Emissions of Sterically Hindered Stilbene Derivatives and Related Compounds. Part IV.[1] Large Conformational Differences between Ground and Excited States of Sterically Hindered Stilbenes: Implications regarding Stokes Shifts and Viscosity or Temperature Dependence of Fluorescence Yields

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Large effects of molecular overcrowding on fluorescence spectra (Stokes shifts) and quantum yields were observed in a series of stilbene derivatives. The measured Stokes shifts depend strongly on the extent of molecular overcrowding. The fluorescence quantum yields increase sharply with increasing viscosity and decreasing temperature. As the extent of overcrowding increases, the temperature range over which fluorescence is observed is shifted downwards, and the importance of viscosity increases. This reflects a corresponding complementary variation of the radiationless processes competing with fluorescence. CFF–SCF–PI calculations of the ground and first excited singlet state geometries of the *trans*- and *cis*-isomers of stilbene and of $\alpha\alpha'$-dimethylstilbene chosen as model molecules indicate that excitation results in large changes in the ring–α and α–α' torsion angles of the relaxed sterically hindered molecules, and therefore in substantial relaxation energies. Good agreement is obtained between observed and calculated Stokes shifts. The viscosity dependence of fluorescence quantum yields is correlated with the calculated Franck–Condon factors for the radiationless transitions competing with fluorescence.

IN previous publications [1] we have shown the existence of fluorescence in *cis*-stilbene and several related compounds. In all cases the emission quantum yield, Q_F, was found to increase sharply on cooling the respective solutions, in many cases approaching unity at 77 K. We could show that, with the exception of *cis*-4,4'-diphenylstilbene,[1a] this was predominantly a viscosity effect.

In the present paper we describe the fluorescence spectra and quantum yields of a series of *cis*-stilbene derivatives over a wide temperature range, in two aliphatic hydrocarbon solvents of widely differing viscosity: decalin, and a 1 : 1 mixture of methylcyclohexane (MCH) and 3-methylpentane (3-MP). The macro-viscosities of both solvents in a wide range of temperatures are known [2] (Figure 1) and can serve as a basis for a comparison of temperature and viscosity effects. In the former case, the observed variation of Q_F with the temperature should be similar in both solvents, while in the latter case, at any given temperature, Q_F in the much more viscous decalin may be expected to be much higher than in MCH–3-MP (within the temperature range in which Q_F increases with decreasing temperature). Several *trans* $\alpha\alpha'$-disubstituted stilbenes were also investigated.

EXPERIMENTAL

Fluorescence spectra were measured with a home-built instrument consisting of a 450 W Xenon lamp, two 500 mm Bausch and Lomb grating monochromators, and an EMI 9558Q photomultiplier whose anode current was measured directly with a Micrograph BD5 recorder having a maximum sensitivity of 20 nA full scale. Sealed-off regular 10 × 10 mm cross-section cells containing the solutions were thermostatted by the copper block technique described earlier.[3] Emission was measured at right angles to the exciting light. A spectral correction curve was determined with known standards, and so were the absolute quantum yields.[4] The *trans*-isomers of compounds (1), (4), and (5) were commercial products purified by t.l.c. Those of compounds (2), (3), and (6) were synthesized according to the literature, as was *cis*-(6). Compound (7) was prepared according to Suzuki,[5] whose procedure results in a mixture of *cis*- and *trans*-isomers. The *trans*-isomer was isolated by repeated recrystallization, the *cis* was purified by chromatography of a solution in methylcyclohexane on a Woelm basic alumina column, followed by recrystallization. All other *cis*-isomers were prepared from the corresponding *trans*-isomers by partial *trans*$\rightarrow$*cis*-photoconversion, followed by recrystallization and t.l.c. M.p.s were as reported in the literature. The purity of all compounds was checked by analytical g.l.c.

RESULTS AND DISCUSSION

Two classes of compounds were investigated, 4- and 4,4'-substituted stilbenes (I) and $\alpha\alpha'$-disubstituted stilbenes (II).

The absorption and emission spectra of all *cis*-compounds are shown in Figure 2, while Figure 3 describes Q_F as a function of the temperature for each compound, both in decalin (denoted D) and in MCH–3-MP (denoted M). According to Figure 2, all *cis*-compounds exhibit a pronounced Stokes shift,[1] but in $\alpha\alpha'$-dimethyl- and -dichloro-stilbene this shift is particularly large, with the emission and absorption peaks being almost 200 nm (16 500 cm^{-1}) apart in $\alpha\alpha'$-dimethyl-*cis*-stilbene. Regarding the variation of Q_F with temperature, Figure 3 shows two prominent features. First, as we go from left to right, Q_F in D starts as being *smaller* than in M for

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[1] (*a*) Part III, G. Fischer and E. Fischer, *Mol. Photochem.*, 1972, **3**, 373; (*b*) Part II, J. Klueger, G. Fischer, E. Fischer, Ch. Goedicke, and H. Stegemeyer, *Chem. Phys. Letters*, 1971, **8**, 279; (*c*) Part I, S. Sharafi and K. A. Muszkat, *J. Amer. Chem. Soc.*, 1971, **93**, 4119, where earlier literature is cited extensively.

