Molecular Orbital View of the Stereochemical Behavior in the Interaction of Bicyclo[2.1.0]pentane and Unsaturated Molecules[1a]

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Abstract: Bicyclo[2.1.0]pentane exhibits unusual stereochemistry: alkenes and alkynes add across the bridge by approach into the fold of the C_5 system, and 2,3-diazabicyclo[2.2.1]hept-2-ene dissociates to N_2 and a net inverted bicyclopentane. While much of the experimental data favor stepwise mechanisms for these reactions, a concerted mechanism described here can account for the stereochemistry in these systems.

The bicyclo[2.1.0]pentane system participates in two related reactions of novel stereochemistry. Alkenes are observed to approach the bridge bond of system from "below" as they add, rather than from above the bridge, although the latter path would seem to be favored by steric influences.[2] Further, the decomposition of 1,2-diazabicyclo[2.2.1]-2-heptene yields molecular nitrogen and a net inverted bicyclo[2.1.0]pentane, regardless of the fact that inversion of the bicyclopentane alone is not facile.[3] The purpose of this report is to provide a rationale for this behavior in the context of approximate molecular orbital theory. We shall see that recognition of local bonding strength is essential to an understanding of the experimental data.

Bonding in Bicyclo[2.1.0]pentane

The discussion of bonding in bicyclo[2.1.0]pentane is simplified by reference to a correlation diagram representing the formation of bicyclopentane from cyclobutene and a singlet methylene (Figures 1 and 5). The details of the path of approach of the "reactants" have been discussed in general elsewhere[4] and need not concern us here. We are more interested in the reorganization of charge attending their approach. The reorganization may be presented in two ways: by direct comparison of the density function of the noninteracting and the interacting species, or by a projection of the molecular wave function onto the basis set provided by the molecular orbitals of the noninteracting fragments. (These and other computations are described in the computations section.) Figures 2 and 3 are contour diagrams of the molecular charge distribution in a plane bisecting the dihedral angle of the bicyclic system, for (a) a mythical species with the same geometry as bicyclopentane, but with a charge distribution which is a superposition of the charge distributions of the ground states of noninteracting cyclobutene and methylene fragments, and (b) essentially an unperturbed bicyclopentane. Figure 4 expresses the difference between these two charge distributions. The diagrams make apparent a *depletion* of charge below the bridge attending the interaction of the fragments as bicyclopentane is formed. The details of the depletion can be expressed in terms of the population of antibonding orbitals in the independent-fragment basis (Table I). In order that bicyclopentane is formed, substantial population of the p-type orbital vacant in the ground state of the singlet methylene is essential. Accompanying this promotion of charge is a population of a combination of antibonding MO's of the cyclobutene species which represent a bent antibonding region below the bridge of the bicyclic species. This situation is given a schematic form in Figure 5. It cannot be said that the space below the bridge is antibonding, but the weak bonding in that region is represented in the independent fragment basis as the result of a population of antibonding orbitals comparable with the population of bonding orbitals in that area. As we shall see, shifts of population among bonding and antibonding MO's in the neighborhood of the bridge provide a convenient way to express charge reorganization during nuclear motions.

Table I. Projection of Bicyclopentene Wave Functions on a Cyclobutene–Methylene Basis of MO's[a]

	BCP				
	A1	A2	A3	A4	A5
CB:A1	0.9709	0.1594	−0.0718	−0.1136	−0.0828
CB:A2	−0.0757	0.9078	0.2427	0.2650	0.1618
CB:A3	−0.0255	0.1054	−0.9167	0.3490	0.1429
CB:A4	−0.0229	0.0709	−0.1139	−0.6500	0.7383
M:Al	−0.2188	0.3433	−0.2503	−0.4798	−0.4038
CB:A5*	−0.0434	0.1100	−0.1228	−0.3328	−0.4407
CB:A6*	−0.0247	0.0605	−0.0644	−0.1654	−0.1988

[a] BCP means *bic*yclo*p*entane; the five occupied antisymmetric MO's are expanded in terms of antisymmetric MO's of cyclobutene (CB) and methylene (M). M:A1 designates the antisymmetric MO comprised entirely of a carbon p orbital on methylene. CB:A5* is an MO of cyclobutene, localized at the bridge, antibonding in a π fashion; CB:A6* is a similarly localized σ antibonding MO. The combination $-[0.2\text{CB:A6}^* + 0.45\text{CB:A5}^*]$ can be considered the antibonding "banana bond" indicated to be occupied in the schematic correlation diagram, Figure 5.

