an interesting effect of the triple bond on  $-s$  can be noticed (see Table VII): the relative value of  $-s$  for size **3** compounds compared to size **2** ones depends on the nature of the acceptor. For the weakest acceptors (series **a** and **c**), a pronounced increase or a weak decrease of  $-s$  is observed from series **2** to series **3**, whereas for the stronger acceptors (series **d**) there is a marked decrease. This can be rationalized as the combined and anta-

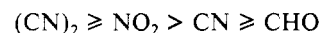
gonistic effects of the lengthening of the linker on one hand and of the addition of the triple bond on the other hand. The extension of the conjugated polyenic system causes a larger charge delocalization in the excited state but the triple bond introduces an inhomogeneity in the conjugation path, which leads to larger charge concentration. In the case of the weakest acceptor, the insulating effect of the triple bond predominates, resulting in a larger charge concentration on end groups, whereas, in the case of the strongest acceptors, the delocalization effect prevails. The decrease of  $-s$  for **3a'** compared to **2a'** (whereas it increases for **3a** compared to **2a**) agrees with the above discussion on the effect of the triple bond, provided that the dimethylamino donor is stronger than the benzodithia one. Also the comparison of  $E_0$  values of **2a'** and **3a'** (and of **2a** and **3a**) indicates that the relative hypsochromic effect of the triple bond is more pronounced in the case of the weaker donor.

**Fluorescence Spectra.** The hypsochromic effect of the triple bond is also noticeable from the data presented in Tables I-VI and from the comparison of  $E_0$  values (Table VII). The most striking observation is the increase of the fluorescence yield induced by the triple bond. A very large effect is obtained for **3a** (Figure 5B). A similar but smaller effect is observed for the analogous cyano and dicyano benzodithia derivatives **3c**, **3b** and for the dimethylamino molecule **3a'**. This effect of the triple bond may have different causes: the nonradiative decay rate may be reduced, compared to compounds of similar size, either by a slower internal conversion (due to the increasing rigidity provided by the triple bond) or by less intersystem crossing (due to a change of the triplet energy level). Further work is needed to clarify the origin of this effect.

**Effect of End Groups. Effect of the Acceptor Groups.** The investigation of the effect of the donor or acceptor groups should be carried at a given chain length. For the same structure (**1**, **2**, **3**, or **4**) but for different donor/acceptor combinations, the effective conjugated path differs; compounds of series **b**, **c**, and **d** contain one more double bond than compounds of series **a**, and compounds of series **c** and **d** bear an additional phenyl group. The relative importance of these differences is smaller for the longer compounds, like size **2** compared to size **1**. Thus, we have chosen to compare the aldehyde, dicyano, cyano, and nitro acceptors on the middle-sized molecules (structure **2**). Besides, no leveling off is observed in either absorption or fluorescence at this linker size.

The absorption spectra of compound **2a** and **2b** in various solvents are presented in Figure 1. The relative position of the ICT absorption bands and the greater sensitivity to solvent polarity of compound **2b** compared to **2a** indicate a larger polarity of the dicyano derivative than of the aldehyde one.

The comparison of the absorption and emission energies for compounds **2a-d** (Tables I-IV) leads to the following classification of the acceptors according to their electron-withdrawing ability:



Examination of the  $E_0$  and  $-s$  values for the same molecules (Tables VII) agrees with the above sequence since it is known that an increase in acceptor strength results in a decrease of the transition energy and an increase of the sensitivity to solvent polarity.<sup>22</sup>

**Dependence of the Fluorescence Yield on Solvent Polarity and Acceptor Group.** The variation of the fluorescence yield with solvent polarity is dependent on the nature of acceptor and donor and on the linker size. Considering comparable polyenic structure and length and same donor, the yield increases with solvent polarity for the aldehyde, dicyano, and *p*-cyanophenyl acceptors (Tables I-III, V). An example is depicted in Figure 4B for molecule **2a'**. A large increase with solvent polarity has also been reported for *p*-(dimethylamino)cinnamaldehyde (**1a'**).<sup>26</sup> On the other hand, a marked decrease of fluorescence yield in polar solvents is observed for the benzodithia derivatives bearing the nitro acceptor (see Figure 4A for molecule **1d** and Table IV). A similar phenomenon has been reported for other push-pull compounds with a nitro acceptor and the dimethylanilino or the anilino donor groups.<sup>13,32</sup> This pattern suggests that the fluorescence originates

