

privately labeled cycloheptatriene it may be possible to observe hydrogen scrambling without carbon scrambling.

(d) Loss of a hydrogen atom to give a $C_7H_7^+$ (m/e 91) moiety is more likely through **6** rather than **5**.

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Theoretical Studies of the Photochemistry of Acyclic Azoalkanes

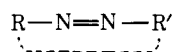
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Abstract. Nonempirical molecular orbital calculations have been carried out on the S_0 (ground), S_1 , T_1 , and T_2 states of azomethane and on selected states of diimide and azoethane. Potential energy surfaces for several possible isomerization pathways from trans to cis isomers have been obtained. Motions in which one alkyl group rotates about the $N=N$ bond or moves in the $N=N-R$ plane through a linear configuration appear to be of considerable importance, while the motion which simultaneously linearizes both $N=N-R$ groups is forbidden by a substantial energy barrier. Spectral and thermodynamic quantities calculated are in good agreement with the experimental data where available. The shapes of the energy surfaces provide explanations for such phenomena as the lack of observed fluorescence and phosphorescence in acyclic azoalkanes and the variation in the quantum yields of isomerization and dissociation with pressure and with the method of excitation.

I. Introduction and Background

In recent years there have been extensive experimental studies of the thermal and photochemical behavior of azoalkanes,²⁻⁵ which have the general formula



The dashed line in the formula indicates that the compound may be cyclic. While there have been several detailed theoretical investigations⁶⁻⁹ of the prototype molecule diimide ($R = R' = H$), calculations on the larger and more stable azo compounds have been almost nonexistent.¹⁰ The chemistry of diimide is significantly different from that of azoalkanes,¹¹ so calculations on a molecule like azomethane ($R = R' = CH_3$) should provide a sounder model for understanding the properties of azo compounds of moderate complexity. In this paper we report on a series of such calculations which have been undertaken in an attempt to elucidate several aspects of the thermal and photochemical behavior of acyclic azoalkanes. We focus here primarily upon the static properties (geometry, spectra, etc.) and upon the mechanism of cis-trans isomer-

ization. The interesting and important problem of decomposition into molecular nitrogen and radical products is mentioned only briefly, but will be discussed more fully in a later paper.

The computational technique employed in this work is the partial retention of diatomic differential overlap (PRDDO) method of Halgren and Lipscomb.¹² This self-consistent nonempirical technique affords accuracy comparable to that of more elaborate minimal basis set self-consistent-field (SCF) approaches, but with computation times only slightly longer than those of much less accurate semiempirical methods. Details of the calculation are discussed briefly in the next section, and the results are presented and analyzed in section III.

Before proceeding with the main results of this work, it will be useful to summarize some of the more important features of the properties and the photochemistry of acyclic azoalkanes which we shall seek to explain in subsequent sections.

(i) At low pressures in the gas phase, $n \rightarrow \pi^*$ excitation of acyclic azoalkanes results in photodissociation to N_2 and alkyl radicals with quantum yields approaching unity.¹³

(ii) As the pressure is increased, either by increasing the concentration of the azo compound or by adding "inert" gas, decomposition decreases and photoisomerization becomes a major channel.¹⁴ Not surprisingly, therefore, direct photolysis in solution generally results in extensive isomerization. For example, for azoisopropane $\Phi_{t \rightarrow c} \sim \Phi_{t \rightarrow t} \sim \Phi_{c \rightarrow t} \sim \Phi_{c \rightarrow c} \sim 0.5$.¹⁵ This photoisomerization proceeds even at liquid nitrogen temperature. In fact, low-temperature photoisomerization was the first method used for preparing a cis azoalkane.¹⁶ However, if the alkyl groups are sufficiently bulky (\geq *tert*-butyl), the cis compound, which is generally the higher energy isomer, becomes sufficiently unstable that it may decompose rapidly at room temperature.¹⁷ In these cases, photolysis, even in solution, may indirectly result in extensive decomposition.⁴

(iii) The results of triplet sensitization are somewhat ambiguous. It is clear, however, that in a number of cases direct excitation and triplet sensitization do not initiate the same photochemistry.⁴ For example, in the case of $R = \text{EtOCCMe}_2$, the quantum yield of N_2 formation for direct photolysis in solution is 0.42 and only 0.06 for triplet sensitization. For both *trans*-azomethane and *trans*-azoisopropane, triplet sensitized isomerization yields are ~ 0.1 while for direct photolysis the yields are close to 0.5.¹⁵

(iv) In contrast to their cyclic counterparts, acyclic azoalkanes show no evidence of vibronic fine structure in the $S_0 \rightarrow S_1$ band.⁴⁻⁶ A weak fine structure is, however, discernible for $S_0 \rightarrow S_2$ in the case of azomethane. Cyclic azoalkanes fluoresce, while the acyclic compounds do not.^{5,18,19} Finally, no phosphorescence has ever been observed from any azoalkane, cyclic or acyclic.

