14. Triplet-Triplet Absorption Spectroscopy of Some Highly Dipolar Unsaturated Nitro Compounds

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In Memory Prof. *Heinrich Labhart*

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Summary

The triplet-triplet absorption spectra of *p-N,N*-dimethylnitroaniline, 4-nitro-*p*-terphenyl, 1-amino-4-nitrofluorene, 5-nitroacenaphthene, *trans*-1-(4-methoxyphenyl)-2-nitroethylene (MeONS), and *trans*-1-(4-dimethylaminophenyl)-2-nitroethylene (DANS) in EPA glass at 77 K are reported, together with molar extinction coefficients and PPP-SCF-MO-CI calculations. The two nitrostyrenes, MeONS and DANS, have been examined in fluid media at room temperature using nanosecond laser photolysis, and their triplet lifetimes found to increase substantially with increase in solvent polarity and charge-transfer character of the compound. This is interpreted in terms of the diradical/zwitterionic nature of the triplet state affecting the T_1-S_0 energy gap at the 90° twisted configuration of the olefinic linkage.

The decrease in both the triplet yield and the fluorescence yield of DANS with increase in solvent polarity is explained by the intervention of an internal conversion process involving a rotation of the dimethylamino group in the lowest singlet excited state.

1. Introduction. - The important photochemical role of triplet states is one reason for the interest during the past two decades in triplet-triplet absorption (T-T) spectra. Professor *Heinrich Labhart* has made notable contributions to such studies both in instrumentation and observation. While T-T spectra of aromatic hydrocarbons have been widely reported (see, for example, the review by *Labhart & Heinzelmann* [1]), there exists a lack of data on nitroaromatics, the intriguing photophysical properties of which remain relatively obscure. Little is known of the nature of the first triplet state T_1 in many nitro compounds, and even less of the higher states $T_2 \ldots T_n$, despite their possible involvement in intersystem crossing from the singlet to the triplet manifold. In nitro compounds for which low or negligible phosphorescence is observed it is often not clear whether this arises from a low radiative rate constant ($S_0 \leftarrow T_1$) or from a low intersystem crossing efficiency ($T_1 \leftarrow S_1$), or indeed both.

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The nitronaphthalenes [2-5] have received some detailed attention by flash photolysis methods, and recently *Capellos & Lang* [6] have reported on the triplet transient from 4-nitronaphthylamine. A few nitrostilbenes have also been investigated [7] [8]. Determinations of the molar extinction coefficients for the main absorption bands are, however, rare despite their importance in the theoretical analysis of the T-T spectra with regard to the symmetry and composition of the higher triplet states. The influence of solvent polarity on triplet state properties is also of major interest [6] [8] since such will be influenced by the extent of charge-transfer in the excited nitro compound.

Reported here are T-T spectra of several nitro compounds in EPA glass (diethyl ether/isopentane/ethanol 5:5:2 by volume) at 77 K with particular emphasis on those compounds substituted by a good electron donor group. Molar extinction coefficients have been measured in some cases and molecular orbital calculations have been performed to assist the spectral analysis. Solvent effects on the triplet state lifetimes of two nitrostyrene systems, examined *via* nanosecond flash photolysis of fluid solutions at room temperature, are significant and the implications of such effects are explored.

2. Experimental part. - The compounds 5-nitroacenaphthene *(Eastman Kodak)*, 3-nitropyrene, 1-nitronaphthalene, 4-nitro-*p*-terphenyl, *N,N*-dimethyl-*m*-nitroaniline, *N,N*-dimethyl-*p*-nitroaniline *(Pfaltz and Bauer)*, 1-amino-7-nitrofluorene, 2-amino-7-nitrofluorene, 1-amino-4-nitronaphthalene, and 2-nitronaphthalene *(Aldrich)* were recrystallised from aqueous ethanol before use. The styrene derivatives were prepared as described elsewhere [9]. EPA solvent components were of Merck fluorimetric quality.

Phosphorescence spectra of *ca.* 10^{-4}M solutions were measured at 77 K on a rotating chopper instrument of standard design [10]. Decay curves were determined with signal averaging using a *Nicolet* storage computer (Model SW-71B). Good linearity in the plots of log (phosphorescence intensity) against time were obtained, except for those systems indicated in the text. T-T spectra at 77 K were obtained using a direct method [11]. Light from a 450 watt xenon arc passed through a UGl glass filter and a 1 cm cell containing distilled water, transmitting wavelengths between 300 and 400 nm, before focussing on the sample contained in a quartz tube of approximately square cross-section, dimensions 10× 10 mm.

An analysing light beam from a tungsten lamp passed through the sample cell, close to the irradiated face, into a monochromator of bandpass 2.06 nm, and thence onto a UVP150 low noise photomultiplier run at 1000-1300 V.

The sample cell was masked by a thin copper shield made with slots to allow entry of both irradiation and monitor beams in a more defined way. In addition, side-arms were found to be essential to eliminate the signal noise arising from boiling of liquid nitrogen in the containing quartz Dewar. The coolant was maintained about 6 mm below the observation beam level to ensure that the temperature of the sample (in the light beam) remained close to 77 K. This was assisted by the copper shield which also dipped into the coolant.

For triplets of suspected short lifetimes ($\tau < 50$ ms), a phase-sensitive detection system was operated, the irradiation beam being chopped at a frequency of *ca.* 120 Hz.