(33) Bensasson, R. W.; Land, E. J.; Truscott, T. G.; *Flash Photolysis and Pulse Radiolysis*; Pergamon Press: New York, 1983; p 67-91 and references cited therein.



from the mixing of the lowest  $\pi\pi^*$  state with a low-lying  $n\pi^*$  state, induced by the nitro acceptor. The increase of the fluorescence yield with solvent polarity observed with the other acceptors points out that the other groups, such as aldehyde, may not possess such a low-lying  $n\pi^*$  state. The decrease of fluorescence yield in polar solvents, together with a near lack of photoreactivity observed for nitro push-pull molecules, has been suggested<sup>32</sup> to be consistent with decay of the emissive state to a nonemissive TICT state,<sup>34,35</sup> which then decays rapidly to the ground state.

**Effect of the Donor Groups.** The comparison between the two donors studied, i.e., benzodithia and dimethylanilino, is based on both the **a** and **a'** series bearing the aldehyde acceptor and the **b** and **b'** series with the dicyano substituent (Tables I, II, V, and VI). In the dimethylanilino series, the dimethylamino function and the phenyl ring have been considered together as the donor group. The ICT absorption band occurs at similar wavelength for compounds of comparable size and bearing the same acceptor. On the other hand, the fluorescence maxima are found at lower energies for compounds **1a'**,<sup>26</sup> **2a'**, **3a'**, **4a'** compared to analogous compounds of series **a**.

The main difference between the two donors is the much higher fluorescence yields obtained for the dimethylamino derivatives than for the benzodithia analogues (see in particular **1a** and **1a'**,<sup>26</sup> **2a** and **2a'**, **2b** and **2b'**, **3a** and **3a'**).

All these results taken together indicate that the benzodithia group is a good donor, slightly less effective than the dimethylanilino group and leading to smaller fluorescence yields. This may be attributed to a slight nonplanarity of the benzodithia compounds.<sup>24</sup>

**Nature of the Excited States.** In this study, two emitting states have been separated for some benzodithia derivatives, to which correspond two different excitation spectra (Table VIII). Excitation at the ICT absorption maximum leads to a very polar state, band B, which emits at low energy, up to the near-infrared. This fluorescence is highly sensitive to solvent polarity, and its solvatochromic behavior corresponds to a  $\pi\pi^*$  transition. In the case of the nitro compounds, the decrease of the emission intensity upon increasing solvent polarity suggests some mixing of the  $\pi\pi^*$  state with an  $n\pi^*$  one. The higher sensitivity of fluorescence to solvent polarity compared to absorption may be accounted for by significant solvent reorganization in polar medium, following excitation, thus after a large increase of the dipole moment. Similar behavior has been reported for push-pull polyenes.<sup>32</sup> Solvent motion markedly affects the rate of fast intramolecular electron transfer.<sup>36</sup>

Compounds bearing the benzodithia donor show evidence for a higher lying fluorescent state (band A). Its excitation maximum is at a higher energy than the absorption maximum and is only little affected by the chain length and structure and by the acceptor. The energy of band A fluorescence, the smaller Stokes shift, and sensitivity to solvent polarity indicate that this excited state is less polar than that of B. This state (band A) is very weakly fluorescent for series **a** and **c**, but its yield is higher for series **d**. Band A has not been observed for the dimethylamino derivatives series **a'** and **b'** in the aprotic solvents studied. However, such a transition may be hidden under band B fluorescence, whose yield is higher for the dimethylamino derivatives than for the benzodithia ones.