II. Method of Calculation

The calculations were performed using the parametrized PRDDO program written by Halgren¹² augmented by Kleier and Halgren to treat open shells by the orthogonality constrained basis set expansion (OCBSE) method of Goddard and co-workers.²⁰ Exponents for the minimal basis set of Slater-type atomic orbitals were chosen by Slater's rules. Geometry optimizations employed a standard quadratic minimization procedure.

Results reported thus far with PRDDO have been in excellent agreement with experimental data and/or results of more elaborate calculations. PRDDO potential surfaces for diatomic molecules closely parallel the corresponding SCF curves;¹² the barrier to internal rotation in ethane is given to within 1 kcal/mol of experiment;¹² a new stable intermediate has been found on the energy surface of $\text{C}_2\text{B}_4\text{H}_6$,²¹ helping to explain some of the rearrangement reactions of this species; even electronic momentum distributions calculated by PRDDO differ very little from those obtained by the more costly SCF approach.²² Computing times with the PRDDO program are about 100 times shorter than those required for an SCF calculation, and about 4-6 times longer than for the semiempirical CNDO or INDO methods. The key feature of the PRDDO approach which makes possible these savings in time, and hence the application of the method to potential surfaces of complex molecules, is the "telescoping" of the information content of approximately N^4 two-electron integrals over atomic orbitals into roughly N^3 transformed integrals over orthogonalized orbitals oriented with respect to local principal axes.

While the successes of PRDDO noted above have been achieved on closed shell systems, preliminary applications to organic radicals have been equally encouraging.²³ Use of the OCBSE approach to the open-shell problem and explicit (though in some cases approximate) calculation of the two-electron integrals should guarantee that the results obtained for excited states will be a significant improvement over calculations which approximate singlet-triplet splittings by a

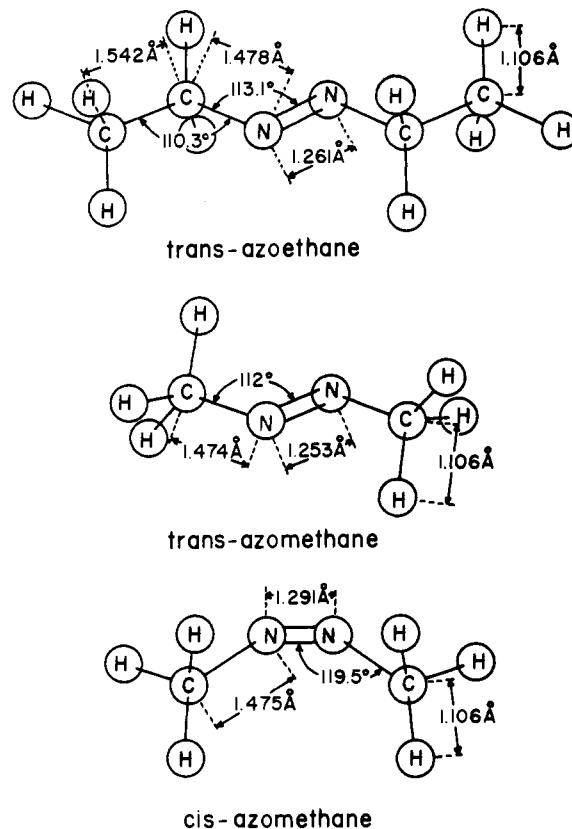


Figure 1. Optimized structures for ground-state azoalkanes.

single term and/or which yield mixtures of multiplets instead of pure states.

In summary, we feel that our calculations should give relative energies with an error on the order of hundredths of an atomic unit ($1 \text{ au} \approx 625 \text{ kcal/mol}$) with respect to the corresponding SCF energies. The major source of error in this work is anticipated to be not the approximations of the PRDDO scheme, but the use of a single-determinant wavefunction constructed from a minimal basis set of atomic orbitals. While these errors may in some cases be quite large, Winter and Pitzer⁸ argue in their study of diimide that compensating effects may make such SCF (and by extension, PRDDO) properties as vertical excitation energies good approximations to the values calculated by a full configuration interaction treatment.

III. Results and Discussion

A. Optimization of Structures. Starting geometries for the optimizations were taken from the results of an electron diffraction study of *trans*-azomethane.²⁴ Selected bond angles and bond lengths were then varied sequentially until minima were obtained for all of the parameters considered. The C_{2h} and C_{2v} symmetries of the *trans* and *cis* isomers, respectively, were maintained throughout these variations. The parameters varied were, in order, the $\text{N}=\text{N}$ bond length, the two $\text{C}-\text{N}$ bond lengths, and the two CNN bond angles. A small additional energy stabilization was also afforded by rotating the methyl groups. No attempt was made to vary either the HCH or the NCH angles from tetrahedral; the $\text{C}-\text{H}$ bond lengths were held fixed at 1.10 \AA . The *trans* configuration of azoethane was optimized in similar fashion, the major difference being the additional optimization of the $\text{C}-\text{C}$ bond lengths. The structures thus obtained are shown in Figure 1. The optimized bond angles agree nicely with those obtained by Baird and Swenson,⁷ while the *trans*-azomethane structure agrees excellently with that obtained by Bauer et al.²⁴

