Tetrahedron Vol 34, pp 747 to 752 Pergamon Press 1978 Printed in Great Britain

EFFECTS OF GEOMETRIC DISTORTIONS AND SUBSTITUENTS ON RATES OF INTERSYSTEM CROSSING; DIAZOMETHANE AND PYRAZOLINE[1]

CARL TRINDLE[2]
Chemistry Department, The Technion-Israel Institute of Technology, Haifa, Israel

and

H. ÖNDER PAMUK
Teorik Kimya Bolümü, Orta Dogu Teknik Üniversitesitesi, Ankara, Türkiye

(Received in UK 29 April 1977; Accepted for publication 4 August 1977)

Abstract—We report a qualititive perturbation-theoretic analysis of the effects of substituents on the spin-orbit coupling and on the density of states in diazomethane and pyrazoline systems. The importance of the form of the distortion which accompanies approach to the singlet–triplet crossing zone is also discussed with the aim of determining when reactions involving a spin multiplicity change can compete in rate with spin-conserving reactions.

Recently the possibility that singlet–triplet crossover may occur in the course of a reaction has been recognized, with the spin orbit coupling playing a role in the definition of the favored reaction path.[4] Known examples include the formation of triplet benzene from Dewar benzene[5] and the production of a mixture of singlet and triplet acetones from tetramethyldioxetane.[6] Such spin-forbidden processes might be competitive with spin-conserving processes to a greater extent than is now appreciated, due to the difficulty of observation of triplet species by trapping. For example, if triplet methylene is produced directly, from a singlet precursor, it may escape detection if its trapping rate is slow relative to its equilibration with the singlet and the trapping of the singlet.[7]

If the possibility of spin-multiplicity changes in the course of organic reactions is to be investigated experimentally, it would be useful to have a qualitative understanding of the influence of substituents and of geometric distortions on the intersystem crossing rate. In this report we use qualitative perturbation theory to describe such effects in two systems which show some signs of preferring a spin-forbidden reaction path, diazomethane, and methylene pyrazoline. However, we find it useful to begin with a simpler system, CH_2.

Substituent effects on spin-orbit coupling in methylene

Consider Fig. 1, which establishes a coordinate system for the species CXYZ, where we identify CXY as a (substituted) methylene fragment. The methylene has a sigma orbital on the carbon which we call σ_C, and a pi orbital π_C. The σ_C orbital is nearly a sp^2 hybrid, and can be written $(S_C + 2P_{zc})/\surd(5)$, while the pi orbital can be written $\pi_C = Pxc$. We estimate the spin orbit coupling between these orbitals as about 15 cm^{-1}.[8] The operator responsible for the mixing is $\zeta_C(LxSx + LySy + LzSz)$, where S is the spin angular momentum and (Sx, Sy, Sz) its cartesian components, L is the orbital angular momentum and (Lx, Ly, Lz) its components, and ζ_C the spin orbit coupling parameter for carbon atom. The L operator rotates p_z into p_x, with S producing compensatory rotation in spin space. If we choose a reference geometry of C_{2v} symmetry, the space factor of the spin orbit coupling operator which rotates x into z (Ly) is of species b_1. The spin factor (Sy) must be of species b_1 as well, since the spin-orbit coupling must be totally symmetric $(b_1 \times b_1 = a_1)$, being a term in the totally symmetric Hamiltonian.

Consider a CH_3 substituent to the methylene carbon. The CH_3 fragment bears $CH\sigma$ bonding orbitals; these bond orbitals mix to a very limited extent with the much less stable σ_c and π_c orbitals responsible for the spin-orbit coupling. Mixing of $CH\sigma^*$ orbitals called e_x^* and e_y^*, with the $C\sigma$ and $C\pi$ orbitals is also possible. (The notation is strictly correct only in C_{3v} symmetry, but is convenient in this discussion.)

