A Consideration of Orbital Interaction in Nitrogen Extrusions of Cyclic Azo Compounds

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The stereochemical paths of nitrogen extrusions from cyclic azo compounds have been examined from the point of view of particular orbital interaction. The stereoselectivity of the recyclization of 1-pyrazoline derivatives and the homologues on the extrusion can be understood in terms of interaction between the frontier orbitals of the C–N–N–C σ-bond system and of N–N π-bond. Other cyclic azo compounds are found also to behave consistently with the direction of the particular orbital interaction between the relevant parts *e.g.*, strained σ-bonds, π-bonds and lone pairs, and two weakened C–N bonds, and of the interaction between approximate *p* orbitals at the α carbons with respect to the nitrogen and unstrained σ-bond to be cleaved.

Both pyrolytic and photolytic reactions of cyclic azo compounds have been reported in many papers. However, no comprehensive, detailed mechanism and steric course have yet been discussed. Here, we intend to interpret the experimental results from the point of view of orbital interaction. The use of a particular orbital interaction scheme is recommended for the purpose of recognizing steric paths in chemical reactions in general.[1] The fundamental proposition lies in the following statement; "A majority of chemical reactions should take place at the position, and in the direction, of maximum overlapping of the highest occupied (HO) molecular orbital (MO) and the lowest unoccupied (LU) MO of the reacting species; in the reacting species with a singly-occupied (SO) MO, this plays the part of the HOMO or the LUMO, or of both." The consideration of the interaction of these particular MO's is convenient in describing the nature of chemical reactions.[2,3] The procedure for discussing the direction and the position of chemical reactions has been established on the basis of the proposition given in a preceding article.[1] In short, reacting species involved in intramolecular reactions are divided into two parts so that new bonds may form across the surface which borders the parts. The sign relation of the orbital lobes in these parts plays an important role in the reaction. The resultant sketch of the reacting molecules shows the path which they should trace; the reaction should proceed so that the signs are congruent on the atoms where the bonds are newly formed. This formularized procedure will here be applied to the nitrogen extrusion of cyclic azo compounds, of which the stereospecificity has so far been suspended without any comprehensive understanding. The following speculation may assist in understanding the extrusion reactions.

First of all, the decompositions of cyclic azo compounds are classified, in terms of their intrinsic difference as chemical species, into three groups; (1) the nitrogen extrusions of the derivatives of 1-pyrazolines and the homologues, (2) those of the compounds with a conjugative part interacting with weakening C–N bonds, and (3) those of the compounds undergoing a cleavage of the unstrained σ-bond bridging the β and β′ carbons. Now our discussion is compelled to enter upon a treatment of each class, since the way of dividing the reactants and the assignment of the frontier orbitals depend on the nature of the reactants as well as on the reaction environments.

The Derivatives of 1-Pyrazolines and the Homologues

In the case of the pyrolysis, the respective interactions between the HOMO and the LUMO of the N–N π-bond system and the LUMO and the HOMO of the C–N–N–C σ-bond system presumably initiate the extrusion reaction, whereas in the photo-induced reactions the energy incorporated through $n\rightarrow\pi^*$ or $\pi\rightarrow\pi^*$ excitation at the nitrogens is transferred to the σ-bond system by way of the orbital interaction between the LUMO of the σ-bond system and the SOMO at the N=N moiety to weaken the C–N bonds and promote the extrusion. The results of the sensitized photolysis of azo compounds tempt us to expect that cyclic azo compounds decompose through both excited singlet and triplet states, while acyclic azo compounds dissociate and undergo *cis-trans* isomerization by way of singlet and triplet states respectively.[4]

Now it is necessary to know the nodal properties of each bond system in order to further our thinking. In the ground state, two electrons, localized at the N–N π-orbital, occupy the MO which is symmetrical (S) with respect to the mirror plane passing through the middle of the N–N bond. The LUMO or the SOMO has an anti-symmetrical (A) character with respect to the plane. In contrast with π-orbital systems, the symmetry of the σ-bond system has not been established completely. The knowledge obtained from the hybrid-based MO calculations[5] is helpful on the present occa-

1) K. Fukui, *Accounts Chem. Res.*, **4**, 57 (1971) and reference therein.