Singlet states energy diagrams have been established for polyenes corresponding to  $C_{2v}$  symmetry, and two singlet  $\pi\pi^*$  states,  $^1A_g$  and  $^1B_u$ , are predicted. In symmetrical polyenes, the  $^1B_u$  state is allowed according to the selection rules and has an ionic character.  $^1A_g$  has a "covalent" character, and the corresponding transition is symmetry forbidden. When an electron-withdrawing group is added to a short polyenic chain, and even more if this polyenic linker is longer, the  $^1B_u$  state energy is

expected to decrease. In the case of push-pull polyenes, the introduction of donor and acceptor groups breaks the  $C_{2v}$  symmetry. As the linker length increases, some mixing with close-lying excited states may be expected. On this basis, band B should arise from the lowest lying  $\pi\pi^*$  state and band A from a higher lying polyenic  $\pi\pi^*$  state. Band A presents a lower polarity than band B, reminiscent of the covalent character of the  $^1A_g$  state in symmetrical polyenes. Band A is lying close to band B in nonpolar solvents, and the energy difference between the two states increases with solvent polarity. The different excitation spectra observed could be accounted for by two excited states, namely, an  $^1A_g$ -like  $\pi\pi^*$  state (band A) and an intramolecular charge-transfer state (band B). This assignment is also consistent with the strong wavelength dependence reported for a *p*-nitrophenyl *p'*-amino-phenyl acetylenic compound, ascribed to mixing of a  $\pi\pi^*$  transition of the diphenylpolyene with an ICT band.<sup>13</sup> The existence of  $^1A_g$  along with  $^1B_u$  transitions has been recently suggested for push-pull diphenylhexatrienes on the basis of lifetime measurements.<sup>37</sup> Additional  $n\pi^*$  levels may be introduced by the donor group, arising from the sulfur lone pair for benzodithia compounds or by the acceptor group.

The existence of a twisted charge-transfer state and/or solvent reorganization could account for the unusually large Stokes shift observed in band B.<sup>38</sup> "Dual fluorescence" for example in (dimethylamino)benzonitrile, has been accounted for by enhanced formation of a TICT state from an ICT one in polar solvent.<sup>34,35</sup> Dual fluorescence in *p,p'*-disubstituted diphenylhexatrienes,<sup>37</sup> and for (dimethylamino)cyanostilbene,<sup>38,39</sup> has been accounted for by TICT formation in polar solvents.

Conformations arising from double bond twisting in the excited state has been shown in polydiacetylene.<sup>40</sup> Theory predicts that the lowest excited singlet state of stilbene-type molecules has an energy minimum in orthogonally twisted conformation ("sudden polarization"), and single and double bond twisting can be competing reaction channels.<sup>39,41,42</sup> This may also be the case with the push-pull compounds used in this work and result in deformation, in the form of twisting, producing a TICT state and/or cis-trans isomers. The change of shape and the increase of fluorescence yield with solvent polarity for emission band B, except for the nitro compounds, suggest cis-trans isomerization in non-polar solvents.<sup>25</sup>

## Conclusion

The photophysical properties of the lower lying transition of the push-pull polyenes studied here are consistent with *long-distance intramolecular charge transfer*, assessing the role of *molecular wire* to the polyenic linker. The ICT excited state emits at low energy, up to near infrared, depending on the conjugating chain length and on the donor and acceptor groups. Evidence for an additional excited state has been observed for some benzodithia compounds and has been ascribed to a higher lying  $\pi\pi^*$  state, whose energy gap with the ICT state depends on solvent polarity.

The increase of polyenic linker length induces bathochromic displacements of both absorption and fluorescence bands, which level off for the longest molecules studied. The introduction of the triple bond leads to a reduction in the electronic transmission process. The acceptors may be ranked, according to their electron-withdrawing ability, the best being the dicyano and nitro groups. The benzodithia groups appears as a good donor group, although leading to lower fluorescence yields than the dimethylamino one. Preliminary results indicate that the fluorescence decay of the lowest excited state occurs in the subnanosecond range, as required for very fast signal processing applications.

