Temperature Dependence of Photoisomerization. IV. Evidence for the Involvement of Triplet States in the Direct Photoisomerization of Stilbenes

Sir:

Contrary to the opinion expressed recently,[1,2] we wish to suggest that the direct photoisomerization of stilbenes proceeds following intersystem crossing from the first excited singlet level S_1 into an isoenergetic or quasi-isoenergetic triplet level T. We base this conclusion on several different lines of experimental evidence.

1. *External Enhancement of the trans-to-cis Photoisomerization Quantum Yield in Stilbene at Low Temperatures by a Heavy-Atom Solvent.* The above quantum yield ϕ_t in *fluid* hydrocarbon solutions, with light at 313 mμ, decreases from 0.50 at room temperature to 0.006 at $-183°$.[3,4] This decrease is equivalent to an activation energy of about 1.2 kcal/mole, assumed to be equal to the energy gap between the vibrationally relaxed first excited singlet level (S_1) and a quasi-isoenergetic triplet level (T) into which crossing takes place.[5a] In an outgassed fluid methylcyclohexane–isohexane (MCH/IH) solution of stilbene (3×10^{-5} *M*) at $-105°$, ϕ_t is[4] 0.12. The fluorescence quantum yield, ϕ_F, of *trans*-stilbene under the same conditions is[5b] 0.54 ± 0.08. In fluid solutions in *n*-butyl bromide, serving as a heavy atom solvent (dried over Al_2O_3 *in vacuo*), under the same conditions, ϕ_t is 0.49 ± 0.05 and ϕ_F is 0.30 ± 0.05. Thus in a heavy-atom solvent at $-105°$ ϕ_t retains its value at room temperature, while ϕ_F is smaller than in MCH/IH. We explain these results by assuming an enhanced yield of intersystem crossing ϕ_{ISC} by the heavy atom, an effect well known from other cases[6,7] and ascribed to mixing between the singlet and triplet states of the solute. In the present case an increased mixing would result either in a depression of the level T or in an increased probability of intersystem crossing to a different triplet level T′, of energy lower than T.

2. *Internal Enhancement of ϕ_t Values at Low Temperatures by Substituents (either a heavy atom or groups with a low energy localized n–π* triplet transition).*[5a] We have found that in sterically nonhindered stilbenes, in fluid media, the temperature dependence of ϕ_t is determined by the nature of the substituent on the aromatic ring. Stilbene proper and its derivatives substituted with a group showing only a weak effect on intersystem-crossing yields, such as 4-chloro-, 4-methoxy-, or 4-dimethylaminostilbene, require an activation energy (from 1 to 10 kcal/mole) for the intersystem-crossing steps. In these compounds the ϕ_t values (0.3–0.6 at room temperature) decrease to almost zero at low temperatures. Stilbenes substituted with groups that enhance intersystem crossing[8] have ϕ_t values independent on temperature. This behavior was observed in 4-bromostilbene[3,4] and 4-nitro-, 4-aceto-, and 4-benzoylstilbene.[5a] We propose that the reason for this effect and for the external enhancement is similar, namely, an enhanced yield ϕ_{ISC}.

3. *Uncoupling of the Fluorescence from the trans-to-cis Photoisomerization by Using High-Viscosity Media.* The ϕ_t values of stilbene and many of its sterically unhindered derivatives are strongly lowered in media of very high viscosity,[5b] while the ϕ_F values are practically unaffected. Thus for stilbene in glycerol at $-80°$ $\phi_t = 0.001$ and $\phi_F = 0.46$, while in MCH/IH[5a,9] $\phi_t = 0.22$ and $\phi_F = 0.35$. For 4-bromostilbene in glycerol at $-80°$ the respective values are $\phi_t = 0.009$ and $\phi_F = 0.11$, while in MCH/IH at the same temperature[4] $\phi_t = 0.35$ and ϕ_F 0.11. We have ascribed[5b] this effect to the fact that *cis*-stilbene occupies a larger volume than *trans*-stilbene in solution, and that the increase in volume during *trans* → *cis* transformation cannot be accommodated in a highly viscous solvent. Under such conditions isomerization stops while its precursor, intersystem crossing, continues and remains the major pathway competing with fluorescence in the deactivation of the first excited singlet of *trans*-stilbene.