2) K. Fukui and H. Fujimoto, This Bulletin, **41**, 1989 (1968).

3) K. Fukui and H. Fujimoto, *ibid.*, **42**, 3399 (1969).

4) (a) B. S. Solomon, T. F. Thomas, and C. Steel, *J. Amer. Chem. Soc.*, **90**, 2249 (1968). (b) P. S. Engel, *ibid.*, **91**, 6903 (1969); P. D. Bartlett and P. S. Engel, *ibid.*, **90**, 2960 (1968); P. S. Engel, *ibid.*, **89**, 5731 (1967); I. I. Abram, G. S. Milne, B. S. Solomon, and C. Steel, *ibid.*, **91**, 1220 (1969); P. S. Engel and P. D. Bartlett, *ibid.*, **92**, 5883 (1970).

5) See *e.g.* K. Fukui, in "Sigma Molecular Orbital Theory," ed. by O. Sinanoğlu and K. B. Wiberg, Yale Univ. Press (1970), p. 121.

sion. Among the three MO's essentially occupied by the six bonding electrons in the C–N–N–C system, the lowest has no node; the three bonds being bonding therefore symmetrical (S) with respect to the mirror plane (Fig. 1A). The next has one node between the nitrogens (A), while the last one, which is also the HOMO of this system, has two (S) (Fig. 1B and 1C respectively). Moreover, the LUMO has three nodes, alternating the signs along the bond chain (A) (Fig. 1D).

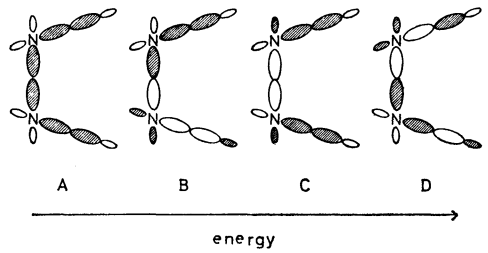


Fig. 1. Relation between orbital symmetry and energy level of three σ-bonds chain.

Assuming that the orbital interaction between the C–N–N–C bond system and the N=N π-bond responsible for the weakening of the C–N bonds governs the stereochemical path both in the pyrolysis and in the photolysis, it is unquestionably necessary to divide 1-pyrazoline and to assign an orbital symmetry for the pyrolysis (A) and the photolysis (B), as is shown in Fig. 2.

In the thermolysis, the particularly important orbital interactions are that between the HOMO of the N–N π-bond system and the LUMO of σ-bond system and that between the LUMO of the former and the HOMO of the latter. One of the interactions, that between π-HOMO and σ-LUMO, is illustrated in Fig. 2A. Fig. 2B represents the mode of the interaction between the LUMO of the σ-bond system and the lowest-excited N–N π-bond, which is caused by an excitation transfer from the neighboring excited N=N π-bond. As a result, 1-pyrazoline decomposes into cyclopropane and nitrogen under both thermal and light-irradiated conditions, with single inversion and with retention at C_α or/and $C_{\alpha'}$ during the recyclization respectively. At first sight, the orbital interaction consideration seems unable to cover all the experimental results listed in Tables 1 and 2. However, it still proves effective in explaining the steric course with the help of the stereochemistry of the reactants. In the pyrolysis, by taking account of the reluctance to rotation of the bulky group at C_α and $C_{\alpha'}$ inward to the breaking five-membered ring, and in the photolysis, by taking account of the multiplicity of the excited state, the particular orbital

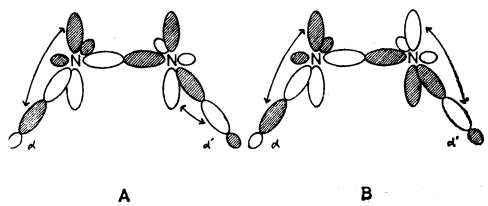


Fig. 2. The modes of orbital interaction in the pyrolysis (A) and in the photolysis (B) of 1-pyrazoline and the homolgue.

