NASA NGR-05-061-004

PROGRESS REPORT

GEOMETRICAL INFLUENCES ON NON-RADIATIVE PROCESSES IN ORGANIC MOLECULES

by

Earl M. Evleth

July, 1969

Prepared under Grant NGR-05-061-004

Division of Natural Sciences
University of California
Santa Cruz, California
95060

INTRODUCTION

The following report details the accomplishments of the first year of the grant. The specific research objectives of the first year of this grant as stated in the original proposal were i) Calculation of the Effect of Substitution on Polyene Spectra, ii) Calculation of the Effect of Non-Planarity on the Energies of the Ground and Excited States of Polyenes and Substituted Polyenes, and iii) Calculation of the Resonance Energies of Polyene Radicals. Of these three objectives item ii) has been the most throughly investigated and part of the results have now been published in the open literature.[1] On further review it was concluded that item i) has been accomplished largely by previous workers. Finally, item iii) is presently under study and has been enlarged to entail the investigation of the resonance energies and spin properties of a number of heterocyclic radicals. Both computational and experimental work will be carried on by a postdoctoral researcher starting in September of 1969. A graduate student is presently studying item ii). The work accomplished in the first year of the grant has, however, been expanded beyond the areas originally planned. Thus the following report is divided into three sections. These are: A) Calculation of the Ground and Excited State Energies of Planar and Distorted Configurations of Organic Molecules, B) Quantum Mechanically Based Rules for Thermal and Photochemical Reactions, and C) Photophysical and Photochemical Studies in Aryldiazonium Cations.

A) CALCULATION OF THE GROUND AND EXCITED STATE ENERGIES OF PLANAR AND DISTORTED CONFIGURATIONS OF ORGANIC MOLECULES

1) Purpose of the Calculations. It is the contention of the work that follows that both photophysical and non-radiative (including photochemical) processes are strongly influenced by the geometries which the excited states of molecules assume after light has been absorbed. In addition there is strong experimental evidence that electronically excited molecules have different geometries, sometimes greatly different, than in the ground state.[2] There is the possible consequence that this geometry change in the excited state may bring the potential energy surface of the ground state into much closer proximity to the excited state potential energy surface.[3] In this region of closer proximity the rates of both photophysical and photochemical processes would be greatly different than would be anticipated for geometries near the Franck-Condon (spectroscopic) state.[4] Thus even an approximate estimate of the relative energies of the ground and excited states and their equilibrium geometries would be an immense aid in rationalizing the mechanisms of photochemical reactions. Ultimately, however, more accurate computational estimates of the energies and molecular parameters of the ground and excited states of molecules at various geometries would provide a means of estimating the partition functions and thus both the thermodynamics and rates of chemical and photochemical reactions. Such an immense

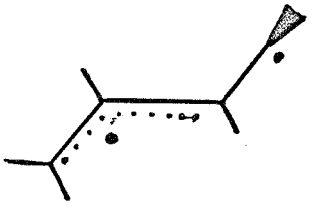
computational power would provide us with the ability of designing molecular systems to do specific chemical, physical, and photochemical jobs.

2) Theoretical Nature of the Problem. The Quantum Chemist seeking to computationally estimate the energies of any configuration of the ground and excited states of a particular set of nuclei and electrons must choose between semiempirical and ab initio methods. The critical difference is economic. A single calculation for a single geometry for a small polyatomic will cost approximately $1,000. A semi-empirical calculation on the same molecule for a single geometry is approximately $10. Economics have relegated this study to a semiempirical investigation. However, the state of the art in semiempirical calculations is not to the point where investigators have ventured extensively into calculating potential energy surfaces. The only method which has been extensively used is the Extended Huckel Technique of Hoffman.[5] This method specifically neglects important electron repulsion terms in the molecular Hamiltonian. The consequence of this neglect is that states of different multiplicities but same electronic configuration have the same calculated energies where in fact the energies may be far apart. But more important is that potential energy surfaces are predicted to cross when in fact they don't. Thus this method, although extensively used, must be discarded. The most recent advances in this area is a semiempirical technique developed by Santry

and Pople[6] and recently applied[7] to predicting the potential energy surface of excited states in the energy region around the equilibrium geometry of the ground state. However, even this technique was not able to predict that formaldehyde is nonplanar in its triplet and singlet excited states.[7] The most recent such calculations[8] at large geometries changes have neglected the inclusion of configuration interaction in the estimates of the ground and excited state energies. This neglect is critical and totally without theoretical justification. Classically, a similar neglect of doubly excited configurations and an inadequate basis set leads to the prediction that ground state H_2 would break up into H^+ and H^- at infinite distances when in fact hydrogen atoms are yielded. Thus the purpose of the following study is to develop reliable semiempirical techniques for the calculation of the entire potential energy surfaces for the ground and excited states. The study was initiated using a modified Pariser-Parr-Pople SCFMO-CI technique[9] applied to non-planar molecules. Such a technique is semiempirical with the Hartree-Fock technique[9] only applied to a limited number of electrons comprising the system under investigation. The systems initially under investigation were limited to those undergoing thermal and photoisomerization.

All the known polyenes apparently undergo photoisomerization. Spectroscopically ethylene is known to be more stable in the non-planar configuration in both its lowest energy

triplet and excited singlet.[2] Theoretical treatment of ethylene has been carried out by a number of workers.[10-12] The most recent results indicate that the potential energy surfaces of the ground state and triplet state are nearly degenerate in the non-planar configuration. Isomerization is known to take place on excitation of ethylene to the spectroscopic triplet.[13-15] Butadiene has been the subject of investigation by a number of photochemists.[13-15] The conclusion of these studies is that triplet butadiene is non-planar and can be viewed as being a biradical with the terminal methylene rotated 90° from the plane of the allyl radical. However, triplet butadiene can only be produced by



triplet butadiene

energy transfer techniques.[13] Direct photoexcitation of butadiene in the 230-260 mμ region produces none of the products (butadiene dimers) which are found in the photosensitized reaction.[15] Singlet butadiene produces cyclobutene and bicyclobutane in about 5% yield.[15] It has also been shown that singlet butadiene does not radiate[15] so that approximately 95% of excited singlet butadiene molecules return to the ground state by non-radiative processes. Thus our first theoretical efforts were directed towards rationalizing the photophysical and photochemical processes in

butadiene. Of the possible processes in butadiene the initial effort was directed towards calculating the energy of the planar and twisted configurations.

3) Method of Calculation. Because of the ease of converting an existing computer program we have selected a simplified semiempirical method for the preliminary calculations. A standard theoretical method used in the past has been the SCFMO-CI (self consistent field molecular orbital configuration interaction) method of Pariser, Parr,[16] and Pople.[7] This technique has largely been limited to planar molecules. Here we apply it to non-planar molecules. The heart of the method is the selection of certain molecules (usually benzene and ethylene) as standards. Using the known spectral data of these materials it is possible to calibrate the parameters necessary in the method. These parameters are the resonance integrals, β, the valence state ionization potentials, I_p, and the one and two centered electron repulsion integrals, $\langle aa|bb\rangle$. However, the calculation of excited state energies where the geometries are known to change with respect to the ground state is more complicated. The core repulsion energies are strongly geometry dependent. Thus the results obtained are dependent on the assumed changes in the geometry. For ethylene a geometry for the C-C bond has been set at 1.337A in the ground state and 1.480 in the excited. A thermal activation energy of 2.67 ev has

been measured.[18] Using this quantity and the known spectral data[2] new <aa|aa> and <aa|bb> are calculated. These new quantities turn out to be not much different than the same quantities in the planar molecule (for <aa|aa> the change is from 10.53 to 10.35 ev and for <aa|bb> from 7.40 to 7.95 ev). It turns out that most of the stabilization of the excited state twisted configuration comes from the assumed increase in C-C bond distance. It is possible to form a critique of this approach but for the purposes of simplicity we shall not.