A genuine quenching of the S_1 level of stilbenes would not detract in any way from the validity of the present conclusions about the triplet mechanism. However, the interpretation of the quenching experiment of excited stilbene molecules by azulene[1] is somewhat controversial. Azulene was reported *as a very efficient quencher of triplets*,[10] while tris(dibenzoylmethanato)-iron(III), which is known as an efficient quencher of singlet excited molecules, does not affect the unsensitized photoisomerization.[11,12]

The lack of any effect of perdeuteration on the rate of direct photoisomerization, and on the photostationary composition of the system stilbene + sensitizer, at room temperature, was suggested[2] as evidence against the triplet mechanism of direct photoisomerization.

We have confirmed these results with stilbene perdeuterated in the rings and obtained similar ones in a wide temperature range, down to $-180°$, both for ϕ_t and ϕ_F. However, we believe that this absence of an isotope effect is definitely compatible with a triplet mechanism. In stilbenes, the $T_1 \rightarrow S_0$ decay (during or following which the final geometry is determined) takes place by a mechanism different from that of the radiationless transition $T_1 \rightarrow S_0$ in rigid polycylic aromatic molecules, as described by Robinson and Frosch.[13] Thus in stilbenes a crossover, without tunneling, from a common T_1 state (configuration proper to zero-point energy) to a twisted S_0 state is energetically feasible.[3,11] Moreover, results of photosensitization experiments[11] and the absence of phosphorescence in stilbenes[14,15] indicate that this $T_1 \rightarrow S_0$ radiationless transition has a very high rate constant which, contrary to the stituation with rigid aromatic molecules,

---

(1) J. Saltiel, E. D. Megarity, and K. G. Kneipp, *J. Am. Chem. Soc.*, 88, 2336 (1966).

(2) J. Saltiel, *ibid.*, 89, 1037 (1967).

(3) R. H. Dyke and D. S. McClure, *J. Chem. Phys.*, 36, 2326 (1962).

(4) S. Malkin and E. Fischer, *J. Phys. Chem.*, 68, 1153 (1964).

(5) Forthcoming publications in this series: (a) part V; (b) part VI.

(6) G. W. Robinson, *J. Mol. Spectry.*, 6, 58 (1961).

(7) S. P. McGlynn, M. J. Reynolds, G. W. Daigre, and N. D. Christodoyleas, *J. Phys. Chem.*, 66, 2499 (1962).

(8) S. K. Lower and M. A. El-Sayed, *Chem. Rev.*, 66, 199 (1966).

(9) Interpolation of the results of ref 4, Figure 1.

(10) G. S. Hammond and P. A. Leermakers, *J. Phys. Chem.*, 66, 1148 (1962).

(11) G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Am. Chem. Soc.*, 86, 3197 (1964).

(12) *Cf.* R. P. Foss and D. O. Cowan, unpublished results, mentioned on p 3211 of ref 11.

(13) G. W. Robinson and R. P. Frosch, *J. Chem. Phys.*, 38, 1187 (1963).

(14) F. Aurich, M. Hauser, E. Lippert, and H. Stegemeyer, *Z. Physik. Chem.* (Frankfurt), 42, 123 (1964).

(15) A. A. Lamola, G. S. Hammond, and F. B. Mallory, *Photochem. Photobiol.*, 4, 259 (1965).

does not depend on the overlap factor between the vibrational wave functions of the T_1 state and the isoenergetic, C–H vibrationally excited S_0 level. It is the latter which is strongly affected by deuteration. The magnitude of the energy gap $T_1 \rightarrow S_0$, which otherwise determines the overlap factor,[13] may therefore be expected to be without any effect on the high rate of the radiationless $T_1 \rightarrow S_0$ process.

We conclude that positive evidence in favor of triplet intermediates is available, whereas evidence against them is either disputable or not relevant.