Table 1. Product ratios of pyrolyses of 1-pyrazoline derivatives and its homologues

Reactants	Products (%)		Remarks	Ref.
	cis	*trans*		
cis-Ia	33.2	66.1	in vapor	5
trans-Ia	72.6	25.4		
cis-Ib	43.6	57.0	in toluene	6
trans-Ib	6.7	93.3		
cis-IIa	14.7	48.3	in neat liquid	7
trans-IIa	16.6	27.9		
cis-IIb	14.2	31.0	in neat liquid	7
trans-IIb	19.6	38.2		
cis-IIIa	1.00	0.70	under nitrogen	8
trans-IIIa	1.00	1.22	in ratio	
cis-IIIb	31	9	in neat liquid	9
trans-IIIb	11	72		
cis-IIIb	47	19	in vapor	9
trans-IIIb	18	74		
cis-IIIc	1	1	in the gas phase	10
trans-IIIc	1	1	in ratio	
cis-IIId	43.7	35.2	in vapor	5
trans-IIId	46.0	21.8		
meso-IV	43	2.5	in benzene	11
dl-IV	3.5	42		

Table. 2. Product ratios of photolyses of 1-pyrazoline derivatives and its homologues

Reactants	Products (%)		Remarks	Ref.
	cis	*trans*		
cis-Ia	47.5	42.5	in the gas phase	5
trans-Ia	59.5	26.7		
cis-Ia	33.9	61.7	in EtOH	5
trans-Ia	44.5	45.6		
trans-Ia	42.4	43.9	in neat liquid	5
cis-Ia	39.3	60.4	in the presence	5
trans-Ia	38.3	61.2	of benzophenone	
cis-Ib	57.2	42.8	in THF	6
trans-Ib	0.7	99.3		
cis-IIIa	63—76		in neat liquid	8
trans-IIIa		72		
cis-IIId	43.0	37.6	in vapor	5
trans-IIId	24.4	37.2		
cis-IIId	60.4	26.4	in EtOH	5
trans-IIId	13.0	50.7		
cis-IIId	32.1	66.2	in the presence	5
trans-IIId	27.0	72.2	of benzophenone	
meso-IV	35	3.5	in benzene	11
d,l-IV	4	33		
meso-IV	11.5	8	in the presence	11
d,l-IV	8	12	of thioxanthone	

6) R. Moore, A. Mishra, and R. J. Crawford, *Can. J. Chem.*, **46**, 3305 (1968).
7) C. G. Overberger, N. Weinshenker, and J.-P. Anselme, *J. Amer. Chem. Soc.*, **87**, 4119 (1965).
8) C. G. Overberger, J. W. Stoddard, C. Yaroslavsky, H. Katz, and J.-P. Anselme, *ibid.*, **91**, 3226 (1969).
9) T. V. Van Auken and K. L. Rinehart, Jr., *ibid.*, **84**, 3736 (1962).
10) D. E. Mcgreen and W. S. Wu, *Can. J. Chem.*, **45**, 461 (1967).
11) R. J. Crawford and G. L. Erickson, *J. Amer. Chem. Soc.*, **89**, 3907 (1967).

interaction turns out to work clearly in directing the path of these reactions as follows.

The Pyrolysis. The thermolytic reactions of α,α'-disubstituted cyclic azo compounds will be discussed first. They obey the directions of orbital interaction to invert singly at either α or α' carbons, when the repulsive force is not considerably outstanding between the approaching groups with the progress of the reaction (*cis*- and *trans*-Ia, *cis*-Ib, *cis*-IIa, and *cis*-IIb). *Trans*-species which have bulky groups at both α and α' carbons suffer such a repellent action during the single inversion that they neglect the orbital interaction, giving the corresponding compounds with a retention of the original configurations (*trans*-Ib and *trans*-IIa and b). In these cases, thermodynamics overcome the orbital interaction.