After mixing, the new methylene orbitals appearing in the spin-orbit coupling matrix element can be written

$$C\sigma' \sim \frac{(C\sigma + \lambda e_x^*)}{(1+\lambda^2)^{1/2}}$$

$$C\pi' \sim \frac{(C\pi + \eta e_y^*)}{(1+\eta^2)^{1/2}}$$

where λ and η are small mixing parameters; the spin-orbit matrix element becomes

$$\langle C\sigma'|V|C\pi'\rangle \simeq \frac{V_{\sigma\pi} + \eta\lambda V_{\sigma^*\pi^*}}{(1+\eta^2)^{1/2}(1+\lambda^2)^{1/2}}$$

Here $V_{\sigma\pi}$ is the original spin-orbit coupling, $\simeq 15$ cm according to Bader and Generosa.[9] Expanding $V_{\sigma^*\pi^*}$ and adopting the reported value for the methylene spin orbit coupling we estimate $V_{\sigma^*\pi^*} \simeq 15$ cm^{-1} as well. The new

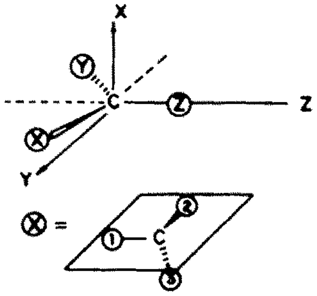

Fig. 1. The coordinates for a general system which produces the substituted methylene X – C – Y upon departure of Z are shown.

spin-orbit coupling integral may be written

$$\langle C\sigma'|V|C\pi'\rangle \simeq \bar{V}\,\frac{(1+\eta\lambda) \simeq \bar{V}\left(1+\eta\lambda-\frac{1}{2}\eta^2-\frac{1}{2}\lambda^2\right)}{[(1+\eta^2)^{1/2}(1+\lambda^2)^{1/2}]}$$

$$\simeq \bar{V}\left[1-\frac{1}{2}(\eta-\lambda)^2\right].\dagger$$

Here $\bar{V}$ is the average of $V_{\sigma\pi}$ and $V_{\sigma^*\pi^*}$. This expression tells us that if the pi mixing is comparable with the σ mixing ($\eta \simeq \lambda$), that the spin-orbit coupling is not much altered by hydrocarbon substituents. But if one type of mixing dominates—which could occur if the substituents has lowlying π^* levels, as phenyl—then the spin orbit coupling will be reduced in a way dependent on the second order of the mixing, or proportional to the charge transfer into the π acceptor substituent.

If the substituent has heavy atoms, A so that the atomic spin-orbit parameter is $V_A = V_C + \Delta$, then the spin-orbit coupling parameter is changed by $\eta\lambda\Delta$. *Both* pi and sigma mixing are required if a heavy atom substituent is to affect the spin-orbit coupling appreciably. Amino, hydroxy, and halocarbenes should have enhanced spin-orbit coupling relative to methylene.

Effects of reactive distortion on spin-orbit coupling in diazomethane

The coordinate system for diazomethane is shown in Fig. 2; C_{2v} symmetry is presumed. A correlation diagram, Fig. 3, shows that the reaction in which symmetry is not broken requires that the excited singlet $(b_1)^2$ A_1 state of CH_2 is produced, rather than the ground $a_1{}^2A_1$ singlet. This is not energetically preferred, as might be inferred from the state correlation diagram (Fig. 4). The system can evade this energy penalty by crossing to the ground singlet under the influence of a b_1 reaction coordinate which would mix the a_1 MO's of the ground state products with the b_1 MO's of the reactants, and favor mixing the excited and ground singlet A_1 states. Alternatively, the spin-orbit coupling could transform one orbital from b_1 to a_1, with an accompanying change in spin state from singlet (A_1) to the y-component of the triplet (B_1).[9]

The spin-orbit coupling induces a transition at the crossing (2) in Fig. 4, which according to more detailed computation occurs *late* in the reaction.

The *magnitude* of the spin-orbit coupling changes as N_2 departs.

At the beginning of the reaction, the orbitals which eventually participate in the spin-orbit coupling are the N lone pair, and the high lying σ^*MO. These may be written

$$b_1 \simeq \frac{PxN2-\lambda(PxN1+Pxc)}{(1+2\lambda^2)^{1/2}};$$

$$a_1 \simeq \frac{(S_c+2p_{zC})-(S_N-2p_{zN2})+\eta p_{zN1}}{(10+\eta^2)^{1/2}}$$

The spin orbit coupling early in the reaction is then

$$V_{b_1a_1} \simeq \left(\frac{1}{1+2\lambda^2}\right)^{1/2}\left(\frac{1}{10+\eta^2}\right)^{1/2}\{2V^N_{xz}-2\lambda V^C_{xz}-\lambda\eta V^N_{xz}\}.$$

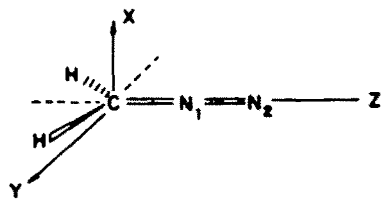

Fig. 2. The system diazomethane, in which X = Y = H and Z = N_2, is shown.

