

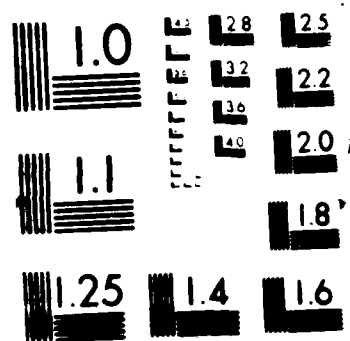
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IN SOME FLUORENE DERIVATIVES(U) NAVAL OCEAN SYSTEMS
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SPECTRAL LOCATIONS OF LOW-ENERGY ELECTRONIC TRANSITIONS
IN SOME FLUORENE DERIVATIVES

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ABSTRACT

The low energy singlet-singlet (S-S) and triplet-triplet (T-T) absorption spectra of fluorene and 2-amino fluorene were measured. Also, the spectral locations of low-energy S-S and T-T intensity maxima of 2-methoxy, 2-hydroxy, 2,7-diamino, and 2-dimethylamino fluorene were recorded.

When expressed in wavenumbers (energy) and within measurement accuracy, the following holds for the 2-position substituted fluorene: (a) The red shift caused by a certain substituent is about the same in both (singlet and triplet) manifolds; (b) The energy difference between S-S and T-T absorption maxima in fluorene as well as in all the substituted compounds is about the same; and (c) The spectral red shifts observed in fluorene in the singlet and triplet manifold due to substitution by auxochromic groups can probably be used in fair approximation to estimate anticipated red shifts in other chromophores.

For 2,7-diamino fluorene; p-terphenyl, p,p'-diamino, p,p'-diethylamino terphenyl, p-quaterphenyl; p,p'-diamino, p,p'-diethylamino quaterphenyl, spectral relations (a) to (c) also hold rather well.

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INTRODUCTION

In the literature very few experimental data are available on the effect of substituents on the triplet-triplet (T-T) absorption spectra of aromatic compounds. Recently, experimental data on red shifting (bathochromic effect) of singlet-singlet (S-S) and T-T absorption bands due to auxochromic group (i.e. $-OCH_3$, $-OH$, $-NH_2$, $-NHR$, $-NR_2$, single butterfly, double butterfly, in order of increasing effectiveness and R representing the alkyl group) substitution in the 7-position of coumarin were reported [1]. The findings showed that: (a) Within measurement accuracy, the order of effectiveness of the auxochromic group in the singlet and triplet manifold is the same. (b) In most cases, when expressed in energy units (e.g. wavenumbers), the red shift ΔS caused by a certain auxochrome in the singlet manifold, in most cases, is the same as the red shift ΔT in the triplet manifold. (c) The energy difference ΔE_1 between the lowest energy S-S absorption band and the similarly polarized T-T absorption band located in the blue spectral region of coumarin, and the energy difference ΔE_2 between the red-shifted S-S absorption band and the red-shifted T-T absorption band in the substituted coumarin are the same, in most of the cases, regardless of the auxochromic substituent.

The fact that coumarin has two closely spaced lowest energy S-S absorption bands of similar intensity at 313 and 274 nm, and

parallel polarization creates uncertainty in (b) and (c). Upon substitution and depending on the substituent, these two bands fuse together. In methoxy and hydroxy (and possibly in amino) coumarin, this fusion may not have been complete. Using the false intensity maximum introduces an error. The measured ΔS are too small.

Observations (a) to (c) may be of a more general nature when tested on some other chromophore. The spectral red shifts ΔS and ΔT , caused by auxochromic group substitution could then be verified to be the same, or about the same, in other chromophores. These experimental data would also verify the accuracy of semi-empirical quantum chemical calculations on spectral locations of electronic transitions in the singlet and triplet manifold. The importance of these red shifts for the synthesis of improved laser dyes is discussed in [1].

The spectral red shifts caused by auxochromic group substitution in 2-position (near long axis) of fluorene was measured. To study the effect of two auxochromic groups positioned at opposite ends, we next measured the spectral red shifts caused by the substitution in the 2,7-positions of fluorene by two amino groups. These data were compared with literature data on p-terphenyl, p,p'-diamino and p,p'-diethylamino terphenyl and p-quaterphenyl, p,p'-diamino and p,p'-diethylamino quaterphenyl.

EXPERIMENTAL

Chemicals. Fluorene, 2-methoxy, 2-amino, and 2,7-diamino fluorene were obtained from Aldrich Chemical Company. 2-hydroxy and 2-dimethyl-amino fluorene were purchased from Chemical Procurement Laboratories. With the exception of fluorene, all compounds were recrystallized from ethanol for purification. A 5×10^{-4} Molar solution was used for the T-T absorption measurements. A mixture of 2:1 ethanol/diethyl ether was used as solvent. The ethanol was purchased from J. T. Baker and the ether from Aldrich.