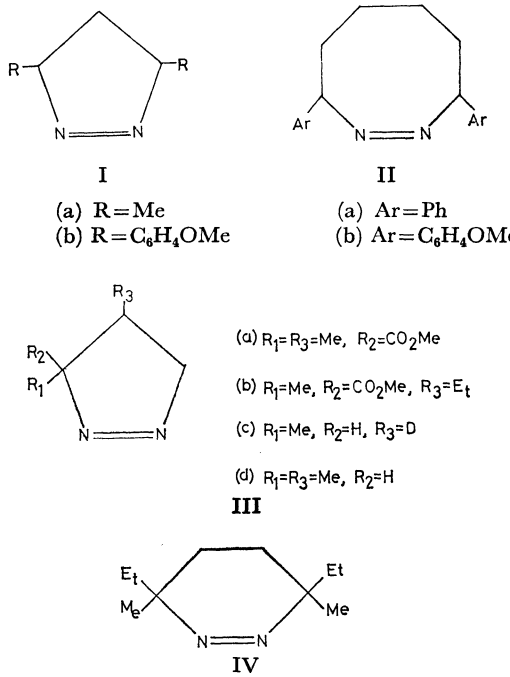
The second object of our discussion is the group of α, α-disubstituted cyclic azo compounds. When α carbon is occupied by two substituents (except for very small groups, for instance, hydrogen and deuterium), the single inversion undoubtedly occurs more probably at the unsubstituted α' carbon to produce apparent retention products (IIIa and b).

Thirdly, α,β-disubstituted-1-pyrazolines will be treated. If these compounds dispose the substituent at the β carbon with respect to leaving nitrogens in the *anti*-position in the transition state of the thermolysis, as has been proposed by Crawford and Mishra,[13] *cis*- and *trans*-α, β-disubstituted-1-pyrazolines will have methyl groups at the α carbon at the axial and the equatorial positions respectively. Since the axial group is compelled to rotate inwardly, the *cis*-reactant must rotate a methyl group but *trans*-species rotate hydrogen. From these requirements, it is evident that *trans*-pyrazolines yield more an apparent inversion product than *cis*-pyrazoline. The experiments on *cis*- and *trans*-IIId exhibit this tendency, but it cannot be explained by these discussions why *trans*-IIId apparently gives more of the single inversion product than the retention product. However, in the case of a small substituent at the β carbon (IIIc), the reactants, whether in the *cis*- or *trans*-form, yield *cis*- and *trans*-products in equal amounts, since the small substituent has no influence on the inward rotation at the α carbon.

The Photolysis. Subsequently, let us proceed to a detailed discussion of the photolysis on the assumption that orbital interaction favors the configurational retention path. If these compounds undergo dissociation through the excited singlets, the stereochemical course will be consistent with our predictions based on Fig. 2B. There can, however, exist some factors independent of the orbital interaction. For example, the interventions of triplets would add to a thermodynamically stable product or *trans*-compound, and the deactivation of an excited singlet to the vibrationally-exicted ground state would compete with the path through excited singlets, in some case giving the inversion product. That is why the stereochemical path in thermolysis is complicated.

All the compounds listed in Table 2 except for *cis*-Ia in 95% ethanol and *trans*-Ia in the gas phase more or less exhibit a tendency toward obedience to orbital interaction control. Here, we may find the causes of the two exceptions and some poorly stereoselective reactions mainly in the intervention of triplets, but it is premature to arrive at conclusive interpretations because of the insufficiency of physical information about 1-pyrazolines, the quantum yield of intersystem crossing, the structural geometry of triplets, *etc.* However, it seems that it will be meaningful to make a tentative proposal.

Some experimental results suggest that cyclic azo compounds extrude nitrogen molecules *via* triplets as well as singlets, but that acyclic azo compounds undergo *cis-trans* isomerization *via* triplets, while they dissociate only through singlets.[4] From this generalization, it can be expected that the dissociation through the triplets depends upon the geometrical structure of the reacting molecules. The geometry in the triplet is considered to suffer some twist, which is probably caused by electronic repulsion between two electrons with parallel spins. Assuming that relief from the twisted strain drives the extrusion, the more the triplet species is



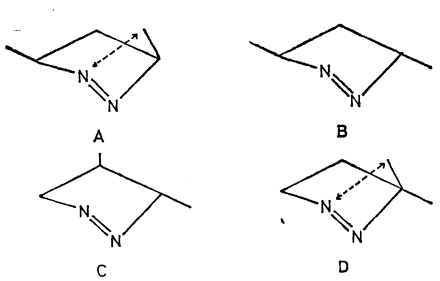


Fig. 3. The repulsion of twisted 1-pyrazoline derivatives in the triplets; (A) *trans*-α,α-dimethyl-1-pyrazoline, (B) *cis*-α,α-dimethyl-1-pyrazoline, (C) α,β-dimethyl-1-pyrazoline, and (D) α,α-substituted 1-pyrazoline.