T-T spectra, as $\Delta V/V$ against wavelength, λ, were obtained point by point at 5 to 20 nm intervals depending on the spectral shape, from the change ΔV in photomultiplier response voltage V on sample irradiation with a minor due allowance for scattered light and sample luminescence. The optical density change, ΔOD., equals $-\log_{10}(1-\Delta V/V)$. In favourable cases the mean fractional population of the triplet state T_1 under steady irradiation, x_T, as detected by the analysing beam, could be found by the kinetic method [12]. By manual operation of a shutter the decay (k_d) and rise (k_r) curves of the triplet species were obtained using the *Nicolet* storage computer (1024 channels swept in e.g. 10s) to store and smooth the curves before digital sampling and processing by a least-squares method for assumed first-order kinetics.

$$x_T = (k_r - k_d)/k_r$$

The method is reliable only when k_r and k_d differ appreciably and the errors in ε_M values noted in the tables arise substantially from this source. The action spectra were corrected for the absorption change caused by depletion in the ground state (S_0) population where x_T was known together with the solution concentration and the normal UV. absorption curves obtained at room temperature and 77 K with the same sample cell and Dewar assembly.

The flash photolysis experiments were conducted in the laboratories of Prof. *Schulte-Frohlinde* at the *Max Planck Institute,* Mulheim-an-der-Ruhr, West Germany, with the assistance of Mr. *L. Currell.* The 337.2 nm nitrogen laser and 265 nm neodymium laser systems, having pulse durations of *ca.* 20 ns, are described in publications from that laboratory. Both air-saturated and argon-flushed solutions (10^{-4} to 10^{-3}M) were examined at 26± 1°.

Pariser-Pople-Parr-SCF-MO-CI calculations were performed using the programmes and the parametrisation developed by *Wagnière et al.* [13]. The more important parameters had the following values, in eV:

$$F_C = -9.00;\ F_N = -20.60\,(NMe_2),\ Z = 2.0,\ \text{or}\ -19.40\,(NO_2),\ Z = 1.5$$

$$F_O(\pi) = -19.40\,(Z = 1.2);\ F_O(n) = -27.00\,(Z = 2.0)$$

$$\beta^{\circ}_{CC} = -2.37;\ \beta_{CN} = -2.00;\ \beta_{NO} = -3.05;\ \beta_{O1}(n)O_2(n) = -0.20$$

$$\gamma_{CC} = 10.53;\ \gamma_{NN} = 12.27;\ \gamma_{OO} = 14.50;\ \gamma_{NO} = 8.80$$

All π electrons and non-bonded electrons of the nitro group were included, with full configuration interaction involving configurations singly-excited with respect to the ground state. For the triplet manifold the latter assumption has been shown to give as satisfactory results as those obtained upon inclusion of doubly excited states (with respect to S_0) provided the parametrisation is correctly chosen. The parametrisation adopted here is close to that recommended for such triplet calculations by *Pancir & Zahradnik* [14].

T-T absorption transition moments were computed from the MO results using a separate computer programme developed by the author.

3. Results. - 3.1. *T-T spectra in EPA glass, 77 K.* Spectra for 4-nitro-*p*-terphenyl, 5-nitroacenaphthene, 1-amino-7-nitrofluorene, and *N,N*-dimethyl-*p*-nitroaniline

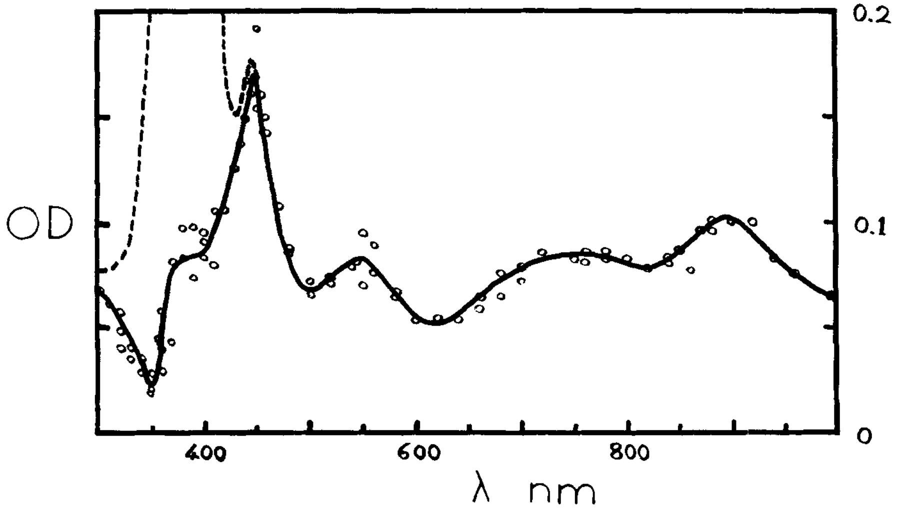

Fig. 1. *T-T spectrum of* p-N,N-*dimethylnitroaniline in EPA glass, 77 K*
OD = Optical density change on irradiation, λ = Wavelength of observation.
The solid curve gives the observed transient spectrum and the broken curve, the spectrum after correction for the ground state depletion.

not reported before, are given in *Figures 1* to *4*. Spectra were also obtained for 1-nitronaphthalene, 2-nitronaphthalene, and 1-amino-4-nitronaphthalene in good agreement with previous reports [2-6] after allowance for differences in media and temperature.