K. A. Muszkat, Dina Gegiou, Ernst Fischer
Chemistry Department, Weizmann Institute of Science
Rehovoth, Israel

Received June 2, 1967

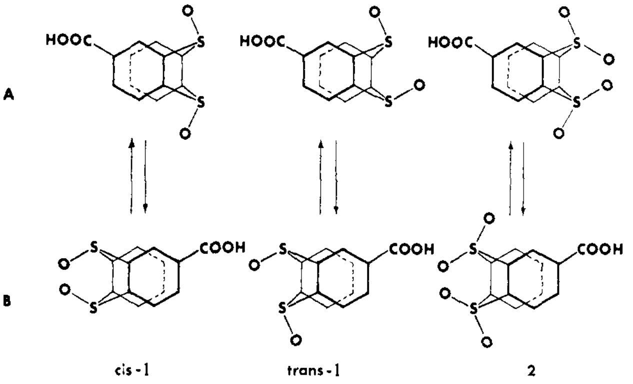
Conformational Flexibility of Thianthrene and Its Oxides[1]

Sir:

Thianthrene, the *cis*- and *trans*-5,10-dioxides, and the 5,5,10,10-tetroxide have folded structures in the crystal state,[2] with dihedral angles in the neighborhood of 130°. While dipole moment evidence[3,4] indicates that folding about the line joining the sulfur atoms is maintained in solution, it is recognized that the molecule of thianthrene and its derivatives oscillates rapidly through a planar position, as deduced from theoretical estimates[5–7] (3–7 kcal/mole) of the activation energy barrier which separates the folded molecule of thianthrene from its inverted form, from failure to separate the stereoisomers which result from folding,[5,8] and from dipole moment[4] and nmr[9] studies. Similar conclusions have been arrived at from studies of analogous heterocyclic systems.[6,8,10,11]

In light of the overwhelming evidence attesting to conformational flexibility in thianthrene and its derivatives, a recent report by Janczewski and Charmas[12] assumes particular importance. The finding by these authors that oxidation of the optically active forms[13] of *cis*- and *trans*-2-thianthrenecarboxylic acid 5,10-dioxide (**1**) affords optically active 2-thianthrenecarboxylic acid 5,5,10,10-tetroxide (**2**) is of far-reaching significance, for the following reasons. Isolation of optically active disulfone **2** demonstrates unequivocally that the tricyclic structure is *rigidly* folded; the resistance of **2** to racemization under the drastic conditions of preparation (oxidation of **1** with 30% hydrogen peroxide in glacial acetic acid at 105–115° for 5 hr) and purification (recrystallization from boiling glacial acetic acid) shows that a surprisingly high energy barrier (*i.e.*, of the order of 25 kcal/mole or greater[14]) separates the enantiomeric conformers of **2**; and the observation[12] that (+)-*cis*-**1** and (+)-*trans*-**1** both give (+)-**2** with $[\alpha]^{20}\mathrm{D}$ +18.18° while (−)-*cis*-**1** and (−)-*trans*-**1** both give (−)-**2** with $[\alpha]^{20}\mathrm{D}$ −18.18° can only mean that both *cis*- and *trans*-sulfoxides **1** contain the two possible diastereomeric conformers in *identical* ratios. The last point is illustrated in Chart I, with arbitrarily chosen configurations and conformations: only the same ratio of *cis*-**1A**:*cis*-**1B** and of *trans*-**1A**:*trans*-**1B** can result in the same ratio of (+)-**2**:(−)-**2**, *i.e.*, in the same optical rotation of **2**. Alternatively, the conformers of *cis*- and *trans*-**1** must exist predominantly in one of the two possible forms (*e.g.*, **A**), exhibiting a thermodynamic preference which is particularly unexpected for *trans*-**1**.

Chart I



We now report that the claims[12] of Janczewski and Charmas cannot be substantiated. The preparation and resolution of *cis*- and *trans*-**1** were repeated, giving results in essential agreement with those reported.[13] When racemic *cis*-**1** was heated for 5 hr with 30% hydrogen peroxide in glacial acetic acid at 105–115°, the product (±)-**2** had mp 306–308° (lit.[12] 312–314°, lit.[13] 300–301°, lit.[15] 302–303°) and an infrared spectrum identical with that reported.[12] *Anal.* Calcd for $C_{13}H_8O_6S_2$: C, 48.14; H, 2.49; S, 19.77. Found: C, 48.32, H, 2.44; S, 19.86; M^+, *m/e* 324. Oxidation of (−)-*cis*-**1** (mp 278–280° with resolidification and remelting at 296–298°[16], $[\alpha]^{25}\mathrm{D}$ −134° (1% aqueous sodium hydroxide); lit.[13] mp 285–287°, $[\alpha]^{20}\mathrm{D}$ −126.57° (1% aqueous sodium hydroxide)) under the same condi-

---

(1) This work was supported by the Air Force Office of Scientific Research under Grant No. AF-AFOSR-1188-67.

