

Table II. Comparison of the Present Results for $(J_{AB}^{1b})_{\text{CHF}}$ with Previous Semiempirical Values (Hz)

molecule	atom pair	present results	semiempirical results (A-E)				
			A ^a	B ^b	C ^c	D ^d	E ^e
ethane	CC	0.2	-1.87	-2.9	0.3	-1.1	-2.3 ^e
ethylene	CC	-9.7	-11.34	-18.6	-3.76	-6.4	
acetylene	CC	13.7 (15.3)	12.5	23.6	4.13	0.0	
acetonitrile	CN	-4.4	-1.02				-7.9 ^f

^a S. Nagata, T. Yamabe, K. Hirao, and K. Fukui, *J. Phys. Chem.*, **79**, 1863 (1975). ^b Reference 6. ^c Reference 8a. ^d C. Barbier, H. Faucher, and G. Berthier, *Theor. Chim. Acta*, **21**, 105 (1971). ^e J. M. Schulman and M. D. Newton, *J. Am. Chem. Soc.*, **96**, 6295 (1974). ^f Reference 2a.

term appears to be well described in the 6-31G basis. On the other hand, use of the minimal STO-3G basis gave very different results. Another test of the bases used here is to compare the present results with those of ref 11 for CH₄, HF, and H₂O, where very large basis sets were used. For ¹J_{HF}^{1b} the present value, 191.5 Hz, agrees well with the value of 182.8 Hz in a (11s7p/6s) uncontracted set. For water, our values of ¹J_{OH}^{1b} = -11.0 and ²J_{HH} = 3.4 Hz are close to the -10.7 and 4.5 Hz of ref 11. Finally, for methane the present ¹J_{CH}^{1b} = 1.4 and ²J_{HH}^{1b} = 1.1 Hz compare well with their 1.7 and 1.4 Hz for a (1s⁵6p³/5s³) contracted basis.

Table II contains the present ab initio coupled Hartree-Fock results ¹J_{CC}^{1b} and ¹J_{CN}^{1b} along with several semiempirical values. All of the latter have the correct signs for ethylene, acetylene, and acetonitrile, although there are some cases of large errors in magnitude. Only method C yields the correct sign for ¹J_{CC} of ethane; however, the ab initio value, 0.2 Hz, is so small that a negative value might be obtained using a much larger basis set.

Acknowledgment. This research was supported in part by a grant from the City University of New York PSC-BHE Research Award Program.

References and Notes

- (1) N. F. Ramsey, *Phys. Rev.*, **91**, 303 (1953).
- (2) (a) J. M. Schulman and T. Venanzi, *J. Am. Chem. Soc.*, **98**, 4701 (1976); (b) *ibid.*, **98**, 6739 (1976).
- (3) J. M. Schulman and T. J. Venanzi, *Tetrahedron Lett.*, 1461 (1976).
- (4) (a) M. Pomerantz, R. Fink, and G. A. Gray, *J. Am. Chem. Soc.*, **98**, 291 (1976); (b) H. Finkelmeier and W. Luttker, *ibid.*, **100**, 6261 (1978).
- (5) K. Thomsen and P. Swanstrom, *Mol. Phys.*, **26**, 735 (1973), and references cited therein.
- (6) A. C. Blizard and D. P. Santry, *J. Chem. Phys.*, **55**, 950 (1971); **58**, 4714 (1973).
- (7) (a) M. J. S. Dewar, D. Landman, Sung Ho Suck, and P. K. Weiner, *J. Am. Chem. Soc.*, **99**, 3951 (1977); (b) J. M. Schulman, *J. Magn. Reson.*, **28**, 137 (1977).
- (8) (a) A. D. C. Towl and K. Schaumburg, *Mol. Phys.*, **22**, 49 (1971); (b) H. Nakatsuji, K. Hirao, H. Kato, and T. Yonezawa, *Chem. Phys. Lett.*, **6**, 541 (1970).
- (9) R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **54**, 724 (1971).
- (10) T. H. Dunning, *J. Chem. Phys.* **53**, 2823 (1970); **55**, 716, 3958 (1971).
- (11) M. F. Guest, V. R. Saunders, and R. E. Overill, *Mol. Phys.*, **35**, 427 (1978).
- (12) W. J. Hehre, W. A. Latham, R. Ditchfield, M. D. Newton, and J. A. Pople, GAUSSIAN 70, Quantum Chemistry Program Exchange, No. 236, Indiana University, Bloomington, Ind.
- (13) O. Matsuoka, *Int. J. Quantum Chem.*, **5**, 1 (1971).
- (14) H. Taketa, S. Huzinaga, and K. Oohata, *J. Phys. Soc. Jpn.*, **21**, 2313 (1966).
- (15) Geometries were taken from L. C. Snyder and H. Basch, "Molecular Wavefunctions," Wiley, New York, 1972, except for HNC, where we chose $r_{\text{NH}} = 1.852a_0$ and $r_{\text{NC}} = 2.203a_0$.

Triplet [2 + 2] Cycloadditions. Spin-Inversion Control of Stereoselectivity

Sason S. Shaik

Contribution from the Department of Chemistry, Cornell University, Ithaca, New York 14853. Received November 27, 1978

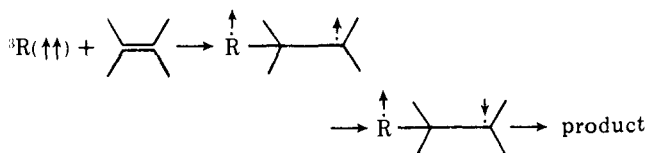
Abstract: Spin-inversion mechanisms in triplet [$\pi 2_s + \pi 2_s$] complexes fall into three classes. These differ in their stereochemical results: (a) bis pyramidalization (BP) which leads to 2s + 2s product; (b) intramolecular disrotation (ID) which leads to 2s + 2a product; (c) bis intramolecular disrotation (BID) which leads to 2a + 2a product. The polarity (i.e., the donor-acceptor relationship) and the triplet excitation energies of the olefins will determine the relative efficiency of these mechanisms; when the olefin pair is nonpolar (i.e., both olefins are electron donors or electron acceptors) 2s + 2s is the main product. As polarity increases, 2s + 2a becomes the major product. Further increase of polarity results again in 2s + 2s cycloaddition. On the other hand, decreasing the triplet excitation energies of the olefins at constant polarity will increase 2s + 2s production. The efficiency of ID and BP is larger in short intermolecular distances and hence anti regiochemistry is expected. Photochemical data (e.g., cycloaddition of olefins to cyclohexenones, type A rearrangement, and the di- π -methane rearrangement) are discussed in the light of these predictions.

I. Introduction

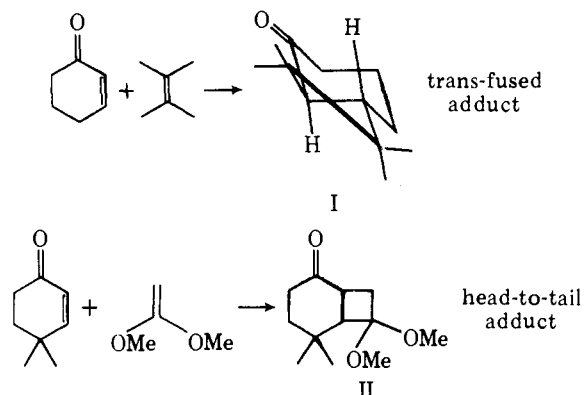
The organic chemistry of molecules in their triplet state is considered to be exclusively a chemistry of diradicals.¹ It was argued that, since product formation is prohibited by the spin conservation principle, the reaction must involve an interme-

diolate diradical which inverts a spin in a subsequent slow step yielding singlet product.^{1a}

Though useful for understanding the loss of stereochemical information often encountered in triplet reactions, several other features, such as formation of highly strained trans-fused four-membered rings and head-to-tail regiochemistry,² re-



mained unyielding to this hypothesis. Two examples which illustrate this nondiradical behavior are given below² (I and II).



Consequently it was felt² that the diradical model, by itself, cannot account for the curious experimental trends.

At the same time, extensive spectroscopic data suggest that the main difference between the decay processes of triplet molecules (or complexes) and their singlet counterparts is the slower decay rate of the former due to spin-inversion requirement. Thus, if spin inversion is indeed difficult, a direct analysis of this step will provide insight into the key features of triplet reactions.

How does spin inversion take place?³ In an earlier publication we attempted to answer this question by finding nuclear motions which maximize the intermolecular HOMO-LUMO type spin-orbit (SO) coupling matrix elements.⁴ Let us refine these ideas further.

In the present study we use group theory to search for the motions which lead to spin inversion and then evaluate their relative efficiency using delocalized MOs as the semiquantitative tool. In this way, the various inter- and intramolecular SO coupling interactions can be derived and their variation with the electronic nature of the reactants discussed. The emerging picture provides a set of stereoselection rules which are used to analyze reactivity patterns in triplet [2 + 2] reactions.

II. Spin-Orbit Coupling—A Model for Spin Inversion

Consider a reaction system on a triplet surface, T_1 . After completing a sequence of events (e.g., bond reorganization) the reaction system reaches a region where it inverts a spin and relaxes to the ground surface, S_0 , in a radiationless manner. Time-dependent perturbation theory shows that the probability of such a process is directly proportional to the SO coupling matrix element, $\langle T_1 | \hat{H}_{SO} | S_0 \rangle$, and to the inverse of the energy gap, $E_1 - E_0$, separating the two states.⁵ Thus, in order to optimize the efficiency of spin inversion, the system must adopt a geometry for which the SO coupling matrix element is maximized and the T_1 - S_0 spacing is minimized. In certain reactions, these requirements may be achieved along the "reaction coordinate", whereas, in others, distortions (Q) may be needed. Our task, then, is to devise a simple method for elucidating these distortions.

We shall first investigate the conditions which lead to maximization of the SO coupling matrix element. There are two ways to approach the problem. The first is approximate in nature but offers a quantitative insight. The second is the-

oretically more rigorous but is purely qualitative. We shall start with the first approach. The one-electronic part of the SO coupling operator, \hat{H}_{SO} , can be expressed as a sum of all interactions between the spin dipole of electron i , $(-e/mc)S_i$, with the field created by the orbital motion of the electron, having momentum P , in a potential V_i due to the nuclear framework. In quantum mechanical language this becomes

$$\hat{H}_{SO} = \sum_i \frac{1}{2m^2c^2} \hat{S}_i \cdot (\text{grad } \hat{V}_i \times \hat{P}_i) \quad (1)$$

Assuming a simple form for the potential $V_i = \sum_N (-Z_N^*e/r_{iN})$, the SO coupling operator can be written as a sum of the pairwise interactions between an electron i and all the nuclei, N , having an effective charge Z_N^* :⁶

$$\hat{H}_{SO} = \sum_i \sum_N \frac{Z_N^*e^2}{2m^2c^2} \frac{\hat{l}(i) \cdot \hat{s}(i)}{r_{iN}^3} \quad (2)$$

This form of the operator allows one to treat complex systems qualitatively with simplicity within the framework of LCAO-MO theory and, hence, will be used throughout the rest of the text. In Cartesian space, the $\hat{l}\hat{s}$ operator is expanded as shown in eq 3, where the angular momentum components, \hat{l}_k ($k = x, y, z$), operate only on the spatial part and the spin components, \hat{s}_k ($k = x, y, z$), only on the spin part of the wave functions.

$$\hat{l} \cdot \hat{s} = \hat{l}_x \hat{s}_x + \hat{l}_y \hat{s}_y + \hat{l}_z \hat{s}_z \quad (3)$$

We shall assume that the triplet wave function, T_1 , and the singlet wave function, S_0 , can be expressed as a sum of configurations which are constructed by permuting electrons among the virtual MOs of the ground-state complex. We also assume that the major configurations in the expansion are the ground configuration for S_0 and only one singly excited configuration for T_1 . Doing so, one has only to identify the motions, Q_k , which maximize the three angular momentum matrix elements, L_k , between the MOs ϕ_i and ϕ_j which are singly occupied in T_1 :

$$L_k = \langle \phi_i | \frac{\hat{l}_k}{r^3} | \phi_j \rangle \quad (k = x, y, z) \quad (4)$$

Inclusion of more configurations will modify some features but will not alter the key conclusions.

Alternatively, one may drop these assumptions. In a rigorous sense, every acceptable wave function must form a basis for some irreducible representation of the molecular point group, spin included. The Hamiltonian must possess the full symmetry of the molecular point group; in other words, the total Hamiltonian, or any of its parts (e.g., \hat{H}_{SO}), must belong to the totally symmetric representation Γ_1 of the molecular symmetry group.