Inversion of Bicyclo[2.1.0]pentane

In bicyclopentane, the bonding above the bridge is markedly different from the bonding below the bridge.

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[1] (a) Work supported by grants from the Petroleum Research Fund of the American Chemical Society (1830-G2) and the Research Corporation; (b) A. P. Sloan Fellow, 1971–1973.

[2] P. G. Gassman, K. T. Mansfield, and T. J. Murphy, *J. Amer. Chem. Soc.*, **91**, 1684 (1969).

[3] (a) W. R. Roth and M. Martin, *Tetrahedron Lett.*, 47, 4695 (1967); *Justus Liebigs Ann. Chem.*, 702, 1 (1967); (b) E. L. Allred and R. L. Smith, *J. Amer. Chem. Soc.*, **91**, 6766 (1969); (c) A. B. Evnin, D. R. Arnold, L. A. Karnischky, and E. Strom, *ibid.*, **92**, 6218 (1970), and references cited therein.

[4] R. Hoffmann, *ibid.*, 90, 1475 (1968).

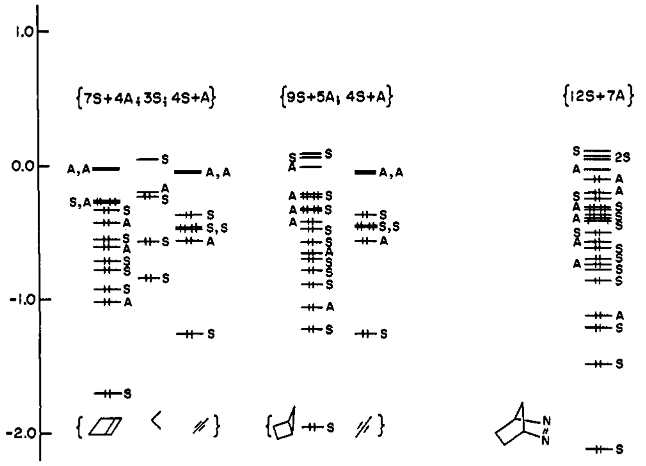

Figure 1. The assembly of 2,3-diazabicyclo[2.2.1]-2-heptene from cyclobutene, methylene, and molecular nitrogen is illustrated by a correlation diagram. The steps shown both involve changes in the symmetry species of the set of occupied orbitals and thus are thermally forbidden as written.

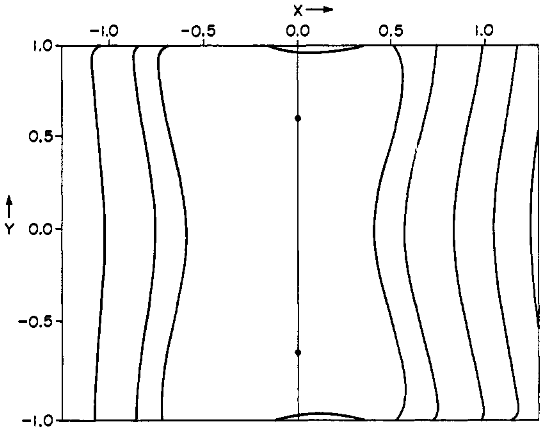

Figure 2. The density in the plane defined by the CN vectors in the region between the eventual bridgehead carbons for 2,3-diazabicyclo[2.2.1]-2-heptene is shown, for a mythical system in which the nuclei are placed at the bicycloheptene system geometry, but contribute charge distributions typical of the isolated fragments cyclobutene, methylene (singlet), and nitrogen. The vertical line represents the vector between bridgehead carbons; the nitrogens lie off the figure at the right, at $X = 1.5$, $Y = \pm 0.75$.