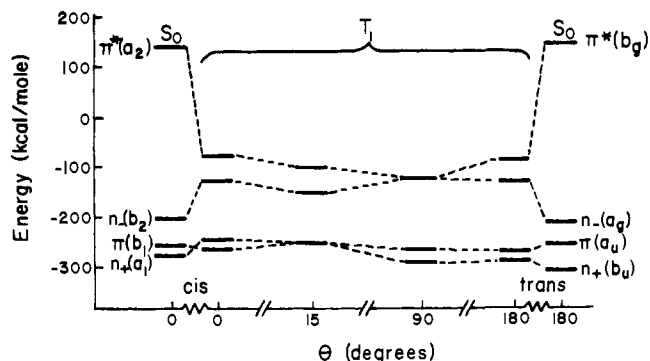
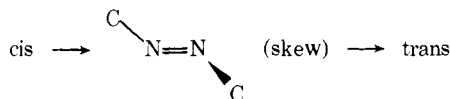


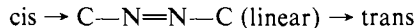
Figure 2. Molecular orbital energies for some of the azomethane structures and states given in Figure 3. State designations (S_0 and T_1) refer to the states for which the orbital energies were calculated.

In addition to the ground state cis and trans forms, geometries corresponding to some intermediate points on the potential surfaces described in the next section were also optimized. Those structures resulting from twisting were treated as above. For the linearized geometries, only bond lengths were varied. The semilinearization motion required that the two C-N bond lengths be optimized separately and that only the "bent" CNN angle be varied.

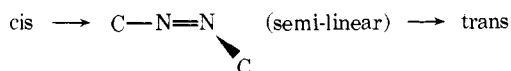
B. Isomerization and Decomposition. Three possible isomerization pathways were considered: (i) Twisting (rotation) about the N=N bond,



(ii) Linearization,



(iii) Semilinearization (inversion)



For each motion, we calculated wave functions and energies at a series of points along the path from cis to trans for each of the states S_0 (ground), S_1 , and T_1 . For the twisting motion, we also studied the behavior of the T_2 state. The orbital energies obtained for the cis and trans ground state species were found to be in the expected order, i.e., $n_+ < \pi < n_- < \pi^*$. In Figure 2, we show the energies of these four molecular orbitals for some of the structures given in Figure 3. The general ordering of orbitals and behavior on geometry variation parallel the qualitative predictions of Baird and Swenson⁷ and of Howell and Kirschenbaum¹⁰ for the azo grouping. Our results and theirs disagree with the ordering of the n_+ and π levels obtained by Kearns,²⁵ but as can be seen from Figure 2, the energy separation of these levels is quite small.

However, several additional points should be noted. On excitation, significant changes occur in the orbital energies. These variations are sufficient in some cases to invert the ordering of two orbital energies *even in the absence of geometry variation*. This suggests that the use of a ground-state orbital correlation diagram to discuss excited state behavior may be unreliable, at least in the case of azo photochemistry. The n and π orbitals are not localized on the nitrogen, but have significant components from atomic orbitals centered on the carbons and the hydrogens. For example, the doubly occupied π orbital of the trans ground state has a population of only 1.54 electrons on the nitrogen atoms, with 0.18 and 0.28 electron being found on the carbon and hydrogen atoms, respectively. The total energy of a state in the molecular orbital formalism is ex-

pressible as the sum of the orbital energies of the occupied MO's plus a linear combination of coulomb and exchange integrals, the precise form of which depends upon the nature of the state. As noted above, the various molecular motions result in significant changes in the orbital energies. However, the concomitant changes in the two-electron integrals are such that the variation in the total energy shows little or no correlation with either the sum of the orbital energies or the energies of individual orbitals or of small sets of MO's.

For the above reasons, our discussion of isomerization pathways will be given in terms of the total energy, which is a true observable, rather than in terms of orbital correlation diagrams such as Figure 2. Figures 3, 4, and 5 show the energetics for the twisting, linearization, and semilinearization motions respectively. We now summarize the major conclusions drawn about each of the states studied.

(i) **First Excited Singlet.** It will be seen that the S_1 state is quite "floppy" in that there is no barrier to rotation, a result also obtained by Baird and Swenson⁷ for diimide, and only a very small barrier to semilinearization. Thus the conclusion⁴ that the cis and trans isomers of simple azoalkanes share a common S_1 state seems to be substantiated. Twisting from either side results in a skew configuration having essentially the same energy as the twisted ground state. The shallow minimum means that vibrational levels corresponding to this motion will be closely spaced. The close approach of the S_0 and S_1 surfaces in both the twist and the semilinearization modes suggests that either motion may result in very rapid internal conversion, $S_0 \rightsquigarrow S_1$, without the intermediacy of the triplet. In contrast, in the case of diimide the calculations indicate that the S_0 and S_1 surfaces never approach more closely than about 30 kcal/mol.⁷ Rapid internal conversion, since it implies a very short singlet lifetime, is also consistent with the absence of fluorescence from acyclic azoalkanes and may contribute to the lack of fine structure in the $S_0 \rightarrow S_1$ bands. This conclusion is in contrast to earlier suggestions^{4,5} that the failure to observe fluorescence and fine structure originated from a rapid intersystem crossing ($S_1 \rightsquigarrow T_x$). The latter seems to be in error because direct excitation and triplet sensitization of simple azoalkanes can result in significantly different photochemistries.