The symmetry of the complete electronic wave functions is a product of the space (ν) and spin parts. The singlet spin wave function always belongs to the totally symmetric representation, whereas the triplet spin functions⁷ transform as the rotation vectors, \mathbf{R}_x , \mathbf{R}_y , and \mathbf{R}_z .⁸ Consequently, the three sublevels of the triplet state (T_{1x} , T_{1y} , and T_{1z}) will have the total symmetries $\Gamma(T_{1\nu}) \times \Gamma(\mathbf{R}_x)$, $\Gamma(T_{1\nu}) \times \Gamma(\mathbf{R}_y)$, $\Gamma(T_{1\nu}) \times \Gamma(\mathbf{R}_z)$, where $\Gamma(T_{1\nu})$ is the representation of the spatial part of the triplet wave function. Since \hat{H}_{SO} transforms as Γ_1 , then the condition for a nonzero SO coupling matrix element, $\langle T_1 | \hat{H}_{SO} | S_0 \rangle$, becomes simply⁶

$$\Gamma(T_{1\nu}) \times \Gamma(\mathbf{R}_k) \times \Gamma(S_0) = \Gamma_1 + \dots \quad (k = x, y, z) \quad (5)$$

i.e., the matrix element does not vanish if the direct product of the representations of S_0 with the three triplet components contains the totally symmetric representation Γ_1 . Whenever this requirement is not met, a distortion Q_k is needed. The distortion will efficiently couple T_1 with S_0 if the condition in eq 6 is fulfilled (see Appendix I):^{3c,e,6a}

$$\Gamma(T_1^\nu) \times \Gamma(\mathbf{R}_k) \times \Gamma(S_0) \times \Gamma(Q_k) = \Gamma_1 + \dots \quad (6)$$

($k = x, y, z$)

Thus, the analysis is reduced to finding motions, Q_k , which can efficiently couple S_0 with one of the components of T_1 . This approach gives, in principle, identical results with the MO analysis (eq 4) and it may be asked: why do we need both? As we shall see later, the two types of analysis give different insights into the problem. Group theoretical analysis is theoretically rigorous and leads to an instant elucidation of the promoting motions and, hence, is very useful as a starting point. However, in many cases group theory suggests motions which are suitable by symmetry criteria but which do not create strong SO coupling interaction.⁹ On the other hand, the approximate analysis based on eq 4 provides a quantitative estimate of the interaction and, hence, can be used as a check on the SO coupling efficiency associated with the motions suggested by group theory. The emerging strategy is as follows: (a) Find archetypal motions which create a strong SO coupling interaction. (b) Determine the symmetries of T_1 and S_0 . (c) Work out the following direct products of eq 7-9.

$$\Gamma(T_1^\nu) \times \Gamma(\mathbf{R}_x) \times \Gamma(S_0) = \Gamma_x \quad (7)$$

$$\Gamma(T_1^\nu) \times \Gamma(\mathbf{R}_y) \times \Gamma(S_0) = \Gamma_y \quad (8)$$

$$\Gamma(T_1^\nu) \times \Gamma(\mathbf{R}_z) \times \Gamma(S_0) = \Gamma_z \quad (9)$$

(d) Find the composite motions Q_k ($k = x, y, z$) which satisfy eq 10-12, using the archetypal motions as guides.

$$\Gamma_x \times \Gamma(Q_x) = \Gamma_1 + \dots \quad (10)$$

$$\Gamma_y \times \Gamma(Q_y) = \Gamma_1 + \dots \quad (11)$$

$$\Gamma_z \times \Gamma(Q_z) = \Gamma_1 + \dots \quad (12)$$

(e) Estimate the SO efficiency, associated with Q_k , using eq 4.

Before entering the analysis sections, a few cautionary remarks are in order. Solving eq 10-12 leads *only* to Q_k 's which transform as *irreducible representations of the point group in question and do not necessarily offer the best SO coupling interaction under all conditions*. Sometimes, motions which belong to *reducible* representations become the most efficient ones when the electronic nature of the reactants is properly manipulated. These motions can be unraveled if the analysis is performed with lower symmetry groups where they transform as *irreducible* representations. In order to elucidate the motions in a lower symmetry group we can either make use of group correlation tables¹⁰ or repeat the entire analysis using the lower symmetry group.

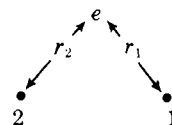
Finally, the group theoretical analysis should be performed judiciously using chemical intuition and selecting motions which keep the molecular complex intact. *The motions, so found, will provide a set of stereoselection rules for concerted spin inversion and product formation.*

III. Archetypal Motions of Spin Inversion

In most organic molecules having carbon atoms at the reaction sites the one-center SO coupling interactions are zero^{6a,11} and thus the two-center interactions become important.¹²

Upon operation on a real p-type atomic orbital (AO) the \hat{I}_k operators rotate the function by $\pm 90^\circ$ about the axis specified by the operator subscript, k . Thus, the only nonvanishing two-center matrix elements are those containing a pair of mutually perpendicular AOs.^{13,14} These matrix elements are shown in eq 13-15, where r_1 and r_2 are the distances between the electron and nuclei 1 and 2 respectively.

Equations 13-15 suggest that when searching for spin-inversion promoting distortions, Q_k , one must focus on motions

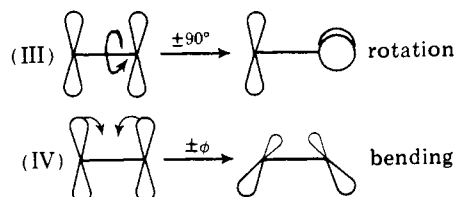


$$\langle p_{1x} | \frac{1}{r_1^3} + \frac{1}{r_2^3} | p_{2y} \rangle = -i\hbar \{ \langle p_{1x} | \frac{1}{r_1^3} | p_{2x} \rangle + \langle p_{1y} | \frac{1}{r_2^3} | p_{2y} \rangle \} \quad (13)$$

$$\langle p_{1x} | \frac{1}{r_1^3} + \frac{1}{r_2^3} | p_{2z} \rangle = i\hbar \{ \langle p_{1z} | \frac{1}{r_1^3} | p_{2z} \rangle + \langle p_{1x} | \frac{1}{r_2^3} | p_{2x} \rangle \} \quad (14)$$

$$\langle p_{1y} | \frac{1}{r_1^3} + \frac{1}{r_2^3} | p_{2z} \rangle = -i\hbar \{ \langle p_{1z} | \frac{1}{r_1^3} | p_{2z} \rangle + \langle p_{1y} | \frac{1}{r_2^3} | p_{2y} \rangle \} \quad (15)$$

which generate mutually perpendicular AOs along two centers. We can distinguish two archetypal motions, namely, $\pm 90^\circ$ rotations (III) and bending or pyramidalization (IV) of tri-

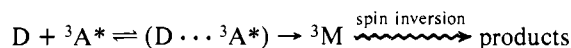


gonal centers. The latter can be considered as a partial rotation (ϕ). These two types will serve as guides for searching composite motions in complex molecular systems. It becomes clear now that, even if group theoretical analysis predicts no need for distortion (i.e., the condition of eq 5 is met for one of the triplet sublevels), *this will not assure an efficient SO coupling if the requisite perpendicular AO relationship is not attained*. In such a case, we must look for a *totally symmetric* motion, Q_k , which couples T_1 and S_0 more efficiently.

We are now ready to discuss the mechanisms of a popular class of triplet reactions, the [2 + 2] reaction.

IV. Potential Energy Surfaces and Mechanisms of [2 + 2] Triplet Cycloadditions

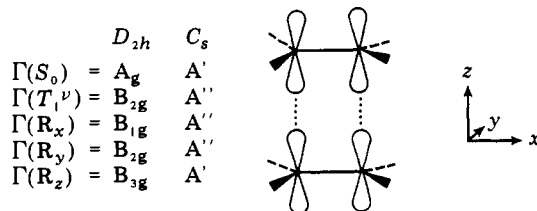
A prototype reaction belonging to this class is [$\pi 2_s + \pi 2_s$]. In most cases, one reactant can be classified as donor, D, and the other as acceptor, A. Figure 1 describes (by arrows) the course of such a triplet photoreaction initiated by excitation of the acceptor, A.



As the two reactants approach one another an encounter complex, ($D \cdots {}^3A^*$), is transformed to a triplet "exciplex," 3M .^{15,16} This travels to the neighborhood of the "hole" generated by the avoided crossing of the ground and the diexcited one-electronic surfaces.¹⁷⁻¹⁹ There, spin inversion must take place to convert the triplet complex to a singlet product. *The efficiency of the spin-inversion step is proportional to the SO coupling interaction of T_1 and S_0 near the "hole."*

Using the strategy outlined in section II, we shall now discover promoting motions, Q_k , which create mutually perpendicular AOs and optimize the SO coupling matrix elements.

The transformation properties of the different wave functions in the maximum symmetry group D_{2h} and the lower symmetry group C_s are shown below.



Solving the direct products of eq 7-9 we obtain the sym-

metries of the Q_k 's which fulfill the conditions in eq 10-12. The final results for D_{2h} and C_s are shown in eq 16-18.

$$\begin{array}{ccc} D_{2h} & C_s & \\ \Gamma(Q_x) = & B_{1g} & A'' \end{array} \quad (16)$$

$$\Gamma(Q_y) = A_g \quad A' \quad (17)$$

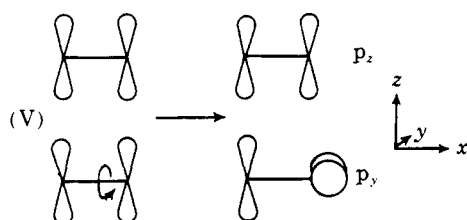
$$\Gamma(Q_z) = B_{3g} \quad A' \quad (18)$$

In the following sections we search for nuclear movements which satisfy these symmetries.

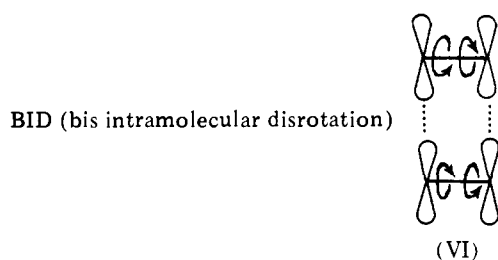
A. Stereoselection Rules (Q_x) for T_{1x} . There are several ways by which one can generate symmetry-adapted functions, nuclear motions, etc. The simplest method utilizes projection operators.²⁰ Equation 16 shows that for a D_{2h} symmetry the x component of T_1 will be coupled to S_0 by a B_{1g} -type motion. The projection operator associated with B_{1g} , $\hat{O}(B_{1g})$, is defined in the equation

$$\hat{O}(B_{1g}) = E + c_2(z) - c_2(y) - c_2(x) + i + \sigma(xy) - \sigma(xz) - \sigma(yz) \quad (19)$$

When it operates on a certain motion vector it will generate the composite motion, if such one exists, which transforms as the irreducible representation B_{1g} . In order to maximize the x component of a two-center SO coupling interaction a y, z perpendicular AO relationship is needed (eq 15). Thus, let us start the search with a rotation which converts p_z to a p_y AO (V).

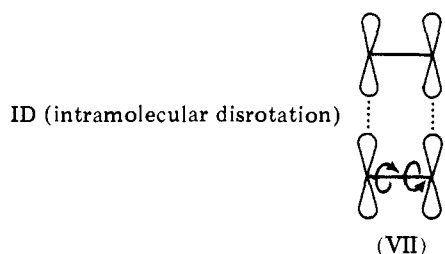


Operation by $\hat{O}(B_{1g})$ on this motion vector generates the symmetry-adapted motion shown below (VI) along with the



nomenclature which describes the type of motion.

When the analysis is performed with C_s , one finds that the A'' type motion, which is antisymmetric with respect to the mirror plane bisecting the two π bonds, can be one which involves a disrotation of only one reactant. This motion is described below (VII).



The third motion involves a single rotation (VIII) and was designated as MR (mono rotation).