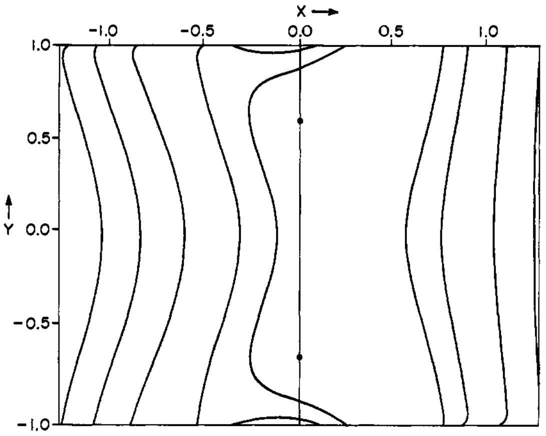

Figure 3. The density in the region between bridgehead carbons is shown in the plane of the C–N vectors, for a mythical system composed of bicyclo[2.1.0]pentane and molecular nitrogen, with all atoms placed at bicycloheptene positions. The vertical line represents the vector between bridgehead carbons.

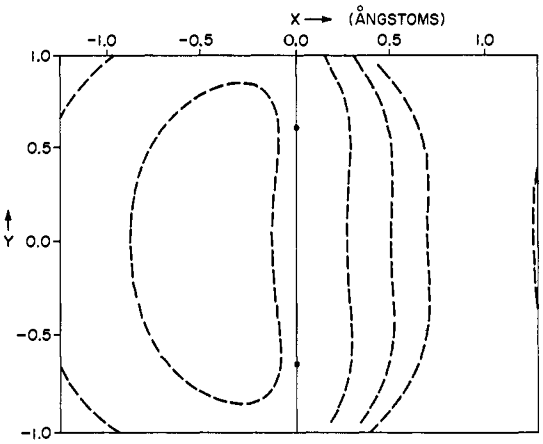

Figure 4a. The difference in density between the bicyclo[2.1.0]-pentane–nitrogen and the cyclobutene–methylene–nitrogen system shows that the formation of bicyclopentane is accompanied by a depletion of charge *below* the bridge. The scale for this figure is identical with the scale of previous figures.

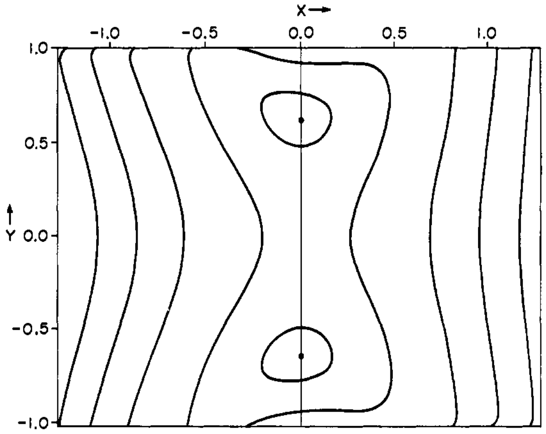

Figure 4b. The density plot for 2,3-diazabicyclo[2.2.1]-2-heptene shows that the C–N bond formation depletes the charge distribution *above* the bridge of the C_5 fragment. This depletion can be accommodated by attack of the C_5 fragment below its bridge and its subsequent inversion (see text).

The charge distribution below the bridge has a considerable antibonding component. The nodal structures of the two interconverting species are quite different, a fact reflected by a low value of the state overlap between the two species' wave functions.[5] The correlation between state overlap and ease of reaction indicates that the inversion is probably opposed by a substantial energy barrier.[6] For a methyl-substituted bicyclopentane, the barrier is observed to be on the order of 30 kcal/mol.[7] The difficulty lies in forcing the antibonding component of the charge distribution into a region where strong bonding was formerly enjoyed.