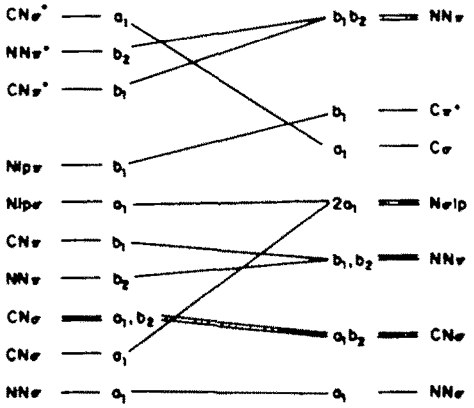

Fig. 3. The orbital correlation diagram for production of CH_2 and N_2 by C_{2v} symmetry-preserving dissociation is shown. Diazomethane at left, products at right.

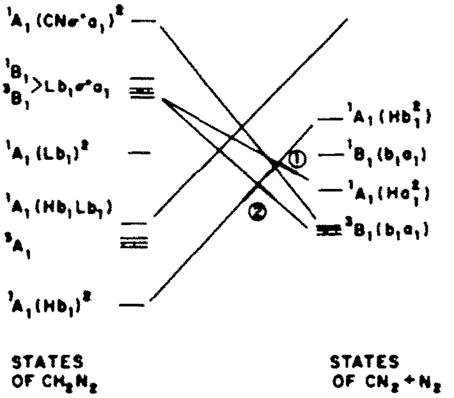

Fig. 4. The state correlation diagram associated with the orbital correlation diagram (Fig. 3) is shown. Crossing 1 is induced by a symmetry breaking b_1 nuclear motion (CNN bending). Crossing 2 is induced by the b_1 component of the spin orbit coupling.

If λ and η take on reasonable values, $V_{b_1a_1}$ will be close to zero. As the reaction proceeds, a_1 becomes identifiable with the CH_2 C_σ orbital, and b_1 becomes identifiable with the CH_2 C_π orbital. The spin orbit coupling becomes large enough (typical of free CH_2) to provide rapid intersystem crossing late in the reaction; since approximate computation places the singlet-triplet potential surface *crossing* very late in the reaction, the reactive distortion has permitted the coupling to become large just when it is required to induce intersystem crossing.

Spin orbit coupling in substituted flexible diradicals

Salem and Rowland[3] have provided a semi-quantitative description of spin-orbit coupling in diradicals. Their

---

†(If the phenyl carbene is a free-internal rotor, so that the acceptor levels interact on the average as much with C_π and C_σ the spin orbit coupling would not be reduced. If $\eta \sim \cos^2\theta$ and $\lambda \sim \sin^2\theta$, and the spin-orbit coupling is averaged over angles, the correction term vanishes.)

very useful conclusion is that orbitals must be orthogonal to each other and to the axis around which orbital angular momentum is being created in the coupling process in order to attain maximum spin-orbit coupling. To provide a basis for the discussion of substituent effects, we illustrate their conclusion with the following example.

Consider a 2-substituted trimethylene (Fig. 5); this system may undergo internal rotation, transforming a "face to face" diradical resembling cyclopropane to a "coplanar" species. In the "face-to-face" species we identify an inphase combination ϕ_+° (a_1 in C_{2v}) of hybrid orbitals, and an outphase combination ϕ_-° (b_2 in C_{2v}).