B. Stereoselection Rules (Q_y) for T_{1y} . The y component of T_1 will be coupled to S_0 by an A_g (or A' in C_s) type motion (eq

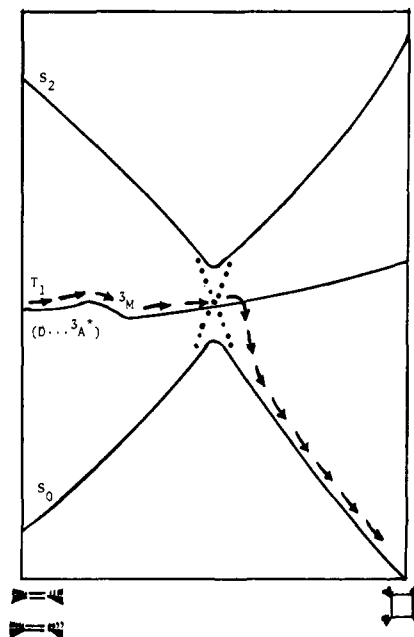
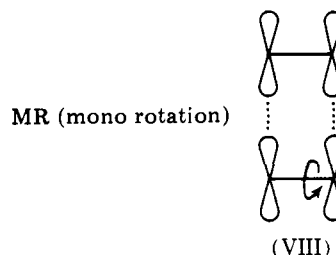
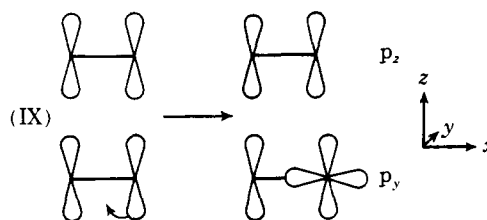


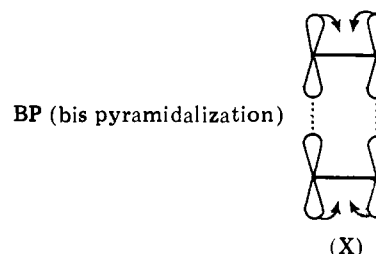
Figure 1. Schematic potential energy surfaces for a $2s + 2s$ cycloaddition. Only S_0 , T_1 , and S_2 are shown. The dotted lines indicate the avoided surface crossing described in the text. The arrows indicate the course of the triplet reaction.



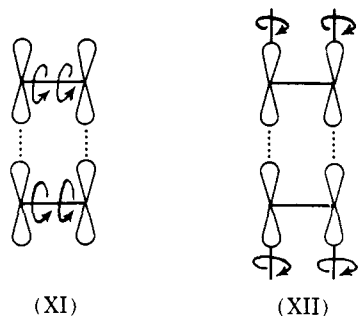
17). This is a totally symmetric motion which preserves the symmetry of the complex and, in order to be efficient, must generate an x, z perpendicular AO relationship. Following the same line of reasoning, we find that a bending motion (pyramidalization) which mixes p_x into the $\pi(p_z)$ MOs fulfills these requirements (IX).



The projection operator $\hat{O}(A_g)$ yields the following symmetry-adapted motion (X).



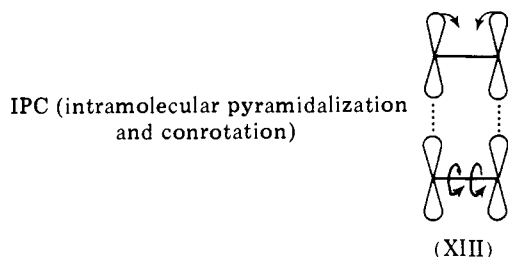
C. Stereoselection Rules (Q_z) for T_{1z} . The z component of T_1 will be coupled to S_0 by a B_{3g} (or A' in C_s) type motion. The projection operator, $\hat{O}(B_{3g})$, generates the following motions (XI and XII), none of which leads to products or creates an efficient-SO coupling interaction.



(XI)

(XII)

However, within C_s symmetry, one finds a composite motion, which is a combination of a conrotation of one olefin and pyramidalization of the other; both types transform as A' and generate the requisite x, z perpendicular AO relationship. This motion transforms in D_{2h} as an irreducible representation which contains $B_{3g}(B_{3g} + B_{2u} + A_g + B_{1u})$ and, hence, also satisfies the requirements of D_{2h} . The motion is shown below (XIII).

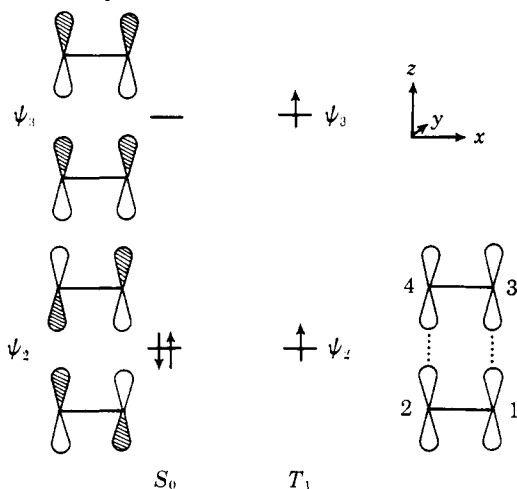


(XIII)

V. Efficiency of Spin-Inversion Mechanisms

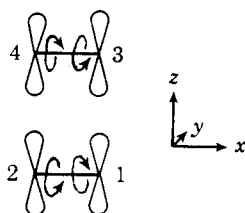
Having the spin-inversion mechanisms, we must now analyze their relative efficiency using eq 4.

The frontier π MOs of the $[\pi 2_s + \pi 2_s]$ complex past the "hole"¹⁸ are depicted below.



Applying eq 4 requires the evaluation of the angular momentum integrals, $\langle \psi_3 | \hat{L}_k / r^3 | \psi_2 \rangle$ ($k = x, y, z$) (where $\hat{L}_k / r^3 =$

BID



$$\begin{aligned} \psi_2 &= a(p_{1z} \cos \theta + p_{1y} \sin \theta - p_{2z} \cos \theta + p_{2y} \sin \theta) \\ &\quad + b(-p_{3z} \cos \theta + p_{3y} \sin \theta + p_{4z} \cos \theta + p_{4y} \sin \theta) \\ \psi_3 &= b(p_{1z} \cos \theta + p_{1y} \sin \theta + p_{2z} \cos \theta - p_{2y} \sin \theta) \\ &\quad + a(p_{3z} \cos \theta - p_{3y} \sin \theta + p_{4z} \cos \theta + p_{4y} \sin \theta) \end{aligned}$$

$\hat{L}_{k1}/r_1^3 + \hat{L}_{k2}/r_2^3 + \hat{L}_{k3}/r_3^3 + \hat{L}_{k4}/r_4^3$) as a function of the rotation angle θ , or the bending (pyramidalization) angle, ϕ . BID (VI) will exemplify this procedure. The analytical forms of ψ_2 and ψ_3 after rotation by θ are shown below where a and b are the AO coefficients.²¹

Assuming that the interactions along C_1-C_2 equal those along C_3-C_4 and those along C_1-C_3 equal C_2-C_4 , the matrix element $\langle \psi_3 | \hat{L}_x / r^3 | \psi_2 \rangle$ becomes

$$\begin{aligned} \langle \psi_3 | \hat{L}_x / r^3 | \psi_2 \rangle &= 2i\hbar \left\{ 2ab \left[\begin{aligned} &\langle 1z | \frac{1}{r_1^3} + \frac{1}{r_2^3} | 2z \rangle \\ &\langle 1y | \frac{1}{r_1^3} + \frac{1}{r_2^3} | 2y \rangle \end{aligned} \right] \right. \\ &\quad \left. + (a^2 + b^2) \left[\begin{aligned} &\langle 1z | \frac{1}{r_1^3} + \frac{1}{r_3^3} | 3z \rangle \\ &\langle 1y | \frac{1}{r_1^3} + \frac{1}{r_3^3} | 3y \rangle \end{aligned} \right] \right\} \sin \theta \cos \theta \quad (20) \end{aligned}$$

where $1z$ stands for p_{1z} and $1y$ for p_{1y} , etc.

The terms in the square brackets describe two types of interactions: π type (e.g., $\langle 1z | (1/r_1^3) + (1/r_2^3) | 2z \rangle$) and σ type (e.g., $\langle 1z | (1/r_1^3) + (1/r_3^3) | 3z \rangle$). For convenience, we shall make use of the following definitions:

$$\begin{aligned} \langle 1z | \frac{1}{r_1^3} + \frac{1}{r_2^3} | 2z \rangle &= V_{12}^\pi \\ \langle 1z | \frac{1}{r_1^3} + \frac{1}{r_3^3} | 3z \rangle &= V_{13}^\sigma \text{ etc.} \end{aligned}$$

Adding all the constants of eq 2 one gets the final form for the x component of the SO coupling interaction.

$$\text{BID: } \langle \hat{H}_{\text{SO}} \rangle_x = \sqrt{2}iKZ^* \{ 4abV_{12}^\pi + (a^2 + b^2)(V_{13}^\pi + V_{13}^\sigma) \} \sin \theta \cos \theta \quad (21)$$

$$K = \frac{e^2 \hbar^2}{2m^2 c^2} \quad (22)$$

Similarly, the SO coupling expressions for the other mechanisms are derived;

$$\begin{aligned} \text{ID: } \langle \hat{H}_{\text{SO}} \rangle_x &= \frac{iKZ^*}{\sqrt{2}} \{ 4abV_{12}^\pi \sin \theta \cos \theta \\ &\quad + (a^2 + b^2)(V_{13}^\pi + V_{13}^\sigma) \sin \theta \} \quad (23) \end{aligned}$$

$$\begin{aligned} \text{MR: } \langle \hat{H}_{\text{SO}} \rangle_x &= \frac{iKZ^*}{2\sqrt{2}} \{ 4abV_{12}^\pi + (a^2 + b^2)(V_{13}^\pi \\ &\quad + V_{13}^\sigma) \} \sin \theta \quad (24) \end{aligned}$$

$$\begin{aligned} \text{BP: } \langle \hat{H}_{\text{SO}} \rangle_y &= \sqrt{2}iKZ^* \{ 2ab(V_{12}^\sigma + V_{12}^\pi) \\ &\quad + (a^2 + b^2)(V_{13}^\pi + V_{13}^\sigma) \} \sin \phi \cos \phi \quad (25) \end{aligned}$$

$$\text{IPC: } \langle \hat{H}_{\text{SO}} \rangle_z = \frac{iKZ^*}{\sqrt{2}} \{ 2(a^2 + b^2)V_{13}^\pi \} \sin \theta \sin \phi \quad (26)$$

$$\begin{aligned} \text{IPC: } \langle \hat{H}_{\text{SO}} \rangle_y &= \frac{iKZ^*}{\sqrt{2}} \{ 2ab[(V_{12}^\pi + V_{12}^\sigma) \cos \phi \sin \phi \\ &\quad + (V_{13}^\pi + V_{13}^\sigma) \sin \phi \cos \phi] \} \quad (27) \end{aligned}$$

The various V^π and V^σ terms fall within two categories: intramolecular ones, V_{12} , and intermolecular ones, V_{13} . These terms behave as the corresponding AO overlap integrals. For example, V_{12}^σ is roughly proportional to the σ -type overlap between the p_x AOs on C_1 and C_2 . Consequently, the relative importance of the inter- and intramolecular contributions depends on the specific nuclear configuration of decay. As the two reactants approach one another the intermolecular distances decrease whereas the intramolecular ones increase making the V_{13} terms increasingly important.

In addition to the V terms, the SO coupling expressions depend on the rotational angle, θ , or on the bending (pyramidalization) angle, ϕ .

We shall now treat separately each mechanism and investigate the conditions for maximization of the angular part of the SO coupling matrix element.

A. 1. Rotational Mechanisms. Equation 21 shows that the SO matrix element associated with BID depends on $\sin \theta \cos \theta$. This term reaches a maximum at $\theta = 45^\circ$, at which angle

$$\text{BID: } \langle \hat{H}_{\text{SO}} \rangle_{x,\text{max}} = \frac{iKZ^*}{\sqrt{2}} \{4abV_{12}^\pi + (a^2 + b^2)(V_{13}^\pi + V_{13}^\sigma)\} \quad (28)$$

Similarly, for MR the SO coupling efficiency depends on $\sin \theta$ with a maximum at $\theta = 90^\circ$, where it becomes

$$\text{MR: } \langle \hat{H}_{\text{SO}} \rangle_{x,\text{max}} = \frac{iKZ^*}{2\sqrt{2}} \{4abV_{12}^\pi + (a^2 + b^2)(V_{13}^\pi + V_{13}^\sigma)\} \quad (29)$$

When CI is included the value of this angle will be somewhat smaller than 90° .¹³ Quite a different situation obtains for the ID mechanism. Since there are two terms with different angular dependence, the angle at which the expression reaches maximum depends on the relative magnitude of the terms multiplying the angular parts. Thus, one cannot make a clear-cut determination of this angle unless one knows the magnitude of the terms for a spectrum of inter- and intramolecular distances. However, two extremes can be easily distinguished, namely, $\theta = 45^\circ$ and $\theta = 90^\circ$. The former value leads to maximization of the intramolecular part and the latter to the intermolecular part. The two expressions are

$$\text{ID}(45^\circ): \langle \hat{H}_{\text{SO}} \rangle_{x,\text{max}} = \frac{iKZ^*}{2\sqrt{2}} \{4abV_{12}^\pi + \sqrt{2}(a^2 + b^2)(V_{13}^\pi + V_{13}^\sigma)\} \quad (30)$$

$$\text{ID}(90^\circ): \langle \hat{H}_{\text{SO}} \rangle_{x,\text{max}} = \frac{iKZ^*}{\sqrt{2}} \{(a^2 + b^2)(V_{13}^\pi + V_{13}^\sigma)\} \quad (31)$$

The important implications of this distinction will be discussed later.