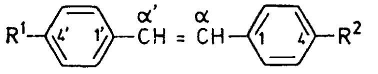
[2] (*a*) H. Greenspan and E. Fischer, *J. Phys. Chem.*, 1965, **69**, 2446; (*b*) G. A. v. Salis and H. Labhart, *ibid.*, 1968, **72**, 752; (*c*) A. C. Ling and J. E. Willard, *ibid.*, p. 3343.

[3] E. Fischer, *Mol. Photochem.*, 1970, **2**, 99.

[4] I. B. Berlman, 'Handbook of Fluorescence Spectra of Aromatic Molecules,' Academic Press, New York, 1971, 2nd edn.

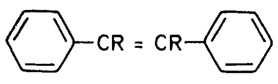
[5] H. Suzuki, *Bull. Chem. Soc. Japan*, 1960, **33**, 405.

compound (4), but already in (3) the situation is reversed, and the M curves are increasingly shifted towards lower temperatures, relative to the D curves. Secondly, the temperature range in which Q_F attains appreciable values, say above 0.04, is shifted towards lower temperatures in the order (4), (3), (2), (1) in the *para*-substituted compounds, *i.e.* the parent *cis*-stilbene (1) is at the extreme right. In the αα′-disubstituted compounds the situation is reversed: the temperature at which Q_F attains any particular value is shifted downwards, with (6) being the most extreme case ($Q_F^{-180°}$ 0.04), while (5) behaves almost like (1). Solid (6) and (7) do not emit. Incidentally, no emission was observed with solutions of the very overcrowded *cis*-2,2′,4,4′,6,6′-hexamethylstilbene.



(I)

(1) $R^1 = R^2 = H$
(2) $R^1 = R^2 = CH_3$
(3) $R^1 = H, R^2 = C_6H_5$
(4) $R^1 = R^2 = C_6H_5$



(II)

(5) R = F
(6) R = CH_3
(7) R = Cl

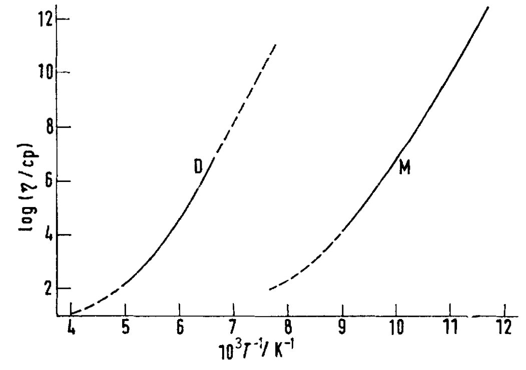


FIGURE 1 Variation of the viscosity η (cp) with the reciprocal temperature T^{-1} (K^{-1}): M = methylcyclohexane–3-MP (1 : 1), D = decalin

The fluorescence behaviour of the corresponding αα′-disubstituted *trans*-stilbenes was also studied.[6] The absorption and emission spectra are shown in Figure 4, while the variation of Q_F^{trans} with the temperature is presented by the broken curves in Figure 3. The data for *trans*-stilbene are given for comparison. The relation between absorption and emission spectra in difluoro-*trans*-stilbene, *trans*-(5) is rather similar to that in the parent *trans*-stilbene *trans*-(1), but in the dimethyl and dichloro-derivatives the Stokes shift is almost as big as in the *cis*-derivatives. [The absorption spectra of *cis*- and *trans*-(7) have been reported by Ballester *et al.*[7] and those of (6) by Suzuki.[8]] The quantum yields are much *smaller* than those observed with the corresponding *cis*-derivatives at the same temperature, even with the difluoro compound. This is just the opposite behaviour of that observed with *trans*-stilbene and its *meta*- or *para*-substituted derivatives, where as a rule $Q_F^{trans} \gg Q_F^{cis}$ at room temperature, *cf.* curves M-(1) and *trans*- (1) in Figure 3. Q_F of *trans*-(4) = 1 even at 100°.[1a] Solid

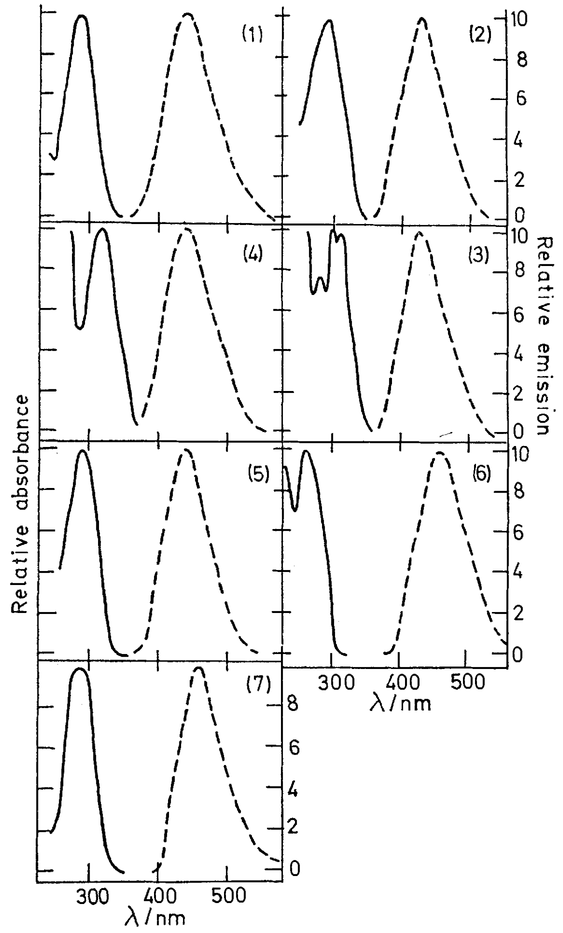


FIGURE 2 Absorption (full curves) and corrected fluorescence (broken curves) spectra of *cis*-stilbenes in MCH–3-MP at −180 to −190° in 10 mm cells. Concentrations were in the range 1—5 × 10^{-5}M. Fluorescence spectra are normalized for equal peak height with absorption peaks. The compounds are numbered as denoted in the text