(34) (a) Rettig, W. *Angew. Chem., Int. Ed. Engl.* **1986**, 25, 971. (b) Rettig, W. In *Supramolecular Photochemistry*; Balzani, V., Ed.; Reidel: Dordrecht, The Netherlands, 1987; p 329.

(35) Siemiarczuk, A.; Grabowski, Z. R.; Krowczynski, A.; Asher, M.; Ottolenghi, M. *Chem. Phys. Lett.* **1977**, 51, 315.

(36) Kosower, E. M. *J. Am. Chem. Soc.* **1985**, 107, 1114.

(37) Lin, C. T.; Guan, H. W.; McCoy, R. K.; Spangler, C. W. *J. Phys. Chem.* **1989**, 93, 39.

(38) Gilibert, E.; Lapouyade, R.; Rullière, C. *Chem. Phys. Lett.* **1988**, 145, 262.

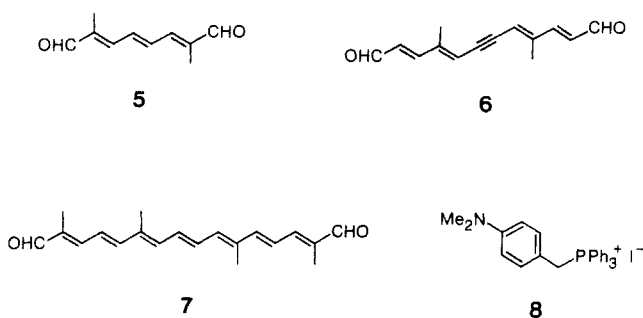
(39) Rettig, W.; Majenz, W. *Chem. Phys. Lett.* **1989**, 154, 335.

(40) Rughooputh, S. D. D. V.; Phillips, D.; Bloor, D.; Ando, D. *J. Chem. Phys. Lett.* **1984**, 106, 247.

(41) Lippert, E.; Rettig, W.; Bonacic-Koutecky, V.; Heisel, F.; Miehle, J. A. *Adv. Chem. Phys.* **1987**, 1.

(42) Hochstrasser, R. M. *Pure Appl. Chem.* **1980**, 52, 2683.

## CHART II



## Experimental Section

**Materials.** The solvents used were spectroscopic grade Merck products. Synthesis of compounds 1-4, a-d, has already been reported.<sup>7</sup>

**Synthesis.** The *p*-(dimethylamino)phenylpolyene aldehydes 2a', 3a', 4a' were prepared by condensation of the respective aldehydes 5, 6, and 7 (Chart II) with 1 equiv of the Wittig reagent generated from the phosphonium salt 8<sup>43</sup> in similar liquid-liquid phase-transfer conditions as those used for the synthesis of 2a, 3a, 4a. The products obtained, with respectively 82%, 65%, and 46% yield, were purified by chromatography on silica gel with dichloromethane as eluant and then crystallized in a CH<sub>2</sub>Cl<sub>2</sub>/ethanol mixture under argon. They gave satisfactory elementary analysis and had <sup>1</sup>H NMR and IR spectral properties in agreement with

(43) Brederick, M.; Simchen, G.; Griebenov, W. *Chem. Ber.* **1973**, *106*, 3732.

the assigned structure. Reaction of 2a', 3a', and 4a' with malonitrile in refluxing absolute ethanol in the presence of a catalytical amount of piperidine, afforded the dicyanomethylene derivatives 2b', 3b', and 4b' with 76%, 76%, and 67% yield. The products were isolated by filtration and then purified by careful chromatography on silica gel, eluting with dichloromethane under argon and avoiding direct light. The correct elemental analysis and spectral properties (<sup>1</sup>H NMR, MS, IR) are in accord with the assigned structures.