For butadiene the case of applying the parameters obtained in ethylene is immediately complicated by what geometry to assume for the twisted configuration. For the twisted configuration arising from rotating the terminal methylene group 90° the allyl part of the biradical is assumed to have C-C distances of 1.400 A (two bonds) while the twisted portion looks like ethylene (twisted). Now additional parameters enter, the resonance parameters for the allyl portion and the other two centered integrals. The latter quantities are calculated by the method of Parr.[19] The former quantities are assumed to be -2.40 ev (as compared to the value of -2.80 ev for the C=C bond in planar ethylene or butadiene). Using these quantities the ground and excited singlet and triplets of butadiene in the planar, twisted 90° about the C=C or C-C bond were calculated (see Figure 1). The thermal barrier was predicted to be the same as ethylene. Chemical

intuition indicates that the actual thermal barrier for butadiene C=C isomerization should be that of ethylene less the resonance energy of the allyl radical (0.5 ev[20]). Thus, the calculation is quantitatively wrong but qualitatively correct. It is calculated that with the twisted C=C configuration both lowest energy excited singlet and triplet states are more stable than the planar configurations, and thus photoisomerization should occur from both states. However, twisting about the central single C-C bond is energetically unfavorable in the excited states. This result confirms Hammond's work[21] that dienes retain stereochemical integrity about the C-C single bond in their triplet excited states. Thus the results are satisfactory from the photochemist's view. However, the results do not wholly rationalize the view that non-radiative decay of singlet butadiene is due to the close proximity of the potential energy surfaces of the twisted ground state and singlet excited state; this separation is still about 3 ev. The electronic transition from this twisted excited configuration to the twisted ground state is forbidden and the predicted fluorescence lifetime would be in the 10^{-6} sec. region. Under these conditions most of the singlet excited state would be expected to bleed into the triplet. Since this is not experimentally observed other geometrical routes to the radiationless decay of butadiene singlet excited state must be investigated. Recently a crude valence bond calculation was reported showing[22] the potential

energy surface for cis-butadiene (which amounts to 5% of butadiene) to cyclobutene reaction. These calculations indicate that the potential energy surfaces come within 1.5-2 ev of one another. However, since excited singlet butadiene probably retains (as does the triplet) sterochemical integrity about the central single bond, cis-butadiene cannot be the route of radiationless decay of trans-butadiene. Other possible geometrical routes will be the object of future study.

The result of the calculations for hexatriene, stilbene, 4-aminobutene-1-one and 1-methyl-2-cyclopentadienylidene-1,2-dihydropyridine are shown in figures 2-5, respectively. Additional calculations on aminoethylene and butenone behaved similarly to ethylene and butadiene. The general theoretical behavior of hexatriene, stilbene, and aminobuteneone are also similar to ethylene and butadiene. The energies of the twisted intermediates resulting from the ground and the lowest spectroscopic triplet states are nearly the same. Conceptually this can be viewed as a biradical with the spin functions of the biradical adiabatically related either to the ground or triplet state of the planar molecule. Another alternative is possible, however. If substituents A and B are attached to an essential double bond then twisting about that bond can produce either a biradical or a zwitterion. The full rationalization of this

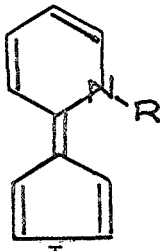
$$A - CH = CH - B \nearrow \searrow \begin{matrix} \dot{A} = CH - CH = \dot{B} \\ \text{biradical} \\ + \qquad\qquad - \\ \dot{A} = CH - CH = B \\ \text{zwitterion} \end{matrix}$$

twisting in valence bond terms has been published.[1] It seemed possible that the aminobutenone could produce a zwitterion in the manner;

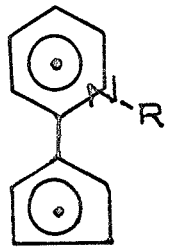
$$R_2N - CH = CH - CH = O \rightarrow R_2\overset{+}{N} = CH - CH = CH - \overset{-}{O}$$

However, as shown in Figure 4, the calculations indicate a near degeneracy of the twisted ground singlet and triplet, a factor characteristic of biradical intermediates, together with a decrease in the computed dipole moment.

The possibility of the zwitterionic intermediate was theoretically confirmed with the calculation on 1-methyl-2-cyclopentadienylidene-1, 2-dihydropyridine (I). The calculation

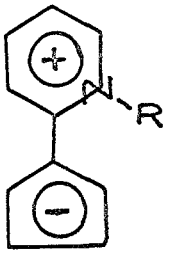


I



Biradical

or



Zwitterion

(Figure 5) predicts that the dipole moment of this material should increase in magnitude by twisting the internuclear double bond. In addition the calculations show that the triplet state should increase in energy rather than decrease. Finally the calculations predict an extremely low activation energy for twisting about the internuclear double bond. The calculated value of 13 kcal for thermal isomerization is to be contrasted to the high activation energies for ethylene

(ca. 60 kcal)[18] or even substituted stilbenes (ca. 40 kcal).[23] Actual NMR data[24] on this material indicates an experimental activation energy in the 11-13 kcal region together with a solvent effect which can only be rationalized if it is concluded that the dipole moment of the twisted intermediate increases with respect to the planar configuration. There is no experimental verification for the predicted high barrier for isomerization in the lowest triplet state. Attempted phosphorescence measurements on I were without success. However both the aminonitrostilbenes[25] and aminostyrylpryidine methiodides[26] do not photoisomerize in polar solvents. Here the possible[21] although unspecified role of ionic valence bond structures have been introduced to rationalize these results.

Thus it must be concluded that the theoretical results reported here are in agreement with reported experimental results. The success is sufficently encouraging to permit a continuation of computations with the view of rationalizing photochemical mechanisms.

B) QUANTUM MECHANICALLY BASED RULES FOR THERMAL AND PHOTOCHEMICAL REACTIONS

Although the above computational approach is preferable it is nevertheless constructive to formulate some qualitative rules based on quantum mechanical considerations which will permit a non-computational understanding of the possible

shape of photochemical and thermal potential energy surfaces. Recently a number of authors[27,28] have formulated such rules largely based on symmetry considerations. The origins of orbital symmetry rules are found in both the United Atom treatment[29] and Walsh's rules[2] governing the shape of molecules in the ground and excited states. Herzberg[2,29] has collected together the rules which show the relationship of the symmetry of photoproducts and the spectroscopic state of the molecule undergoing photodecomposition. Here the rule will be generalized to large organic systems.