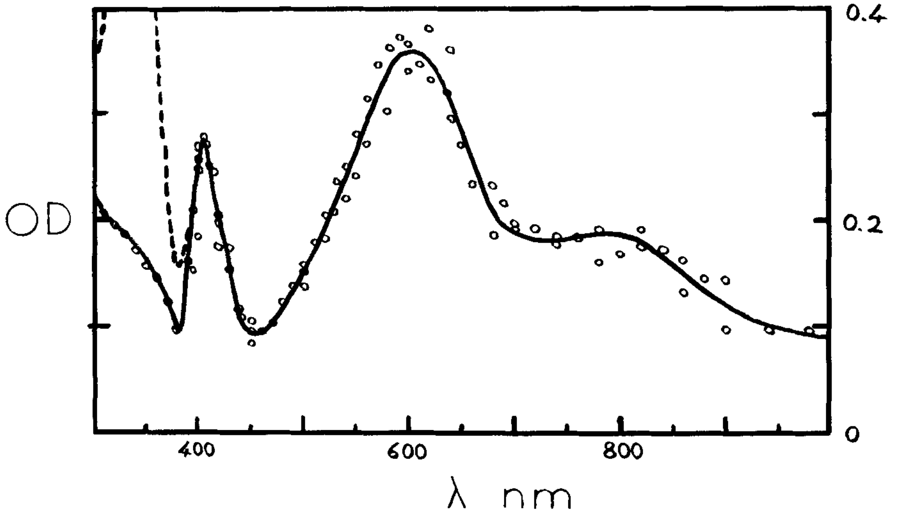

Fig. 2. *T-T spectrum of 4-nitro-*p*-terphenyl in EPA glass, 77 K*
OD = Optical density change on irradiation, λ = Wavelength of observation.
The solid curve gives the observed transient spectrum and the broken curve, the spectrum after correction for the ground state depletion.

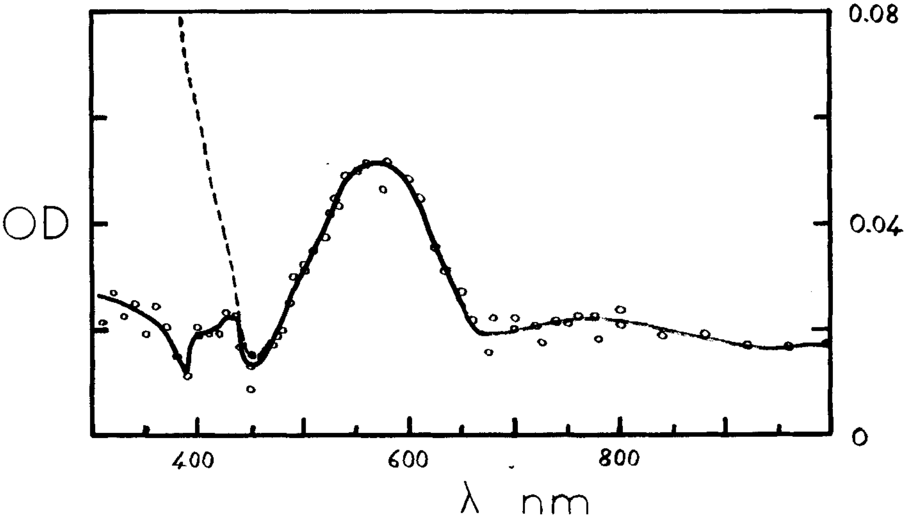

Fig. 3. *T-T spectrum of 1-amino-7-nitrofluorene in EPA glass, 77 K*
OD = Optical density change on irradiation, λ = Wavelength of observation.
The solid curve gives the observed transient spectrum and the broken curve, the spectrum after correction for the ground state depletion.

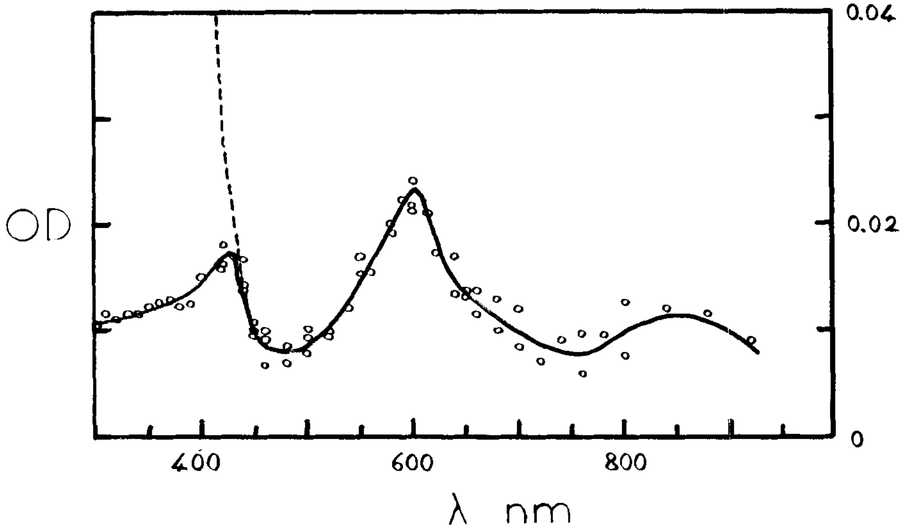

Fig. 4. *T-T spectrum of 5-nitroacenaphthene in EPA glass, 77 K*
OD = Optical density change on irradiation, λ = Wavelength of observation.
The solid curve gives the observed transient spectrum and the broken curve, the spectrum after correction for the ground state depletion.