A. 2. Pyramidalization Mechanisms. The SO coupling expression associated with BP varies proportionally to $\sin \phi \cos \phi$ where ϕ is the bending angle. Theoretically, the expression has a maximum value at $\phi = 45^\circ$, but actually, ϕ is geometrically constrained to $\sim 19.47^\circ$ (which completes a tetrahedral angle), at which angle $\langle \hat{H}_{\text{SO}} \rangle_y$ becomes

$$\text{BP: } \langle \hat{H}_{\text{SO}} \rangle_{y,\text{max}} = 0.31\sqrt{2}iKZ^* \{2ab(V_{12}^\pi + V_{12}^\sigma) + (a^2 + b^2)(V_{13}^\pi + V_{13}^\sigma)\} \quad (32)$$

In practice, the magnitude will be even smaller due to mixing of s AOs which reduces the a and b coefficients.

The IPC mechanism involves a mixture of conrotation and pyramidalization creating both $\langle \hat{H}_{\text{SO}} \rangle_y$ and $\langle \hat{H}_{\text{SO}} \rangle_z$. The z component varies as $\sin \theta \sin \phi$. This term will reach its possible maximum when $\theta = 90^\circ$ and $\phi \approx 19.47^\circ$. At these values

$$\text{IPC}(90^\circ, 19.47^\circ): \langle \hat{H}_{\text{SO}} \rangle_{z,\text{max}} = 0.33\sqrt{2}iKZ^* \{(a^2 + b^2)V_{13}^\pi\} \quad (33)$$

$$\langle \hat{H}_{\text{SO}} \rangle_y = \frac{0.31iKZ^*}{\sqrt{2}} \{2ab(V_{12}^\pi + V_{12}^\sigma)\} \quad (34)$$

Alternatively, $\langle \hat{H}_{\text{SO}} \rangle_y$ reaches its possible maximum when $\theta = 0^\circ$ and $\phi \approx 19.47^\circ$ leading to the expressions

$$\text{IPC}(0^\circ, 19.47^\circ): \langle \hat{H}_{\text{SO}} \rangle_z = 0 \quad (35)$$

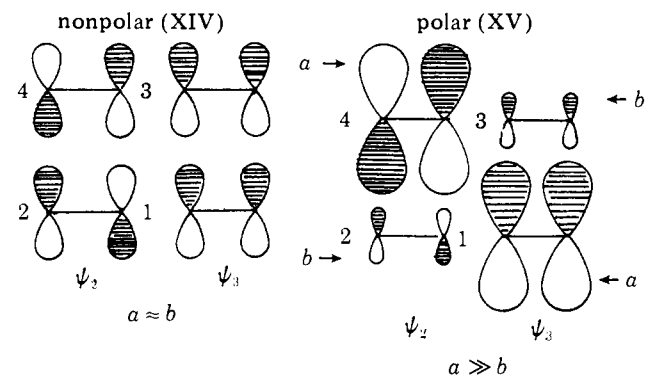
$$\langle \hat{H}_{\text{SO}} \rangle_{y,\text{max}} = \frac{0.31iKZ^*}{\sqrt{2}} \{2ab[(V_{12}^\pi + V_{12}^\sigma) + (V_{13}^\pi + V_{13}^\sigma)]\} \quad (36)$$

At these latter values, IPC is reduced to a pyramidalization mechanism involving only one olefin. Thus we shall neglect this mechanism in our further discussions.

Before comparing the magnitude of the SO coupling terms for the different mechanisms we have to clarify two points.

(a) It was mentioned before that V^σ and V^π behave as the corresponding AO overlap integrals. Thus, V^σ varies as σ -type overlap and will have a negative value.²² On the other hand, V^π is always positive and smaller than the corresponding $|V^\sigma|$.

(b) The products of coefficients in eq 26–32 fall into two categories: $2ab$, which multiplies the intramolecular terms, and $a^2 + b^2$, which multiplies the intermolecular contributions. For electronically similar olefins (i.e., *nonpolar reaction*) $a \approx b$ and hence $2ab \approx a^2 + b^2$. On the other hand, when the two olefins are electronically dissimilar, e.g., one is an electron donor, the other electron acceptor (i.e., *polar reaction*), the MOs become polarized with $a \neq b$. In the extreme case, the MO polarization makes $2ab$ zero while $a^2 + b^2$ approaches unity.²³ Consequently, as the olefins are made a better donor–acceptor pair the intermolecular terms (V_{13}) become increasingly important. The reverse is true for the intramolecular terms since they are weighted by the decreasing multiplier $2ab$. For a given donor–acceptor relationship, the $2ab$ multiplier will increase as the excitation energies of the olefins are decreased.²³ These considerations are illustrated below (XIV and XV).



We can now proceed with the comparison of the various mechanisms using the SO coupling expressions in eq 28–34.

(a) The SO coupling matrix element associated with BID contains an intramolecular π -type contribution, V_{12}^π , and two intermolecular contributions, V_{13}^σ and V_{13}^π . Since V_{13}^σ and V_{13}^π have different signs and $|V_{13}^\sigma| > |V_{13}^\pi|$ the intramolecular and intermolecular contributions would tend to cancel each other provided that the latter are significant. This depends on the intermolecular distances and the polarity of the reaction. As the intermolecular distance decreases (V_{13} increases in absolute magnitude) the SO coupling expression falls off rapidly. Similarly as polarity increases $a^2 + b^2$ becomes larger than $2ab$, decreasing the magnitude of the SO coupling expression. These considerations lead to the clear-cut prediction. *BID will take place preferentially in a "loose" geometry and will be encouraged in nonpolar cases.*

(b) The same considerations apply to MR. Thus, "loose" geometries and low polarity will encourage this mechanism.

(c) The SO coupling expression for ID(45°) contains intermolecular terms, $V_{13}^\pi + V_{13}^\sigma$, multiplied by $\sqrt{2}(a^2 + b^2)$ and thus the SO coupling matrix element will fall off very rapidly with increasing polarity and decreasing intermolecular distance. The intermolecular term may outweigh the intramolecular one at limiting polarity and the SO coupling expression

Table I. Effects of Polarity, Triplet Excitation Energies (E_T), and Intermolecular Distance on the SO Coupling Matrix Elements

mechanism	preferred intermolecular distance	preferred olefin-pair polarity ^a	preferred E_T
BID	loose	nonpolar pair	low
MR	loose	nonpolar pair	low
ID (90°)	tight	polar pair	high
BP	tight	nonpolar pair	low

^a A polar pair is a donor-acceptor pair.

will slowly increase again. In any event, this mechanism is expected to be inefficient.

(d) The SO coupling expression for ID(90°) contains only intermolecular contribution and hence will prefer "tight" geometries. Since the only multiplier of $V_{13}^{\pi} + V_{13}^{\sigma}$ is $a^2 + b^2$, which increases as polarity increases, the SO coupling matrix element will rise sharply as polarity increases, ultimately becoming the largest matrix element.

(e) Similar conclusions apply to the $\langle \hat{H}_{SO} \rangle_z$ for IPC(90°, 19.47°). However, since this contains only a π contribution (eq 31), its magnitude will not be significant throughout the polarity spectrum.

(f) In the case of BP, both the inter- and intramolecular contributions contain V^{σ} and will reinforce each other. Consequently, the SO coupling expression will rise as intermolecular distance decreases. Polarity will have an opposite effect. Along the reaction coordinate $|V_{12}^{\sigma}|$ is almost always greater than $|V_{13}^{\sigma}|$. In addition, V_{12}^{σ} is weighted by $2ab$ while V_{13}^{σ} by $a^2 + b^2$, so that, as polarity increases, the SO coupling expression will decrease.

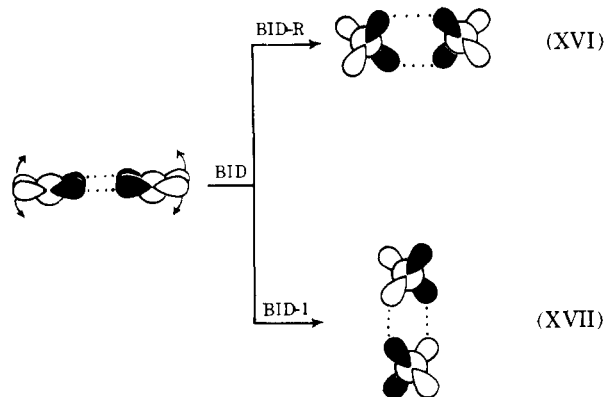
(g) In each case, lowering the triplet excitation energies of the reactants will have an opposite effect to that of increasing the polarity.

The conclusions of this discussion are summarized in Table I.

VI. Stereochemical Consequences of Spin-Inversion Mechanisms

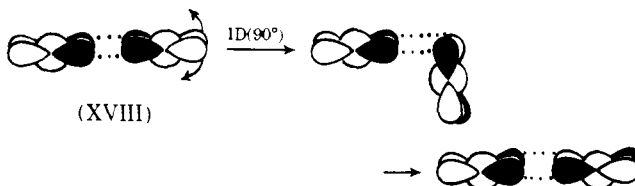
We note that the intermediate structures generated by each motion may or may not be actual intermediates housed in energy wells. This subject lies beyond the scope of the present treatment and will not be discussed. Instead, we shall focus on the final stereochemical result imposed by each spin-inversion mechanism. In discussing the stereochemical result we shall make use of Newman projections showing the p orbitals with the two lobes differently colored to indicate the directional changes following distortion.

In bimolecular $2\pi + 2\pi$ reactions the two olefins approach one another with the π bonds in a face-on manner. Since BID requires 45° rotations it may lead to the two isomeric structures shown below (XVI and XVII). The dotted lines indicate bonds to be formed.

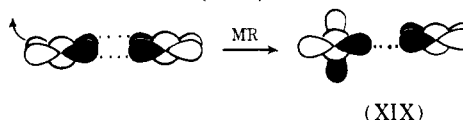


The first mechanism leads to an overall retention of the geometric integrity of both olefins and will be designated BID-R to signify stereochemical retention. The second, labeled by BID-I, obtains by concurrent rotations and a translation of one olefin with respect to the other, leading ultimately to geometric inversion of both olefins. The *translational motion will not be needed should the olefins approach one another with their π bonds mutually parallel as in many intramolecular reactions.*

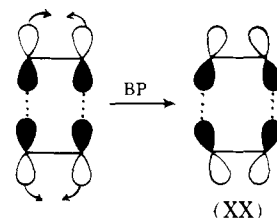
When ID(90°) is performed (XVIII), the result is inversion of the geometry of the rotating olefin.



The third rotational mechanism, MR, leads to a loss of stereochemical information via what may be loosely termed a perpendicular diradical (XIX).



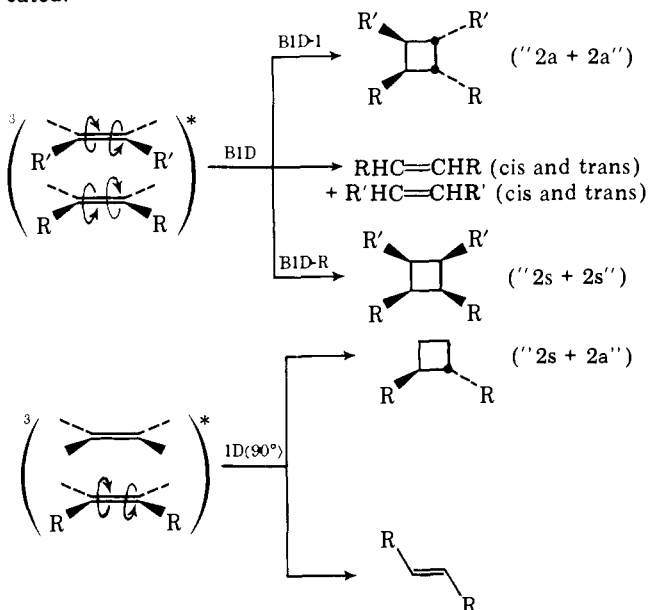
On the other hand, the pyramidalization mechanism BP preserves the geometric integrity of the olefins (XX).