1) Photodecomposition of Large Systems in which Atoms are not the Photoproducts

a) Homolytic Cleavage (Radical Cleavage)

Process

i) $^1AB^* \xrightarrow{h\nu} {}^2A^{\cdot *} + {}^2B^{\cdot}$ or $^2A^{\cdot} + {}^2B^{\cdot *}$ (decomposition of excited singlet)

ii) $^3AB^* \xrightarrow{h\nu} {}^2A^{\cdot} + {}^2B^{\cdot}$ (decomposition of triplet)

iii) $AB \xrightarrow{\Delta} {}^2A^{\cdot} + {}^2B^{\cdot}$ (thermal decomposition)

Rule: At infinite distance separation of A and B the potential energy surfaces of processes ii) and iii) meet. Decomposition by process i) must yield excited radicals unless non-radiative processes dominate.

b) Heterolytic Cleavage

Process

i) $^1AB^* \rightarrow {}^1A^+ + {}^1B^{-*}$ or $^1A^{+*} + {}^1B^-$ (decomposition of excited singlet)

ii) $^3AB^* \rightarrow {}^1A + {}^3B^*$ or $^3A^* + {}^1B^-$ (decomposition of triplet)

iii) $^1AB \rightarrow {}^1A^+ + {}^1B^-$ (decomposition of ground state)

Rule: Decomposition of excited singlet or triplet must yield at least one of the excited singlet or triplet state, respectively.

c) Role of Resonance Structures in Such Processes

Rule: i) Singlet and triplet resonance structures are totally differentiated and are never present in the same wavefunction (exception: spin-orbit coupling). When talking about photochemical processes taking place from triplet states singlet type resonance structures may not be included in the argument.

ii) There is presently no known non-computational method of assigning the relative importance of various resonance structures in the excited states of molecules.

Discussion of Rules a), b) and c)

Process i) of Rule a) is yet to be confirmed. Bond breaking, in general, costs from 50-100 kcal/mole. The generation of the excited state of a radical A* or B* would cost an additional 50-100 kcal/mole. Generally, then, the generation of excited radical species would cost at least 100 kcal/mole above the ground state of the molecule. Since normal UV-visible photolyses are at or lower than this

energy it seems improbable that such events will be observed in low energy region. In the vaccum UV such processes are possible. Unfortunately emission processes are not normally looked for. A thorough search of the literature has not yet been conducted but the author has not found obvious reference to such events. However, in processes i) and ii) in Rule b) it has been generally observed that the ionization of excited singlet or triplet organic acids or bases yield excited photoproducts in, respectively, the same multiplicity.[30]

Neglect of Rule c) has been less frequent in recent times. Part i) of this rule is fundamental. Part ii) is less recognized but has been dealt with in some detail by the author.[31]

ORBITAL SYMMETRY RULES FOR ISOMERIZATION IN THE POLYENES

Although the actual calculations are to be preferred it is possible, through the aid of symmetry considerations, to form qualitative rules of what the potential energy surfaces look like. Recently Woodward and Hoffmann have developed these rules[27,28] for rationalizing thermal and photochemical reactions in large organic molecules. These rules have their logical basis in the United Atom treatment[29] and Walsh's rules.[2] In the polyenes, $H(CH = CH)_nH$, n is either even or odd. When n is even the central bond of the all trans configuration is a C-C single bond. When n is odd the bond is a double bond. The symmetry of these all trans-polyenes is C_{2h}. If cis-trans isomerization occurs about this bond the molecule becomes C_{2v}. If this

isomerization is done in a smooth fashion the molecule of intermediate geometries is C_2. The only element of symmetry which joins these three symmetry types is C_2, rotation by 180° about the rotational symmetry axis (which is in the plane of the C_{2v} molecule but perpendicular to the plane of the C_{2h} molecule). The orbital symmetry rules of Woodward and Hoffmann merely state that the symmetry of the individual molecular orbitals remain the same throughout the cis-trans isomerization. In the case of ethylene (Figure 6) the π bonding orbital of transethylene adiabatically changes into the π^* anti-bonding orbital of cis-ethylene. The actual energy of the ground state, shown in the state diagram of Fig. 6, will become the energy of the doubly excited state of the isomer. However, the total symmetry of the ground state wavefunction is SS, totally symmetric (S = symmetric, A = antisymmetric with respect to the C_2 operation) for the trans-configuration, and AA (also totally symmetric) for the cis-configuration. The potential energy surfaces of wavefunctions having the same symmetry cannot cross (configuration interaction) and thus it is qualitatively predicted that the ground state potential surface of ethylene should reach a maxima and then drop. However, the rules predict a fairly flat response for the first excited state (SA) which is qualitatively equivalent to a low barrier for photoisomerization. Thus the rules predict a high barrier for thermal isomerization but a low barrier for photoisomerization. The

opposite is predicted for butadiene (Figure 7) while hexatriene is like ethylene. In fact the rules state that when n is even the photochemical behavior is like butadiene and when n is odd like ethylene. However, orbital symmetry rules are not applicable where the change encountered causes a breakdown in the symmetry.

C) EXPERIMENTAL STUDIES IN DISTORTABLE MOLECULES

1) Photophysical and Photochemical Studies in Aryldiazonium cations

Through the good graces of R. J. Cox, IBM San Jose, we have been able to obtain samples of some aryldiazonium salts in which the p-dimethylamino group is progressively distorted from resonance interaction with the ring system and thus the N_2+ itself. The effect of this distortion (see Table 1) is sufficient to cause a shift to lower energies of the visible absorption band. This is counter to most steric hinderance effects on spectra and qualitatively indicates that the distortion has a much greater effect on lowering the energy of the ground state than the excited state. Aryldiazonium salts are photolabile and in aqueous solution photosolvolyze to give the corresponding phenol. The thermal solvolysis product is the same. In spite of the photochemical reactivity the published literature on these materials is open to question. The section in Calvert and Pitts[32] on these materials is almost totally in error. In particular,

4-dimethylaminobenzenediazonium cation (II) has a quantum yield around 0.5[33,34] not the 1.0[35] reported. One author reports no photodecomposition at 77°K[36] while another reports[33] the quantum yield is almost independent of temperature. For benzenediazonium cation itself it has been reported[37] that it exhibits both fluorescence and phosphorescence when exposed to light at 295 mμ (and no photodecomposition) yet only exhibits photodecomposition at 260 mμ. Schulte-Fröhlinde and co-workers footnote[25] that aryldiazonium salts do not fluoresce and show a wavelength dependence on the quantum yield. This latter factor was previously reported[33,34] and is confirmed by our work (Table 1). Thus, photochemically, the materials appear unique. Because of the availability of materials and the relationship to the studies dealing with the effect of geometry on radiationless processes we decided to see what the effect of structure on quantum yield was.

2) Experimental

The quantum yields were measured at the wavelengths stated in Table I. The quantum yields were determined by monitoring the light coming through an aqueous solution of the salt. Using the appropriate correction for light reflection and absorption the equation can be derived showing that

$$\log(I_o/I_t - 1) = -I_o \phi^* \epsilon + \log(10^{OD_o} - 1)$$

where I_o is the light flux entering the system and I_t

is the light intensity at the detector at time t, ϕ is the quantum yield and ϵ is the extinction coefficient, and OD_o is the optical density at time zero.

Obviously this equation yields a straight-line when the quantity on the left is plotted against time. This equation holds for monochromatic light and if the solution is not mixed during exposure. Thus exposure must be short (several hundred seconds) so that diffusion into the light path from the unexposed portions of the solution does not occur. Lack of linearity in the results indicate mixing or a mixture of photosensitive materials. The equation does not hold if the photoproduct absorbs light. The quantum yields reported in Table I are all determined this way after determining the photon flux, I_o, with the ferrioxalate actinometer.[32]

Additional experimental work showed that neither fluorescence or phosphorescence was found (in water) in the spectral region to the red or blue of the diazonium absorption peaks. Attempts to sensitize or desensitize the photodecomposition of diethylaminobenzenediazonium cation with either oxygen or 2 M bromide solutions was without success, the quantum yield of this material is uneffected by such treatment. It was found the 2 M bromide solution almost completely quenched the fluorescence of quinine sulfate. Finally, the quantum yield is constant through a concentration range of 10^{-3} to 10^{-5} molar. No light intensity effect was also found.