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[6] D. Gegiou, K. A. Muszkat, and E. Fischer, *J. Amer. Chem. Soc.*, 1968, **80**, 3907. Q_F of *trans*-(5) at −183° was erroneously given as 0.35. The correct value is 0.15.

[7] M. Ballester, C. Molinet, and J. Rosa, *Tetrahedron*, 1959, **6**, 109.

[8] H. Suzuki, ' Electronic Absorption Spectra and Geometry of Organic Molecules,' Academic Press, New York, 1967.

trans-(6) and (7) emit appreciably at 20°. Table 1 summarizes the absorption and emission data of both isomers of compounds (1) and (5)—(7) in solution at −190°.

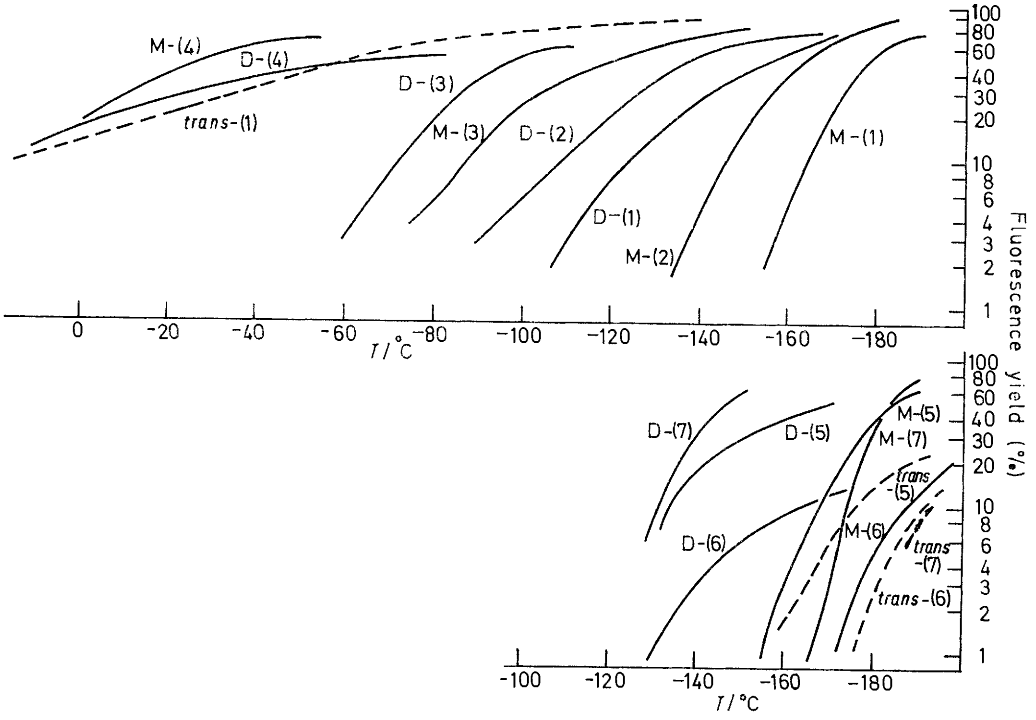

FIGURE 3 Temperature dependence of fluorescence quantum yields in two solvents: D = decalin, M = 1 : 1 MCH–3-MP. For numbering of compounds see text. Full curves denote *cis*-isomers in the solvent indicated, broken curves denote *trans*-isomers in MCH–3-MP

Two main points in the current results are of particular interest: (a) the Stokes shift, and (b) the variation of the fluorescence quantum yield with the temperature, and the way both are affected by the substituents of *cis*- and *trans*-stilbene.

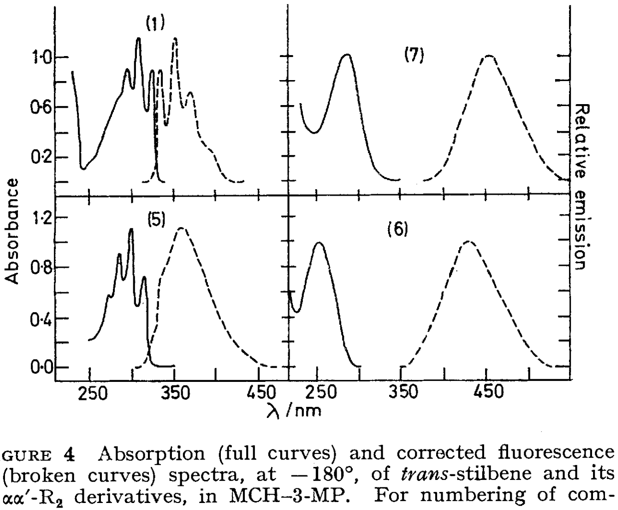

FIGURE 4 Absorption (full curves) and corrected fluorescence (broken curves) spectra, at −180°, of *trans*-stilbene and its αα′-R$_2$ derivatives, in MCH-3-MP. For numbering of compounds see text

