Table I. Molecular Orbital Results

A. Net Atomic Charges			
O(1)	−0.74	H(1) (av)	+0.03
O(2)	−0.69	H(2) (av)	+0.05
N(1)	+1.57	N(2)	+0.92
O(1)	−0.18	O(3)	−0.88
C(2)	−0.15		
B. Mulliken Overlap Populations[a]			
O(1)–N(1)	0.82	C(2)–H(2) (av)	0.62
O(2)–N(1)	0.84	C(2)–N(2)	0.72
N(1)–C(1)	0.75	N(2)–O(3)	0.71 (0.07)
C(1)–C(2)	0.81	N(2)–N(2)′	1.00 (0.24)
C(1)–H(1) (av)	0.69		

[a] π contribution to overlap population is indicated by parentheses.

populations,[15] are shown in Table I. Overlap populations should not be confused with bond orders: calculated overlap populations for a variety of molecules are available for purposes of comparison in ref 13. The nitro groups give a partial check on the degree of charge exaggeration in our wave function. The group dipole moment obtained from our calculated net charges is 4.5 D., compared to the experimental value in nitromethane of 3.5 D. Hence, we feel that while our net charges are moderately overestimated because of the lack of an explicit SCF procedure in the computations, the error thus introduced should not seriously modify our conclusions.

The molecular orbital results for the nitroso part of the system provide evidence that resonance structure II makes a very substantial contribution to the bonding in C-nitroso dimers. The overlap populations indicate that the π system perpendicular to the O–N–N–O plane contributes considerable double bond character to the N–N bond, but relatively little to N–O. This result is closely associated with the form of the highest filled molecular orbital (of symmetry u) which has nodes near the midpoints of the N–O bonds. Furthermore, the calculated charge distribution shows that the N–O bond is highly polar, even allowing for some charge exaggeration. The N–N bond length of 1.315 A is consistent with this interpretation, being considerably shorter than the value[16] of 1.41 A for the single bond in $N_2H_6^{2+}$, where adjacent nitrogen atoms may also be expected to bear large positive charges. The short distance and high stretching frequency of N–O with respect to single bond values are then attributed chiefly to coulombic attraction and only secondarily to the small amount of π character indicated in the overlap population. Contributions from other resonance structures, acting so as to reduce the polarization associated with the formal charges of II, are to be expected and are in fact implied by the population analysis.

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(15) R. S. Mulliken, *J. Chem. Phys.*, 23, 1833, 1841 (1955).
(16) Reference 11, p 57.

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Perdeuteriostilbene. The Role of Phantom States in the *cis–trans* Photoisomerization of Stilbenes

Sir:

The following deals with the sensitized and direct *cis–trans* photoisomerization of perdeuteriostilbene. In interpreting the data, we have modified the triplet mechanism for sensitized isomerization and suggest a new mechanism for direct photoisomerization.

trans-Perdeuteriostilbene was synthesized from *cis*-perhydrostilbene by four exchanges with heavy water over platinum at about 200°.[1] Mass spectroscopic analysis showed that the *trans*-perdeuteriostilbene used is 80% d_{12}, 14% d_{11}, 4.3% d_{10}, and 1% d_9.[3] Irradiations were carried out in a merry-go-round apparatus.[4] Samples were degassed. A uranium glass filter (cutoff $\lambda \leq 3300$ A) was used for sensitized isomerizations and a 3130 A "filter train" for unsensitized isomerizations. Photostationary states were approached from *trans*-perdeuteriostilbene. Generally, *trans*-perdeuteriostilbene and *cis*- and *trans*-perhydrostilbenes were irradiated simultaneously. Analyses were by vapor phase chromatography.

Triplet-State Path. A phantom (twisted) triplet state, nearly isoenergetic and in equilibrium with the *trans* triplet, was suggested as a key intermediate in the sensitized photoisomerization of the stilbenes.[4] To account for small temperature effects on photostationary states it was assumed that phantom triplet decay to *cis* S° is more probable than *trans* triplet decay to *cis* S^0, and that the phantom triplet has higher enthalpy content than the *trans* triplet.[4] The estimate of the lifetime of stilbene triplets, 10^{-8} sec, depends on the assumption that excitation transfer from stilbene triplets to azulene (eq 1) is diffusion controlled.[4]

$$t^{T^1} + Az^{S^0} \xrightarrow{k_q} t^{S^0} + Az^{T^1} \qquad (1)$$

We find that: (1) several sensitizers lead to photostationary compositions which are, within experimental uncertainty, identical for perdeuterated and undeuterated stilbene;[5] (2) for benzophenone-sensitized isomerization *trans* → *cis* quantum yields are identical for the two stilbenes.