Molar extinction coefficients at band maxima are given in *Table 1*. In some cases the genuine existence of a weak absorption band on the side of an intense band in the region 300-400 nm is doubtful. Such bands are asterisked in the table. Evidence that the observed transient absorptions arise from the triplet states is provided by the reasonable agreement in the T-T-absorption and phosphorescence decay constants *(Table 1)*. For 1-nitronaphthalene, two species were present on

Table 1. *Triplet Absorption Spectra and Decay Characteristics in EPA glass at 77 K*

Compound	Band maxima, nm (ε_M, M^{-1} cm^{-1})				P[a])	Decay constant, s^{-1}	
						T-T absorption	Phosphorescence
1-Nitronaphthalene		420 (–)	580 (–)		–	–	16.0
2-Nitronaphthalene	360(3,600)		475(750)	760(510)	5	4.05±0.04	4.4±0.4
5-Nitroacenaphthene	370(7,100)		600(500)	850(250)	12	3.8±0.4	4.2±0.6
4-Nitro-p-terphenyl	340(38,500)		600(25,500)	800(14,500)	5	3.18±0.16	3.15±0.10
p-N,N-Dimethyl-nitroaniline	390(20,600)	550(2,700)	760(2,780)	900(3,370)	5	2.29±0.05	2.30±0.10
1-Amino-4-nitro-naphthalene	440(28,000)	480[b])(7,500)	650(2,730)		50	5.3 ±0.3	4.0
MeONS			530(–)	740(–)		–	33.7
DANS	440(35,000)[c])		600(19,100)[c])		20	12.6±2.4	13.5±2.0

[a]) P = estimated percentage error in ε_M values.
[b]) This may be a shoulder.
[c]) Assuming $x_T = 0.02$, a value which leads to a reasonable net spectrum after correction for S_0 depletion (see *Figure 6*, curve a).

irradiation. One of short lifetime corresponding closely to the phosphorescence, the other much longer-lived (~seconds). Since the absorption was completely reversible at all wavelengths at 77 K, the latter species could be the monohydro radical 1-$C_{10}H_7NO_2H\cdot$.

Despite intensive searches, using both direct and phasesensitive detection methods - so effectively covering all likely triplet state lifetimes - no net transient absorptions were observed for 3-nitropyrene, *N,N*-dimethyl-*m*-nitroaniline, or 2-amino-7-nitrofluorene. The expected intense fluorescences of the latter two compounds were observed.

Attempts to investigate the dipolar nitro compounds in aliphatic hydrocarbon glasses were frustrated by the clear evidences of aggregation (UV. absorption, complex phosphorescence spectra and decays).

3.2. *Flash photolysis of fluid solutions at 299 K.* Transient absorption spectra following a 20 ns laser pulse for *trans*-1-(4-methoxyphenyl)-2-nitroethylene and *trans*-1-(4-*N,N*-dimethylaminophenyl)-2-nitroethylene (hereafter referred to as MeONS and DANS respectively) in various solvents at room temperature are shown in *Figures 5* and *6*, which also include T-T spectra of these compounds obtained in EPA glass at 77 K. In every case the observed transient absorption was a linear function of the laser pulse energy, but for DANS in polar media the decay subsequent to the pulse was not strictly exponential. First-order decay constants, for argon-flushed solutions, are given in *Table 2*.

Table 2. *Maximum yields of triplet transients and firstorder decay constants following pulse photolysis of argon-flushed solutions at 299 K*

Solvent	MeONS		DANS	
	Relative^{a}) Yield	$10^6 k_T$ s^{-1}	Relative^{a}) Yield	$10^6 k_T$ s^{-1}
C_6H_{12}	1.8	102	3.57	2.64
C_6H_6	3.9	65	3.06	1.8
C_6H_6/CH_3CN 99:1	-	-	2.81	
C_6H_6/CH_3CN 97.5:2.5	-	-	1.59	
C_6H_6/CH_3CN 95:5	6.4	58	0.96	0.26
C_6H_6/CH_3CN80:20	7.8	51	0.56	
$C_6H_{12}/CHCl_3$ 80:20	-	-	2.15	0.32
$C_6H_{12}/CHCl_3$ 40:60	-	-	0.77	0.14
CH_3OH	16.0	13.8		0.60

^{a}) Yields estimated from the maximum change in optical density following the laser pulse.

For a given compound, an estimate of the triplet yield can be derived from the maximum change in absorbance at a band maxima following the (approximately constant) laser pulse after correction for variations in parent compound optical density at the excitation wavelength and assuming that the molar extinction coefficient at the chosen band maxima is not a sensitive function of solvent polarity. The yield obtained in this manner for MeONS *(Table 2)* increases steadily with increase in the polarity of the medium. The lower apparent yield at low solvent polarity should be offset, however, by a correction arising from the fact that the triplet lifetime in such media is comparable to the laser pulse duration. While an identical trend in triplet decay constant occurs for DANS as for MeONS with increase in the solvent polarity, the estimated triplet yield appears to diminish considerably and parallels the decrease in the fluorescence quantum yield for DANS dissolved in benzene/methyl cyanide [15].