(a) *Stokes Shift*.—The present and previous results[1] can be summarized by the statement that a combination of flexibility and increasing overcrowding in a molecule results in increasing Stokes shifts, indicating substantial relaxation processes following (1), excitation to the S_1 level, and (2), emission to the S_0 level

$$(S_0) \xrightarrow{(1)} S_1 \xrightarrow{(2)} (S_1) \xrightarrow{(3)} S_0 \xrightarrow{(4)} (S_0)$$

The parentheses denote relaxed levels, steps (1) and (3) are Franck–Condon controlled radiative steps, and (2) and (4) are relaxation processes in the excited and ground states, respectively. All *trans*-stilbenes not substituted in the *ortho* ring or in the α and α′ positions may be expected to have a coplanar geometry[8,9] both in the ground and in the excited state, with a resulting more or less pronounced vibrational structure in the absorption spectra, and a small Stokes shift, as shown in Figure 4, curves (1) and (5). As molecular crowding increases by substituting the above positions with larger groups, *i.e.* methyls, in the *trans*-form, or by isomerisation to the *cis*-form, steric repulsion of the groups in the immediate environment of the central double bond increases and coplanarity is lost by twisting about both the essential α–α′ double bond and the two essential 1–α and 1′–α′ single bonds. In the excited

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[9] A. Bromberg and K. A. Muszkat, *Tetrahedron*, 1972, **28**, 1265. The headings for the columns of Table 2 in that paper for both S_1 and S_0 states should respectively read ϕ_a, ϕ_b, ϕ_c, P_a, P_b, and P_c.

singlet state the π-bond orders are reversed, and overcrowding is relieved in a different way than in the ground state, resulting in a different molecular geometry and in a greatly enhanced energy gain during relaxation (2) in the excited state. The same, in reverse, holds concerning emission (3) from the relaxed excited to the unrelaxed ground state, the overall effect being the observed large Stokes shift. This shift is due to the energy difference between the transitions (1) and (3), and increases with the molecular overcrowding caused by replacing the α- and α'-hydrogens with methyl or chlorine. The CFF–SCF–PI calculations detailed below for compounds (1) and (6) provide the quantitative aspects of these ideas. As expected, replacement of hydrogen by fluorine has almost no effect on the absorption and emission spectra, since both atoms have similar van der Waals radii.

TABLE 1

Positions of absorption and emission peaks, and Stokes shifts * in *cis*- and *trans*-isomers of $\alpha\alpha'$-disubstituted stilbenes, observed in MCH–3-MP solutions at −180 to −190°.

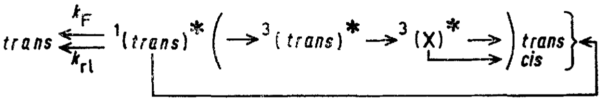
Compound	Absorption peak (nm)	Emission peak (nm)	Stokes shift (nm)		
			λ_F	λ_A	$\Delta = \lambda_F - \lambda_A$
cis-(1)	290	440	366	340	26
trans-(1)	297, 310 327	335, 352 372, (395)			‘ 0 ’
cis-(5)	295	442	364	336	28
trans-(5)	275, 286 300, 315	(326), (335) 360, (380)			‘ 0 ’
cis-(6)	260	460	388	312	76
trans-(6)	250	430	360	293	67
cis-(7)	293	460	402	338	64
trans-(7)	282	450	387	330	57
trans-$(CH_3)_6$-stilbene	278	345, 363 380	328	324	4

* When comparing compounds having structured absorption and emission spectra with those which do not, it is difficult to define the Stokes shift in an unambiguous way. In the present study, we have defined it as the wavelength difference Δ between the longwave onset of the absorption band, λ_A, and the shortwave onset of emission, λ_F, because in the absence of vibronic structure there is no way of estimating the 0–0 transitions. (In this context ‘ onset ’ will be defined as the wavelength at which the absorbance or emission is 1% of its peak value.) This results in a slightly negative Δ for *trans*-(1) and *trans*-(5). The ‘ observed ’ Stokes shifts listed in Table 4 are defined as the difference between the longest absorption and the shortest emission peaks, according to the second and third columns above.

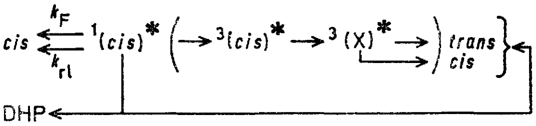
We are dealing here with solutions of hydrocarbons (only two having polar substituents) in an aliphatic hydrocarbon solvent. The above relaxation processes cannot therefore be ascribed to a rearrangement of the solvent cage around the solute, caused by differences in dipolar interactions between the solvent and the S_1 and S_0 states of the solute.

Also, since the shape of the fluorescence spectra does not vary with the temperature or the viscosity, it follows that the fluorescence is due solely to the relaxed S_1 state.