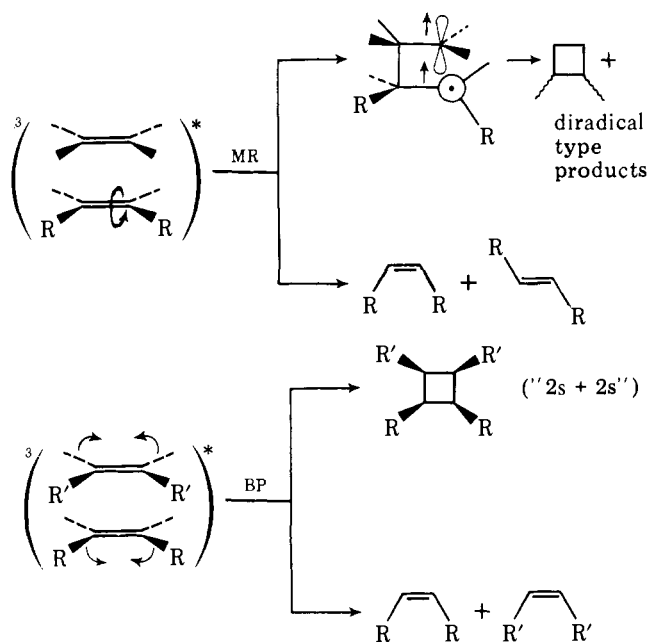


It is now possible to write mechanisms for triplet $[\pi 2_s + \pi 2_s]$ reactions.

VII. Mechanisms and Stereochemistry of Triplet $[\pi 2_s + \pi 2_s]$ Cycloadditions

The mechanisms of triplet $[\pi 2_s + \pi 2_s]$ reactions are depicted below along with the nomenclature that is commonly used to describe product stereochemistry (i.e., Woodward-Hoffmann nomenclature). In each case quenching results are also indicated.





These mechanisms describe the fate of the $[\pi 2_s + \pi 2_s]$ triplet complex as it proceeds to the neighborhood of the "hole".¹⁸ There it performs one of the requisite spin-inversion motions which leads to the distribution of the reaction complexes among products and quenched reactants, all having the characteristic stereochemistry of the motion. Thus, BID-R (XVI) leads to a formal $2s + 2s$ cycloadduct while BID-I leads to a formal $2a + 2a$ product if one olefin can glide over the other without a substantial barrier. The latter will be the *only result of an unimolecular $2\pi + 2\pi$ reaction* when the two π bonds are mutually parallel. In addition, when the complex falls apart it leaves two perpendicular olefins which relax to a cis and trans mixture.

Alternatively, when ID(90°) (XVIII) takes place a formal $2s + 2a$ cycloadduct is produced in addition to an isomerized reactant. If, however, MR is performed, all the stereochemical information contained in the reactants is lost in the final products as well as in the quenched reactants. In addition to cycloadducts, this mechanism will yield other products typical of diradicals (e.g., polymerization).

Finally, BP results in formal $2s + 2s$ cycloadduct. In this case unchanged reactant will be obtained by quenching the complex.

In summary, a triplet $2\pi + 2\pi$ photocycloaddition may be *s + s stereospecific, a + s stereospecific, a + a stereospecific, or stereorandom*. In most cases, combination of these mechanisms will result in a nonstereospecific appearance of the cycloaddition. Immediately, the question arises: Is it ever reasonable to expect a stereoselective triplet photocycloaddition? A partial answer to this question follows from the discussion of polarity effect on the size of the SO coupling matrix element. As polarity increases ID(90°) will have the largest SO coupling matrix element, whereas those associated with BID, MR, and BP become smaller (Table I). For a fixed polarity, reducing the triplet excitation energies of the olefins will have an opposite effect.

The second factor to be considered is the decay energy gap, ΔE (between T_1 and S_0), associated with each motion. In this sense, the MR (XIX) mechanism constitutes a special case. At the early stage of the rotation T_1 lies above S_0 and ultimately becomes the lowest state at $\theta = 90^\circ$, crossing at $\theta < 90^\circ$. A similar situation arises at $180^\circ \geq \theta \geq 90^\circ$ as shown in Figure 2. At the crossing points (A and B) the triplet complex may invert a spin and proceed to form cyclobutane. Alternatively, the complex may proceed along the triplet surface,

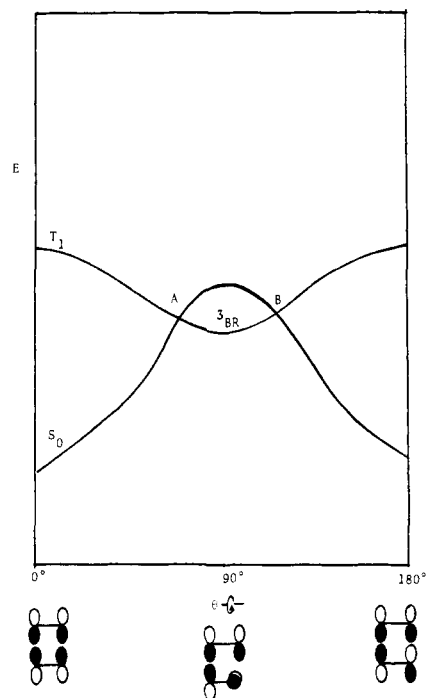


Figure 2. Schematic energy variation of S_0 and T_1 during the MR mechanism in a nonpolar cycloaddition. A and B are the crossing points where spin inversion can take place. 3BR is the perpendicular triplet diradical. The coloring convention of the p AOs is used to indicate stereochemical changes following rotation.

generating a perpendicular triplet diradical. The latter process will be efficient in nonpolar cycloadditions where the perpendicular triplet diradical may be the global minimum of the triplet surface. As polarity increases, the triplet $[\pi 2_s + \pi 2_s]$ complex¹⁶ is increasingly stabilized relative to the perpendicular triplet diradical (Figure 2) and the formation of the diradical becomes less favorable. At the same time, increasing polarity ultimately diminishes the size of the SO coupling matrix element owing to the reasons discussed before (Table I) and to the shifting of the T_1 - S_0 crossing points (Figure 2) to smaller θ values. Consequently, spin inversion (at the crossing points) which leads to cycloadduct formation becomes less efficient. In summary, MR will play a lesser role in polar cycloadditions.

BP is the only mechanism which preserves the "hole"¹⁸ since it preserves the $[\pi 2_s + \pi 2_s]$ geometry. Consequently, BP will involve a small decay gap, ΔE_{BP} , if spin inversion occurs in the close proximity of the "hole" (Figure 1). On the other hand, during ID the PE surfaces are transformed and are no longer characteristic of a $[\pi 2_s + \pi 2_s]$ complex. This may create a large energy gap, ΔE_{ID} , between T_1 and S_0 .

In nonpolar reactions $\Delta E_{ID} > \Delta E_{BP}$ and hence the main spin-inversion mechanism for this range of polarity is BP, which also has a larger SO coupling matrix element. As polarity increases ΔE_{ID} becomes comparable to ΔE_{BP} ²⁴ because the triplet state during ID is more ionic than that associated with BP.^{4,14,25} These arguments are applicable especially to a geometry past the "hole", where any distortion from $[\pi 2_s + \pi 2_s]$ results in sharp energy rise of S_0 , a fact that contributes to equalizing ΔE_{ID} and ΔE_{BP} . Furthermore, as polarity increases the SO coupling matrix element associated with ID(90°) increases (Table I) and becomes larger than that of BP. Consequently, at this limit, ID(90°) becomes the main spin-inversion mechanism. On the other hand, a decrease of the triplet excitation energies of the olefins for a given polarity will encourage BP relatively to ID(90°).

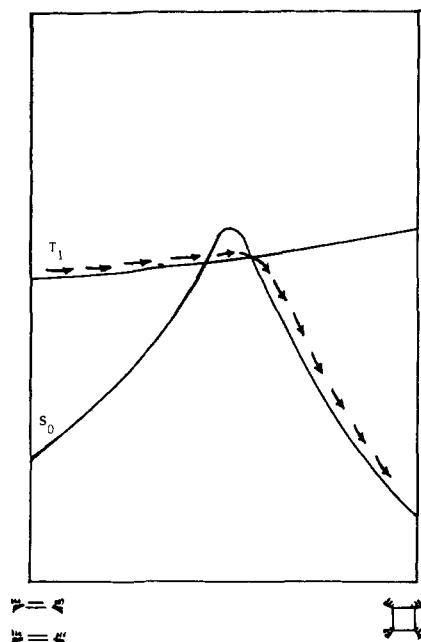


Figure 3. Schematic potential energy surfaces for a $2s + 2s$ cycloaddition in which T_1 crosses S_0 . The dotted lines indicate the avoided surface crossing. The arrows indicate the course of the triplet reaction.

This polarity-selectivity relationship will be reversed when polarity is so large that T_1 crosses S_0 instead of lying above it as in Figure 1. The triplet complex then performs a transition onto the singlet surface at the crossing point on the product side (Figure 3). Consequently, BP, which preserves the T_1 - S_0 surface crossing situation, will prevail, leading to $2s + 2s$ cycloadduct with efficiency decreasing as polarity increases. At the same time, ID(90°) will compete with BP with increasing efficiency and may ultimately take over at the extreme end of polarity, namely, at the ionic range,^{26,27} where T_1 - S_0 crossing can be maintained in both mechanisms.

The BID mechanism is enigmatic; during its course a substantial steric repulsion is developed owing to congestion of the substituents. Thus, in bimolecular reactions BID will serve mainly as a quencher of "loose" [$\pi 2_s + \pi 2_s$] complexes and will give rise to a mixture of *cis* and *trans* isomers. Since the SO coupling matrix element associated with BID decreases with polarity, its role will diminish as the two olefins become a better donor-acceptor pair. On the other hand, in unimolecular [2 + 2] reactions where rotatory motions are needed to generate products (e.g., electrocyclicization) BID will be operative as a product-forming mechanism with decreasing efficiency as polarity increases.

The selectivity trend which emerges from this discussion is described below and the main conclusions are summarized in Table II.

(a) The polarity of the reactants plays a decisive role in determining the final stereochemistry of the reaction.

(b) The geometric changes observed in the quenched reactants are not always indicative of the mechanisms of product formation.

(c) The selectivity-polarity relation is not monotonic and under ideal conditions selectivity will oscillate yielding, alternately, $2s + 2s$ and $2s + 2a$ products as polarity varies from one extreme to the other.²⁷

(d) For a given polarity, reduction of the triplet excitation energies of the olefins will result in an increase of $2s + 2s$ cycloadduct formation.

(e) Diradical formation is important mainly in the nonpolar range.

Table II. Stereoselectivity of Triplet $\pi 2_s + \pi 2_s$ Cycloadditions

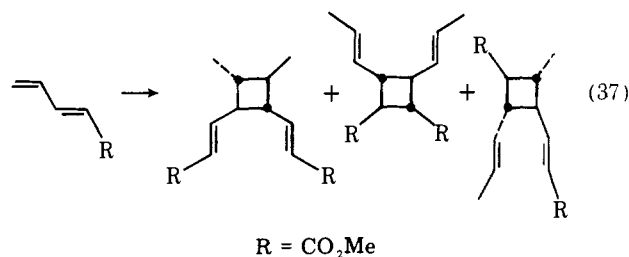
nature of olefin pair	product stereochemistry ^a	main spin-inversion mechanism ^c
nonpolar	$2s + 2s > 2s + 2a$	BP
polar	$2s + 2a > 2s + 2s$	ID (90°)
very polar	$2s + 2s > 2s + 2a$	BP
low triplet energies	$2s + 2s > 2s + 2a$ ^b	BP

^a The stereochemistry of the recovered quenched reactants is affected also by BID which stereorandomizes reactants without yielding cycloadducts. ^b For a given polarity $2s + 2s$ production will gradually increase as the triplet excitation energies of the olefins are decreased. ^c MR (i.e., diradical formation) competes mainly in the nonpolar region.

VIII. Experimental Trends in Triplet [2 + 2] Cycloadditions

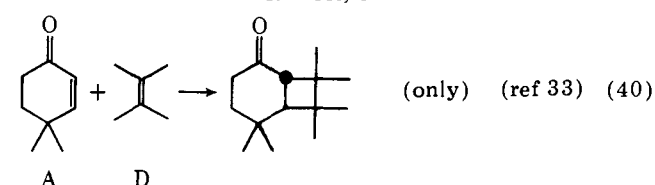
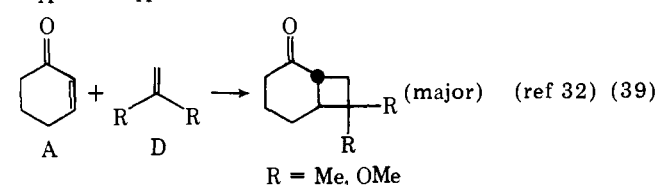
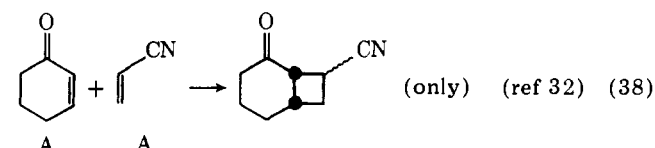
In general, even if diradicals do not intervene triplet reactions can appear nonstereospecific owing to the availability of stereochemically different spin-inversion mechanisms. In this section we provide evidence suggesting that by choosing the reactants properly one of the mechanisms can be made predominant.