It has been suggested by a referee that the near-crossing of the S_0 and S_1 surfaces on twisting may be an artifact of our calculation, in which no configuration interaction (CI) is included. Since the HOMO and LUMO are nearly degenerate in the skew conformation, one would expect a considerable lowering of the energy of the skew S_0 state from a 2×2 CI between the HOMO² LUMO⁰ and the HOMO⁰ LUMO² configurations. While we are not able to completely rule out the possibility that this crossing may be an artifact, comparison of our results for diimide and azomethane strongly suggests that the S_0 and S_1 surfaces approach considerably more closely on twisting in the latter molecule. Without CI, our $S_0 - S_1$ energy difference in the skew conformation of diimide is 24 kcal/mol. The corresponding value in azomethane is only 2 kcal/mol. We carried out the 2×2 CI calculations suggested above for both molecules, and as expected, the effect was to lower the S_0 energies of both molecules by a significant amount (about 35 kcal/mol). However, the magnitude of this effect was *the same* for both molecules. Thus, unless CI has a much larger effect on the S_1 state of diimide than of the S_1 state of azomethane, we would still expect the S_0 and S_1 surfaces to lie ~ 20 kcal/mol closer in the skew state of the azoalkane.

Of course the energy surfaces of acyclic azoalkanes are such that any fluorescence that did occur would be grossly red shifted from the absorption spectrum. In contrast, cyclic azoalkanes, which cannot rotate, have significant fluorescence yields, and in these cases the O-O' bands in emission and absorption correspond closely.^{18,19}

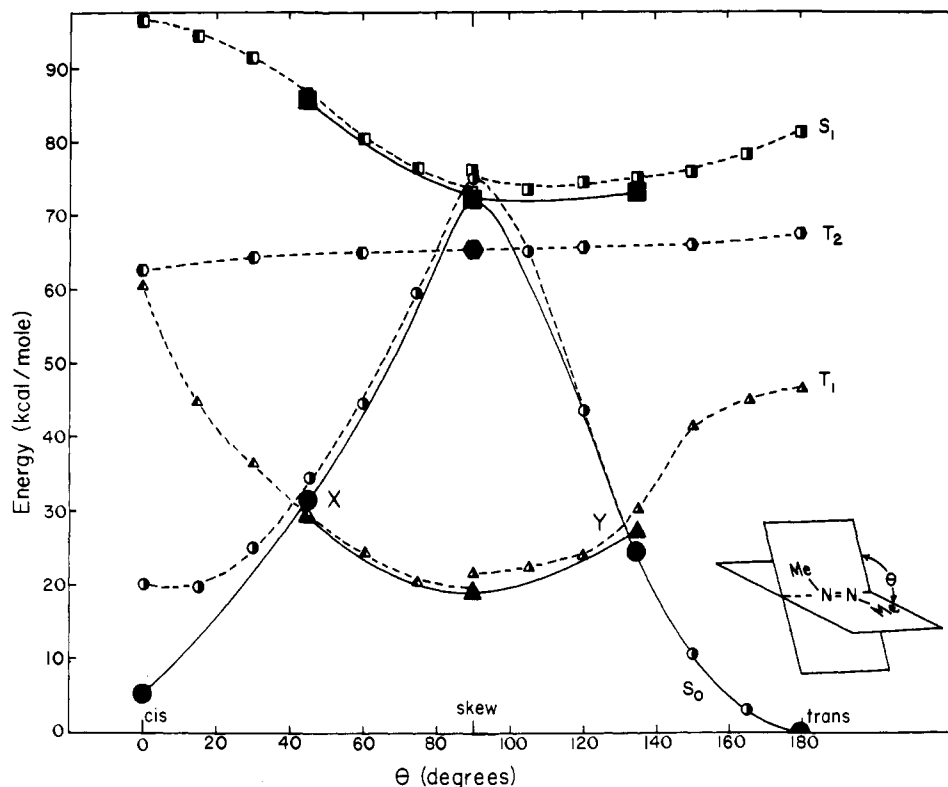


Figure 3. Potential surfaces for isomerization of azomethane by twisting: (●, ▲, ○, ■) fully optimized structures in S_0 , T_1 , T_2 , and S_1 states, respectively; (○, ▲, ○, ■) structures derived from optimized ground-state *cis*-azomethane by simply varying θ , other geometric parameters held constant; (●, ▲, ○, ■) corresponding structures obtained from ground state *trans* by varying only θ .

