calculated structure factor amplitudes for $[(FeC_8H_{18}N_2S_2)_2NO]$-$PF_6 \cdot C_3H_6O$ will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St. N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche, referring to code number JACS-74-6519.

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Positional Dependence of the Heavy Atom Effect in the Cis–Trans Photoisomerization of Bromostilbenes[1]

Sir:

Comparison of the temperature dependence of fluorescence, ϕ_f, and isomerization, $\phi_{t\rightarrow c}$ and $\phi_{c\rightarrow t}$, quantum yields for the stilbenes and the p-halostilbenes has revealed a substantial bromine substituent effect.[3-5] Increasing the temperature in the parent hydrocarbon from −180 to 25° increases $\phi_{t\rightarrow c}$ while decreasing ϕ_f, these two processes being coupled throughout the temperature range.[4-7] In p-bromostilbene $\phi_{t\rightarrow c}$ is reported to be temperature independent while ϕ_f increases modestly as the temperature is decreased.[3,4] Bromine substitution brings into play an additional pathway for stilbene photoisomerization which is not activated and is generally assigned to heavy-atom-enhanced intersystem crossing.[2-5] The temperature independence of $\phi_{c\rightarrow t}$ in the systems studied has revealed no difference in behavior between excited cis-stilbene and its halogen substituted derivatives.[4,5] However, halogen substitution, especially in the meta position, has been reported to lower $\phi_{c\rightarrow t}$ significantly[8] and it has been suggested that enhanced spin–orbit coupling induces very rapid $^1c \rightarrow {}^3c \rightarrow {}^0c$ decay.[8,9] This suggestion contradicts the commonly expressed view that, with the exception of a minor cyclization component to dihydrophenanthrene, DHP, torsion about the central bond to twisted geometries, ^1p and ^3p, is the major decay mode of cis excited states.[2] In the following, observations are reported which allow a quantitative evaluation of triplet state involvement following direct excitation of the bromostilbenes.

Preliminary quantum yields obtained in our work[10]

(1) Presented in part at the Southeastern Regional Meeting of the American Chemical Society, Tallahassee, Fla., 1968, Abstract 113, and at the "Frontiers of Organic Photochemistry" Symposium sponsored by the New York Section of the American Chemical Society, Tarrytown, N. Y., 1970.[2]

(2) J. Saltiel, et al., Org. Photochem., 3, 1 (1973).

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

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

(5) D. Gegiou, K. A. Muszkat, and E. Fischer, J. Amer. Chem. Soc., 90, 3907 (1968).

(6) S. Sharafy and K. A. Muszkat, J. Amer. Chem. Soc., 93, 4119 (1971).

(7) J. Saltiel and J. T. D'Agostino, J. Amer. Chem. Soc., 94, 6445 (1972).

(8) K. Krüger and E. Lippert, Z. Phys. Chem. (Frankfurt am Main), 66, 293 (1969).

(9) E. Lippert, Z. Phys. Chem. (Frankfurt am Main), 42, 125 (1964).

(10) Irradiations were carried out in a merry-go-round apparatus.[11] Large cis–trans conversions due to bromine atom catalysis were avoided by including mossy zinc in the irradiation ampoules.[12] The benzophenone-sensitized photoisomerization of cis-1,3-pentadiene was used

Table I. Isomerization Quantum Yields and Photostationary Compositions[a]

Compound	$\phi_{t\rightarrow c}$	$\phi_{c\rightarrow t}$	% [t]$_s$	% [t]$_s$[b]
Stilbene	0.52 (0.50)	0.33 (0.35)	8.3 (7)	52
m-Bromostilbene	0.53 (0.46)	0.33 (0.18)	11.4 (6)	59
m,m'-Dibromo-stilbene	0.57 (0.53)	0.22 (<0.05)	8.0 (~0)	69
p-Bromostilbene	0.54 (0.35)	0.4 (0.16)	11.0 (−)	62

[a] Experiments were carried out in n-pentane at 30°, 313 nm. Values in parentheses are from ref 4 and 8, n-hexane, 25°, 313 nm. [b] Photostationary states are attained using 254-nm excitation.

are shown in Table I along with corresponding values reported by Krüger and Lippert.[8] Our observations indicate a modest but significant decrease in $\phi_{c\rightarrow t}$ for m,m'-dibromostilbene but do not show the previously reported dramatic decrease.[14] Furthermore, Table I shows the trans-stilbenes to be significant components in photostationary states obtained with 313-nm irradiation and more so when excitation is at 254 nm where cis and trans isomers have similar extinction coefficients (e.g., for m,m'-dibromostilbene $\epsilon_c/\epsilon_t = 0.157$ and 1.67 at 313 and 254 nm, respectively).