Discussion

Previous workers claim[25] that the photodecomposition of aryldiazonium cations occurs from the singlet state. The evidence to date can not differentiate between the singlet or triplet mechanisms. As yet no sensitized triplet-triplet energy transfer decompositions of aryldiazonium salts have been attempted. The above observation that diazonium decompositions are unquenched by bromide ion indicates that the photoreactive state has an extremely short life time. The lack of fluorescence and lack of bromide quenching indicates that the singlet excited state lifetime is much less than the natural lifetime (estimated to be in the 1-10 nsec range). In the case of diethylamino-benzenediazonium cation only 50% of the light absorbing molecules can be accounted for. The other 50% return to the ground state by an as yet unknown non-radiative path. The effect of steric hinderance is to decrease the quantum yield but not drastically so. The reason for the red shift in the absorption spectra can be rationalized by assuming the bond order of the N-C bond of the dimethylamino linkage is higher in the ground state than in the excited state. The consequence of twisting about this bond is to lower the stability of the ground state to a larger degree than the excited state resulting in a red spectral shift with increasing steric hinderance. The reason for the drop in quantum yield is less obvious. The work of Kasha on steric hindered anilines[38] indicates that twisting about the C-N

bond produces a faster rate in singlet-triplet intersystems crossing. If the triplet were less photoreactive than the singlet such an event would produce a drop in the quantum yield. However the lack of bromide ion quenching would indicate that the systems are insensitive to heavy atom or spin orbit effects or that all the photochemistry is taking place from the triplet state which is spontaneously photodissociative.

A possible alternative hypothesis is available. Photodissociation from the singlet excited state is spontaneous (predissociation) but that there is some phenyl cation-molecular nitrogen recombination to give back starting material. The activation energy for thermal hydroysis[39] of diazonium salts are probably in the 20-35 kcal region with an overall enthalpy of an additional -40 kcals.[39] It is possible that the overall photo energy imput (70 kcal) is sufficiently greater than the thermal activation energy to keep the phenyl cation-molecular nitrogen combination sufficiently "hot" to bring about thermal deactivation to products or starting material in a fairly random fashion. This would be analogous to the radical cage effect. A few low temperature photolysis studies are planned in order to search for both radiative processes and to determine the quantum yield at -77°K.

D) FUTURE WORK BASED ON PROGRESS TO DATE

1) Calculations of the Ground and Excited State Energies of Planar and Distorted Configurations of Organic Molecules

This work will continue along the lines of the perfection of Pople-Santry-Segal CNDO type calculations on the all valence electronic structures of organic molecules. Superimposed on these calculations will be the introduction of configuration interaction treatment of both the ground and excited states. Within the framework of self consistent field calculations the inclusion of doubly excited configurations will be necessary. Progress to date consists of (i) operation of the CNDO program (II) and preparation of the configuration interaction subprogram. Computing facilities at Santa Cruz (360-40) are being updated to 64K memory in August of 1969. At that time memory requirements of the above program will be sufficient for the final operation of the CNDO-CI program and the initiation of test calculations. The work in the area has been approved for future study under the section of 2nd year of grant entitled: "Geometrical Influences On Non-Radiative Processes in Organic Molecules."

2) Radical Stabilities in Nitrogen Containing Heterocyclic Systems

The work in this area has been approved for future study under the 2nd year of the grant. Progress to date consists of the operation status of an open-shell SCF program

which will allow for the estimates of the spin densities and resonance energies. Studies will consist of calculations and electron spin resonance studies on both polyenyl and heterocyclic radicals. Test calculations are presently under way on allyl, pentadienyl, and higher polyene type radicals. Future calculations on hetero-containing and heterocyclic radicals of biological interest will be performed in conjuction with ESR studies.

References

1. E. M. Evleth, Chem. Phys. Letters 3, 122 (1969) "Ionic and Biradical Mechanisms in Thermal and Photo Cis-trans Isomerizations."

2. G. Herzberg,"Electronic Spectra of Polyatomic Molecules," Van Nostrand, 1966.

3. D. Phillips, J. Lemaire, C. S. Burton and W. A. Noyes, Jr. "Advances in Photochemistry," Vol. 5, pp. 329-364, Interscience (1968).

4. G. W. Robinson and R. P. Frosch, J. Chem. Phys. 38, 1187 (1963).

5. R. Hoffmann, J. Chem. Phys., 39, 1397 (1963).

6. J. A. Pople, D. P. Santry, and G. A. Segal, ibid., 43, S129 (1965).

7. H. W. Kroto and D. P. Santry, ibid., 47, 792 (1967).

8. J. J. McCullough, H. Ohorodnyk and D. P. Santry, Chem. Comm. 570 (1969).

9. For a review see M.J.S. Dewar "The Molecular Orbital Theory of Organic Chemistry," Chapter 3, McGraw-Hill, (1969).

10. R. S. Mulliken and C. C. J. Roothaan, Chem. Rev., 41, 219 (1947).

11. U. Kaldor and I. Shavitt, J. Chem. Phys., 48, 191 (1968).

12. R. J. Buenker, ibid., 48, 1368 (1968).

13. G. S. Hammond, in "Reactivity of the Photoexcited Organic Molecule." Proceedings of the 13th Conference on Chemistry at the University of Brussels, October 1965, published by Interscience (1967), p. 119-138.

14. W. G. Dauben, ibid., p. 171-196.

15. R. Srinivasan, "Advances in Photochemistry," Interscience (1966), p. 113-141 (Vol. 4).

16. R. Pariser and R. G. Parr, J. Chem. Phys., 21, 446, 767 (1953).

17. J. A. Pople, Trans. Faraday Soc., 49, 1375 (1953).

18. B. S. Rabinovitch, J. E. Douglas, and F. S. Loonly, J. Chem. Phys., 20, 1807 (1952).

19. R. G. Parr, ibid., 33, 1184 (1960).

20. K. W. Egger, D. M. Golden, and S. W. Benson, J. Am. Chem. Soc., 86, 5416 (1964).

21. See ref. 7 and also P. J. Wagner and G. S. Hammond, "Advances in Photochemistry," Interscience (1968), p. 21-156 (Vol. 5).

22. W. Th. A. M. van der Lugt and L. J. Oosterhoff, Chem. Comm. 1235 (1968).

23. For a list of isomerization energies see A. A. Frost and R. G. Pearson, "Kinetics and Mechanisms," p. 105, Wiley and Sons (1953).

24. J. H. Crabtree and D. J. Bertelli, J. Am. Chem. Soc.,

89, 5384 (1967).

25. D. Schulte-Frohlinde, H. Blume and H. Gusten, J. Phys. Chem., 66, 2486 (1962).

26. J. L. R. Williams, J. M. Carlson, R. E. Adel, and G. A. Reynolds, Can. J. Chem. 42, 1345 (1965).

27. R. Hoffmann and R. B. Woodward, Accounts of Chem. Res., 1, 17 (1968).

28. J. J. Vollmer and K. L. Servis, J. Chem. Ed., 45, 214, (1968).

29. G. Herzberg, "Spectra of Diatomic Molecules," Van Nostrand, (1961), Chapter 6.

30. E. L. Wehry and L. B. Rogers, "Fluorescence and Phosphorescence Analysis" Ed. D. M. Hercules, Chap. 3, Interscience (1963).