(b) *Fluorescence Quantum Yields and their Variation with the Temperature.*—These are controlled by the rates of all competing deactivation processes, relative to that of fluorescence, within the wide temperature range investigated, since it appears unlikely that the actual rate of emission k_F varies considerably with the temperature. For the *trans*-isomers these competing reactions are *trans* $\xrightarrow{h\nu}$ *cis* isomerisation (probably *via* the triplet state), and radiationless transition to the ground state. For the *cis*-isomers they are *cis* $\xrightarrow{h\nu}$ *trans*, *cis* $\xrightarrow{h\nu}$ 4a,4b-dihydrophenanthrene (DHP) derivatives, and again radiationless transitions. Reactions (5) and (6) summarizes the fate of the singlet-excited *trans*- and *cis*-molecules. k_F and k_{rl} denote radiative and radiationless transitions, respectively. Any variation of Q_F with the temperature therefore actually reflects a variation of some or all of these rates, including intersystem crossing. It is only for the trivial reason that it is so much easier to determine Q_F in a wide temperature range, that most investigations deal with Q_F, rather than with Q(*cis* $\rightleftharpoons$ *trans*), Q(*cis* $\longrightarrow$ DHP), and Q(radiationless).



(5)



(6)

The Q_F values presented in Figure 3 show two interesting features. First, steric overcrowding, both in the $\alpha\alpha'$-disubstituted *trans*-isomers, and in all *cis*-isomers, sharply lowers Q_F at and around room temperature, by comparison with the parent compound. In other words, the competing deactivation processes predominate, and are only gradually cut out as the temperature is lowered. Substitution in the $\alpha\alpha'$-positions even causes a reversal of the relative positions of the *cis*- and *trans*-curves. The case of *trans*-(5) is exceptional. Since this cannot be a steric effect, either electronic or mass factors have to be involved. Secondly, in most cases it is impossible to distinguish unequivocally between temperature and viscosity effects on Q_F. In compound *cis*-(4), Q_F in decalin is *smaller* than in MCH, indicating a true temperature effect. However, in *cis*-(3) the situation is reversed, though curves M-(3) and D-(3) are still rather close. As we move to the right in Figure 3, corresponding D and M curves move apart, and the temperature range in which Q_F attains appreciable values moves downwards. The fact that all D curves, except D-(4), are shifted towards higher temperatures, relatively to the corresponding M curves, proves the existence of a pronounced viscosity effect, superimposed on a true temperature effect. In Table 2 we summarize the values of the viscosity, in both solvents, at which $Q_F = 0.04$, obtained by combining data from Figures 1 and 3. According to this compilation, for each compound $Q_F = 0.04$ in decalin at a macro-viscosity which is *ca.* 40—80 times higher than in methylcyclohexane. In other words, if we are dealing with a viscosity effect, the micro-viscosity 'felt' by the solute molecules in D is 40—180 times smaller than that expected from a comparison of the macro-viscosities in D and M. This holds for all *cis*-compounds, despite the fact that the temperature and viscosity range of observable fluorescence varies within extremely wide limits (Table 2). On the other hand, this observation may also be the result of superimposed temperature and viscosity effects, with the effect of higher temperatures being compensated by higher viscosities, in D, and that of lower viscosities by lower temperatures, in M.

TABLE 2

Temperatures and viscosities at which the fluorescence quantum yield $Q_F = 0.04$, for several *cis*-stilbene derivatives in decalin (D) and in a MCH-3-MP mixture (M)

Compound (solvent)	Temperature (°C)	Viscosity (log η/cp)
(3) (D)	−64	1.7
(3) (M)	−76	~0
(2) (D)	−95	3.4
(2) (M)	−138	1.8
(1) (D)	−113	5.4
(1) (M)	−159	3.6
(7) (D)	−127	7.7
(7) (M)	−171	6.2
(6) (D)	−144	(11)
(6) (M)	−179	8.3

From the general trend of all D and M curves in Figure 3 it emerges that in the $\alpha\alpha'$-R_2 compounds, as the overcrowding increases, lower temperatures and higher viscosities are required to attenuate the radiationless deactivation processes, and thereby to increase Q_F. Whether these processes are *cis* $\longrightarrow$ DHP, *cis* $\rightleftarrows$ *trans*, intersystem crossing, or internal conversion we cannot decide without measuring the quantum yields of the former three photoconversions in the same temperature range. However, it should be recalled that in all *cis*-stilbene derivatives and related compounds investigated so far, both the above photoconversions have been found to be attenuated on cooling,[10] with one exception.[11] Moreover, at least in the two halogenated *trans*-stilbenes (5) and (7), internal conversion $S_1 \longrightarrow S_0$ or intersystem crossing not followed by isomerisation must be substantial, in view of the low quantum yields of fluorescence and of *trans* $\longrightarrow$ *cis* photoisomerisation. [At −175° for compound (5) $Q_F = 0.13$, $Q_{t\to c} = 0.22$, $Q_{c\to t} = 0.40$, while for (7) $Q_F = 0.002$, $Q_{t\to c} = 0.08$, $Q_{c\to t} = 0.15$].

Substitution in the 4 and 4′ positions has the opposite effect on Q_F^{cis}, *i.e.* higher temperatures and lower viscosities suffice to attenuate the radiationless deactivations of ${}^1(cis)^*$, as the substituents increase in size and number, in the order (1),(2),(3),(4). The relative importance of the temperature effect, compared with the viscosity effect, increases in the same order. In the absence of further experimental information we may assume that the solvent and its interaction with the solute play an important role in the effect of both the temperature and the viscosity on Q_F. A qualitative treatment of the viscosity dependence of Q_F will be suggested in the following section.