Deuteration decreases the rate of $T^1 \rightarrow S^0$ radiationless decay.[6] Theory predicts the effect to diminish as the energy separation between electronic states decreases.[7] Deuteration, then, should affect *trans* triplet decay more than phantom triplet decay. The absence of a deuterium effect leads to the conclusion that *decay from trans triplets is negligible for both perhydro- and perdeuteriostilbene*. The supposed requirement that the phantom triplet be at higher energy than the *trans* triplet is removed.[8] Figure 1 shows a modified potential energy diagram for the triplet state ($k_1 \ll k_2$

(1) We find disproportionation to bibenzyl and phenanthrene to be a significant side reaction.[2]
(2) J. L. Garnett and W. A. Sollich-Baumgartner, *J. Phys. Chem.*, 69, 3526 (1965).
(3) We thank Mr. David Weiss and Professor N. J. Turro for the mass spectroscopic data.
(4) 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).
(5) Sensitizers ranged in triplet energy from 69 to 48 kcal/mole.
(6) S. K. Lower and M. A. El-Sayed, *Chem. Rev.*, 66, 199 (1966).
(7) G. W. Robinson and R. Frosch, *J. Chem. Phys.*, 37, 1962 (1962); 38, 1187 (1963).
(8) A higher activation energy for decay of phantom triplets to *cis* ground state than to *trans* ground state could account for the temperature effect.

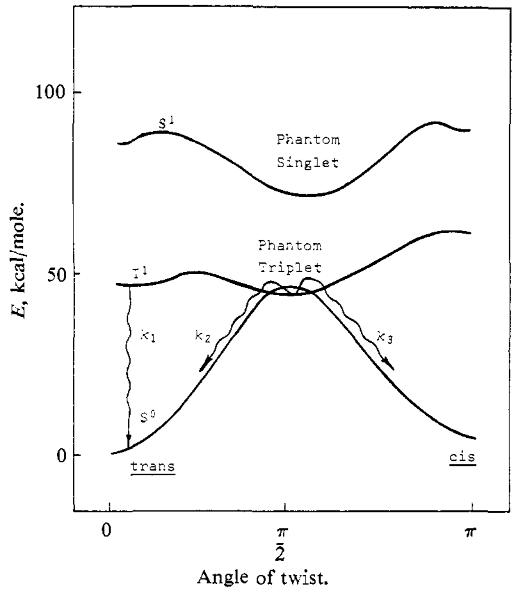

Figure 1. Possible potential energy diagram for the lowest electronic states of the stilbenes ($k_1 \ll k_2$ or k_3).

or k_3). The twisted triplet is shown at lower energy than the *trans* triplet. This would allow crossing of S^0 and T^1 potential energy surfaces[9] and account for the short lifetime of stilbene triplets.[12]

Relative lifetimes of perdeuterio- and perhydrostilbene triplets were determined in experiments with benzophenone as sensitizer and azulene as quencher. The data are plotted in Figure 2.[13] Table I shows ratios of rate constants obtained. It follows that $(k_2^H + k_3^H)/(k_2^D + k_3^D) = 1.2\text{–}1.3$; *i.e., perdeuteration increases the lifetime of stilbene triplets only 20–30%.* In contrast, perdeuteration increases the lifetime of pyrene triplets sixfold at 25°.[14]

Table I. Ratios of Rate Constants

Substrate	Temp, °C	k_q/k_2, M^{-1} $\times 10^{-2}$	k_2/k_3
Perhydrostilbene	25	1.20	0.72
	60	1.88	0.65
Perdeuteriostilbene	25	1.57	0.72
	60	2.25	0.65

The temperature effect on the k_q/k_2 ratios confirms the assumption that reaction 1 is diffusion controlled. The Debye equation for diffusion-controlled rates yields $k_q^{60}/k_q^{25} = 1.7$.[15] Assuming that k_2^H and k_2^D are temperature independent, the experimental values are 1.4 for perdeuteriostilbene and 1.6 for perhydrostilbene (Table I), in good agreement with the calculated value.