31. E. M. Evleth, J. Am. Chem. Soc., 89, 6445 (1967).

32. J. G. Calvert and J. N. Pitts, Jr. "Photochemistry," Wiley (1966), p. 471-473.

33. R. Moraw and J. Munder, "Kolliquium uber Wiss. Photographie," Section IV, II Zurich, (1961), also see J. Kosar, "Light Sensitive Systems," Wiley and Sons, (1965), p. 194-320.

34. Work done at IBM Research Laboratories, 1962-65.

35. A. Baril, Jr., J. Chem. Phys., 22, 1275 (1964).

36. W. E. Lee, J. G. Calvert, and E. W. Malmberg, J. Am. Chem. Soc., 83, 1928 (1961).

37. M. Sukigara and S. Kikuchi, Bull. Chem. Soc. Japan, 40, 461 (1967).

38. M. Kasha, Photochemistry Symposium held at U.C. Riverside, Dec. 1967.

39. H. J. Borchardt and F. Daniels, J. Am. Chem. Soc., 79, 41 (1957).

40. M. L. Crossley, R. H. Kienle and C. H. Benbrook, ibid., 62, 1400 (1940).

TABLE I

Quantum Yields of Photodecomposition of Some Aryldiazonium Salts

	Aryldiazonium Salt	λ_{max}^{a}	ϵ_{max}^{b}	ϕ_{365}	ϵ	ϕ_{405}	ϵ	ϕ_{435}	ϵ
I	4-N,N-diethylamino	378	40,200	0.50	30,800	0.44	13,300		
II	4-N,N-dimethylamino	378	36,100	0.57	28,900	0.44	10,000		
III	3-mthyl-4-N,N-dimethylamino	393	34,000	0.47	15,000	0.55	30,300	0.45	4,300
IV	3,5-dimethyl-4-N,N-dimethylamino	425	26,900	0.34	3,400	0.31	19,800	0.23	25,800
V	3-ethyl-4-N,N-dimethylamino	394	32,400	0.51	14,000	0.48	30,200	0.42	4,800
VI	3-t-butyl-4-N,N-dimethylamino	406	17,600	0.42	5,200	0.45	17,500	0.32	8,300