Analysis of Stokes Shifts and of Viscosity Effects.—The present results as well as those of previous communications [1,10c] indicate remarkable differences in photochemical and in spectroscopic properties between planar and nonplanar stilbenes. In this section we shall present an analysis limited to two aspects in which the planar and nonplanar molecules differ strongly, namely Stokes shifts and viscosity dependence of fluorescence quantum yields. These two subjects are amenable to a straightforward analysis based on the calculation of geometry differences between the two electronic states involved. As will be shown later, among the molecules examined in the present study, *trans*-stilbene is planar while the *cis*-isomer as well as both *cis*- and *trans*- $\alpha\alpha'$-dimethylstilbene are nonplanar.

The topmost occupied and the lowest unoccupied MOs of stilbenes are essentially perturbed MOs of the $\alpha\alpha'$-ethylene unit. Thus excitation from S_0 to S_1 (and to a large extent to T_1) involves transfer of an electron from a π 1–α (and 1′–α') antibonding and α–α' bonding orbital to an α–α' antibonding and 1–α bonding orbital. On excitation of the nonplanar molecules, as will be shown subsequently, these changes in the bonding character of the wave function combined with the effect of the steric repulsions result in large geometry changes.

We obtained the ground and excited state geometries as well as π-excitation energies and normal modes by the CFF–SCF–PI–CI method described recently by Warshel and Karplus.[12] This semiempirical method is based on a combination of a Pariser–Parr–Pople π-electron treatment for the π-electrons with a potential function method for the calculation of the σ core energy,[12] and involves an efficient minimalization of the total energy with respect to all co-ordinates. The total potential energy $V(r)$ is expressed as an analytic function of the co-ordinates r in the form (7) where $V_\sigma(r)$ and $V^\circ_\pi(r)$ are the respective σ and π electron contributions to the ground state energy, $V_\sigma(r)$ is an empirical potential

$$V(r) = V_\sigma(r) + V^\circ_\pi(r) + \Delta V_\pi(r) \qquad (7)$$

function, and $\Delta V_\pi(r)$ is the π-electron excitation energy. All the parameters for the three energy contributions were optimized extensively by Warshel and Karplus so as to provide best results for a wide range of properties of

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[10] (*a*) S. Malkin and E. Fischer, *J. Phys. Chem.*, 1964, **66**, 1153; (*b*) K. A. Muszkat and E. Fischer, *J. Chem. Soc.* (*B*), 1967, 662; (*c*) D. Gegiou, K. A. Muszkat, and E. Fischer, *J. Amer. Chem. Soc.*, 1968, **90**, 12 and 3907; (*d*) T. Knittel, G. Fischer, and E. Fischer, *J.C.S. Chem. Comm.*, 1972, 84; (*e*) T. Wismonski-Knittel, G. Fischer, and E. Fischer, *J.C.S. Perkin II*, 1974, 1930.

[11] R. Naef and E. Fischer, *Helv. Chim. Acta*, 1974, **54**, 2224.

[12] A. Warshel and M. Karplus (*a*) *J. Amer. Chem. Soc.*, 1972, **95**, 5612; (*b*) *Chem. Phys. Letters*, 1972, **17**, 7; (*c*) *J. Amer. Chem. Soc.*, 1974, **96**, 5677.

[13] A. Warshel and M. Levitt, Quantum Chemistry Program Exchange, Program No. 247, QCFF/PI.

a large series of molecules. On this account, as far as ground and excited state geometries of large molecules are concerned, this method has many advantages. In particular, the excited state geometries of several polyenes calculated by Warshel and Karplus with this procedure led to a satisfactory simulation of the vibrational envelopes of the electronic absorption bands of such molecules.

TABLE 3

Bond lengths, R, (Å), and torsional angles τ (°)

	Stilbene				αα′-Dimethylstilbene			
	trans		*cis*		*trans*		*cis*	
	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1
$R(1,\alpha)$	1.48	1.42	1.48	1.42	1.50	1.43	1.50	1.43
$R(\alpha,\alpha)$	1.35	1.43	1.35	1.44	1.36	1.46	1.36	1.46
$\tau(1,\alpha)$	0	0	35	13	47	13	47	13
$\tau(\alpha,\alpha')$	180	180	10	37	6	49	7	49

In Table 3 we report the results calculated by this method for the internal co-ordinates undergoing the largest changes upon excitation.[13, *] These co-ordinates are the torsional angles τ about the 1–α, 1′–α′, and α–α′ bonds in the nonplanar molecules, and the 1–α, 1′–α′, and α–α′ bond lengths. According to the present results the nonplanar molecules are strongly twisted about the 1–α and 1′–α′ bonds in the ground state, while in the excited state the major twist is about the α–α′ bond.[†]

The calculated lengths of the 1′–α, 1′–α′, and α–α′ bonds are almost the same in the four molecules examined, both in the S_0 and the S_1 state. Thus the differences between *trans*- and *cis*-stilbene on the one hand, and *trans*-stilbene and *cis*- or *trans*-αα′-dimethylstilbene on the other, are mainly due to changes, upon excitation, in the torsional angles about the α–α′ and 1–α bonds in the nonplanar molecules.