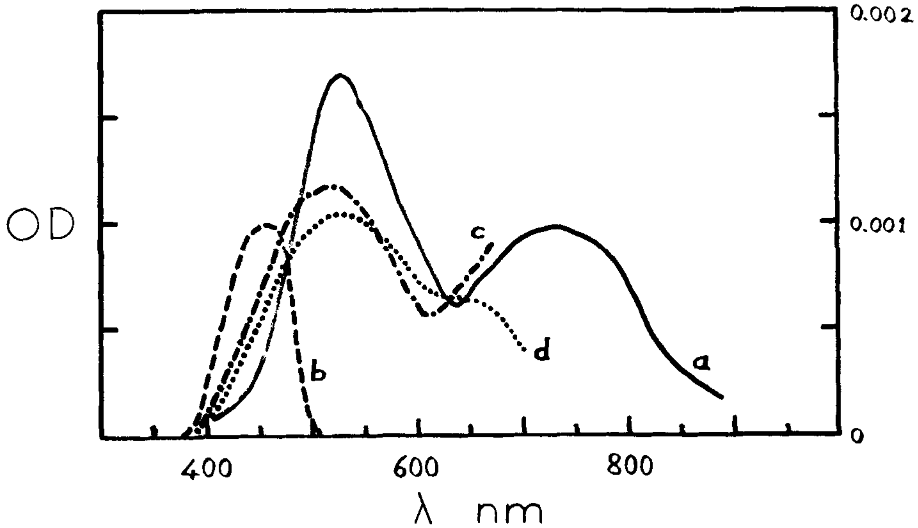

Fig. 5. *T-T spectrum of MeONS*
Curve (a) EPA, 77 K; Curve (b) In cyclohexane, 299 K; Curve (c) In benzene, 299 K; Curve (d) In benzene/acetonitrile 8:2 (*v*/*v*), 299 K.
OD = Optical density change on irradiation, λ = Wavelength of observation.

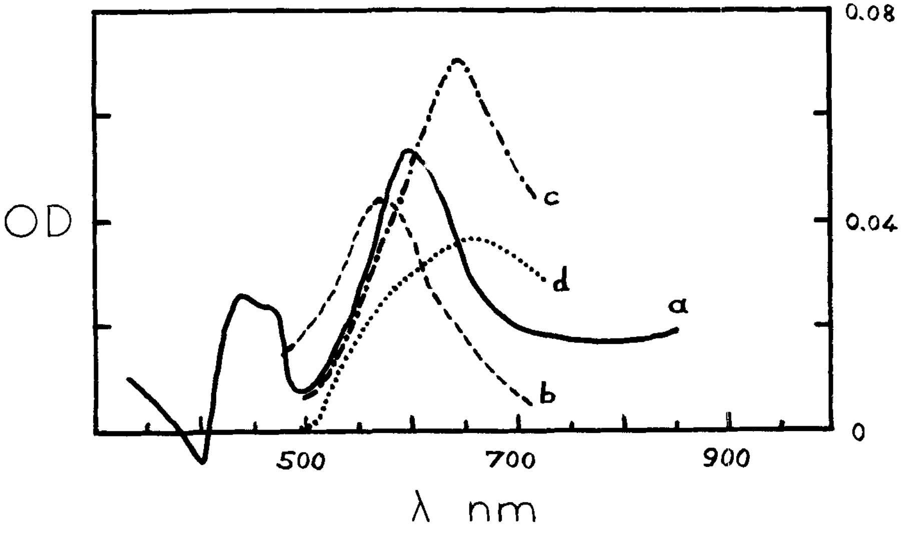

Fig. 6. *T-T spectrum of DANS*
Curve (a) EPA, 77 K; Curve (b) In cyclohexane, 299 K; Curve (c) In benzene solution, 299 K; Curve (d) In benzene/acetonitrile 8:2 (*v*/*v*), 299 K.
OD = Optical density change on irradiation, λ = Wavelength of observation.

3.3. *Theoretical calculations of T-T spectra.* The S_0-T_1 energy gaps were reproduced well by the calculations, as were the singlet-singlet ($S_n \leftarrow S_0$) transitions. Calculated T-T transition energies and 'x' and 'y' components of the transition moments are given in *Table 3* for three of the compounds studied experimentally and for which no calculations have been reported previously. The compounds were assumed to be planar with the x axis passing through the amino nitrogen (or methoxy oxygen) and the attached carbon atom. Molecular size restrictions, related to the number of required excited configurations for adequate representation of states and the corresponding computing time, prevented other larger systems from being included in this study. The nitronaphthalenes have been discussed in some detail previously [2].