Before any rotation away from the face-to-face C_v geometry, we can write

$$a_1 = \phi_+{}^0 = (S_1 + \lambda P_{z1} + \eta P_{y1} + S_2 + \lambda P_{z2} - \eta P_{y2})/N_0(\lambda, \eta)$$

$$b_2 = \phi\ {}^0 = (S_1 + \lambda P_{z1} + \eta P_{y1} - S_2 - \lambda P_{z2} + \eta_{py})/N_0(\lambda, \eta).$$

After a rotation of 90°, $\phi_+{}^0$ and $\phi_-{}^0$ become

$$\phi_+ = (S_1 + \xi Px1 + S_2 \pm \xi Px2)/N(\xi)$$

$$\phi\ = (S_1 + \xi Px1 - S_1 \mp \xi Px2)/N(\xi).$$

At intermediate points in a synchronous rotation

$$\phi_+(\theta) = \cos\theta \cdot \phi_+{}^0 + \sin\theta \cdot \phi_+$$

$$\phi_-(\theta) = \cos\theta \cdot \phi_-{}^0 + \sin\theta \cdot \phi\ .$$

The upper sign in the expressions for ϕ_+ and ϕ_- refers to disrotation (b_1 symmetry) and the lower sign refers to conrotation (a_2 symmetry).

The spin-orbit coupling matrix element

$$\langle\phi_+(\theta)|V|\phi_-(\theta)\rangle$$

can be written

$$\frac{\xi \sin\theta \cos\theta}{N(\xi)N_0(\lambda, \eta)} \times \begin{cases} 2\lambda V_{zz}\ (\text{conrotation}) \\ 2\eta V_{xy}\ (\text{disrotation}) \end{cases}$$

We recover the sin θ cos θ dependence of the spin-orbit coupling established by Salem and Wright. Another point of interest emerges; if Ly is the orbital angular momentum operator effecting intersystem crossing (as for conrotation, above) Sy must simultaneously act in spin space. Sy can produce *only* the triplet component of symmetry b_1 by acting on the totally symmetric singlet spin state. We predict a *spin polarization*, weighting the b_1 state, and conceivably observable by spin echo experiments. The spin polarization is diagnostic of the reaction path.

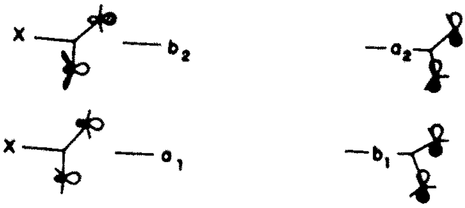

Fig. 5. The "diradical" orbitals are shown for face-to-face X-substituted trimethylene (*left*) and for coplanar X-substituted trimethylene (*right*).

Substituent effects

If X ≠ H, the spin-orbit coupling will be influenced. Let $X = CH_2$ so that the product is trimethylene methane. This system has a triplet ground state, the HOMO(s) being degenerate and half full in D_{3h}. The trimethylene methane is composed of the twisting terminal methylenes described above, and π and π^* ethylenic fragments associated with the substituent. Owing to symmetry, the π and π^* levels mix only with the symmetric $(P_{x1} + P_{x2})$ diradical combination, without affecting the antisymmetric $(P_{x1} - P_{x2})$ combination. This mixing *reduces* the spin orbit coupling between these two combinations by a factor $(1-\mu)/\sqrt{(1+\mu^2)}$, where μ is the mixing coefficient between the symmetric diradical orbital and the new π^* level.

Since the mixing reaches a maximum in the coplanar species and a minimum in the face-to-face species, $\mu \simeq \mu_0 \sin\theta$; $\theta = 0$ in the face-to-face system, $(\pi/2)$ in the coplanar system. Then

$$V \simeq V_0 \sin\theta \cos\theta \left[1 - \frac{\mu_0 \sin\theta}{(1 + \mu_0{}^2 \sin^2\theta)^{1/2}}\right].$$

Assigning μ_0 the value $\sqrt{2}$, appropriate for coplanar trimethylene methane, we find that the spin-orbit coupling reaches its maximum at $\theta \simeq 25°$, with a value $\simeq 0.186 V_0$. This is to be compared with the value of $0.5 V_0$ at 45°, the maximum for the unsubstituted systems.

Reaction path effect on position of singlet-triplet crossing

Spin-orbit coupling is a weak influence in organic systems, and can be expected to have dramatic effects only at points where singlet and triplet states are very nearly degenerate. The *positions* on the reaction coordinate of the crossing must affect the rate of intersystem crossing, since the magnitude of the spin-orbit coupling varies along the reaction coordinate. In the case of trimethylene rotation from face-to-face to coplanar structures, any agent which forces the singlet-triplet crossing to occur early in the course of the rotation, will tend to enhance the rate of intersystem crossing. Such an agent may be a further substituent, or may be the particular choice of stereochemistry in the reaction path. Consult Fig. 6, in which the states of trimethylene methane are sketched as a function of reaction path. The singlet and triplet B_2 states correlate directly as the system passes from face-to-face to coplanar structures. However, the details of the correlations of the A_1 states are different for the two possible choices—conrotation or disrotation—of reaction path.