The calculated and observed values of the absorption and emission energies are reported in Table 4. ΔE_A and ΔE_E are, respectively, the vertical $S_0 \longrightarrow S_1$ and $S_1 \longrightarrow S_0$ transition energies (*cf.* Figure 5). $\Delta E_A - \Delta E_E$ is a measure of the Stokes shift and ΔE_0 is the 0,0 transition energy between the S_0 and S_1 states. The observed ΔE_A and ΔE_E values refer to the experimental absorption and fluorescence maxima. The measured Stokes shifts increase along the series *trans*-stilbene, *cis*-stilbene, *trans*-, and *cis*-αα′-dimethylstilbene. This increase parallels the calculated increase in the equilibrium value of the torsion angle about the central α–α′ bond, on excitation (Table 3).

In this context, the previously reported results on the blue shift of fluorescence in sterically-hindered stilbenes in the neat glassy state[15] are of particular interest. Those results lead to the conclusion that lower values of Stokes shifts are obtained under extreme viscosity conditions where changes in the torsional angles are prevented from taking place. This conclusion is fully borne out by the results given in Tables 3 and 4.

TABLE 4

Electronic transitions in kK. ΔE_A, and ΔE_0 are defined in Figure 5. Experimental values are from Table 1 (Absorption and emission peaks)

		Stilbene		αα′-Dimethylstilbene	
		trans	*cis*	*trans*	*cis*
ΔE_A	calc.	33.76	35.43	37.84	37.8
	obs.	32.26	34.48	40.0	38.46
ΔE_E	calc.	29.01	26.34	22.91	22.9
	obs.	28.41	22.73	23.26	21.74
$\Delta E_A - \Delta E_E$	calc.	4.75	9.09	14.93	14.9
	obs.	3.85	11.75	16.74	16.72
ΔE_0	calc.	31.44	30.85	30.9	31.21

The calculated Stokes shifts (Table 4) are in good agreement with the experimental values, not only as far as the magnitude of the effect is concerned but also with respect to the relative values in the series. Thus the calculated Stokes shifts for both isomers of αα′-dimethylstilbene are equal, as found experimentally, while *cis*-stilbene occupies an intermediate position between *trans*-stilbene and *cis*- or *trans*-αα′-dimethylstilbene.

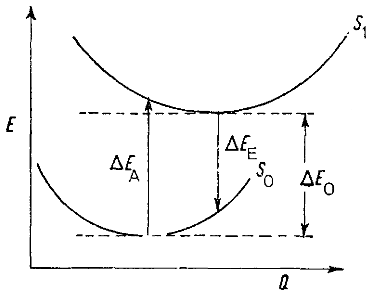

FIGURE 5 Schematic potential curves for S_1 and S_0 states. Q is one of the active co-ordinated, such as torsion about the α–α′ bond

In Part I, the strong increase in the fluorescence quantum yields of nonplanar stilbene derivatives at high viscosities has been attributed in a qualitative sense to the effect of high viscosity in reducing the amplitudes of torsional and out-of-plane bending vibrations of the solute.[1c] These vibrations were assumed to play an important role in determining the rate of the internal conversion process (radiationless $S_1 \longrightarrow S_0$ transition).[1c] The results of Table 3 confirm this interpretation. The large differences in the α–α′ and 1–α torsional angles between ground and excited states of the nonplanar molecules indicate that the corresponding normal modes will be strongly excited during transitions between such states.[16] The Franck–Condon factors F of such normal

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[*] A detailed calculation of *cis*- and *trans*-stilbene has been recently completed.[14]

[†] In the previous investigation on this subject,[9] due to the poor minimalization procedure, these changes in the αα′-torsional angles in the dimethylstilbenes were overlooked, as only values of $\tau(\alpha,\alpha')$ lower than 15° were explored for the excited state.

[14] A. Warshel, *J. Chem. Phys.*, 1975, **62**, 214.

[15] G. Fischer, E. Fischer, and H. Stegemeyer, *Ber. Bunsenges. Phys. Chem.*, 1973, **77**, 685.

[16] G. Herzberg and E. Teller, *Z. phys. Chem.* (*Leipzig*), 1933, **B21**, 410.

modes (for both radiative and radiationless transitions) are correspondingly large.[18,19] However, as will be shown later, vibrations of this type are prevented by a highly viscous medium.

According to several theoretical treatments of radiationless transitions,[17,18] the final vibrational levels of the lower state are quasi-degenerate with the initial electronic state in its zeroth vibrational level. Thus to satisfy the quasi-degeneracy requirement very high vibrational levels of the final electronic state have to be involved in radiationless transitions.

The rate constant k for a radiationless transition is given according to these treatments by expression (8) [17,18] where J denotes the electronic coupling matrix

$$k = 2\pi/hJ^2\rho\bar{F}(E) \qquad (8)$$

element, ρ is the density of states, and $\bar{F}(E)$ is the total mean Franck–Condon factor for an energy gap E. Obviously the rate will be reduced under conditions where $\bar{F}(E)$ decreases. This is seemingly the situation which prevails in viscous solutions of nonplanar stilbenes.