It is possible to trace the passage of the antibonding component of the bridgehead carbon–carbon interaction as the bicyclopentane molecule inverts by a series of SCF–CI computations in which the dominant "excited" configuration contains a doubly occupied orbital with a node between the bridgehead carbons.

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(5) C. Trindle, *J. Amer. Chem. Soc.*, **92**, 3251, 3255 (1970).

(6) C. Trindle and F. S. Collins, *Int. J. Quantum Chem.*, **4**, 195 (1971), and unpublished work.

(7) J. P. Chesick, *J. Amer. Chem. Soc.*, **84**, 3250 (1962).

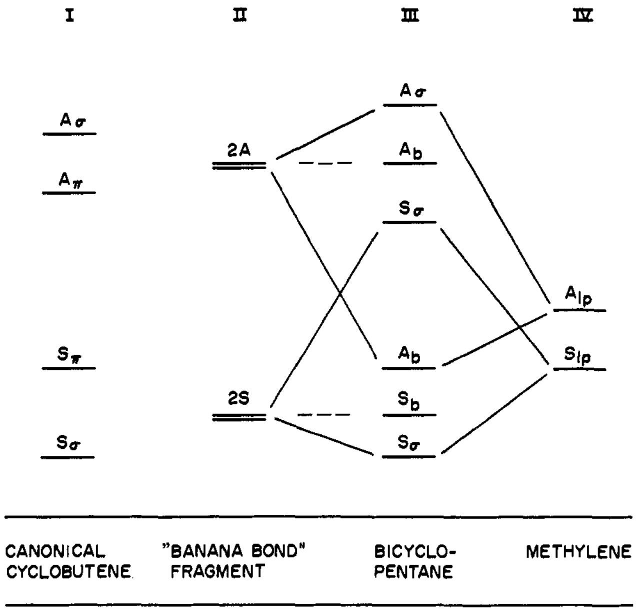

Figure 5. A schematic representation of the charge reorganization as bicyclo[2.1.0]pentane is formed from cyclobutene and the excited $(A^*)^2$ state of methylene. Only the cyclobutene σ and π components of the double bond and the methylene lone-pair-type orbitals are shown. When the σ and π portions of the double bond are transferred to bent bonds, the interaction with methylene alters only one of the bent bonds significantly. The bent bond "below" the forming bridge is weakened by the superposition of the corresponding antibonding orbital.

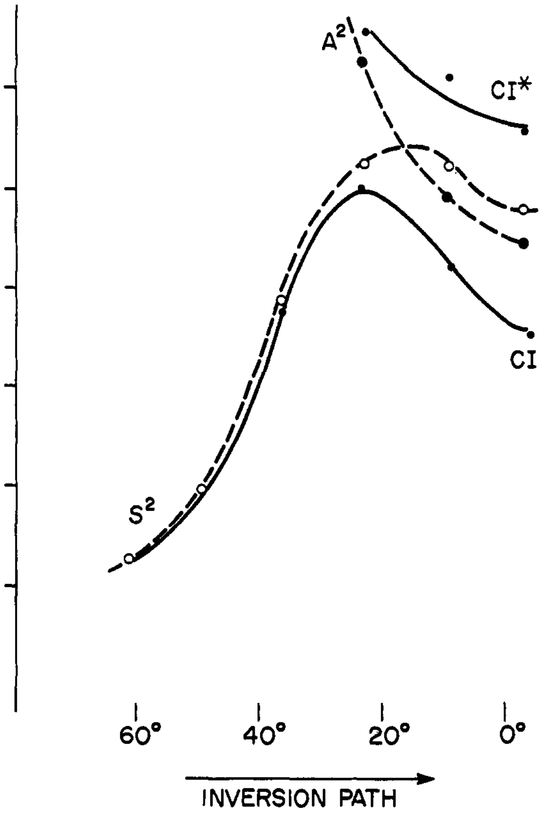

Figure 6. The inversion of bicyclo[2.1.0]pentane is accompanied by the population of a configuration (A^2) in which the interaction across the bridge is antibonding, and the depopulation of the configuration (S^2) in which a bonding interaction is maintained across the bridge. At the planar intermediate geometry the interaction across the bridge is very slight, so the system may be termed a "diradical."