A. Polarity-Selectivity Relationship in Triplet $2\pi + 2\pi$ Cycloadditions. Table II shows that for electronically similar olefins $2s + 2s$ stereoselectivity is expected. The photosensitized dimerization of methyl sorbate (eq 37) is a case in point.²⁸

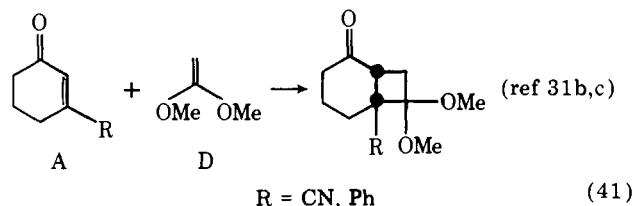


Other examples are the photosensitized reactions of dimethylmaleic anhydride and *cis*- or/and *trans*-dichloroethylene, which proceed with $2s + 2s$ stereospecificity.²⁹

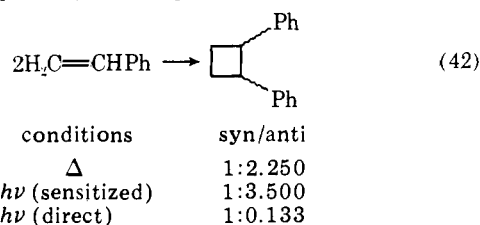
The effect of increasing polarity on the $(2s + 2a)/(2s + 2s)$ ratio is documented in the triplet photocycloaddition of enones.³⁰ Specifically, when the partner olefin is electron poor (i.e., electronically similar to the enone) only *cis*-fused cycloadducts are produced, while an electron-rich partner leads to *trans*-fused adducts. Only some of the known³¹ examples are given below (eq 38-40).



As polarity increases further and/or the triplet excitation energy decreases the trend reverses again, resulting in only cis-fused adducts (eq 41).

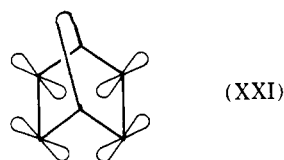


B. Steric Effects in Triplet $2\pi + 2\pi$ Cycloaddition. Inspection of Table I shows that the SO coupling matrix elements associated with ID(90°) and BP increase rapidly as the intermolecular distance decreases. Consequently, spin inversion via these mechanisms will take place at "tight" complex geometries. At this stage, steric repulsions associated with the congested substituents override the stabilizing HOMO-HOMO and LUMO-LUMO secondary orbital interactions.³⁴ Consequently, whenever syn and anti isomers are possible, the latter will be the preferred product. That this is so can be concluded from the comparative studies of Brown.³⁵ His results show how steric effects are magnified in the triplet reaction in comparison with the thermal or the singlet photoreaction (reaction 42). A survey of the literature shows this trend with almost no exceptions (for example, see ref 1d and 30d).



C. BID Mechanisms in Triplet Intramolecular [2 + 2] Reactions. We have argued before that BID will not be an efficient product-forming mechanism in bimolecular $2\pi + 2\pi$ cycloadditions owing to congestion of the substituents. Quite a different situation is expected in intramolecular [2 + 2] cycloadditions such as $2\sigma + 2\pi$ or $2\pi + 2\pi$. Here, the geometric characteristics of the system allows BID to take place without imposing severe steric repulsion. Below we discuss two classes of photoreactions in which this mechanism explains the unique stereochemical course.

1. Di- π -methane Rearrangement of Bicyclic Systems. The first step of the di- π -methane rearrangement in bicyclic systems can be viewed as a $2\pi + 2\pi$ reaction. Unlike bimolecular reactions, here the π bonds are not aligned in a face-on manner but are canted as shown in XXI. Consequently, rotations will

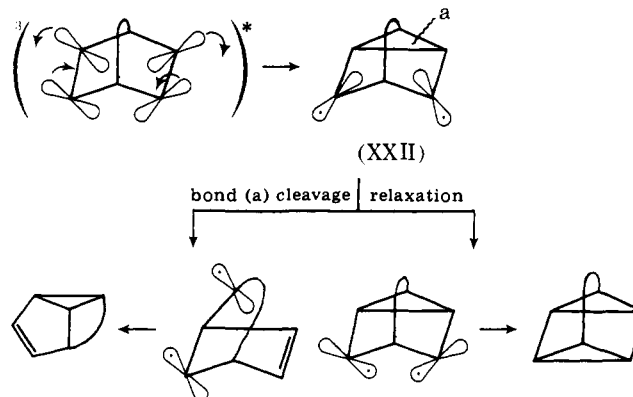


be needed for cycloadduct formation. The geometric constraints of the system make BP and BID the only likely candidates for spin inversion. Derivation of the SO coupling matrix elements for BID now yields an expression which differs from eq 28 by a sign:

$$\text{BID: } \langle \hat{H}_{\text{SO}} \rangle_{x,\text{max}} = \frac{iKZ^*}{\sqrt{2}} \{4abV_{12}^\pi - (a^2 + b^2)(V_{13}^\pi + V_{13}^\sigma)\} \quad (43)$$

This difference arises from the cant in the alignment of the π MOs³⁶ and makes the matrix element associated with BID larger than that associated with BP. The reason is that $V_{13}^\pi +$

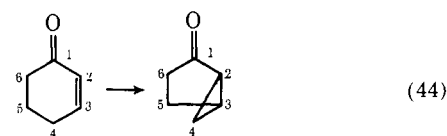
V_{13}^σ is a negative term and will add to V_{12}^π . Furthermore, BID is superior to BP also due to a smaller T_1-S_0 energy gap. Specifically, during BID T_1 and S_0 reach a near-touching situation because the geometric constraints enforce a diradicaloid species. The resulting singlet species (XXII), after spin



inversion, can either relax its geometry and then close to cycloadduct or rearrange if ring closure requires a higher barrier.

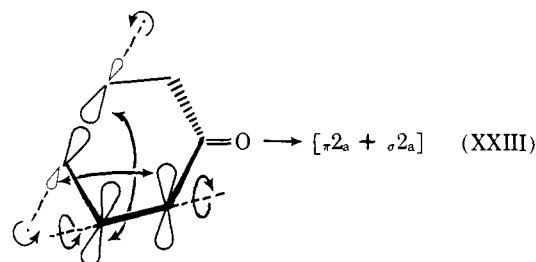
Both possibilities have been observed experimentally.^{37,38}

2. Type A Lumiketone Rearrangement. Type A lumiketone rearrangement has been known to originate from a triplet state with evidence suggesting a ${}^3\pi\pi^*$ reactive state.^{39,40} The reaction can be viewed as a formal $2\pi + 2\sigma$ cycloaddition, in which $\sigma_{4,5}$ is cleaved and adds in a cross-bonding fashion to $\pi_{2,3}$ (eq 44).



Recently, Schuster et al.⁴¹ have demonstrated that the reaction of optically active 4-substituted cyclohexenones is [$\pi 2_a + \sigma 2_a$] stereospecific.

The mechanism is shown schematically by XXIII. The thick



double-headed arrows indicate bonds to be formed and the single-headed arrows indicate the modes of the π bond rotation and the σ bond cleavage.

The reader will recognize that the mechanism is analogous to BID since it requires a double inversion, one for each reactant. Whenever both spin-inversion and orbital-symmetry requirements are met along the *same* reaction coordinate, the reaction can be stereospecific. This conspiracy of orbital symmetry and spin inversion can be typically realized in intramolecular $2\pi + 2\pi$ and $2\pi + 2\sigma$ cycloadditions.

IX. Conclusion

Most of the theoretical effort in organic chemistry with a few exceptions^{3,4,13} has focused so far on the study of the spin free Hamiltonian. This has led to an understanding of factors related to the intimacies of reaction profiles such as potential barriers and energy wells (reaction intermediates).¹⁸ At the same time, the factors which control the behavior of spin nonconservative processes remained unclear. Consequently,

triplet reactions, although investigated extensively by the experimentalist, became a source of puzzlement.⁴²

We have shown that spin inversion is related to nuclear movements which are characteristic of the symmetry properties of the reaction complex. These nuclear movements define a set of stereoselection rules for triplet reactions. In general, one expects, for most reactions, at least three *stereochemically different* spin-inversion motions. This is a direct result of the commonly different symmetries of the three sublevels of the triplet state (T_x , T_y , T_z). Thus, one may be led to the disappointing conclusion that triplet reactions are "doomed" to be nonstereospecific. This work shows that the situation is not necessarily hopeless. Proper selection of the reactants may lead to stereoselective and even to stereospecific results. One class of reactions (the enone cycloadditions) has been shown to exhibit this trend and another class (type A rearrangements) has been shown to be stereospecific owing to the conspiracy of efficient spin-inversion and orbital symmetry allowedness.

Further understanding of the role played by spin inversion may be gained by selective excitation of the triplet sublevels (T_x , T_y , T_z). Recent developments in this area^{43,44} can hopefully be extended to study the stereochemistry of triplet cycloadditions.

Acknowledgment. The author is grateful to Professor R. Hoffmann for his encouragement and support. Thanks also to E. Jemmis and A. Pinhas for many critical comments.

Appendix I

We have dealt in the text with two types of motions, pyramidalizations and rotations. The basic difference between these is in their effect on the frontier MOs of the complex. Pyramidalization motions preserve the ordering of these MOs and mix into them orbitals having the same local symmetries. On the other hand, the rotational motions usually result in changing the ordering of these levels and transforming them into one another by changing the symmetry of the complex. For example, rotation of ethylene transforms π into π^* and leads to orbital crossing, whereas pyramidalization will simply mix σ and σ^* into the π and π^* MOs. As a result of this distinction pyramidalization, even nonsymmetric, can be treated as a continuous sequence of perturbations, whereas rotations cannot. Accordingly, the derivation of selection rules for spin inversion must follow two different formalisms which we will now describe.

1. Pyramidalization Motions. The Hamiltonian of the system is expressed as a sum of the electronic Hamiltonian of a fixed set of nuclei, \hat{H}^0 , and the electronic energy due to a small nuclear displacement, Q_i .⁴⁵

$$\hat{H} = \hat{H}^0 + \sum_i \left(\frac{\partial \hat{H}}{\partial Q_i} \right) Q_i = \hat{H}^0 + \sum_i V_i Q_i \quad (45)$$

If one concentrates on a particular displacement, Q_i , we get a new set of solutions for the Schrödinger equation. We are interested only in two particular solutions, T_1 and S_0 . These wave functions, corrected to the first order, are

$$T_1 = T_1^0 + \sum_{m \neq 1} Q_i \frac{\langle T_m^0 | V_i | T_1^0 \rangle}{E_1^0 - E_m^0} T_m^0 \quad (46)$$

$$S_0 = S_0^0 + \sum_{n \neq 0} Q_i \frac{\langle S_n^0 | V_i | S_0^0 \rangle}{E_0^0 - E_n^0} S_n^0 \quad (47)$$

where m runs over the triplet zero-order set of solutions and n over the singlet ones. The superscript zero denotes the zero-order solutions for the fixed reference system.