12) P. D. Bartlett and N. A. Porter, *J. Amer. Chem. Soc.*, **90**, 5317 (1968).
13) R. J. Crawford and A. Mishra, *ibid.*, **88**, 3963 (1966).

strained, the more facile a decomposition it is submitted to.

Now let us proceed to a detailed discussion of this assumption. The distortion of α,α'-disubstituted 1-pyrazolines (I) brings about strains of different extents between *cis*- and *trans*-isomers. With respect to *cis*-I, a suitable repulsion arises from the unavoidable approach of the substituent and the originally remoter nitrogen (Fig. 3A), thus accelerating the extrusion through the triplets so remarkably as to compete with the singlet path. The participation of triplets contributes to the formation of thermodynamically stable products or *trans*-isomers. That probably results in the low stereospecificity of *cis*-I (*cis*-Ia in the gas phase and *cis*-Ib in tetrahydrofuran). Further, in the liquid phase, as the deactivation of an excited singlet to the vibrationally-excited ground state by collision with the surrounding molecules adds to inversion products by way of the ground state, the mode of stereospecificity may be reversed in *cis*-reactants (*cis*-Ia in ethanol). In contrast, *trans*-I can be twisted without bringing the substituents close to the nitrogens (Fig. 3B); therefore, the triplet species might decompose too slowly, as compared with the excited singlets, to exert any remarkable influence on the distribution of products. That implies the predominant control of orbital interaction in determining the stereochemical path in the gas phase (this conclusion contradicts the experimental finding with regard to *trans*-Ia in the gas phase).[14] Since there is little intervention of triplets, the stereospecificity of *trans*-I in the solution is lower by an extent corresponding to the deactivation of the excited singlets to the ground state by solvents (*trans*-Ia in ethanol). However, large substituents at both α and α' carbons keep themselves from approaching at the cost of thermodynamical stability. That is why *trans*-Ib is converted with a high stereospecificity of configurational retention.

Some 1-pyrazolines, α,β-disubstituted compounds (IIId), can avoid the strain, as is illustrated in Fig. 3C. Accordingly, these species obey the direction of orbital interaction in the excited singlets without any disturbance.

The α,α-disubstituted compounds, IIIa and IV, also suffer an appropriate strain (Fig. 3D) enough to take the triplet path of competing explicitly with the singlet path. However, the triplet reactions of these compounds do not affect the product ratios, since the resulting biradical intermediates have nearly equal thermodynamical stabilities whether they assume the *cis*-form or *trans*-form. In fact, the experiments seem to show that IIIa and IV behave as if the triplets were not concerned in distributing the product in spite of the suitable strains. This interpretation is supported by the fact that, while the photo-induced transformation of *meso*- and *d,l*-IV yield the respective products, thus maintaining the configuration, both *cis*- and *trans*-reactants in general give the same product as the major component in the triplet-sensitized reactions under thermodynamical control.

The Compounds with a Conjugative Part Interacting with Weakening C-N Bonds

Before discussing other cyclic azo compounds, we must consider how they diverge from 1-pyrazolines and their homologues. The cyclic azo compounds treated in this section have a "conjugative" part interacting with incipient orbitals appearing at the carbons as the C–N bonds are weakened. This orbital interaction, rather than that which is responsible for the weakening of the C–N bonds, presumably governs the stereochemical path. This assumption is founded on the fact that two C–N bonds can be approximately separated from the N–N σ-bond since weakening σ-bonds tend to have a π character to some extent. In consequence, the whole of the reactant may be divided into the part and two C–N bonds. The respective MO's of the C–N bond system are assigned in Fig. 4.