Due to the direction of the "intended crossings" induced by the b_1 disrotation or the a_2 conrotation, the conrotation allows a singlet-triplet degeneracy earlier

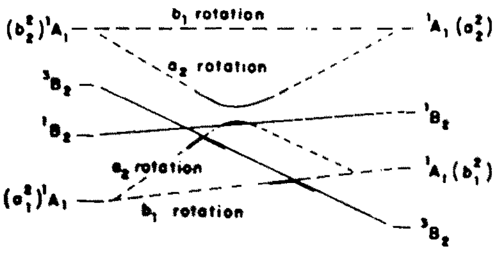

Fig. 6. The state correlation diagram for the passage from the face-to-face species to the coplanar species. The crossings marked by heavy lines are induced by spin-orbit coupling.

than the disrotation does. In conrotation the crossing seems to occur early enough that the spin-orbit coupling is reaching its peak, just at the right time to aid the singlet-triplet transition. Since this coincidence depends on the slopes of the correlation lines, it depends on the relative state energies of reactant and product. In trimethylene methane, where the triplet is stable compared with higher singlet states, we expect the spin-orbit mediated transition state to lie early, as it should to enhance intersystem crossing, compared with a latter transition state for the somewhat less stable trimethylene triplet.

A very similar analysis can be invoked to rationalize the production of triplet trimethylene methane from methylene pyrazoline by N_2 extrusion. The main difference is that the orbital which becomes the a_1 diradical orbital corresponds to a very high lying CN_{σ^*} level in the precursor, according to the correlation diagram for pyrazoline N_2 extrusion.

(a) if rotation begins before significant CN breaking, rotation in the b_1 sense is required for any orbital crossing. Early rotation is probably difficult, and the crossing occurs *late*, when spin orbit coupling is feeble.

(b) if N_2 departure is virtually complete before the onset of rotation, conrotation is required for orbital crossing, and crossing can occur early in the rotation where the coupling finds its maximum. Computation of the singlet and triplet surfaces[7] confirms that the lowest energy singlet-triplet state crossing occurs when the CN bonds are almost completely broken.

Substituent effects on state density

The RRKM rate of passage through a "critical" point depends on the density of states at the equilibrium configuration and the density of states at the "critical" configuration of nuclei.[10] In the case where passage from surface to surface is required, a transition factor $f(\zeta)$ multiplies the usual rate expression.

$$\text{Rate} = \frac{f(\zeta)Pc(E^*)}{N_{eq}(E)}.$$

Here E^* is the energy in excess of the critical energy, E is the total energy and ζ is a parameter describing the coupling between surfaces. If the classical expressions for the energy density are used, and if the Landau-Zener expression[11] for $f(\xi)$ is used in the approximate form

$$f(\xi) = \frac{\zeta^2}{(E - E_x)^{1/2}} \quad \text{(where } E_x \text{ is the energy at the crossing point)}$$

it is possible to integrate the rate expression over the energy. One obtains

$$\text{Rate (triplet production)} = \frac{\zeta^2 Q_T{\ddagger}\, e^{-E_x/RT}}{Q_{eq}}.$$

Q_{eq} and $Q_T\ddagger$ are partition functions for the ground state reactant and for the triplet state at the crossing point respectively. Here the rate of triplet production at the crossing point is taken to be identical with the rate of the entire triplet reaction. That is, we presume that there is no activation barrier to the completion of the triplet reaction, once the triplet is formed. However, the critical energy for the singlet reaction may be different—in the systems of interest here, it will be higher ($E_c > E_x$). The rate of the singlet reaction is then

$$\frac{Q_s\ddagger}{Q_{eq}} e^{\;E_c/RT}.$$

The ratio of rates of the triplet and singlet reactions is

$$\frac{K_T}{K_S} = \frac{\zeta^2 Q_T\ddagger}{Q_S\ddagger} \exp(-(E_x - E_c)/RT).$$

Depending on the magnitude of $E_x - E_c$, ζ^2 and the partition functions, this ratio may be unity or greater.