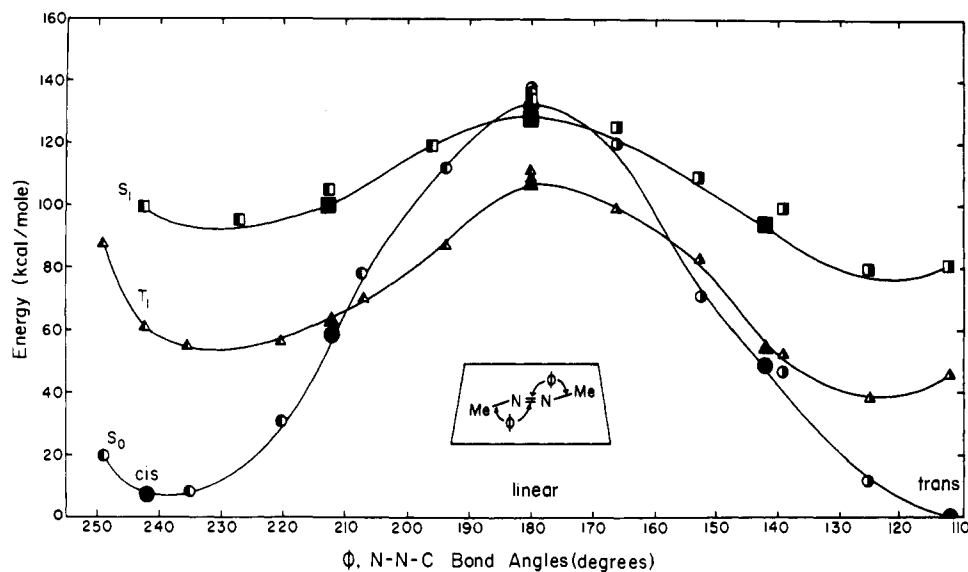


Figure 4. Potential surfaces for isomerization of azomethane by simultaneously varying both NNC angles (linearization). Legend for points is the same as for Figure 3.

In a recent experimental paper on the gas-phase dissociation of *trans*- and *cis*-azoisopropane,¹⁵ it was suggested that the dissociation observed at low pressures occurs from the vibrationally excited ground-state *cis* and *trans* molecules, which are formed in roughly equal yields by the photolysis of either isomer. A rapid internal conversion in the isolated molecule region appears to be a likely route for the formation of these vibrationally excited species. Collisional deactivation to stable *cis* and *trans* S_0 molecules results in decreased dissociation and increased isomerization. Figure 4 shows that compared to rotation and semilinearization, linearization is an energetically unfavorable motion, so that at least for $n \rightarrow \pi^*$ photochemistry it can be neglected.

(ii) **Ground State.** Linearization is also unfavorable in the ground state, where semilinearization should be the favored pathway for isomerization. This result is in agreement with theoretical studies of the diimide isomerization.⁷⁻¹⁰ The barrier to thermal isomerization of *cis* azomethane is calculated to be 51 kcal/mol, in good agreement with values of 53⁷ and 55¹⁰ kcal/mol obtained in other minimal basis set SCF calculations. The ground state rotational barrier, starting from the *cis* side, in our case is 70 kcal/mol, again in agreement with Baird and Swenson's⁷ value of 73 kcal/mol. Ground state isomerization has not been reported for azomethane but has been observed in the case of *cis*-azoisopropane.²⁶