The SO coupling matrix element of the two new states can now be expanded in terms of the reference system:

$$\begin{aligned} \langle T_1 | \hat{H}_{SO} | S_0 \rangle &= \langle T_1^0 | \hat{H}_{SO} | S_0^0 \rangle \\ &+ \sum_{n \neq 0} Q_i \frac{\langle S_n^0 | V_i | S_0^0 \rangle}{E_0^0 - E_n^0} \langle T_1^0 | \hat{H}_{SO} | S_n^0 \rangle \\ &+ \sum_{m \neq 1} Q_i \frac{\langle T_m^0 | V_i | T_1^0 \rangle}{E_1^0 - E_m^0} \langle T_m^0 | \hat{H}_{SO} | S_0^0 \rangle \\ &+ \sum_{m \neq 1} \sum_{n \neq 0} Q_i^2 \frac{\langle T_m^0 | V_i | T_1^0 \rangle \langle S_n^0 | V_i | S_0^0 \rangle}{E_1^0 - E_m^0} \frac{1}{E_0^0 - E_n^0} \\ &\quad \times \langle T_m^0 | \hat{H}_{SO} | S_n^0 \rangle \quad (48) \end{aligned}$$

These terms can be further expanded if \hat{H}_{SO} is expressed as⁴⁶

$$\hat{H}_{SO} = \hat{H}_{SO}^0 + \left(\frac{\partial \hat{H}_{SO}}{\partial Q_i} \right) Q_i + \dots \quad (49)$$

This leads to the final form of the SO coupling matrix element in eq 50 where we neglected the quadratic term in Q_i .

$$\begin{aligned} \langle T_1 | \hat{H}_{SO} | S_0 \rangle &= \langle T_1^0 | \hat{H}_{SO}^0 | S_0^0 \rangle + \left\langle T_1^0 \left| \frac{\partial \hat{H}_{SO}}{\partial Q_i} \right| S_0^0 \right\rangle Q_i \\ &+ \sum_{m \neq 0} Q_i \frac{\langle S_n^0 | V_i | S_0^0 \rangle}{E_0^0 - E_n^0} \left\{ \langle T_1^0 | \hat{H}_{SO}^0 | S_n^0 \rangle \right. \\ &+ \left. \left\langle T_1^0 \left| \frac{\partial \hat{H}_{SO}}{\partial Q_i} \right| S_n^0 \right\rangle Q_i \right\} + \sum_{n \neq 1} Q_i \frac{\langle T_m^0 | V_i | T_1^0 \rangle}{E_1^0 - E_m^0} \\ &\times \left\{ \langle T_m^0 | \hat{H}_{SO}^0 | S_0^0 \rangle + \left\langle T_m^0 \left| \frac{\partial \hat{H}_{SO}}{\partial Q_i} \right| S_0^0 \right\rangle Q_i \right\} \quad (50) \end{aligned}$$

The various terms in eq 50 can be equated with different coupling mechanisms. This has been done many times before⁴⁶ and will not be repeated here. Instead we shall attempt to derive selection rules using group theoretical language.

Since $V_i Q_i$ and $(\partial \hat{H}_{SO} / \partial Q_i) Q_i$ are parts of the Hamiltonian they must belong to the totally symmetric representation Γ_1 , and so does \hat{H}_{SO}^0 . Thus the following equalities hold unless degeneracies are involved.

$$\Gamma(Q_i) = \Gamma(V_i) \quad \Gamma(Q_i) = \Gamma(\partial \hat{H}_{SO} / \partial Q_i)$$

Recalling that the triplet spin functions transform as the rotations \mathbf{R}_k ($k = x, y, z$), we can write the conditions which lead to nonvanishing terms in eq 50. We shall concentrate on the first two terms and the reader can convince himself that the rest of the terms yield the same results. These are shown in eq 51 and 52 where $(T_1^{0,\nu})$ is the representation of the spatial part of T_1^0 .

$$\begin{aligned} \langle T_1^0 | \hat{H}_{SO} | S_0^0 \rangle &\rightarrow \Gamma(T_1^{0,\nu}) \times \Gamma(\mathbf{R}_k) \times \Gamma(S_0) \\ &= \Gamma_1 + \dots \quad (k = x, y, z) \quad (51) \end{aligned}$$

$$\begin{aligned} \left\langle T_1^0 \left| \frac{\partial \hat{H}_{SO}}{\partial Q_i} \right| S_0^0 \right\rangle &\rightarrow \Gamma(T_1^{0,\nu}) \times \Gamma(\mathbf{R}_k) \\ &\times \Gamma(S_0) \times \Gamma(Q_i) = \Gamma_1 + \dots \quad (52) \end{aligned}$$

Equations 51 and 52 define the basis for the derivation of selection rules as was done in the text (eq 5 and 6). The first equation states the condition for nonvanishing SO coupling interaction in the fixed reference system and the second states the conditions for creating SO coupling interaction upon distortion Q_i . Similar conclusions have been reached by Halevi and Trindle^{3c} and by Lee.^{3e}

2. Rotation Motions. Consider a triplet complex (in state T_1^0) belonging to a point group P^0 and experiencing rotations which transform it into a new symmetry group, P^1 . The condition for nonvanishing SO coupling interaction in the new group, as usual, is that the direct product involving the representations of the new states, T_1^1 and S_0^1 , includes the totally symmetric representation, Γ_1^1 .

$$\Gamma(T_1^{1,\nu}) \times \Gamma(\mathbf{R}_k^1) \times \Gamma(S_0^1) = \Gamma_1^1 + \dots \quad (53)$$

Recalling that $T_1^{1,\nu}$, S_0^1 , and the spin functions of T_1^1 are generated by the transformation, Q of T_1^0 and S_0^0 or of other states having equal symmetries to S_0^0 and T_1^0 , we can rewrite the left-hand side of eq 53 as follows:

$$\Gamma(QT_1^{0,\nu}) \times \Gamma(QR_k^0) \times \Gamma(QS_0^0)$$

Since $\Gamma(Q) \times \Gamma(Q) = \Gamma_1 + \dots$, this expression can be simplified (when degeneracies are not involved) and the selection rules become

$$\Gamma(T_1^{0,\nu}) \times \Gamma(R_k^0) \times \Gamma(S_0^0) \times \Gamma(Q) = \Gamma_1^0 + \dots \quad (54)$$

Thus, in this case also, the spin-inversion motion can be searched using the original point group, P^0 . This will not be the case when Q leads to multiple orbital crossing such that T_1^1 and S_0^1 are generated from states T_m^0 and S_n^0 having symmetries different from T_1^0 and S_0^0 . In this case there is no easy recipe for searching spin-inversion promoting motions.

References and Notes

- (1) For example, see (a) R. S. H. Liu and G. S. Hammond, *J. Am. Chem. Soc.*, **89**, 4936 (1967); (b) P. De Mayo, J.-P. Pete, and M. Tchir, *Can. J. Chem.*, **46**, 2535 (1968); (c) P. D. Bartlett, R. Helgeson, and O. A. Wersel, *Pure Appl. Chem.*, **16**, 187 (1968); (d) W. L. Dilling, *Chem. Rev.*, **66**, 373 (1966); **69**, 845 (1969); (e) W. L. Dilling, T. E. Tabor, F. P. Boer, and P. P. North, *J. Am. Chem. Soc.*, **92**, 1399 (1970); (f) P. D. Bartlett, *Q. Rev., Chem. Soc.*, **24**, 473 (1970).
- (2) (a) O. L. Chapman and G. Lenz, *Org. Photochem.*, **1**, 283 (1967); (b) P. E. Eaton, *Acc. Chem. Res.*, **1**, 50 (1968); (c) P. De Mayo, *ibid.*, **4**, 41 (1971); (d) R. M. Bowman, C. Calvo, J. J. McCullough, P. W. Rasmussen, and F. F. Snyder, *J. Org. Chem.*, **37**, 2084 (1972); (e) O. L. Chapman and D. S. Weiss, *Org. Photochem.*, **3**, 197 (1973).
- (3) For other treatments of spin inversion, see (a) N. J. Turro and A. Devaquet, *J. Am. Chem. Soc.*, **97**, 3859 (1975); (b) E. A. Halevi, *Angew. Chem., Int. Ed. Engl.*, **15**, 593 (1976); (c) E. A. Halevi and C. Trindle, *Isr. J. Chem.*, **16**, 283 (1977); (d) C. Trindle and H. O. Pamuk, *Tetrahedron*, **34**, 747 (1978); (e) T. Lee, *J. Am. Chem. Soc.*, **99**, 3909 (1977).
- (4) S. Shaik and N. D. Epiotis, *J. Am. Chem. Soc.*, **100**, 18 (1978).
- (5) (a) G. W. Robinson and R. P. Frosch, *J. Chem. Phys.*, **37**, 1962 (1962); (b) *ibid.*, **38**, 1187 (1963); (c) J. Jortner, S. A. Rice, and R. M. Hochstrasser, *Adv. Photochem.*, **7**, 149 (1969); (d) J. Jortner, *Pure Appl. Chem.*, **27**, 389 (1971).
- (6) (a) S. P. McGlynn, T. Azumi, and M. Kinoshita, "The Triplet State", Prentice-Hall, Englewood Cliffs, N.J., 1969; (b) S. P. McGlynn, L. G. Vanquickenborne, M. Kinoshita, and D. G. Carroll, "Introduction to Applied Quantum Chemistry", Holt, Rinehart and Winston, New York, 1972, Chapter 11.
- (7) The spin functions defined over the Cartesian axes are