**Apparatus.** The absorption spectra were recorded either on Kontron spectrophotometers, Model 860 or 820, or on a Perkin-Elmer Model 554 apparatus. A Spex Fluorolog spectrofluorimeter was used for the static emission experiments. The spectra were corrected for the wavelength dependence of the transmission and detection systems. The reference solution for quantum yields measurements was quinine bisulfate in 1 N sulfuric acid. The area of the fluorescence curves was then calculated to obtain relative fluorescence yields. Each apparatus was thermostated at 20 ± 1 °C, unless otherwise stated. In the case of low-temperature measurements, a nitrogen flow was blown on the cell, in order to eliminate condensation.

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**Registry No.** 1a, 87815-67-6; 1a', 20432-35-3; 1b, 121881-11-6; 1c, 121881-23-0; 1d, 121881-26-3; 2a, 121881-08-1; 2a', 124445-99-4; 2b, 121881-12-7; 2c, 121881-24-1; 2d, 121881-27-4; 3a, 121881-09-2; 3a', 124446-00-0; 3b, 121881-13-8; 3c, 121881-25-2; 3d, 121881-28-5; 4a, 121881-10-5; 4a', 124446-01-1; 4b, 121881-14-9; 5, 5056-17-7; 6, 58096-44-9; 7, 502-70-5; 8, 34904-03-5.

## Temperature-Dependent Formaldehyde Cross Sections in the Near-Ultraviolet Spectral Region

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The near-ultraviolet (300-360 nm, 33 300-27 800 cm<sup>-1</sup>) absolute absorption cross sections for formaldehyde (CH<sub>2</sub>O) have been measured as a function of temperature (223-293 K), and formaldehyde concentration in nitrogen at 500 Torr. Fourier transform spectroscopy was performed using an instrumental resolution sufficiently high (1.00 cm<sup>-1</sup> or approximately 0.011 nm at 330 nm) to ensure the cross sections which are used in calculated atmospheric photolysis rates are free of artifacts due to overlap (or lack thereof) in the spectral structure of the solar flux or in the structure of the formaldehyde absorption spectrum. Comparisons with previous measurements are made and recommendations presented for use in atmospheric photolysis rate calculations. Representative ground-level photolysis rates are calculated and compared in order to ascertain the effect of the temperature dependence in the absorption cross sections as well as the effect of integration interval.

## Introduction

The first member of the aldehyde family, formaldehyde, has been the subject of scientific investigations for more than 180 years. Reviews of formaldehyde chemistry and spectroscopy up to 1975 are found in refs 1 and 2. Since the 1970s, studies have continued involving laboratory investigations<sup>3-11</sup> as well as atmospheric measurements.<sup>12-17</sup> The highly structured ultraviolet spectrum of this atmospherically important molecule was the first of the polyatomic molecules to be interpreted unambiguously in the early work of Dieke and Kistiakowsky.<sup>18</sup>

In the atmosphere, the photochemical activity of formaldehyde makes it an important component in the initiation of odd hydrogen

<sup>†</sup>The National Center for Atmospheric Research is funded by the National Science Foundation.

- (1) Moule, D. C.; Walsh, A. D. *Chem. Rev.* **1975**, *75*, 67-84.
- (2) Calvert, J. G. *Proc. NATO Adv. Study Inst. Atm. Ozone*; Report No. FAA-EE-80-20, 1979; pp 153-190.
- (3) Bass, A. M.; Glasgow, L. C.; Miller, C.; Jesson, J. P.; Filkin, D. L. *Planet. Space Sci.* **1980**, *28*, 675-679.
- (4) Moortgat, G. K.; Slemr, F.; Seiler, W.; Warneck, P. *Chem. Phys. Lett.* **1978**, *54*, 444-447.
- (5) Moortgat, G. K.; Warneck, P. *J. Chem. Phys.* **1979**, *70*, 3639-3651.
- (6) Moortgat, G. K.; Klippel, W.; Möbus, K. H.; Seiler, W.; Warneck, P. *FAA Report No. FAA-EE-80-47*, 1980.
- (7) Moortgat, G. K.; Seiler, W.; Warneck, P. *J. Chem. Phys.* **1983**, *78*, 1185.