Table 3. *Calculated and Experimental Triplet Transition Energies and Transition Moments*

Compound	Energy (eV)		Transition moments (Debye)		Transition
	Obs.[a]	Calc.	X	Y	
DMNA	2.36	2.14			$S_0 \leftarrow T_1$
		0.95	8.1	0.0	$T_2 \leftarrow T_1$
		1.01	0.0	0.0	(n,π^*) $T_3 \leftarrow T_1$
		1.09	2.6	0.0	$T_4 \leftarrow T_1$
		1.41	0.0	0.0	(n,π^*) $T_5 \leftarrow T_1$
	1.40	1.60	12.0	0.0	$T_6 \leftarrow T_1$
	1.64	1.78	5.3	0.0	$T_7 \leftarrow T_1$
	2.26	2.22	12.2	0.0	$T_8 \leftarrow T_1$
	3.17	3.11	4.6	0.0	$T_9 \leftarrow T_1$
		3.65	0.2	0.0	$T_{10} \leftarrow T_1$
MeONS	2.27	1.95			$S_0 \leftarrow T_1$
		1.09	0.0	0.0	(n,π^*) $T_2 \leftarrow T_1$
		1.13	7.2	0.7	$T_3 \leftarrow T_1$
		1.47	1.2	0.2	$T_4 \leftarrow T_1$
		1.52	0.0	0.0	(n,π^*) $T_5 \leftarrow T_1$
	1.67	2.17	3.3	0.3	$T_6 \leftarrow T_1$
		2.24	2.9	0.4	$T_7 \leftarrow T_1$
	2.33	2.53	4.6	0.5	$T_8 \leftarrow T_1$
	(3.3)	3.22	6.1	0.6	$T_9 \leftarrow T_1$
		3.65	1.5	0.0	$T_{10} \leftarrow T_1$
		3.97	3.1	0.3	$T_{11} \leftarrow T_1$
DANS	2.02	1.87			$S_0 \leftarrow T_1$
		1.18	5.1	0.5	$T_2 \leftarrow T_1$
		1.21	0.0	0.0	(n,π^*) $T_3 \leftarrow T_1$
		1.28	9.1	1.0	$T_4 \leftarrow T_1$
		1.63	0.0	0.0	(n,π^*) $T_5 \leftarrow T_1$
	(1.5)	1.94	4.9	0.6	$T_6 \leftarrow T_1$
		2.16	0.8	0.2	$T_7 \leftarrow T_1$
	2.07	2.45	9.2	1.2	$T_8 \leftarrow T_1$
	2.82	3.07	7.1	0.9	$T_9 \leftarrow T_1$
		3.15	9.1	1.3	$T_{10} \leftarrow T_1$
		3.78	2.3	0.1	$T_{11} \leftarrow T_1$

[a] Phosphorescence O,O band energy, EPA, 77 K.

4. Discussion. - 4.1. *T-T spectra and MO calculations.* Comment is made generally regarding the spectral band positions and intensities and briefly on broad conclusions derived from the PPP calculations for *p-N,N*-dimethylnitroaniline (DMNA), MeONS, and DANS. In the latter calculations precise interpretation proved to be difficult if not hazardous! Many of the computed triplet states were complex combinations of the singlyexcited configurations, such that ready physical description was awkward. Further, the computed transition moments derived their appreciable magnitudes from 'cross-product' terms, again making assignments difficult. The calculated transition moments do not correlate well with the observed relative band intensities, and the suggested assignments must be considered to be tentative.

In every compound examined here a prominent spectral feature is the occurrence of an intense T-T absorption band at an energy corresponding closely to that of intense lowest energy π,π^* absorption by ground state molecules ($S_{(1)} \leftarrow S_0$). In D-Ar-NO_2 type compounds (D is an electron donor) this transition $S_{(1)} \leftarrow S_0$ has strong charge-transfer (CT) character involving a large contribution from the excitation, highest occupied molecular orbital (HOMO) into the lowest vacant molecular orbital (LVMO) where the LVMO is a π^* orbital localised on the nitro group. In the cases of DMNA, MeONS, and DANS the lowest energy triplet state T_1 possesses similar (typically 50% weight), but not quite as strong, charge-transfer character as the excited singlet CT state (typically 70% weight for the CT configuration). From the calculations in these cases, the most likely assignment of the observed intense T-T absorption in the 2.8-3.3 eV region is $T_9 \leftarrow T_1$. The T_9 state consists of predominantly ringlocalised excitations, and in its dipolar character is like the singlet ground state S_0.

Thus, the band $T_9 \leftarrow T_1$ seems to correspond to a gross *back*-transfer of electronic charge from the acceptor nitro group into the rest of the unsaturated system.

In the region below the $S(CT) \leftarrow S_0$ transition in energy, most of the compounds examined exhibit a number of bands of moderate intensity. As expected, 5-nitroacenaphthene has a similar spectrum to that of 1-nitronaphthalene, but of note are the strong intensities of the bands in the spectrum of 4-nitro-*p*-terphenyl by comparison. It would appear that extension of conjugation and/or introduction of electron donating groups leads to band intensification.

For DMNA, MeONS, and DANS, in EPA at 77 K the absorption bands (in eV) in two groups A and B are as follows

	DMNA	MeONS	DANS
A	2.25	2.32	2.07
B	1.65 and 1.40	1.67	*ca.* 1.5

The 'A band' correlates in all three compounds with the computed $T_8 \leftarrow T_1$ transition. The T_8 state is dominated by an excitation from a perturbed benzene e_{1g} orbital into the LVMO on the nitro group, and thereby somewhat dipolar. The 'B band' can be assigned to either the $T_7 \leftarrow T_1$ or $T_6 \leftarrow T_1$ calculated transitions (or both in the case of DMNA where two distinct maxima are observed). The state T_7 has a major component an excitation from a perturbed benzene e_{1g} orbital into a perturbed benzene e_{2u} orbital. The state T_6 is composed of other related ring excitations but with some important CT contributions.