Apparatus. Conventional (S-S) absorption spectra were measured with a Varian Super-Scan 3 UV visible spectrophotometer at room temperature. The T-T absorption spectra were recorded with equipment described by Pavlopoulos [2]. Depending on the spectral location of the S-S absorption of the compound studied, either the 313 nm line from a high-pressure mercury arc lamp together with a 5 cm pathlength nickel sulfate [3] UG5 Scott filter combination, or the 325 nm line from a cw Cadmium/helium Liconix laser were used. A high-pressure xenon lamp monitored the T-T absorption. Because the photochemical stability of the studied compounds was rather low, measurement accuracy was not better than $\pm 300 \text{ cm}^{-1}$ for the spectral locations of the T-T maxima. The error in the spectral locations of the S-S maxima was about $\pm 100 \text{ cm}^{-1}$. We wish to emphasize that, besides measurement inaccuracy, the experimental results presented also contain a conceptual error. Ideally the red shift should be measured between the vibrational 0,0 bands of the unsubstituted

and substituted compounds. Because these 0,0 bands cannot usually be resolved even at 77° K, intensity maxima are used. Although these intensity maxima do not coincide with the 0,0 band, they offer a convenient, but somewhat less accurate substitute.

RESULTS AND DISCUSSION

Fluorene.

The electronic spectra of fluorene can be best understood from the spectra of biphenyl. Biphenyl exhibits a rather broad S-S absorption band at $40,500\text{ cm}^{-1}$ (247 nm) which is long-axis polarized [4]. At the long wavelength side, two additional transitions, one short-axis and one long-axis polarized are hidden. The quantum fluorescence yield is rather low (0.17) [5] due to the nonplanarity of the two phenyl rings. With a CH_2 bridge between the two non-planar phenyl rings, the molecule becomes more closely planar, exhibits a more structured low energy S-S and the fluorescence spectrum and the quantum fluorescence yield rises to 0.80 [5]. We measured the S-S absorption spectrum of fluorene (Figure 1a). We used the long-axis polarized band at $38,200\text{ cm}^{-1}$ (262 nm) as reference to measure spectral red shifts due to near-long-axis substitution (i.e. in the 2-position). The T-T absorption spectrum of biphenyl has been measured by several authors [6]. In agreement with theoretical calculations [7], the strong T-T absorption band at $35,800\text{ cm}^{-1}$ (279 nm) is long-axis polarized [8]. The T-T absorption spectrum of fluorene has also been measured repeatedly [6]. This spectrum was remeasured and

also presented in Figure 1a. The T-T absorption maximum at $26,000\text{ cm}^{-1}$ (385nm) served as reference for measuring spectral red shifts due to auxochromic group substitution in the 2-position of fluorene.

Because of the similarity to biphenyl, both strong S-S and T-T absorption bands (at 262 and 385 nm respectively) in fluorene should be long-axis polarized.

Our equipment was only able to measure triplet optical densities $OD_T(\lambda)$. Thus, we converted our data to triplet extinction coefficients ϵ_T by using the value of $12,000\text{ M}^{-1}\text{ cm}^{-1}$ at 382 nm obtained by Alfimov *et al.* [9]. The spectral data of fluorene are compiled in Table 1.

2-Amino Fluorene.

In this compound, the S-S absorption maximum has been red shifted to $34,400\text{ cm}^{-1}$ (291 nm) (Figure 1b). The T-T absorption spectrum of this compound was also measured by Alfimov *et al.* [9]. Our spectrum is also shown in Figure 1b. Again, we used the value of $\epsilon_T = 10,600\text{ M}^{-1}\text{ cm}^{-1}$ obtained by Alfimov *et al.* [9] for the T-T absorption maximum to convert our OD_T data. This compound was photochemically rather stable. The spectroscopic data of this compound is presented in Table 1.

2-Methoxy Fluorene, 2-Hydroxy Fluorene, and 2-Dimethylamino Fluorene.

The spectroscopic data of these compounds are shown in Table 1.