Substituents may influence this ratio by altering vibrational frequencies (and hence $Q\ddagger$) for triplet *relative* to singlet, or by changing $E_x - E_c$, besides changing ζ. The most dramatic effects occur by a change in $E_x - E_c$. If $E_x - E_c$ is positive (case 1, Fig. 8) there is a chance of overcoming the spin-conservation rule, since the triplet reaction has an energetic advantage. However, if $E_x - E_c$ is negative (case 2, Fig. 8) the chance of direct triplet production must be small. We will consider the energetic effects of substituents of donor type, bearing occupied levels of energy E_D, and then substituents of acceptor type, bearing vacant levels of energy E_A. In the following we assume that HOMO and LUMO are nondegenerate ($E_{HOMO} < E_{LUMO}$).

E_D may exceed, match, or be less than the energy of the LUMO of the parent singlet system. If $E_D > E_{LUMO}$, charge will be transferred to the LUMO; if transfer is complete the singlet will be stabilized by $2(E_D - E_{LUMO})$. There will be a further (second order) stabilization of $2\alpha^2/(E_D - E_{LUMO})$ where $\alpha = \langle\phi_D|\mu|\phi_{LUMO}\rangle$. As E_D approaches E_{LUMO} these relations become inappropriate, and the (2 × 2) secular equation must be solved. When $E_D = E_{LUMO}$ the stabilization becomes 2α. As E_D drops below E_{LUMO} only the second order stabilization $2\alpha^2/(E_{LUMO} - E_D)$ remains.

In the case of a donor interacting with a triplet, where HOMO and LUMO are both singly occupied, it becomes

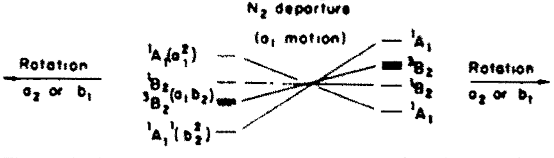

Fig. 7. Orbital and state correlation diagrams for N_2 extrusion from pyrazoline and rotation to the planar diradical. In the center of the figure, the correlation of orbitals and states in the N_2 extrusion from pyrazoline, forming the face-to-face trimethylene diradical is shown. Only the out of phase combination of CN sigma bonds (b_2) and the in phase combination of CN sigma antibonds are shown, since they correlate directly with the trimethylene diradical orbitals. At the left, the correlations established by conrotation (a_2) and disrotation (b_1) are shown for rotations early in the N_2 extrusion. At right the correlations are shown for rotation late in the N_2 extrusion. No change in state symmetry is induced by the rotations, early or late.

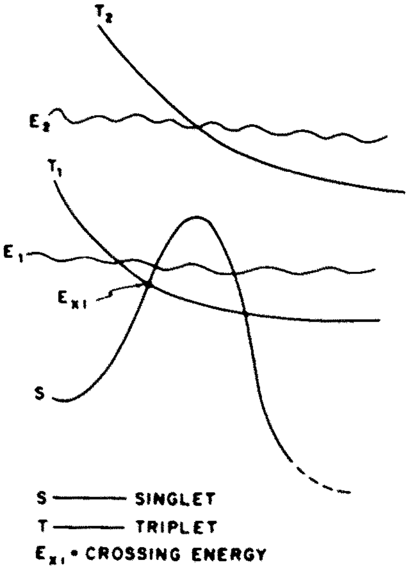

Fig. 8. If a triplet state lies sufficiently low that there is a surface intersection on the reaction coordinate, a spin forbidden event is energetically favored. If the triplet lies above the highest point on the singlet reactions coordinate, there is no energetic advantage to spin-forbidden reaction.

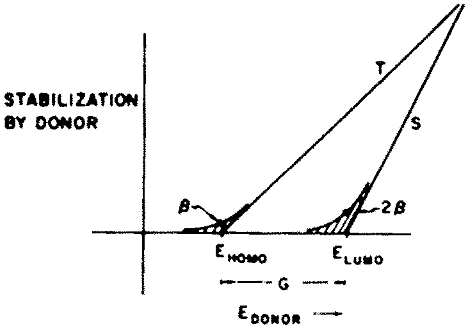

Fig. 9. A donor substituent stabilizes a triplet more than a singlet species, unless the donor level lies at least G above the energy of the Lowest Unoccupied Molecular Orbital (LUMO).