Unfortunately, for the fluid solutions of MeONS and DANS only a restricted spectral range (400–700) in the T-T absorption was examined and thus information from the solvent shifts of the bands is very limited. Band A, as denoted earlier, suffers an appreciable red shift with solvent-polarity increase - *ca.* 2100 cm^{-1} and 3400 cm^{-1} for DANS and MeONS respectively between cyclohexane and benzene containing 20% *v/v* acetonitrile. Such a red shift would suggest that the higher triplet level (T_8) reached from T_1 in the absorption act is significantly more dipolar than T_1.

While this explanation is straightforward it is difficult to accept on the basis of the MO calculations that the triplet could be so much more dipolar than the quite dipolar T_1 state in these two compounds. Further, it is likely that the triplet species observed in fluid media, and perhaps in EPA at 77 K also, is highly twisted about the olefinic linkage. If the latter is correct the red shift can be accounted for by the rise in energy of the twisted T_1 state with increase in solvent polarity whilst the higher triplet state (T_8?), of lower dipolarity, remains constant or drops slightly in energy. The origin of such behaviour is discussed in a subsequent section concerning triplet T_1 lifetimes in fluid media.

4.2. *Triplet yields and lifetimes.* Whilst no exact estimates of the yields of triplet species, in EPA glass at 77 K, were made important qualitative estimates were possible. Of the nitroaromatics, only in the case of 3-nitropyrene was a transient absorption not detectable. In fluid solution 3-nitropyrene does not appear to undergo any efficient photodecomposition [16]. Thus we presume that the triplet yield is very low (<0.05) and that the T-T spectral bands are very weak.

Comparison of *m-N,N*-dimethylnitroaniline with its *p*-isomer and DANS, or 2-amino-7-nitrofluorene with 1-amino-7-nitrofluorene is revealing. In the former compound of each couplet, intense fluorescence is present but negligible phosphorescence or T-T absorption, whereas in the latter compound(s) the triplet, T_1, level is populated in fair yield while some fluorescence is also observable. The fluorescence yield is sensitive to solvent polarity and the rigidity of the medium [15] [17].

The observations regarding the triplet yields and the fluorescence emission substantiate the conclusions which can be reached from the detailed fluorescence studies and molecular orbital calculations [18].

They are that:

a) D-Ar-NO_2 type compounds (D is an electron donor) exhibit fluorescence when the singlet π,π^* charge-transfer state S_1(CT) drops below the triplet n,π^* state in energy, *via* an increase in the electron donating ability of D, by substitutional position change *e.g.* para to meta, or by solvent polarity increase, or by a combination of two or more of these factors [9] [15];

b) intersystem crossing from the singlet π,π^* charge-transfer state to the lowest triplet π,π^* state is efficient only when occurring *via* the triplet n,π^* state.

Such an intersystem crossing mechanism appears to hold for *p-N,N*-dimethylnitroaniline and DANS in EPA at 77 K but S_1(CT) must lie slightly below the $^3(n,\pi^*)$ state, with a consequent thermal activation requirement. The data for fluid media is explicable on the same basis. MeONS does not fluorescence in any solvent and the corrected relative triplet yield deduced from the flash photolysis data is insensitive to changes in solvent polarity, as is also the quantum efficiency of *trans* to *cis* photo-isomerisation [16]. The latter reaction is known from sensitisation studies to proceed predominantly through the triplet state. The simplest rationalisation in this case is that S(CT) lies above both singlet and triplet n,π^* states.

On the other hand, the *trans* to *cis* photo-isomerisation of DANS at room temperature in cyclohexane solution is quenched by addition of polar solvents, as is also the case for the analogous stilbene derivative [19]. From the flash photolysis studies, the apparent yield of the DANS triplet species decreases with increase in the polarity of the solvent (see *Table 2*). However, there is a simultaneous decline in fluorescence yield, from which one may deduce that an internal conversion process is effective in polar media (k_{IC} increasing from 10^9 to $>10^{10}$ s^{-1}). In view of the minor change in the S_1–S_0 energy gap, monitored by the fluorescence emission, and the magnitude of the change in k_{IC}, it appears unlikely that the process

$$S_1 \rightarrow S_0 + \text{heat}$$

is the deactivation channel. An alternative route is

$$S_1 \rightarrow S_1{}^t$$

where $S_1{}^t$ is a relatively non-emissive isomer of S_1, whose nature is suggested by an argument advanced first by *Mataga* [20].

Increase of solvent polarity favours the development of charge separation in the emitting singlet state but this involves a corresponding decrease in electron delocalisation. Conversely, a change in molecular conformation which hinders delocalisation will favour a more ionic electronic state, and such a change will be assisted by the stabilising influence of polar solvent media (see also *Salem* [21] [22]).

Molecular orbital calculations on DANS and similar compounds [23] reveal that a somewhat more dipolar excited state is produced on twist of a dimethylamino group from coplanarity with the attached aromatic ring. Such an internal rotation, however, must involve an associated reduction in the radiative rate constant k_F for the transition $S_0 \leftarrow S_1$, k_F being zero for 90° twist.

We suggest that the non-emissive singlet state $S_1{}^t$ is a conformer in which the Me_2N moiety is substantially twisted from coplanarity with the aromatic ring, the whole system being the intramolecular analogue of singlet intimate ion-pair of intermolecular donor-acceptor systems.