SUMMARY OF EXPERIMENTAL RESULTS CONTAINED IN TABLE 1

1. As expected, the order of effectiveness of causing spectral red shifts by auxochromic groups in the triplet manifold is the same as in the singlet manifold.
2. Within measurement accuracy, for the same auxochromic group, the red shifts $\Delta S(\text{cm}^{-1})$ and $\Delta T(\text{cm}^{-1})$ are the same for all compounds studied, including the methoxy and hydroxy derivatives. This supports our previous conclusions on coumarin which suggested the same relationship.
3. For similarly polarized transitions, the energy difference $\Delta E(\text{cm}^{-1})$ between the S-S absorption maximum and the T-T absorption maximum, before and after substitution for all compounds studied, remains the same.
4. The red shifts $\Delta S(\text{cm}^{-1})$ and $\Delta T(\text{cm}^{-1})$ caused by a certain auxochrome in fluorene and in coumarin (within $1,000 \text{ cm}^{-1}$) and therefore are approximately the same. Therefore the average value of ΔS and ΔT obtained from the coumarin and fluorene experiments should serve as a good approximation for estimating anticipated spectral locations of S-S and T-T absorption bands in other chromophores.

2,7-Diamino fluorene

To obtain information on the red shifts caused by two auxochromic groups positioned at the opposite ends of the long axis of the chromophore molecule, the spectral locations of the S-S and T-T absorption maxima of 2,7-diamino fluorene were measured. We also used experimental data on p-terphenyl, p,p'-diamino, and p,p'-diethylamino terphenyl and p-quaterphenyl,

p,p'-diamino, and p,p'-diethylamino quaterphenyl contained in [10]. These data are presented in Table 2.

Since the fluorene, terphenyl and quaterphenyl derivatives were photochemically rather unstable, the measurement error for the T-T absorption maxima is about $\pm 500 \text{ cm}^{-1}$. The measurement errors in the singlet manifold are estimated to be about $\pm 200 \text{ cm}^{-1}$.

SUMMARY OF EXPERIMENTAL RESULTS CONTAINED IN TABLE 2

The results are basically the same as the ones obtained from Table 1. Specifically:

1. From the very limited data available, we can only conclude that in the p-terphenyl and q-quaterphenyl derivatives, the red shifts caused by the two diethylamino groups are larger than the red shifts caused by the two amino groups.
2. (a) In 2,7-diamino fluorene, the red shift $\Delta T(\text{cm}^{-1})$ is about the same as $\Delta S(\text{cm}^{-1})$.
(b) In p,p'-amino terphenyl, $\Delta S(\text{cm}^{-1})$ is larger than $\Delta T(\text{cm}^{-1})$. If this is solely the result of the addition of experimental errors is difficult to say. However, in p,p'-diethylamino terphenyl, $\Delta S(\text{cm}^{-1})$ and $\Delta T(\text{cm}^{-1})$ are about the same.
(c) In p,p'-diamino quaterphenyl, $\Delta S(\text{cm}^{-1})$ and $\Delta T(\text{cm}^{-1})$ are about the same. The same holds for p,p'-diethylamino quaterphenyl.
3. The energy difference $\Delta E(\text{cm}^{-1})$ in each of the three chromophores and its doubly substituted derivatives remains about the same.

4. The red shifts $\Delta S(\text{cm}^{-1})$ caused by the two amino groups are about the same for all three chromophores. The red shifts for $\Delta T(\text{cm}^{-1})$ are similar. The red shifts $\Delta S(\text{cm}^{-1})$ caused by the two diethylamino groups are about the same for p-terphenyl and p-quaterphenyl. The same is true for the red shifts $\Delta T(\text{cm}^{-1})$.

Acknowledgments

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Table 1.

Spectral intensity maxima of low-energy electronic transitions in fluorene and its auxochromic group substituted derivatives. S-S and T-T are the maxima of intensity expressed in wavelength (nm) and wavenumbers (cm^{-1}). ΔS presents the spectral red shifts between the strong S-S maximum at 262 nm of fluorene and the S-S maximum of the substituted compound. Similarly, ΔT presents the spectral red shift between the strong T-T maximum at 385 nm and the T-T maximum of the substituted compound. ΔE presents the energy difference (expressed in cm^{-1}) between the strong S-S and the strong T-T maximum of the same compound.

The S-S absorption spectra were measured at room temperature and the T-T absorption maxima at 77° K.