a) millimicrons

b) liters $moles^{-1}cm^{-1}$

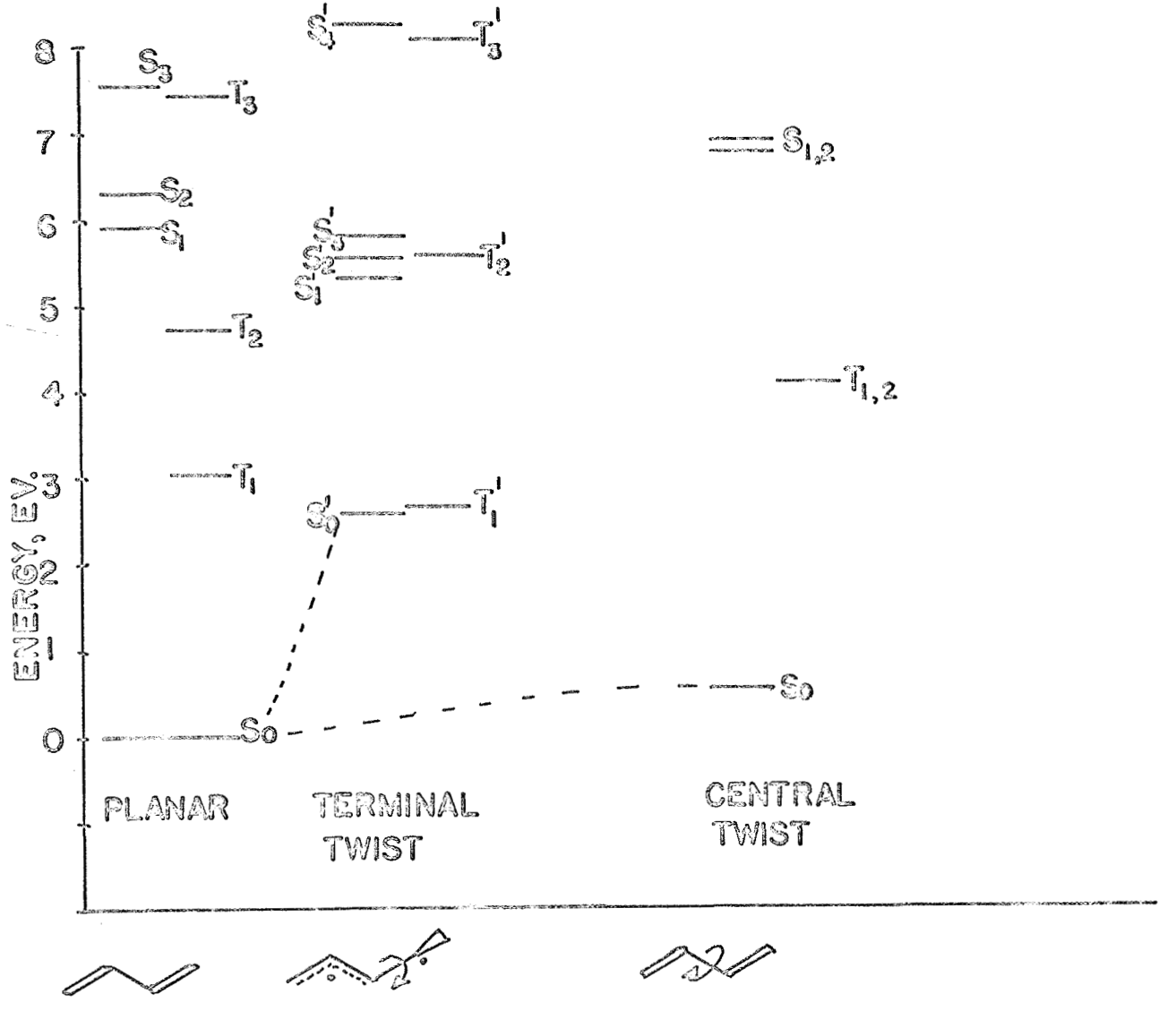


Figure 1

S = singlet, T = triplet

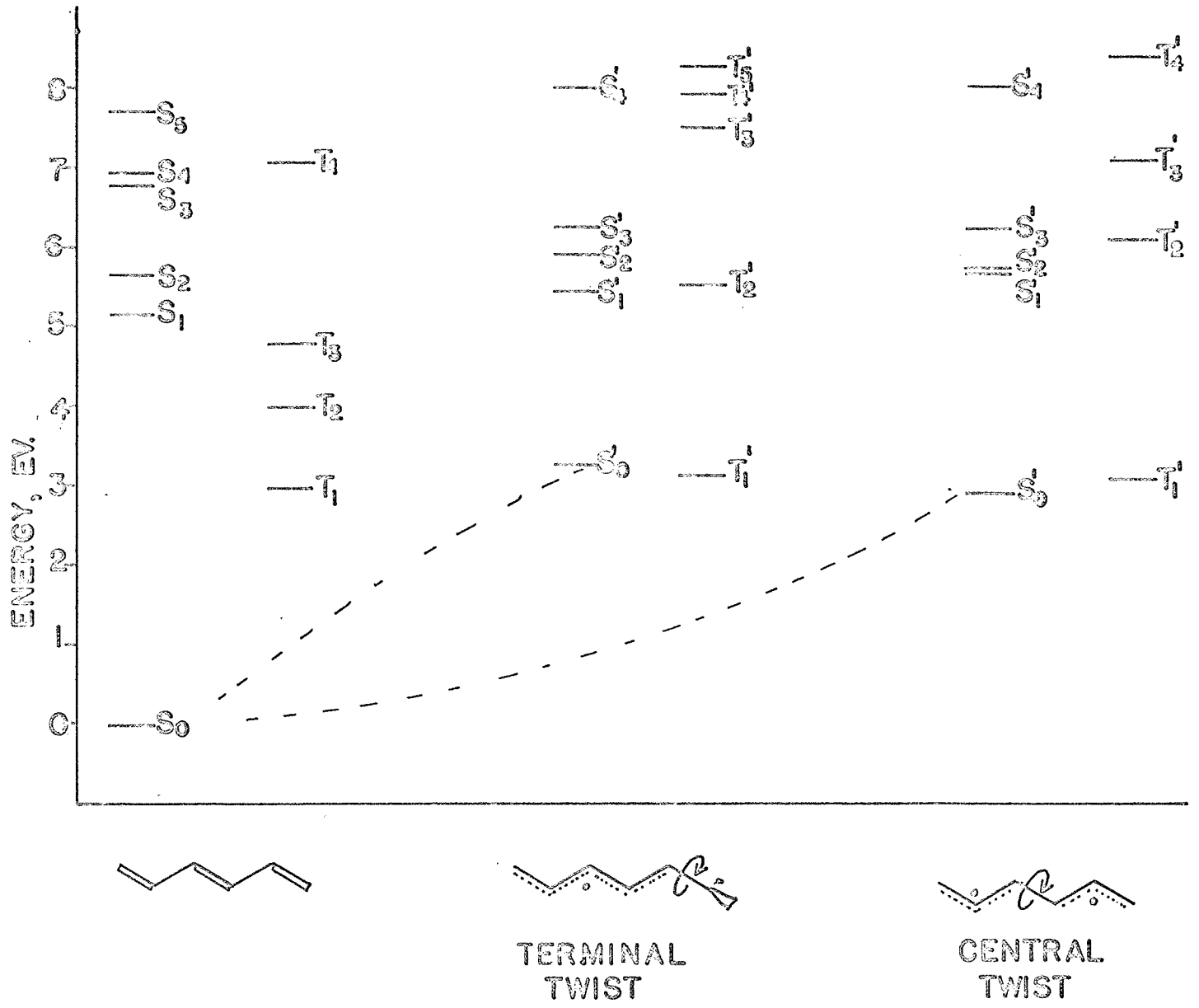

ENERGY, EV.
0
1
2
3
4
5
6
7
8
S_0
S_1
S_2
S_3
S_4
T_1
T_2
T_3
S_1'
S_2'
S_3'
S_4'
T_1'
T_2'
T_3'
T_4'
T_5'
TERMINAL TWIST
CENTRAL TWIST