Planar and nonplanar molecules were thus far compared on the basis of the geometry differences between S_1 and S_0 (Table 3). Examination of harmonic Franck–Condon factors for single modes (Table 5) serves to emphasize further the difference between planar and nonplanar molecules. We shall choose *cis*-stilbene as a model for the nonplanar case and compare it to the planar *trans*-stilbene. The discussion will be limited first to one-normal-mode Franck–Condon factors. Compared to *trans*-stilbene, *cis*-stilbene is seen (Table 5) to have a considerably larger number of low frequency modes ($\nu < 1\,000$ cm^{-1}) with large Franck–Condon factors for the $S_1 \longrightarrow S_0$ transition. The $F(0,n)$ components listed in Table 5 (zeroth vibrational level of S_1, n-th level of S_0) are very much larger for *cis-* than for *trans*-stilbene. As a result, Franck–Condon factors for vibrations with large quantum numbers in the final state will be considerably larger for *cis*-stilbene. Such Franck–Condon factors usually determine the magnitude of radiationless processes. Inspection of Table 5 shows that the low-frequency modes considered here are mostly composed of torsional and out-of-plane bending motions of the 1,1′,α, and α′ atoms.

TABLE 5

Vibrations excited in $S_1 \longrightarrow S_0$ transition

trans-Stilbene [a]				*cis*-Stilbene			
ν/cm^{-1} [b]	n [c]	F [d]	Description [e]	ν/cm^{-1}	n	F	Description
1 662	1	0.6	α–α′ st. + 1–α st.	1 658	1	0.9	α–α′ st. + 1–α st.
1 613	1	0.3	C–C st. + C–C–H bend. + C–C–C bend.	1 614	1	0.2	C–C st. + C–C–H bend. + C–C–C bend.
1 360	1	0.1	α–α′-H bend.	1 264	1	0.2	1–α st. + C–C–H bend.
1 246	1	0.1	α–1 st. + C–C–H bend.	1 053	1	0.2	C–C–C bend. (ring) + o.o.p.-H
1 051	1	0.2	C–C–C bend. (ring)	1 020	1	0.6	α-H, o.o.p. + α–α′ tor. + 1–α tor.
				669	1	0.2	α–α′ tor. + 1–α tor. + ring def.
				549	1	1.4	α–α′ tor. + 1–α tor. + ring def.
				435	1	1.2	α–α′ tor. + 1–α tor. + ring def.
				287	1	0.6	α–α′ tor.
229	1	0.5	1–α–α′ bend.	201	2	2.8	1–α tor. + α–α′ tor.
				50	2	4.5	1–α tor. + α–α′ tor.

[a] Missing frequencies are very weakly excited. [b] S_0 Frequencies. [c] Quantum number of reported ground-state vibrational component. [d] Franck–Condon factor for n-th component relative to $F(0,0)$. [e] st.—stretching, bend—bending, C—ring carbon atom, def.—deformation, tor.—torsion, o.o.p.—out of plane bending.

The mean total Franck–Condon factor [17,18] will be reduced when the one-mode Franck–Condon factors are decreased. This will occur when the molecule in the final electronic state is constrained by the rigid solvent. Such a situation is encountered in the nonplanar stilbenes at high viscosities and results in greatly increased fluorescence quantum yields, due to the slowing down of the internal conversion and probably of other radiationless processes which compete with fluorescence in the deactivation of the S_1 state.[1c,10c]

The mean total Franck–Condon factor of *trans*-stilbene is necessarily lower than that of *cis*-stilbene (Table 5). As a result the $S_1 \longrightarrow S_0$ radiationless process in *trans*-stilbene is expected to be small even at low viscosity. Therefore this molecule has a larger (and weakly viscosity dependent) fluorescence quantum yield even in fluid solutions.

The present discussion was based on a model of Franck–Condon factors for harmonic oscillators. In the real case anharmonicity in the final state should of course be considered. However, the qualitative conclusions drawn from the simple model are expected to remain valid.

Other radiationless processes such as $S_1 \longrightarrow T_1$, $T_1 \longrightarrow T_2$, or possibly photocyclization are undoubtedly important in the present context.[10c] From the CI-SCF-PI-electron wave functions of Beveridge and Jaffé,[20] it is possible to infer that these (as well as the $S_1 \longrightarrow S_0$ transition) involve considerable geometry changes in the 1–α–α′–1′ region. Though the energy gaps and the

[17] D. M. Burland and G. W. Robinson, *J. Chem. Phys.*, 1969, **51**, 4548.

[18] W. Siebrand, *J. Chem. Phys.*, 1967, **46**, 440.

[19] E. Heilbronner, K. A. Muszkat, and J. Schäublin, *Helv. Chim. Acta*, 1971, **54**, 58.

[20] D. L. Beveridge and H. H. Jaffé, *J. Amer. Chem. Soc.*, 1965, **87**, 5340.

geometry changes for these transitions are widely different, they are nevertheless expected to show qualitatively similar dependence on the medium viscosity.*

Obviously, the effects of solvent viscosity on radiative processes such as fluorescence and on radiationless processes such as internal conversion are different. The radiative processes are influenced only by the highest viscosities (*cf.* blue shift and Stokes effects). However, radiationless processes such as internal conversion [1c] are affected already by much lower viscosities. To a large extent this dissimilarity is readily attributed to different vibrational states involved. For radiative transitions, degeneracy is no longer required and therefore, only the lowest vibrational levels (the zeroth level in the absence of geometry changes) of the final electronic state need be considered.[19] On these grounds viscosity changes are expected to affect mainly the shape of the vibrational envelope and to have only a limited effect on the total Franck–Condon factor for radiative transitions.

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* For the T_1 state of *cis*-stilbene, the values calculated by the method of ref. 12 are $\tau(\alpha,\alpha') = 32°$ and $\tau(1,\alpha) = 14°$.