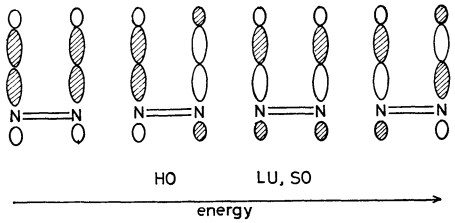
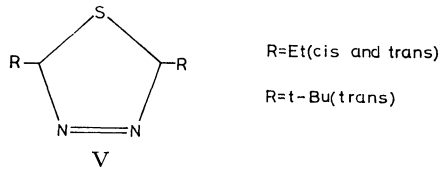


Fig. 4. Relation between orbital symmetry and energy level of two σ-bonds system.

Our discussions will begin with the reaction of 1-pyrazoline and the analogue bearing a conjugative part at the β carbon. When the conjugative part consists of *exo* π-orbitals, *e.g.*, 4-alkylidene-1-pyrazolines, the particularly important orbital interactions are probably that between the HOMO (S) of the π-orbitals and the LUMO (S) of the C–N bonds and that between the LUMO (S) of the former and the HOMO (A) of the latter.[15] Accordingly, the stereospecificity of the compounds depends upon the balance between these two competitive modes of orbital interactions. That is, the configuration may be retained during the reaction when the interaction between symmetrical and symmetrical MO's prevails over the other and may be singly inverted when symmetrical and anti-symmetrical interaction dominates. No information has been obtained so far which shows which mode is predominant. However, when the conjugative part is a lone pair (V), there is no appropriate LUMO localized on this part. This implies the exclusive operation of the orbital interaction between the lone pair as the HOMO (S) and the LUMO (S) the C–N-bond system (Fig. 5). It follows that V goes through thiocarbonyl ylide as an intermediate to produce an adduct with a certain dipolarophile by way of a 4+2 π thermally-allowed-cycloaddition process, with the configuration retained throughout the re-

14) This exceptional distribution of products which slips out of our consistent interpretation does not argue radically against the effectiveness of orbital interaction scheme. The internal conversion of electronic excited state to vibrationally excited state in photolysis take place considerably even in the gas phase. (See Ref. 4a and the references therein.)

15) However there is a communication that the thermolysis of VII yields as a major the recyclization product due to C_α–$C_{\alpha'}$ bond formation against the distribution in the equilibrium. This observation suggests that 4-alkylidene-1-pyrazoline could partially neglect the alkylidene part to behave as 1-pyrazoline. (See Ref. 18c.)



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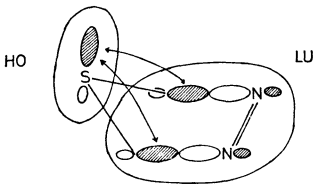
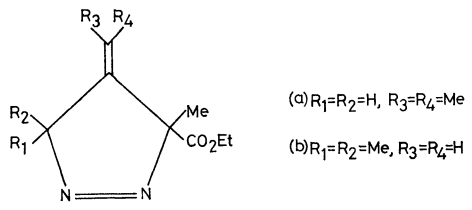


Fig. 5. The mode of orbital interaction in the pyrolysis of thiadiazoline.

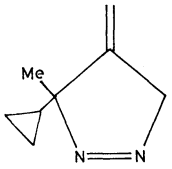
action.[16]

The orbital symmetry assigned to 1-pyrazoline under irradiation is still quite important in any discussion of the photochemical transformation of 4-alkylidene-1-pyrazoline on the grounds that an orbital interaction responsible for weakening C–N bonds is desirable for the incipient orbitals at the carbons to move in the same direction.[17] As a result, the extrusion reaction provides, as a major product, the product arising from the direct bond formation by overlapping between the orbitals which result as the C–N bonds weaken. A few related experiments are known.[18]

In the sensitized reaction, the resultant unpaired electrons with parallel spins have an opportunity to redistribute themselves, which would allow the trimethylenemethane intermediate to reach a stable state. That these reactions occur under the thermodynamical control is supported by the experiment which has demonstrated that the distributions of two possible alkylidenecyclopropanes due to recyclization, originating from VIa and from VIb, are nearly identical.[18] The further the two unpaired electrons with parallel spins are separated from each other, and the greater the extent to which these electrons can be delocalized, the more stable the electronic state becomes. According to this principle, all sorts of unsaturated groups or those substituents with lone-pair electrons, attached to the carbon atom at which an unpaired electron appears, will facilitate