Figure 2

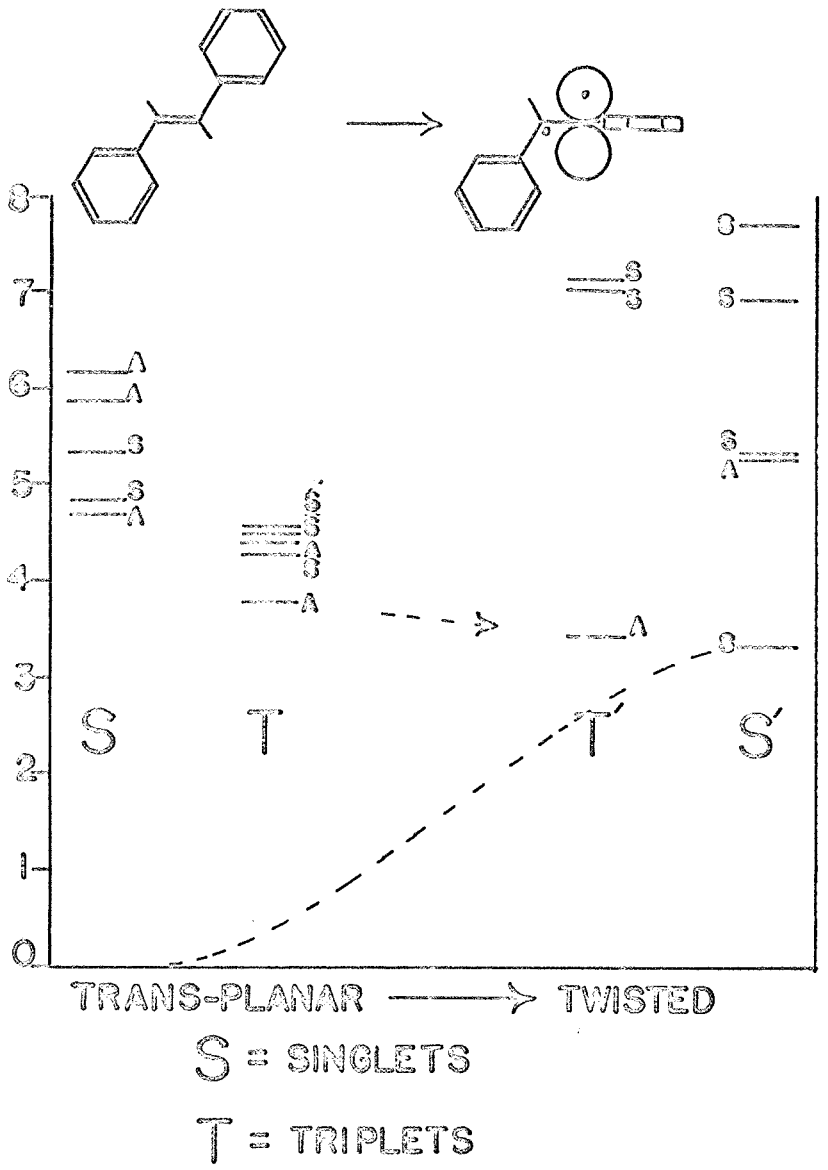


Figure 3

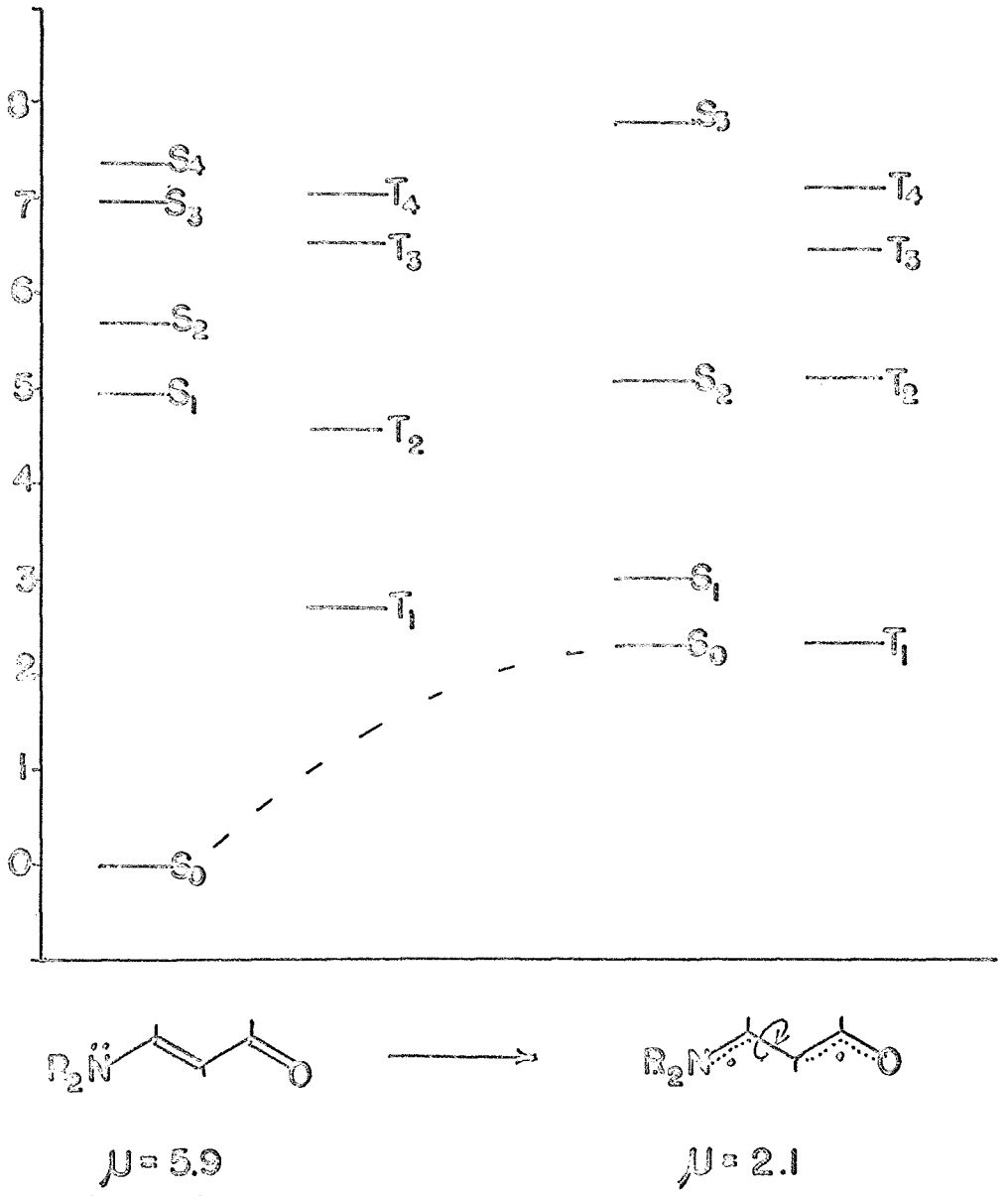

8
7
6
5
4
3
2
1
0
S4
S3
S2
S1
S0
T4
T3
T2
T1
S3
S2
S1
S0
T4
T3
T2
T1
R2N
O
R2N
O
μ = 5.9
(CALCD.)
μ = 2.1

Figure 4

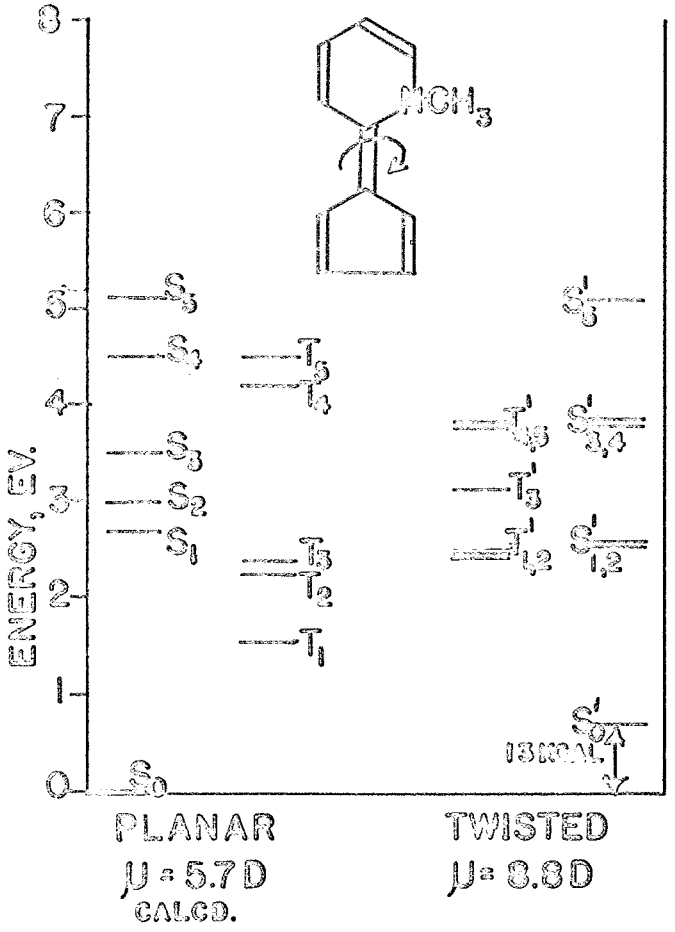
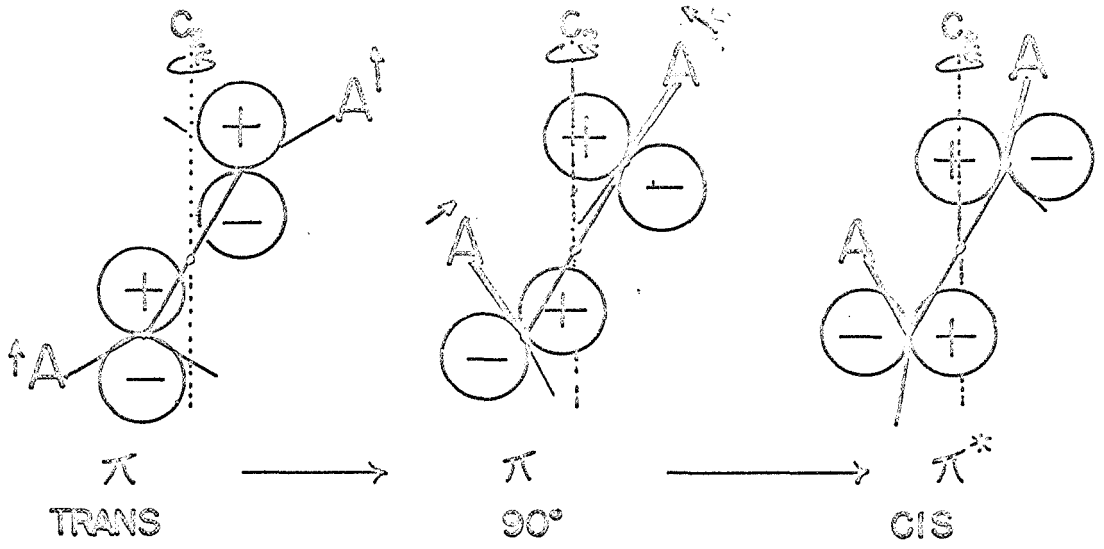
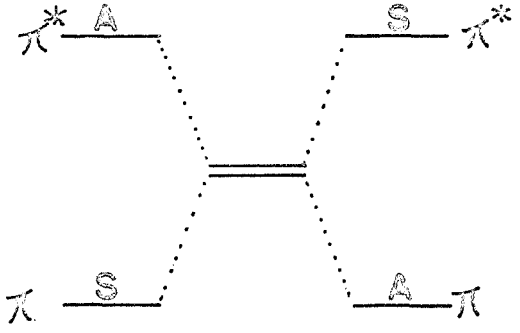
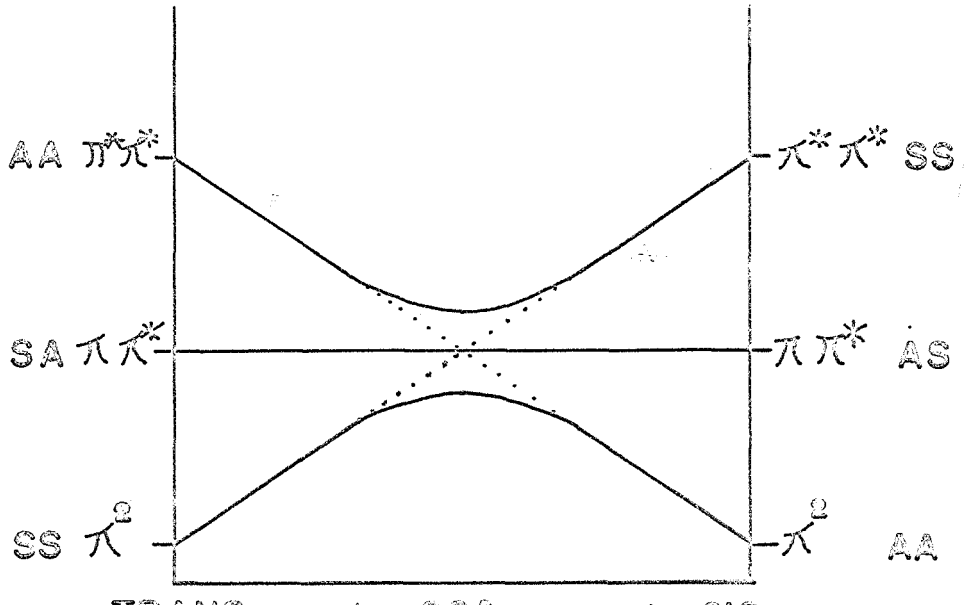