Further support for this hypothesis lies in the variation of the fluorescence quantum yield of both DANS and 4-*N,N*-dimethylamino-4′-nitrostilbene [24] with temperature. From limited data, the higher solvent polarity the stronger the fluorescence quenching but *(Table 4)* the lower is the activation energy of the quenching process (determined from plots of $1/\phi_F$ against $1/T$ in the region where the solvents are fluid and fluorescence still measurable, normally between 180 and 300 K). Assuming that the singlet excited state is represented by a variable combination of locally-excited, LE, and charge-transfer, CT, configurations, the simplified correlation diagrams for nonpolar and polar solvent systems *(Figure 7)* show clearly the origin of the observed trends. The transformation of the excited state from a more locally-excited configuration to a mainly charge-transfer configuration occurs at an earlier point on the curve and involves a lower energy barrier, the more the CT state is stabilised by the solvent.

Table 4. *Activation energies,* E_a, *for fluorescence quenching of DANS and 4-dimethylamino-4'-nitrostilbene* (DMANS) *in fluid media*

Solvent	Activation energy E_a kJ mol^{-1}	
	DANS	DMANS[a])
$C_6H_5CH_3$	35.6	31.5
$(CH_3CH_2)_2O$	24.0	
CH_3CH_2OH	14.4	17.0
CH_3OH		13.4
$(CH_3)_2NCHO$		~0

[a]) Estimated values from the data in [24].

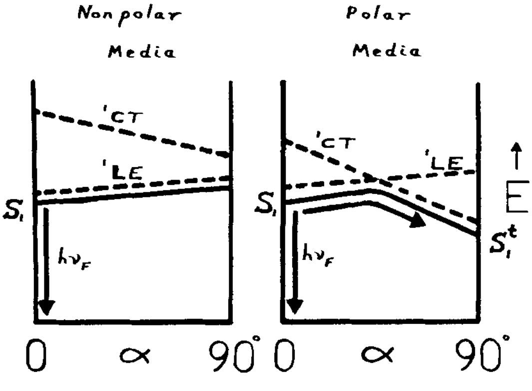

Fig. 7. *Variation of the energy of the lowest* π,π^* *excited state with the internal rotation angle* α *of the dimethylamino group in* Me_2N-*Ar-A type compounds*
^{1}LE = Locally-excited configuration, (D-Ar)*-A. ^{1}CT = Charge-transfer configuration, $(D^+\text{-Ar-}A^-)^*$. S_1 is considered to be a varying mixture of ^{1}LE and ^{1}CT configurations with change in angle α.

Although the lifetime of the dipolar fluorescent state of DANS is shortened in polar media, the lifetime of the lowest energy triplet state appears to increase in polar solvents *(Table 2)*. Further, for a given solvent the triplet lifetime of DANS, in which more charge-transfer character is expected to be present, is longer by an order of magnitude than the triplet lifetime of MeONS. The latter lifetime is affected in the same way by solvent polarity as that of DANS. Identical trends in triplet lifetimes have been reported for the corresponding stilbene derivatives [7] [8]. While other explanations may exist, the following appears to fit the known data admirably. Consider an olefin of general form DCH=CHA where D is a π-electron donor group and A is a π-electron acceptor group. For the electronic ground state, S_0, twist about the double bond involves a substantial energy barrier. The excited triplet state T_1 can be represented as a resonance between a canonical diradical form ^3D, in which the central double bond is broken, and a canonical zwitterionic form ^3Z, in which the double bond is preserved, as shown in *Figure 8*. In a situation where ^3Z carries little weight in the actual triplet state, rotation about the central bond in the triplet state is energetically very favourable as electron repulsions are relieved such that the T_1 potential curve can be quite close to the S_0 potential curve at the 90° twist position *(Fig. 8)*. The radiationless crossing $S_0 \leftarrow T_1$ is correspondingly rapid.

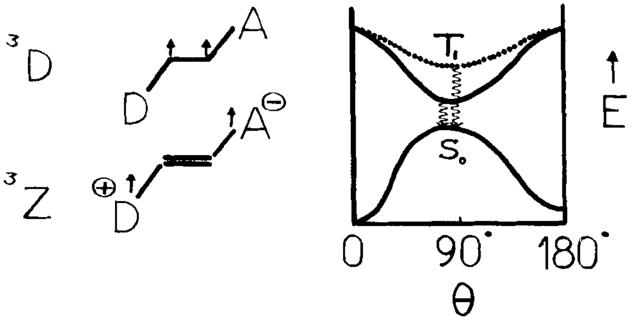

Fig. 8. *Variation in energy* E *of the lowest triplet excited state T_1 and the ground electronic state S_0 with rotation angle, θ, about the olefinic bond in a representative D–CH=CH–A system*
^3D = Triplet diradical configuration. ^3Z = Triplet zwitterionic configuration. T_1 Curves - full line: non-polar media dotted line: polar media.

However, if the zwitterionic component, ^3Z, of T_1 is increased, for example by increase in the donor ability of D and/or increase in solvent polarity, the T_1 potential curve does not dip down as much as before since twist of the ^3Z form involves an energy barrier. Thus the radiationless passage from the T_1 surface to the S_0 surface becomes slower, and the triplet lifetime, therefore, longer.

In conclusion, the weight of the evidence of various kinds presented here suggests strongly the influence of conformational changes on the rates of photophysical processes, especially in molecules possessing the potential for gross transfer of electronic charge from one end of the molecule to the other.

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