(2) H. Lynton and E. G. Cox, *J. Chem. Soc.*, 4886 (1956); I. Rowe and B. Post, *Acta Cryst.*, **11**, 372 (1958); S. Hosoya and R. G. Wood, *Chem. Ind.* (London), 1042 (1957); S. Hosoya, *ibid.*, 159, 980 (1958); S. Hosoya, *Acta Cryst.*, **16**, 310 (1963); **21**, 21 (1966).

(3) E. Bergmann and M. Tschudnowsky, *Ber.*, **65**, 457 (1932); W. S. Walls and C. P. Smyth, *J. Chem. Phys.*, 1, 337 (1933); G. M. Bennett and S. Glasstone, *J. Chem. Soc.*, 128 (1934); T. W. J. Taylor, *ibid.*, 625 (1935); E. Bergmann and A. Weizmann, *Chem. Ind.* (London), 364 (1938); H. Lumbroso and G. Montaudo, *Bull. Soc. Chim. France*, 2119 (1964).

(4) M. J. Aroney, R. J. W. LeFèvre, and J. D. Saxby, *J. Chem. Soc.*, 571 (1965).

(5) G. H. Keats, *ibid.*, 1592 (1937).

(6) K. Mislow, A. Zimmerman, and J. T. Melillo, *J. Am. Chem. Soc.*, **85**, 594 (1963).

(7) A. K. Chandra, *Tetrahedron*, **19**, 471 (1963).

(8) H. Baw, G. M. Bennett, and P. Dearns, *J. Chem. Soc.*, 680 (1934); G. M. Bennett, M. S. Lesslie, and E. E. Turner, *ibid.*, 444 (1937).

(9) K. F. Purcell and J. R. Berschied, Jr., *J. Am. Chem. Soc.*, **89**, 1579 (1967).

(10) M. C. Thompson and E. E. Turner, *J. Chem. Soc.*, 29 (1938); I. G. M. Campbell and E. E. Turner, *ibid.*, 37 (1938); J. P. A. Castrillón and H. H. Szmant, *J. Org. Chem.*, **32**, 976 (1967).

(11) The conformational rigidity ascribed to conformers of 9-[(N-methyl-3-piperidyl)methyl]thioxanthene (W. Michaelis, O. Schindler, and R. Signer, *Helv. Chim. Acta*, **49**, 42 (1966)) is more properly described by the statement that one of the two forms (*i.e.*, the a′,a′ form in the *cis* isomer and the a′,e′ form in the *trans* isomer) exists as by far the most populous component in a *mobile* conformational equilibrium.[6]

(12) M. Janczewski and W. Charmas, *Roczniki Chem.*, **40**, 1243 (1966); for a preliminary report, see ref 13.

(13) M. Janczewski, M. Dec., and W. Charmas, *ibid.*, **40**, 1021 (1966).

(14) For example, taking the half-life of racemization as 10 min at 105°, if $\Delta S^{\ddagger} = 0$ eu, $\Delta H^{\ddagger} = 27.3$ kcal/mole.

(15) H. Gilman and D. R. Swayampati, *J. Am. Chem. Soc.*, **79**, 208 (1957).

(16) At the melting point the optically active forms of *cis*- and *trans*-**1** suffer racemization by pyramidal inversion at sulfur (*cf.* D. R. Rayner, E. G. Miller, P. Bickart, A. J. Gordon, and K. Mislow, *ibid.*, **88**, 3138 (1966)); furthermore, the *trans* form isomerizes to the *cis* form (K. Mislow, P. Schneider, and A. L. Ternay, Jr., *ibid.*, **86**, 2957 (1964)), mp 296–298°.