ENERGY, EV.
0
1
2
3
4
5
6
7
8
NCH3
S5
S4
S3
S2
S1
T5
T4
T3
T2
T1
S'5
S'4,3
T'5
T'3
S'2,1
T'2,1
S'0
13 KCAL.
PLANAR
μ = 5.7D
CALCD.
TWISTED
μ = 8.8D

Figure 5



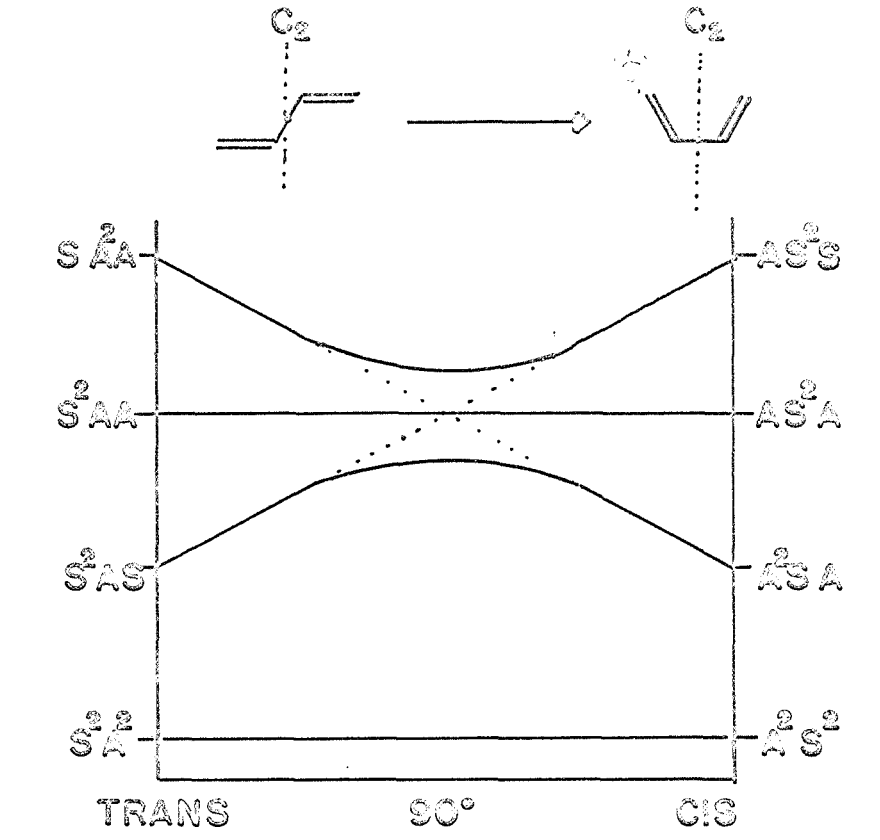


ORBITAL DIAGRAM



STATE DIAGRAM

Figure 6


C_2
C_2
S^2AA
AS^2S
S^2AA
AS^2A
S^2AS
AS^2A
S^2A^2
A^2S^2
TRANS
90°
CIS

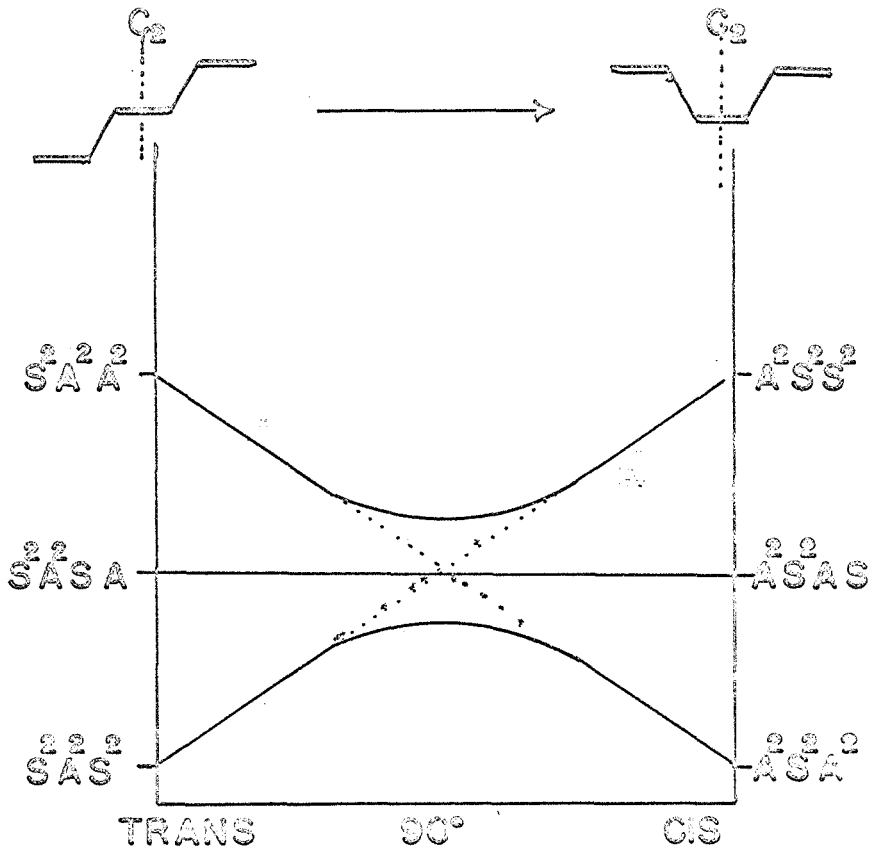

C_2
C_2
$S^2A^2A^2$
$A^2S^2S^2$
$S^2AS\,A$
$AS^2A\,S$
$S^2A^2S^2$
AS^2A^2
TRANS
90°
CIS

Figure 7