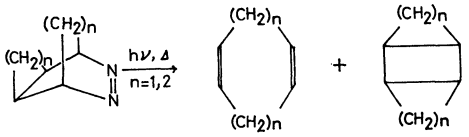
VI



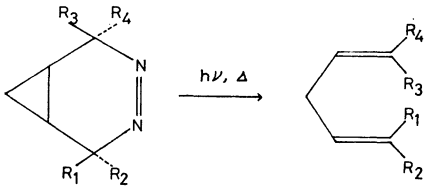
VII

the cyclization. A few experiments are compatible with the results of this discussion, showing that lone pairs at chlorine and at oxygen of the ester group help unpaired electrons to delocalize.[18] With respect to VII, the π character of the cyclopropane ring acts a part corresponding to that of the pure π orbitals.[18c]

The stereochemical behavior of the compounds with one conjugative or strained bond between β and β' carbons will now be discussed. The particularly important orbital interactions in the thermolysis include that between the HOMO (S) of the C_β–$C_{\beta'}$ bond and the LUMO (S) of the C–N bonds and that between the LUMO (A) of the former and the HOMO (A) of the

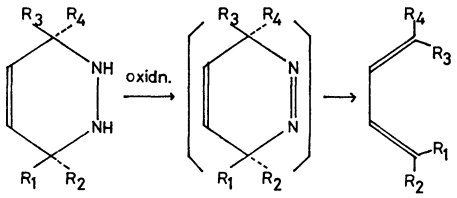


Experiment 1.[19]

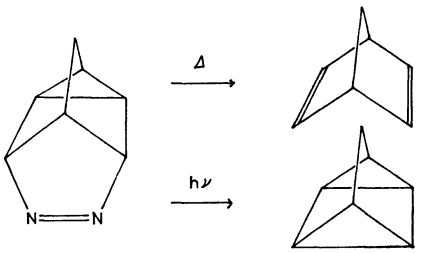


R_1,R_2.R_3,R_4=Me,H

Experiment 2a.[20a]



Experiment 2b.[20b]



Experiment 3.[21]

16) R. M. Kellog, S. Wassenaar, and J. Bunter, *Tetrahedron Lett.*, **1970**, 4689.

17) The orbital interaction identical with that in pyrolysis might also play an important role in these photolysis, since n-π^* excitation at a nitrogen results only in weakening C–N bonds to give the transition state identical with that in thermolysis.

18) a) S. D. Andrews and A. C. Day, *J. Chem. Soc. (B)*, **1968**, 1271; *Chem. Commun.*, **1966**, 667. b) T. Sanjiki, H. Kota, and M. Ohta, *ibid.*, **1968**, 496. c) T. Sanjiki, M. Ohta, and H. Kato, *ibid.*, **1969**, 638.

19) H. Tanida, S. Teratake, Y. Hata, and M. Watanabe, *Tetrahedron Lett.*, **1969**, 5341, 5345, H. Tanida and S. Teratake, *ibid.*, **1970**, 4991; E. V. Allred, J. C. Hinshaw and A. L. Johnson, *J. Amer. Chem. Soc.*, **91**, 3382 (1969).

20) a) J. A. Berson and S. S. Olin, *ibid.*, **92**, 1086 (1970). b) J. A. Berson, *ibid.*, **91**, 777 (1769).

21) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, (1967) p. 230, references cited therein. The analogous reaction are reported in the following paper; L. A. Paquette and L. M. Leichter, *J. Amer. Chem. Soc.*, **92**, 1765 (1970).

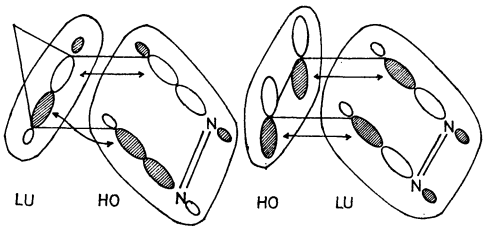


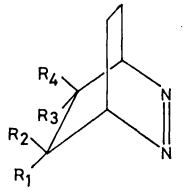
Fig. 6. The mode of orbital interaction in the pyrolysis of bicyclic azo compounds with strained β,β' σ-bond.