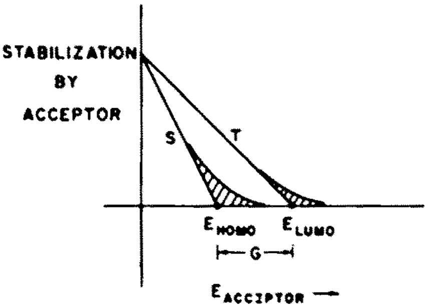

Fig. 10. Likewise, an acceptor substituent stabilizes a triplet more than a singlet, unless the acceptor level lies at least G below the Highest Occupied Molecular Orbital (HOMO).

possible to transfer one electron into the HOMO rather than the LUMO. One electron must remain in the donor level to maintain triplet spin-coupling. For $E_D > E_{LUMO}$ the stabilization is $E_D - E_{HOMO}$ (second order terms cancel). When E_D approaches E_{LUMO}, this formula is still valid, but when E_D approaches E_{HOMO} the stabilization approaches $\alpha + (\beta^2/E_{LUMO} - E_D)$ where α represents donor-HOMO interaction and β represents the donor-LUMO interaction.

We summarize these arguments in Fig. 9 in which stabilization energy due to the donor substituent is plotted against the energy of the donor level. The notable feature of this graph is that so long as the donor energy is less than $E_{LUMO} + G$, where G is the HOMO-LUMO gap, the triplet is more stabilized than the singlet. Consistent redshifts in singlet–triplet spectra of polymethyl benzenes relative to benzene support this conclusion. Therefore, *almost any donor substituent* tends to favor the triplet pathway by increasing $E_c - E_x$. The outstanding example illustrating this possibility is the production of a mix of triplet and singlet acetones from tetramethyl-1,2-dioxetane, while triplet formaldehyde is not encountered in thermolysis of the parent dioxetane.

A very similar argument, leading to a summary Fig. 10 shows that an Acceptor substituent will *also* preferentially stabilize a triplet relative to a singlet, so long as $E_A > E_{HOMO}$-G. The only exception to stabilizing influence of substituents occurs for diradicals (G → 0). By a "diradical" we mean a species in which the HOMO–LUMO gap is less than or comparable with the interaction with the substituent. We illustrate this case (Fig. 11) with a bromine-substituted trimethylene methane, in which the substituent interacts more strongly with one of the degenerate half filled levels than the other. Substituents thus tend to stabilize the singlet in this approximation. However, since we have not included any explicit recognition of electron repulsions, the triplet may still be the ground state. For example, CH_2 has a triplet ground state; methylcarbene a singlet; but diphenylcarbene has a triplet ground state.

CONCLUSIONS

We have used qualitative perturbation theory to describe the effects of substituents and choice of reaction path on the rate of intersystem crossing in two types of organic systems in which a spin forbidden reaction may be competitive in rate with spin conservative reactions.

The main conclusions follow:

(a) Aliphatic hydrocarbon substituents have little effect on spin-orbit coupling while N or O substituents can enhance spin-orbit coupling;

(b) Pi-acceptor substituents tend to reduce spin-orbit coupling;

(c) Spin-orbit coupling increases as the CN bond breaks in diazomethane;

(d) C_{2v}-symmetry preserving extrusion of N_2 from pyrazoline forces spin-orbit coupling to be near zero; conrotation and disrotation of the trimethylene fragment permits a substantial spin-orbit coupling, allowing the production of the triplet $m_s = \pm 1$ and $m_s = 0$ states respectively;

(e) The spin-orbit coupling behaves as $V \cos\theta \sin\theta$, where θ ranges from 0 to $\pi/2$ and describes the con- or disrotation.