Auxochromic Group	S-S nm cm ⁻¹	ΔS nm cm ⁻¹	T-T nm cm ⁻¹	ΔT nm cm ⁻¹		ΔE nm cm ⁻¹	
-H	262		385				
	38,200		26,000			12,200	
-OCH ₃	266	4	396	11			
	37,600	600	25,300	700		12,300	
-OH	275	13	408	23			
	36,400	1,800	24,500	1,500		11,900	
-NH ₂	291	29	444	59			
	34,400	3,800	22,500	3,500		11,900	
-N(CH ₃) ₂	304	42	488	103			
	32,900	5,300	20,500	5,500		12,400	

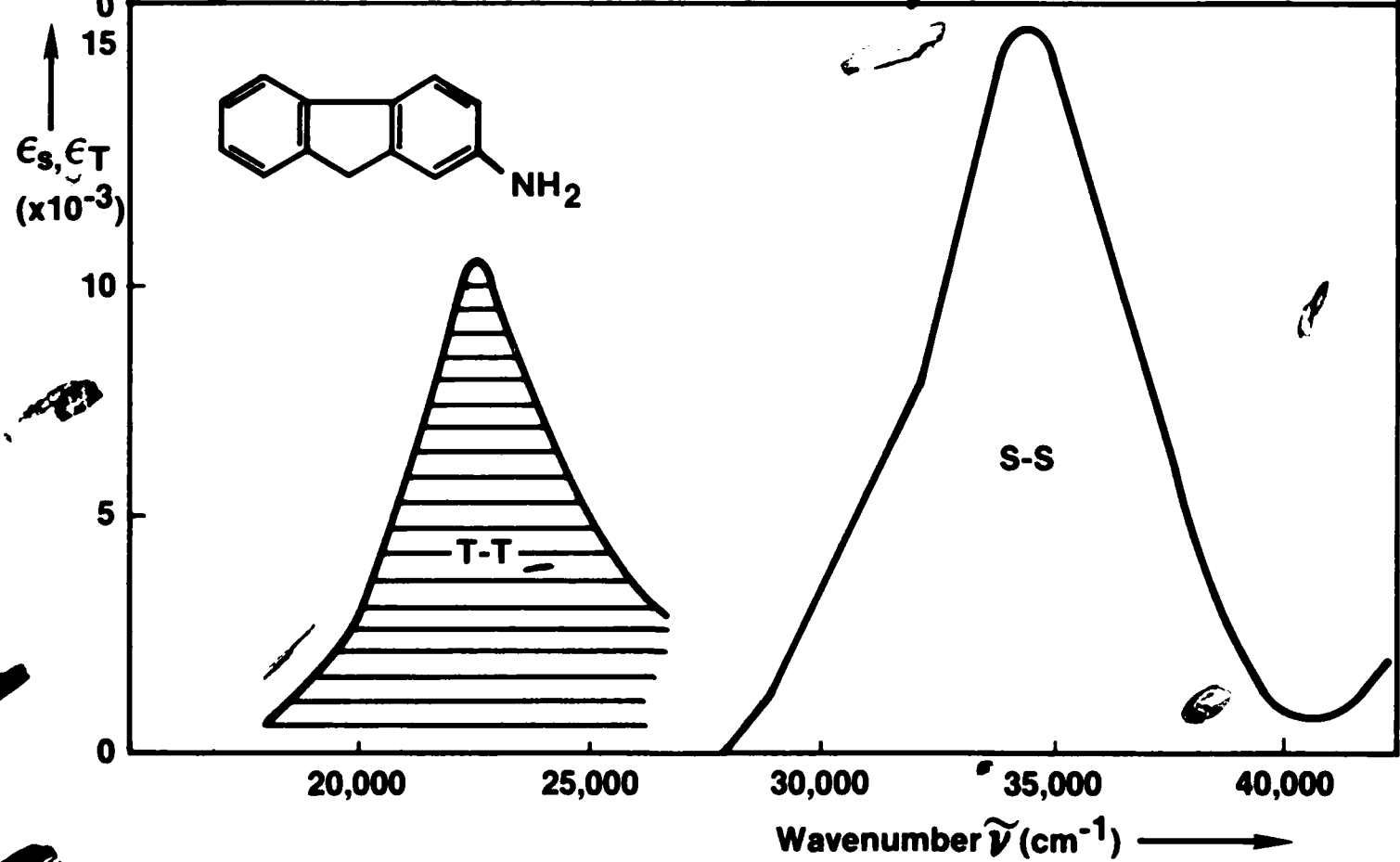
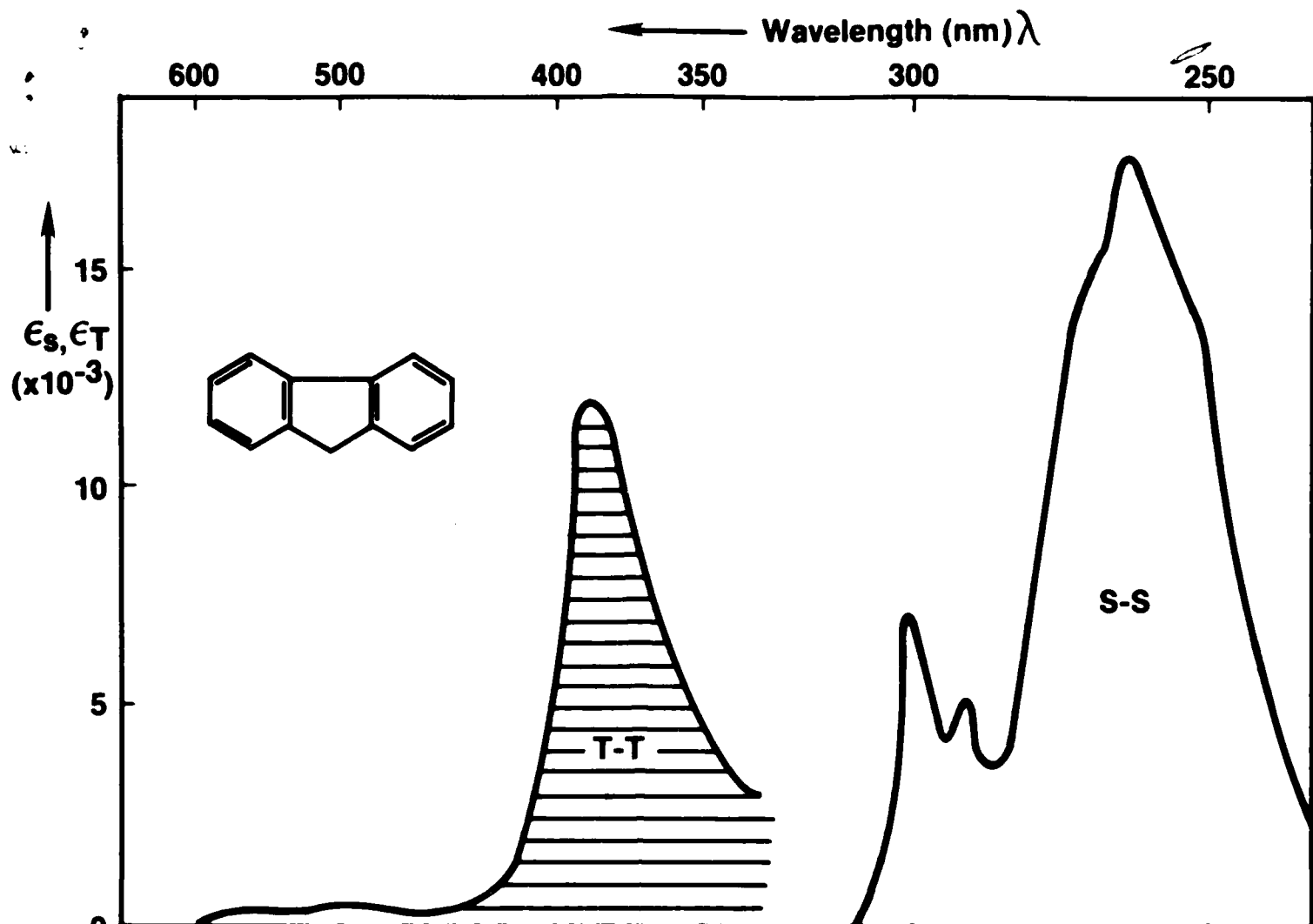
Table 2.