Singlet-State Path. It has been shown that the path for direct photoisomerization of the stilbenes by-passes the triplet states.[16] The conclusion was that the Lewis mechanism in which molecules pass through a condition of free rotation following $S^1 \rightarrow S^0$ conversion[17,18] obtains.

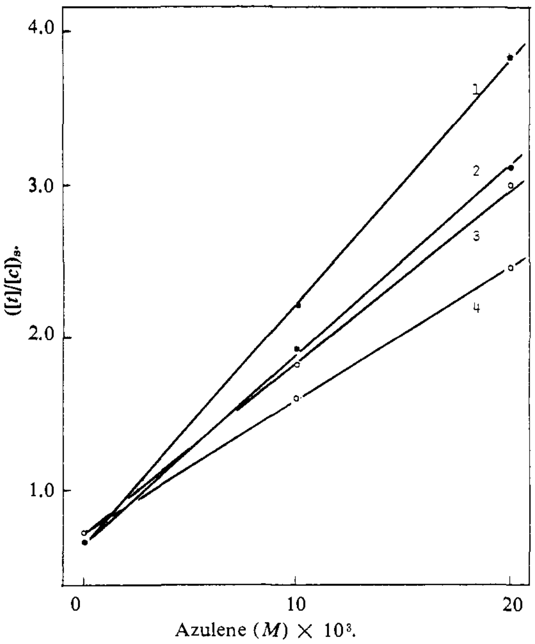

Figure 2. Relative lifetimes of stilbene triplets: lines 1 and 3, perdeuteriostilbene, lines 2 and 4, perhydrostilbene; lines 1 and 2, effect at 60°, lines 3 and 4, effect at 25°. Benzophenone 0.05 M, total stilbene concentration 5×10^{-3} M.

We now find that benzene solutions of *trans*-perdeuteriostilbene and *trans*-perhydrostilbene, irradiated in parallel, approach photostationary states at rates which are identical within experimental uncertainty. *Deuterium substitution does not alter cis → trans and trans → cis quantum yields.*

If vibrational modes of the nascent excited ground state molecules were active, a large deuterium isotope effect should have been observed. The Lewis mechanism accounts for the absence of this effect only if we postulate that essentially all electronic excitation in S^1 is converted into rotational energy of the central bond—an unlikely occurrence.[19] We therefore propose a mechanism involving a common twisted S^1 state, the singlet phantom state (Figure 1). The absence of *trans*-stilbene fluorescence from *cis*-stilbene is accounted for if the energy of the phantom singlet is low relative to the energy of *trans* S^1. Since the geometries of the phantom singlet and triplet states should be similar, the new mechanism allows rationalization of the fact that *cis*/*trans* decay ratios from S^1 and T^1 states are identical.[4]

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[9] The best estimate for the transition stage of thermal *cis* → *trans* isomerization is 43–49 kcal/mole.[10,11]

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[11] G. B. Kistiakowsky and W. R. Smith, *J. Am. Chem. Soc.*, **56**, 638 (1934).

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[13] Data in Figure 2 for perhydrostilbene are new determinations. Previous work was at 30° with [Az] $\leq 10^{-2}$ M.[4]

[14] R. E. Kellogg and R. P. Schwenker, *J. Chem. Phys.*, **41**, 2860 (1964). Note that the S^0–T^1 energy gap in pyrene is also about 49 kcal/mole.

[15] The viscosity of benzene at the two temperatures was obtained by interpolation from data in "Handbook of Chemistry," N. A. Lange, Ed., 9th ed, Handbook Publishers Inc., Sandusky, Ohio, 1956, p 1658.

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[17] G. N. Lewis, T. T. Magel, and D. Lipkin, *ibid.*, **62**, 2973 (1940).

[18] It is important to note that in this mechanism decay is from spectroscopic *trans* S^1 states.

[19] For objections to the Lewis mechanism see also G. Zimmerman, L. Chow, and V. Paik, *J. Am. Chem. Soc.*, **80**, 3528 (1958). For similar arguments applied to a different system, see H. E. Zimmerman and J. W. Wilson, *ibid.*, **86**, 4036 (1964).