(iii) **Triplet States.** Because of the favorable internal con-

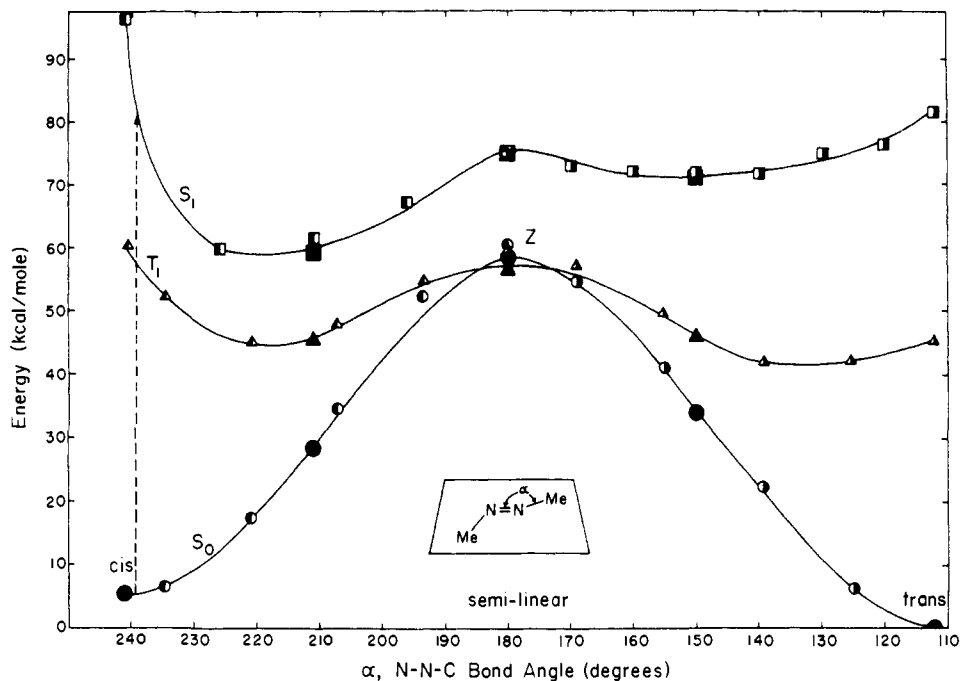


Figure 5. Potential surfaces for isomerization of azomethane by varying only one NNC angle (semilinearization). Legend for points is the same as for Figure 3.

version $S_1 \rightsquigarrow S_0$, intersystem crossing $S_1 \rightsquigarrow T_x$ may be less effective than is commonly realized, although the intrinsic rate of intersystem crossing might be quite rapid. Also, since the S_0 , T_2 , and S_1 states all have such similar energies in the skew geometry in azomethane, we may expect the relative importances of the various processes to vary significantly among the azoalkanes as different groups (R, R') affect the shapes and relative positions of the potential surfaces.

If the T_1 surface is populated, for example, by triplet transfer, then isomerization should be a major chemical channel at room temperature, as is observed. However, the yields may be quite different from those obtained by direct photolysis and for different azoalkanes, since the actual yields of isomerization may depend crucially upon the relative locations of the crossings at X and Y in Figure 3, and the touching at Z in Figure 5. The surfaces also imply that there should be a small barrier to getting out of the skew T_1 state and onto the ground state surface, so that at low temperature the triplet may have sufficient stability that its population may be built up for observation. Further discussion of the T_2 state will be found in the next section.

C. Spectroscopic Correlations. From Figures 3–5 the vertical singlet energy, $E_{S_1^v}(n \rightarrow \pi^*)$, for *trans*-azomethane is 81.3 kcal/mol. Experimentally the $n \rightarrow \pi^*$ absorption maximum occurs at 338 nm which corresponds to 84.6 kcal/mol.²⁷ The diagrams also indicate that the adiabatic transition energy, $E_{S_1^a}$, should be about 71 kcal/mol. This corresponds to a wavelength of 403 nm, while experimentally the onset of the $n \rightarrow \pi^*$ band occurs at about 410 nm. To see if we could expect the same quality of fit with other azoalkanes, a limited series of calculations was also performed on the next higher azo compound, azoethane.

For *trans*-azoethane $E_{S_1^v} = 76.8$ kcal/mol while the observed absorption maximum is at 356 nm (80.3 kcal/mol).²⁷ Thus the calculated red shift of 4.5 kcal/mol from azomethane agrees almost perfectly with the observed value of 4.3 kcal/mol.

Turning next to the triplet manifold, $E_{T_2^v}(\pi \rightarrow \pi^*) = 67.5$ kcal/mol and $E_{T_1^v}(n \rightarrow \pi^*) = 45.5$ kcal/mol. In a recent electron impact study of azomethane, Mosher et al.²⁸ obtained a transition at 63.4 kcal/mol which they associated with

$E_{T_1^v}(n \rightarrow \pi^*)$. Our calculations indicate that this might in fact be the second transition, the first one being missed either because it is weak or because they only scanned down to 2 eV (=46 kcal/mol). The diimide calculations also locate a ${}^3n, \pi^*$ state between ${}^1n, \pi^*$ and ${}^3n, \pi^*$.⁷

In the case of the *cis* spectrum we are confronted with a problem. Figure 5 shows that taken from the *cis* minimum, $E_{S_1^v} = 90.6$ kcal/mol while in all known cases the *cis*-azoalkane $n \rightarrow \pi^*$ maxima are red shifted from the maxima for the corresponding *trans* spectra. For example, for azoisopropane in the gas phase $\lambda_{\max}(\text{trans}) = 355$ nm and $\lambda_{\max}(\text{cis}) = 380$ nm.¹⁵ Similar shifts have been observed for azomethane and azoisobutane. However, if we examine Figure 5 we see that the energy of S_1 drops very rapidly as the *cis* molecule is semilinearized. In the figure we have shown by means of a vertical line the transition which would give an absorption appropriately red shifted (~ 5 kcal/mol) from the *trans* transition, and it can be seen that the nuclear displacement from the "equilibrium" ground state geometry is quite small. In general whenever an upper state has a sharply varying potential in the region of the (flat) minimum on the ground state surface, evaluation of the vertical transition energy becomes extremely uncertain.