Spectral intensity maxima of low energy transitions in fluorene, 2,7-diamino fluorene, p-terphenyl, p,p'-diamino and p,p'-diethylamino terphenyl, p-quater-phenyl, p,p'-diamino and p,p'-diethylamino quaterphenyl. Meaning of symbols as in Table 1.

Compound	S-S	ΔS	T-T	ΔT	ΔE
	nm	nm	nm	nm	
	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}
Fluorene	262		385		
	38,200		26,000		12,200
2,7-Diamino Fluorene	298	36	455	70	
	33,600	4,600	22,000	4,000	11,600
p-Terphenyl	278		460		
	36,000		21,700		14,300
p,p'-Diamino Terphenyl	320	42	560	100	
	31,300	4,700	17,900	3,800	13,400
p,p'-Diethylamino Terphenyl	340	62	610	150	
	29,400	5,600	16,400	5,300	13,000
p-Quaterphenyl	296		530		
	33,800		18,900		14,900
p,p'-Diamino Quaterphenyl	332	36	650	120	
	30,100	3,700	15,400	3,500	14,700
p,p'-Diethylamino Quaterphenyl	346	50	710	180	
	28,900	4,900	14,100	4,800	14,800

Figure 1.

S-S and T-T absorption spectra of (a) fluorene and
(b) 2-amino fluorene.



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