Bromine's influence on spin–orbit coupling in the stilbenes can be inferred from measurements of stationary states for direct and sensitized photoisomerizations in the presence of azulene.[15,16] In all cases $([t]/[c])_s$ stationary ratios are found to be linearly dependent on azulene concentration. Slope/intercept ratios are shown in Table II. These results can be

Table II. Azulene Effects on Photoisomerization of Stilbenes in Pentane at 30°[a]

Compound	r_d,[b] M^{-1}	r_s[c], M^{-1}	% [t]$_s$[d]
Stilbene	14	304	37.0
m-Bromostilbene	12	140	45.3
m,m'-Dibromostilbene	23	400	37.5
p-Bromostilbene	31	56	39.6

[a] Similar observations have been made in benzene. [b] Slope/intercept ratios for direct excitation at 313 nm; similar results were obtained at 254 nm. [c] Slope/intercept ratios for benzophenone sensitization. [d] Photostationary states for benzophenone sensitization in the absence of azulene, % [t]$_s$ = 100β.

accounted for by the mechanism shown in Scheme I, where $\phi_{^1c^1p}$ is the quantum yield for twisted singlet formation from ^1c, $\phi_{is}{}^1t$ and $\phi_{is}{}^1p$ are intersystem crossing quantum yields from ^1t and ^1p, k_s and k_t are rate constants for azulene quenching of stilbene singlets and

for actinometry.[13] Samples were irradiated with 313-nm light in the presence and in the absence of visible light absorbed by the DHP's. Analyses were by glpc and were corrected for back reaction.[13]

(11) F. G. Moses, R. S. H. Liu, and B. M. Monroe, Mol. Photochem., 1, 245 (1969).

(12) P. J. Kropp, T. H. Jones, and G. S. Poindexter, J. Amer. Chem. Soc., 95, 5420 (1973).

(13) A. A. Lamola and G. S. Hammond, J. Chem. Phys., 43, 2129 (1965).

(14) Preliminary evidence suggests that the decrease in $\phi_{c\rightarrow t}$ in m,m'-dibromostilbene may be due to the larger moments of inertia of the aryl groups which tend to favor cyclization to DHP over torsional $^1c\rightarrow{}^1p$ displacement.

(15) J. Saltiel and E. D. Megarity, J. Amer. Chem. Soc., 94, 2742 (1972).

(16) Cf. D. V. Bent and D. Schulte-Frohlinde, J. Phys. Chem., 78, 446, 451 (1974), for direct confirmation of the validity of the azulene method as a mechanistic probe in the photoisomerization of nitrostilbenes.

Scheme I. Combination of Singlet and Triplet Paths for
Stilbene Photoisomerization
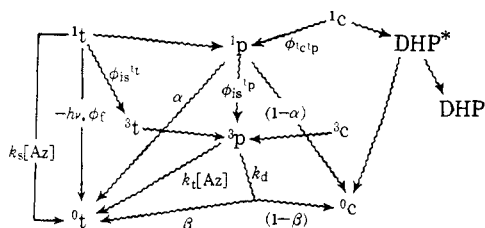
triplets, respectively, and other symbols have their usual meaning.[17] The mechanism predicts that photostationary [t]/[c] ratios for direct excitation should depend on azulene concentration according to eq 1,

$$\left(\frac{[t]}{[c]}\right)_s = \frac{\epsilon_c}{\epsilon_t}\phi_{1c^1p}(1 + K_s[Az]) \times$$

$$\left\{\frac{\alpha(1 - \phi_{is}^{1p})(1 + K_t[Az]) + \phi_{is}^{1p}(\beta + K_t[Az])}{(1 - \phi_t)(1 - \beta) + (1 - \phi_{is}^{1t} - \phi_t)(1 - \phi_{is}^{1p}) \times}{\{\beta - \alpha + (1 - \alpha)K_t[Az]\}}\right\}$$ (1)

where $K_s = k\tau_{1t}$ and $K_t = k_t/k_d = \beta r_s$. In the absence of intersystem crossing, $\phi_{is}^{1p} \sim \phi_{is}^{1t} = 0$, eq 1 reduces to eq 2 so that $r_d = K_s$. The value of K_s has been shown

$$\left(\frac{[t]}{[c]}\right)_s = \frac{\epsilon_c}{\epsilon_t}\frac{\phi_{1c^1p}}{1 - \phi_t}\frac{\alpha}{1 - \alpha}(1 + K_s[Az])$$ (2)

to be ~15 M^{-1} in the case of trans-stilbene,[15] and would be expected to be similar or smaller for the bromostilbenes.[19] If on the other hand intersystem crossing were the only pathway leading to isomerization, eq 1 would reduce to eq 3 and the dependence on azulene

$$\left(\frac{[t]}{[c]}\right)_s = \frac{\epsilon_c}{\epsilon_t}\frac{\phi_{1c^1p}}{1 - \phi_t}(1 + K_s[Az])\frac{(\beta + K_t[Az])}{(1 - \beta)}$$ (3)

would deviate somewhat from linearity, with $r_d > r_s$.[15] Examination of the data in Table II shows that bromine enhances intersystem crossing when bonded at a para position but is totally ineffective in this respect when bonded at a meta position. This striking positional dependence of radiationless heavy-atom induced spin-orbital coupling is to our knowledge unprecedented.[20] The data for p-bromostilbene can be fitted to eq 1 by assuming that the unactivated process competing with fluorescence is $\phi_{is}^{1t} \simeq 0.33$ at 30°,[2-4] and using $\phi_{is}^{1p} = 0.28$. The smaller value of r_s for p-bromostilbene suggests that the same positional dependence applies to the $^1T \rightarrow {}^0S$ radiationless process, since r_s should be approximately related to the inverse of k_d.