$$\tau_x = 2^{-1/2}[\alpha(1)\alpha(2) - \beta(1)\beta(2)]$$

$$\tau_y = i2^{-1/2}[\alpha(1)\alpha(2) + \beta(1)\beta(2)]$$

$$\tau_z = 2^{-1/2}[\alpha(1)\beta(2) + \beta(1)\alpha(2)]$$
- (8) (a) E. P. Wigner, "Group Theory and Its Applications to the Quantum Mechanics of Atomic Spectra", Academic Press, New York, 1959; (b) R. S. Knox and A. Gold, "Symmetry in the Solid State", W. A. Benjamin, New York, 1964.
- (9) The symmetry requirements in eq 6 indicate that the SO coupling matrix element is nonzero when the condition is met, without implying anything about the magnitude of the matrix element.
- (10) Group correlation tables can be found inter alia in (a) E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, "Molecular Vibrations", McGraw-Hill, New York, 1955; (b) M. Tinkham, "Group Theory and Quantum Mechanics", McGraw-Hill, New York, 1964; (c) R. M. Hochstrasser, "Molecular Aspects of Symmetry", W. A. Benjamin, New York, 1966; (d) F. A. Cotton, "Chemical Application of Group Theory", Wiley-Interscience, New York, 1971.
- (11) See, for example, the SO coupling analysis in ${}^3B_{1u}$ of benzene: D. S. McClure, *J. Chem. Phys.*, **20**, 682 (1952).
- (12) The importance of two-center SO coupling interactions in determining the phosphorescence lifetimes of aromatic amines has been discussed: M. Kasha, H. R. Rawls, and M. A. El-Bayoumi, 8th European Congress on Molecular Spectroscopy, Copenhagen, Denmark, 1965.
- (13) According to Salem, spin inversion is brought about by the torque which is associated with the change of angular momentum. For this and other details on two-center SO coupling interactions, see (a) L. Salem and C. Rowland, *Angew. Chem., Int. Ed. Engl.*, **11**, 92 (1972); (b) L. Salem, *Pure Appl. Chem.*, **33**, 317 (1973).
- (14) S. Shaik, Ph.D. Dissertation, University of Washington, Seattle, Wash., 1978.
- (15) The "exciplex" phenomena is reviewed in M. Gordon and W. R. Ware, Eds., "The Exciplex", Academic Press, New York, 1975.
- (16) The wave function of a polar 3M is $\Psi_{3M} = {}^3D^+A^- + \lambda({}^3D^+A^- - {}^3DA^+) - \delta({}^3D^+A^-)$ ($0 < \delta < \lambda$). Evidence of the role of triplet exciplexes in $2\pi + 2\pi$ cycloadditions has been obtained recently; see, for example, (a) S. Farid, J. C. Doty, and J. R. L. Williams, *J. Chem. Soc., Chem. Commun.*, **711** (1972); (b) S. Farid, S. E. Hartman, J. C. Doty, and J. R. L. Williams, *J. Am. Chem. Soc.*, **97**, 3697 (1975); (c) D. Creed, R. A. Caldwell, and M. M. Ulrich, *ibid.*, **100**, 5831 (1978).
- (17) For the original discussion of this avoided crossing, see (a) H. C. Longuet-Higgins and E. W. Abrahamson, *J. Am. Chem. Soc.*, **87**, 2045 (1965); (b) R. Hoffmann and R. B. Woodward, *ibid.*, **87**, 2046 (1965).
- (18) The "hole" is the locus of MO crossing (ref 17). Its importance as an efficient drain for excited complexes has been emphasized by (a) W. Th. A. M. Van der Lugt and L. J. Oosterhoff, *J. Am. Chem. Soc.*, **91**, 6042 (1969); (b) R. C. Dougherty, *ibid.*, **93**, 7187 (1971); (c) J. Michl, *Top. Curr. Chem.*, **46**, 1 (1974); (d) J. Michl, *Pure Appl. Chem.*, **41**, 507 (1975); (e) L. Salem, C. Leforestier, G. Segal, and R. Wetmore, *J. Am. Chem. Soc.*, **97**, 479 (1975); (f) W. G. Dauben, L. Salem, and N. J. Turro, *Acc. Chem. Res.*, **8**, 41 (1975); (g) L. Salem, *Science*, **191**, 822 (1976); (h) A. Devaquet, *Pure Appl. Chem.*, **41**, 455 (1975); (i) D. Grimbert, G. Segal, and A. Devaquet, *J. Am. Chem. Soc.*, **97**, 6629 (1975); (j) Y. Jean and A. Devaquet, *ibid.*, **99**, 1949 (1977); (k) O. Kikuchi, *Bull. Chem. Soc. Jpn.*, **47**, 1551 (1974).
- (19) The construction of qualitative PE surfaces of the type sketched in Figure 1 is described in (a) N. D. Epiotis and S. Shaik in "Progress in Theoretical Organic Chemistry", Vol. 2, I. G. Csizmadia, Ed., Elsevier, Amsterdam, 1977; (b) N. D. Epiotis and S. Shaik, *J. Am. Chem. Soc.*, **99**, 4936 (1977); (c) *ibid.*, **100**, 1, 8, 29 (1978); (d) N. D. Epiotis, "Theory of Organic Reactions", Springer-Verlag, Heidelberg, 1978; (e) N. D. Epiotis, S. Shaik, and W. Zander in "Rearrangements in Ground and Excited States", P. De Mayo, Ed., Academic Press, New York, 1979.
- (20) The theoretical background involved in the formulation of projection operators is given in (a) ref 6b, Chapter 7; (b) ref 10b, pp 40-42; (c) ref 10c, pp 174-190; (d) ref 10d, Chapter 6.
- (21) The same a, b set of coefficients for ψ_2 and ψ_3 was assumed for simplicity. This need not be so and the same conclusions are arrived at if two different sets of coefficients are used.
- (22) The sign of σ -type overlap is negative owing to the convention of the coordinate axes. Thus, a σ_{cc} MO appears as a negative combination of pAOs but it is stabilized since the corresponding overlap is negative.
- (23) This has been checked by means of EH computation of $2\pi + 2\pi$ complexes with increasing donor-acceptor properties. As polarity increases ψ_2 progressively concentrates on the acceptor portion, while ψ_3 on the donor portion. When one olefin becomes simultaneously a better donor and a better acceptor (i.e., its excitation energy is lowered) both ψ_2 and ψ_3 tend to concentrate on this olefin.
- (24) This trend has been checked by using the EH HOMO-LUMO gap as a rough index for the S_0-T_1 separation, ΔE . We have found that ΔE_{IP} is sensitive to polarity, and, for a polar case, this gap becomes practically equal to that for the $[\pi_2s + \pi_2s]$ complex.
- (25) Since the olefin performs rotation, the intermolecular one-electronic HOMO-HOMO and LUMO-LUMO interactions are weakened. This results in less mixing of ${}^3DA^+$ and ${}^3D^+A^-$ into ${}^3D^+A^-$ making T_1 more ionic. For more details see ref 19c-e and footnote in ref 16.
- (26) The ionic range of reactivity starts from the point where D^+A^- attains lower energy than the no-bond configuration, DA. For more details see ref 19.
- (27) Other factors, not discussed here, may intervene to upset the trend, e.g., high rotation barriers at the polar range may suppress $ID(90^\circ)$.
- (28) H. P. Kaufmann and A. K. S. Gupta, *Justus Liebigs Ann. Chem.*, **681**, 39 (1965).
- (29) G. O. Schenck, W. Hartman, and R. Steinmetz, *Chem. Ber.*, **96**, 498 (1963).
- (30) (a) References 2a-c; (b) P. G. Bauslaugh, *Synthesis*, **2**, 287 (1970); (c) H. Meier, "Methoden der Organischen Chemie", Vol. IV/56, Part II, E. Muller, Ed., George Thieme Verlag, Stuttgart, 1975, pp 898-940; (d) P. Margaretha, *Chimia*, **29**, 203 (1975); (e) G. V. Thi and P. Margaretha, *Helv. Chim. Acta*, **59**, 2236 (1976).
- (31) (a) T. S. Cantrell, W. S. Haller, and J. C. Williams, *J. Org. Chem.*, **34**, 509 (1969); (b) T. S. Cantrell, *Tetrahedron*, **27**, 1227 (1971); (c) ref 2d.
- (32) E. J. Corey, J. D. Bass, R. LeMahieu, and R. B. Mitra, *J. Am. Chem. Soc.*, **86**, 5570 (1964).
- (33) P. J. Nelson, D. Ostrem, J. D. Lassila, and O. L. Chapman, *J. Org. Chem.*, **34**, 811 (1969).
- (34) (a) W. C. Herndon, *Top. Curr. Chem.*, **46**, 141 (1974); (b) ref 19d, Chapter 7.
- (35) W. G. Brown, *J. Am. Chem. Soc.*, **90**, 1916 (1968).
- (36) BID changes the molecular point group from D_{2h} to C_{2h} . In C_{2h} the in-plane frontier orbitals of a $2\pi + 2\pi$ complex behave (in pairs) as B_u and A_u . Hence, upon rotation they will be transformed to the out-of-plane orbitals of the same symmetry. On the other hand, the out-of-plane orbitals of the intramolecular complex (such as XXII) behave in C_{2h} as A_g and B_g and will be transformed upon BID to the in-plane MOs having the same symmetries. This distinction leads to the sign difference in eq 28 and 43.
- (37) (a) N. J. Turro, W. R. Cherry, N. F. Mirbach, and M. J. Mirbach, *J. Am. Chem. Soc.*, **99**, 7388 (1977), and references cited therein; (b) A. J. G. Barwise, A. A. Gorman, R. L. Leyland, P. G. Smith, and M. A. J. Rodgers, *ibid.*, **100**, 1814 (1978).
- (38) (a) S. S. Hixson, P. S. Mariano, and H. E. Zimmerman, *Chem. Rev.*, **73**, 531 (1973); (b) J. R. Edman, *J. Am. Chem. Soc.*, **91**, 7103 (1969); (c) L. A. Paquette, D. M. Cottrell, R. A. Snow, K. B. Gifkins, and J. Clardy, *ibid.*, **97**, 3275 (1975).
- (39) W. G. Dauben, W. A. Spitzer, and M. S. Kellogg, *J. Am. Chem. Soc.*, **93**, 3674 (1971).
- (40) (a) D. Bellus, D. R. Kearns, and K. Schaffner, *Helv. Chim. Acta*, **52**, 971 (1969); (b) G. Marsh, D. R. Kearns, and K. Schaffner, *J. Am. Chem. Soc.*, **93**, 3129 (1971).
- (41) D. I. Schuster, R. H. Brown, and B. M. Resnick, *J. Am. Chem. Soc.*, **100**, 4504 (1978).
- (42) For example, see ref 2e (especially p 225).
- (43) Selective population of the triplet sublevels is described in M. A. El-Sayed, *Annu. Rev. Phys. Chem.*, **26**, 235 (1975).

(44) Different rates of decomposition were observed for the sublevels of the first triplet state of dimethyl-*s*-tetrazine. See B. Dillinger, R. M. Hochstrasser, and A. B. Smith, III, *J. Am. Chem. Soc.*, **99**, 5834 (1977).
 (45) (a) R. F. W. Bader, *Mol. Phys.*, **3**, 137 (1960); (b) L. Salem *Chem. Phys. Lett.*,

3, 99 (1966); (c) R. G. Pearson, *J. Am. Chem. Soc.*, **91**, 1252 (1969); (d) ref 10c, pp 229-230.
 (46) For example: (a) A. C. Albrecht, *J. Chem. Phys.*, **38**, 354 (1963); (b) ref 10c, Chapter 9.

Solute-Solvent Interactions in the Ground State and in Electronic Excited States. The Dipolar Aprotic to Polar Protic Solvent Blue Shift of Some Anilines and Phenols

Paul Haberfield,* Douglas Rosen, and Ira Jasser

Contribution from the Department of Chemistry, Brooklyn College of the City University of New York, Brooklyn, New York 11210. Received November 2, 1978

Abstract: The long-wavelength transition of some anilines, phenols, and their nitro derivatives was found to be blue shifted on transfer from dimethylformamide to methanol solvent. The enthalpies of transfer of the Franck-Condon excited states were then determined by combining calorimetric and spectroscopic data. It was found that enthalpies of transfer of the Franck-Condon excited states were uniformly endothermic into the hydrogen-bonding solvent. An estimate of the solvent transfer enthalpies of the corresponding relaxed excited states was made from fluorescence, absorbance, and calorimetric data. A comparison of the solvent transfer enthalpies of the ground state, the Franck-Condon excited state, and the relaxed excited state was used to evaluate the specific solvation mechanisms causing the blue shift.

The frequently observed solvent effects on the wavelengths of electronic transitions are the sum of the changes in solvation energy of the ground state and changes in the solvation energy of the excited state. Combination of calorimetric and spectroscopic data can separate these two effects, thus shedding some light on the nature of the solvation effects in the ground and excited states, as well as on the nature of the particular electronic transition.¹⁻³ Recently we reported the results of such a study on the long-wavelength transition of some nitroaromatics.³ In this transition the dipole moment increases in the excited state transferring negative charge from the aromatic ring to the nitro group. Nevertheless, this transition was found to be blue shifted from a dipolar aprotic to a polar protic solvent. This unexpected result indicated that, as charge is transferred from the aromatic system to the NO₂ group, it strengthens dipole-dipole interactions more than it strengthens the hydrogen bonds to the NO₂ group.

It should be of interest to examine a transition in which the dipole moment also increases, but transfers negative charge in the other direction, namely toward the aromatic ring. An example of such a transition is to be found in the long-wavelength absorption of anilines (corresponding to the 287-nm band of aniline) and phenols (corresponding to the 275-nm band of phenol).^{4,5} The solvation of this excited state should be of interest as it bears on the question of the greatly enhanced excited-state acidities of phenols⁶ and the reduced basicities of the excited states of anilines,^{6b} as well as on the excited states of related biomolecules.⁷ Anilines and phenols having a conjugated nitro group would be expected to have a still larger dipole moment increase in the excited state,^{8,9} while having the complicating factor of the nitro group solvation effects observed earlier³ superimposed on the amino or hydroxy group solvation effect. Such compounds are of added interest because their spectral shifts have been used by Kamlet and Taft for their solvatochromic comparison method to construct a scale of solvent hydrogen bond donor and hydrogen bond acceptor abilities.¹⁰ As before³ the dipolar aprotic-polar protic solvent pair used in this study was dimethylformamide and methanol.

These two solvents have very similar dielectric constants and therefore lend themselves well to the study of specific solvation effects.

Results and Discussion

The enthalpy of transfer of a compound from dimethylformamide to methanol, $\delta\Delta H_{\text{DMF}\rightarrow\text{MeOH}}^{\text{ground state}}$, is the difference between the heats of solution, $\Delta H_{\text{solvent}}$, of the compound in the two solvents of interest:

$$\delta\Delta H_{\text{DMF}\rightarrow\text{MeOH}}^{\text{ground state}} = \Delta H_{\text{MeOH}} - \Delta H_{\text{DMF}}$$

With the spectral solvent shift, $\delta\Delta E_{\text{DMF}\rightarrow\text{MeOH}}^{\text{abs}}$, defined in the usual way as the difference in the excitation energies, ΔE^{abs} , in the two solvents:

$$\delta\Delta E_{\text{DMF}\rightarrow\text{MeOH}}^{\text{abs}} = \Delta E_{\text{MeOH}}^{\text{abs}} - \Delta E_{\text{DMF}}^{\text{abs}}$$

The energy of transfer of the Franck-Condon excited state, $\delta\Delta H_{\text{DMF}\rightarrow\text{MeOH}}^{\text{F.C. excited state}}$, is then readily calculated from the equation

$$\delta\Delta H_{\text{DMF}\rightarrow\text{MeOH}}^{\text{F.C. excited state}} = \delta\Delta H_{\text{DMF}\rightarrow\text{MeOH}}^{\text{ground state}} + \delta\Delta E_{\text{DMF}\rightarrow\text{MeOH}}^{\text{abs}} \quad (1)$$

All but one of the 12 compounds examined were found to be blue shifted into the polar protic solvent (Table I, column 2). Considering the first three amines, one sees that their enthalpies of transfer into the hydrogen bond donor solvent are all endothermic (Table I, column 3). This is mainly a consequence of the greater net interaction¹¹ of the amino group with the hydrogen bond acceptor solvent (DMF) than with the hydrogen bond donor solvent (MeOH). That this is so is shown by the fact that in the case of *N,N*-dimethylaniline, where the former interaction is necessarily absent, the transfer enthalpy is least endothermic (0.8 kcal/mol). This, however, is still larger than the transfer enthalpy of cumene, 0.11 kcal/mol,¹² which can be used as a model for the difference between the cavity-forming enthalpies in the two solvents¹¹ plus any solute-solvent interactions¹³ not specifically involving the functional group. Thus, even in the absence of a hydrogen bond