It will also be noted that our calculations predict that ground state *cis*-azomethane should be about 5 kcal less stable than *trans*-azomethane. Although the thermodynamic data do not exist for this pair, it has been found experimentally that *cis*-azoisopropane is about 8 kcal/mol less stable than *trans*-azoisopropane.²⁹ Finally, mention should be made of our estimates of vertical ionization potentials. For *trans*-azomethane our Koopmans' theorem values for $I^v(n_-)$, $I^v(\pi)$, and $I^v(n_+)$ are 8.81, 11.04, and 13.07 eV. The experimental values are 8.98, 11.84, and 12.3 eV.³⁰ In the case of *trans*-azoethane our calculated ionization potentials are 8.43, 11.22, and 11.81 eV, the experimental values being 8.77, 11.43, and 11.79 eV.³⁰

D. Comparisons with Other Calculations. As indicated earlier, other authors^{7,10} have carried out calculations for a limited number of geometries of ground-state azomethane, but no calculations on excited states were reported. In order to provide a more stringent test of the applicability of the PRDDO method to the present problem, we therefore under-

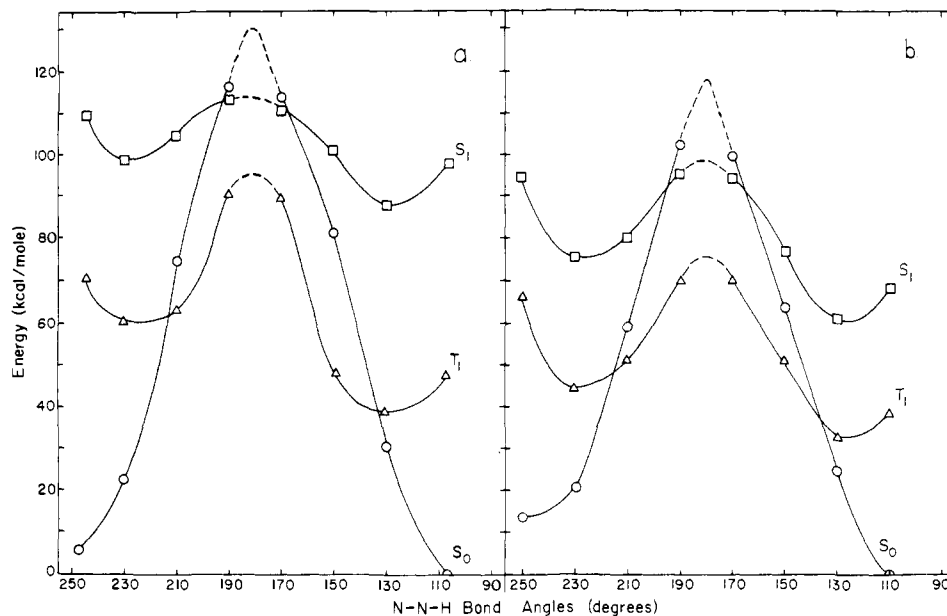


Figure 6. Calculated total energy surfaces for the linearization of diimide: (a) this work; (b) ab initio calculation of PB.⁹ For (a) all geometries except those resulting from vertical excitation of cis and trans were fully optimized.

took a series of calculations of the energies of various states and configurations of diimide, for which numerous elaborate calculations appear in the literature. The states chosen were the S_0 , S_1 , and T_1 , as these are not only the most important in the azomethane photochemistry discussed earlier but they are also the states most likely to be well described by this type of calculation.

Ground state cis and trans geometries were optimized and vertical excitation energies were calculated for the $n \rightarrow \pi^*$ singlets and triplets of both isomers. In addition we calculated energies and wave functions for structures resulting from the linearization motion using an optimization procedure similar to that described earlier for azomethane. The results of our calculations on diimide are shown in Figure 6a. The corresponding results obtained by Peyerimhoff, Buenker, et al. (PB)⁹ from their extended basis set plus configuration interaction calculations appear in Figure 6b. The similarity in the shapes of the curves is obvious, lending support to our assertion that PRDDO should adequately predict the qualitative features and general trends in the total energy surfaces of the azoalkanes.

There are several specific features common to both sets of calculated curves. The optimized ground state geometries of both the cis and trans configurations are nearly identical in the two calculations. Also in both calculations the excited states show pronounced local minima in the same positions. The excited singlet state bond angles predicted by the calculations ($\sim 130^\circ$) agree with the spectral results of Back, Willis, and Ramsay ($132 \pm 2^\circ$).³¹

We should point out that the relative energies obtained in the two calculations differ significantly. For example, our vertical singlet energy for trans diimide is 97.3 kcal/mol. Baird and Swenson⁷ report ~ 87 kcal/mol while the PB value is 68.4 kcal/mol. The latter value is supported by spectroscopic measurements. However, the excellent agreement of our calculations for both azomethane and azoethane with the available spectroscopic data suggests that diimide may be an anomalously poor case for PRDDO calculations and that results on larger azoalkanes may be more reliable.