Fig. 7. The mode of orbital interaction in the pyrolysis of cyclic azo compounds with a π-bond.

latter. These modes of orbital interaction favor the disrotatory opening of a fused small ring (Fig. 6) or the formation of two π-bonds adjacent to the original π-bond (Fig. 7). These processes accompanying the extrusion are thermally possible (Experiments 1, 2, and 3). The steric paths of the photochemical reactions are complicated by the variable extent to which the photochemically generated SOMO participates directly in the orbital interaction determining the stereochemical course. The initial orbital interaction between the LUMO of the C–N–N–C-bond system and the SOMO of the N–N π-bond may only weaken the C–N bonds, without having any other effects. The HOMO, the level of which must be considerably elevated by this bond weakening, will participate in the interaction with the LUMO of the C_β–$C_{\beta'}$ bond. This orbital interaction is identical with that which operates in the pyrolytic extrusion, leading to the corresponding compounds as well as to thermolysis (Ex. 1 and 2a). The bond formation between the carbons next to the nitrogen (Ex. 1 and 3) may be ascribed to the favorable movement of the atomic orbital lobes in the same direction as was illustrated in connection with the photolysis of 1-pyrazoline (Fig. 2B).

The Compounds Undergoing Cleavage of the Unstrained σ-Bond Bridging between β and β' Carbons

Fig. 8 shows a presumptive energy level relationship between the HOMO and the LUMO of strained and unstrained C_β–$C_{\beta'}$, bonds as well as the C–N-bond system. The reactants with a strained C_β–$C_{\beta'}$ bond could initiate the orbital interaction between the strained bond and the C–N bonds on the weakening of the C–N bonds, for the energy gaps between the frontier orbitals



(a) $R_1=R_3=Me$, $R_2=R_4=H$
(b) $R_1=R_3=H$, $R_2=R_4=Me$

VIII

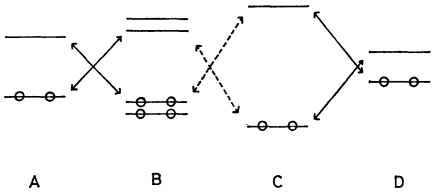


Fig. 8. Estimated energy levels of frontier orbitals of a strained σ-bond (A), two C–N bonds system. (B), an unstrained σ-bond (C) and a quasi-σ-bond (D).

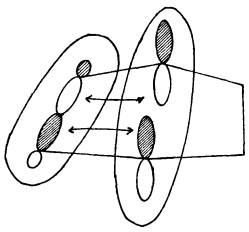


Fig. 9. The mode of orbital interaction in the pyrolysis of cyclic azo compounds with unstrained β,β' σ-bond.

are narrow. In contrast with the strained bond, the level separation between the frontier orbitals of the unstrained bond are so large that the orbital interaction will not be sufficient to break the C_β–$C_{\beta'}$ bond until the C–N bonds become seriously weakened. According to the weakening of the C–N bonds, the appearing orbitals on α carbons come to have an approximate π character. "quasi-π" orbitals can interact with the unstrained C_β–$C_{\beta'}$ bond to cause the fission. The assignment of the orbital lobes and the mode of division of the reactant are analogous to the ring opening of cyclobutene, as is depicted in Fig. 9. This illustration explains the conrotatory bond scission of the unstrained bond in the pyrolysis.[22]

Remarks

The stereospecificity of the extrusion reactions of cyclic azo compounds, which seems to be chaotic, is found to be put into order comprehensively under the government of orbital interaction between the relevant parts in the molecule. During a consideration on the basis of orbital interaction we have found that the parts between which the orbital interaction should be considered to determined the stereochemical course are variable, even in the reaction of similar compounds, and that thermal and photochemical reactions are not always counterparts of each other in the sense of stereospecificity.

22) W. R. Roth and M. Martin, *Tetrahedron Lett.*, **1967**, 3865. It is meaningful to refer to the thermolysis of a bicyclo[2.1.0]pentane derivative. The mechanism is proposed by the reporters that the compound undergoes conrotatory ring opening after the bridge bond cleaves to produce cyclopentane-1,3-diyl biradical; J. A. Berson, W. Bauer, and M. M. Campbell, *J. Amer. Chem. Soc.*, **92**, 7515 (1970).