The positional dependence is probably related to the difference between meta and para coefficients of the highest occupied and lowest unoccupied MO's of stilbene, $c_m = 0.0791$ and $c_p = 0.3138$ in the Hückel approximation. Spin-orbit coupling occurs via interaction with upper $\sigma\pi^*$ and $\pi\sigma^*$ singlet and triplet

states.[22,23] Qualitatively, spin-orbit coupling matrix elements can be approximated by one-center terms and can be reduced to a center by center sum of the π-electron coefficients times the appropriate σ orbital coefficients.[23] If, as in the case of bromine substitution the center bearing bromine dominates then the expression describing the probability of spin-orbit coupling will be dominated by the appropriate π and σ MO coefficients at that center.[22] It is sensible, therefore that since the π-coefficient of stilbene is nearly zero at the meta position, substitution at that position should cause no enhancement in the rate constants for intersystem crossing.

(22) S. P. McGlynn, T. Azumi, and M. Kinoshita, "Molecular Spectroscopy of the Triplet State," Prentice-Hall, Englewood Cliffs, N. J., 1969, p 269.
(23) B. R. Henry, personal communication.
(24) (a) Fellow of the Alfred P. Sloan Foundation, 1971–1973; (b) National Institutes of Health Predoctoral Research Fellow, 1965–1969.

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A Low Temperature Infrared Spectral Study of Iron(II) Dioxygen Complexes Derived from a "Picket Fence Porphyrin"

Sir:

The nature of the dioxygen-iron bond in HbO_2 and MbO_2[1] is becoming clarified through studies of crystalline model compounds. Recently we reported the synthesis,[2] magnetic properties, Mössbauer spectra, and X-ray crystallographic structure[3] for a reversibly formed iron(II) dioxygen complex, 1, derived from a "picket fence porphyrin" and an axial imidazole (Figure 1). This complex has an end-on angular FeO_2 bond with Fe-O-O 136 (4)°, Fe-O 1.75 (0.02) Å, O-O 1.25 (0.08) Å, and Fe-N (N-Me-Im) 2.07 (0.02) Å, in accord with Pauling's[4] suggested structure. There are two types of dioxygen coordination—one coplanar and the other normal to the axial base.[3]

Earlier we were unable to assign an ir or Raman band to $\nu(O_2)$ at 300°K even with the aid of ^{18}O substitution.[2] We now report the low temperature (−175°) solid-state (KBr) ir spectrum of 1 which exhibits a remarkably sharp (half width 1 cm^{-1}), intense peak at 1385 cm^{-1}! Typical data are displayed in Figure 2. The 1385-cm^{-1} peak is not an artifact arising from the supporting medium, as it may also be observed at −175° in a fluorocarbon lube mull. Control experiments suggest that the 1385 cm^{-1} feature represents $\nu(O_2)$. The peak is not observed, for example, upon replacement of dioxygen by other axial bases such as in

(17) Details of interactions of stilbene triplets with quenchers are discussed in a recent paper.[18]
(18) J. Saltiel and B. Thomas, *J. Amer. Chem. Soc.*, **96**, 5560 (1974).
(19) A smaller K_s value would result if τ^{1t} is decreased owing to competing intersystem crossing.
(20) The positional dependence observed in dibromonaphthonorbornenes is not analogous since substitution was not directly on a carbon of the π-system.[21]
(21) N. J. Turro, G. Kavarnos, V. Fung, A. L. Lyons, Jr., and T. Cole, Jr., *J. Amer. Chem. Soc.*, **94**, 1392 (1972).

(1) Abbreviations used in this paper are: Hb, hemoglobin; Mb, myoglobin; N-MeIm, N-methylimidazole; N-n-BuIm, N-n-butylimidazole; THF, tetrahydrofuran.
(2) J. P. Collman, R. R. Gagne, T. R. Halbert, J. C. Marchon, and C. A. Reed, *J. Amer. Chem. Soc.*, **95**, 7868 (1973).
(3) J. P. Collman, R. R. Gagne, C. A. Reed, W. T. Robinson, and G. A. Rodley, *Proc. Nat. Acad. Sci. U. S.*, **71**, 1326 (1974).
(4) (a) L. Pauling, *Stanford Med. Bull.*, **6**, 215 (1948); (b) *Nature, (London)*, **203**, 182 (1964).