IV. Summary and Conclusion

This paper describes an attempt to explain some aspects of acyclic azoalkane photochemistry by the use of approximate

molecular orbital theory. It has, through the investigation of three total energy surfaces of azomethane, established plausible reasons for the following observed effects:

(a) The lack of vibrational fine structure in the $S_0 \rightarrow S_1$ band was attributed to the shallow nature of the S_1 potential surface and rapid internal conversion onto the nearby S_0 surface. (b) The absence of fluorescence is also explained by the shapes of the S_0 and S_1 surfaces and by their close approach. (c) The lowest triplet is most stable in the skew geometry. This gross distortion from the ground state equilibrium configuration with the resultant absence of Franck-Condon transitions explains the lack of phosphorescence. (d) The fact that S_1 is essentially common to both isomers means that the direct photochemistry of both cis and trans azoalkanes should be similar. (e) Since $S_1 \leftrightarrow T_x$ may not occur efficiently, triplet sensitized and direct photolysis need not be similar. Also, in the case of sensitized photochemistry the relative importance of the various channels may be sensitive to the nature of the R groups as the latter can affect the locations of the crossings of the triplet surfaces with the ground-state surface.

The excellent agreement obtained with spectral data available for azomethane and azoethane establishes the PRDDO method as useful for the study of azoalkanes. Utilization of extended basis sets and configuration interaction, as they become economically feasible, should make it possible to extend the qualitative insights derived here into more quantitatively reliable ones.

Future considerations will include the photochemical behavior of cyclic as well as of higher acyclic azoalkanes. The use of a generalized valence bond technique will also permit the examination of the photodecomposition and thermal decomposition of this fascinating class of compounds.

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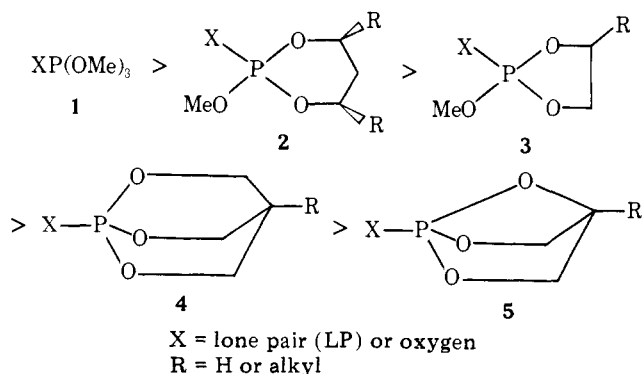
Structure-Basicity Relations among Phosphate and Phosphite Esters. CNDO/2 and Protonation Studies

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Abstract: Protonation in HFSO₃ at -50 °C of the phosphite triesters **1**¹¹¹-**5**¹¹¹ revealed a steady increase in ¹J_{PH} (826-928 Hz) upon increased constraint of the alkoxy groups. CNDO/2 calculations showed a concomitant rise in the positive charge on phosphorus and the phosphorus-bound hydrogen in the protonated species, but no trend was observed in the P hybridization. A plot of the cube of the sum of these charges vs. ¹J_{PH} (correlation coefficient 0.92) suggests that the charge contribution is probably dominant in the Fermi contact term. These results are consistent with stereochemically dependent orbital effects proposed earlier. A similar rise in the calculated negative charges at the ring oxygens of the phosphate analogues **1**^V-**4**^V along with smaller differences in the protonation energies of the phosphoryl oxygen on constraint parallels the decreased hydrogen bonding tendency of the phosphoryl oxygen as shown by phenol shift experiments. A minor reversal in basicity of the first two members of the phosphite series is indicated by the BH stretching frequency trend of the BH₃ adducts **1**^A-**5**^A and is rationalized in terms of the greater polarizing power of the proton than BH₃.

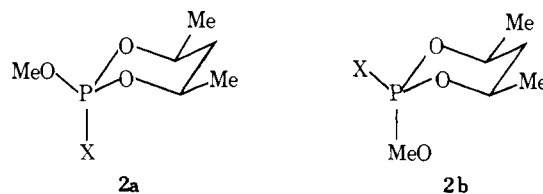
Substantial spectroscopic and chemical evidence has been put forth within the last 2 years which suggests a decreasing trend in the basicity of the phosphorus and the phosphoryl oxygen upon molecular constraint in phosphite and phosphate triesters, respectively,² **1** > **2** > **3** > **4** > **5**. The rationale which has been given for this progression entails a consideration of



changing orbital orientations^{2,3} (particularly those of the ester oxygen p lone pairs with respect to X) which can give rise to

orbital repulsions.^{3a} In addition, a "hinge effect" resulting from ester oxygen hybridization changes induced by increased strain in the rings has been invoked.^{2,3b}

It has also been noted that the conformation which obtains for the second member of the above series is chair, with the X moiety in the equatorial position.^{2b,3} If this system is forced by ring substitution to direct the X group axial, spectroscopic studies reveal that the order of basicities is **2a** > **2b** toward



Mo(CO)₄ where X = LP and toward a proton where X = O.^{2b,3}

The threefold purpose of the present investigation was to ascertain if calculations of the atomic charges of pertinent atoms in these systems would reflect the above basicity orders, to protonate the phosphorus of the phosphite esters in a strong acid medium to ascertain if the calculational parameters of the