In these systems there is no obvious increase in state density ρ(E) due to preferential lowering of vibrational frequencies due to substituents. Substituents can enhance both singlet and triplet state densities by their stabilizing effect. In the one-electron approximation triplets are generally preferentially stabilized by sub-

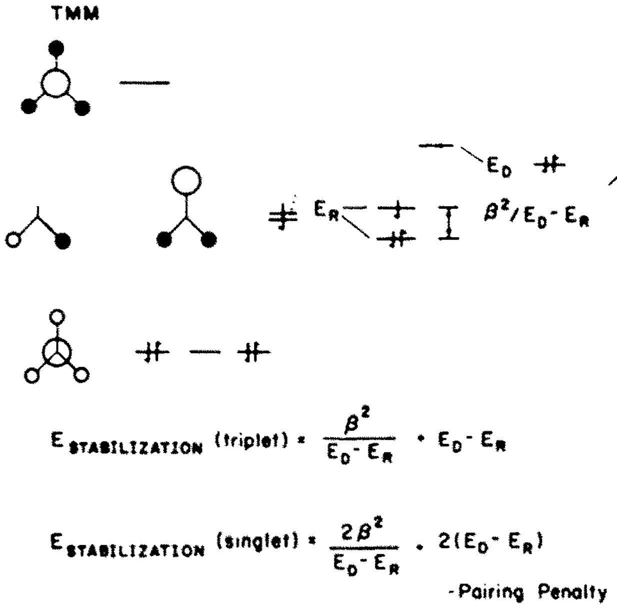

Fig. 11(a). A more detailed description of the effects of substitution on a diradical. Bromo-trimethylene methane enjoys a greater substituent stabilization for the singlet than the triplet.

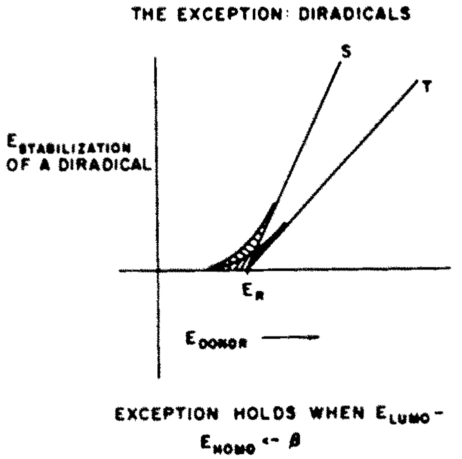

Fig. 11(b). The diradical limit $G \to 0$ of Fig. 9. A similar limiting figure could be drawn for the acceptor substituent, as $G \to 0$ in Fig. 10.

stituents, except in the diradical limit. Therefore, substituents can enhance the intersystem crossing rate either by their influence on the density of states, or by their influence on the spin-orbit coupling.

Acknowledgement—CT takes pleasure in acknowledgement of helpful discussion with Prof. E. A. Halevi of the Chemistry Department at the Technion, Haifa, Israel.

REFERENCES

[1] Partially supported by NATO (Grant No. 1186) and by the University of Virginia Sesquicentennial Foundation.

[2] Permanent address: Chemistry Department, University of Virginia.

[3] L. Salem and C. Rowland, *Angew. Chem. Intern.* Ed. 11, 92 (1972).

[4] E. A. Halevi, R. Pauncz, I. Schek and H. Weinstein, *Jerusalem Symposia on Quantum Chemistry and Biochemistry* (Edited by E. D. Bergmann and B. Pullman) Vol. 6, pp. 167–182. The Israel Academy of Sciences and Humanities (1974). Also *Rates of Spin-Forbidden Organic Reactions* I, II, III—preprints available from C.T.

[5] P. Lechtken, R. Breslow, A. H. Schmidt and N. J. Turro, *J. Am. Chem. Soc.* 95, 3025 (1973).

[6] N. J. Turro and P. Lechtken, *Ibid.* 95, 264 (1973).

[7] C. D. Duncan and C. Trindle, *Tetrahedron Letters* 26, 2251 (1977).

[8] R. F. Bader and J. I. Gererosa, *Can. J. Chem.* 43, 1631 (1965).

[9] E. A. Halevi and C. Trindle, *Israel J. Chem.* in press.

[10] W. Forst, *Theory of Unimolecular Reactions*. Academic Press, New York (1973).

[11] C. Zener, *Proc. Roy. Soc.* A137, 696 (1932).

[12] *Spin States in Carbene Chemistry*, P. P. Gaspar and G. Hammond *Carbenes*, (Edited by R. A. Moss and M. Jones, Jr.), Vol. VI. p. 207. Wiley-Interscience, New York (1975).