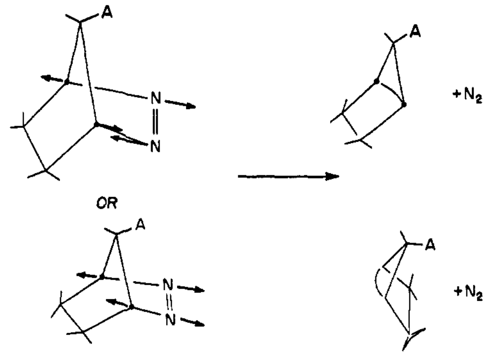

Figure 7. Inspection of low-energy excitations in the manner of Salem and Wright[10] leads to the prediction of two likely modes of dissociation of 2,3-diazabicyclo[2.2.1]-2-heptene to bicyclo[2.1.0]pentane and molecular nitrogen. One motion is basically an antisymmetric stretch of the CN bonds, indicating a stepwise dissociation. The other possible motion is the symmetric CN stretch, implying a possible concerted dissociation and inversion.

In the normal bent geometry of bicyclopentane this excited configuration makes only a small contribution to the total charge distribution, which is virtually unchanged from the SCF charge distribution shown in Figure 3. However, as the molecule is bent, the energy of the excited configuration approaches the energy of the configuration in which bonding is maintained between the bridgehead carbons, and when the molecule attains planarity, the configuration permitting bridge bonding is *less* stable than the configuration prohibiting bridge bonding. In the sense that the symmetry species of the orbitals in the most stable single determinant changes as bicyclopentane is forced into planarity, the process is symmetry forbidden in the usage of Woodward and Hoffmann.[8] The two configurations (which are of the same *state* symmetry) mix considerably, and the CI wave function for the planar species contains almost equal weights of each configuration. There is virtually zero interaction between the bridgehead carbons in the two-configuration wave function, so that the system may be called a "diradical." Diradical intermediates have played an important role in mechanistic speculation on the reactions of bicyclopentane derivatives, and our computations indicate (Figure 6) that a planar form is a true intermediate, occupying a local minimum on the system potential energy surface. The inversion itself is unlikely to be a concerted process.

Formation of Bicyclo[2.1.0]pentane from 2,3-Diazabicyclo[2.2.1]-2-heptene

The molecule 2,3-diazbicyclo[2.2.1]-2-heptene dissociates to molecular nitrogen and bicyclo[2.1.0]pentane, under thermal or photochemical stimulus[3a,b] (Figure 7). The process transforms the two C–N bonds, of symmetry species S (symmetric) + A (antisymmetric) to a π bond of N_2, symmetric with respect to the plane of symmetry, and an antisymmetric region between the bridgehead carbons of the remaining five-carbon fragment. For this reason the dissociation is considered to be symmetry forbidden and not concerted under thermal conditions, and stepwise mechanisms are proposed, though kinetic data seem to

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[8] R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie-Academic Press, Weinheim, 1970.

indicate that both CN bonds are breaking in the rate-determining step.[3b] The curious feature of this symmetry-violating dissociation is that it is accompanied by the symmetry-violating inversion of the five-carbon fragment. It is worth noting that inversion is not perfect, but that inverted bicyclopentane exceeds noninverted bicyclopentane in the dissociation products. "[The] inversion is a consequence of recoil from energy released by CN bond breaking" according to Allred and Smith.[3b] The meaning of this statement is not altogether clear, since bond breaking would seem to *require* energy, not liberate it. The energy supplied to the system in *excess* of the bond breaking energy would conceivably lead to inversion. The departure of N_2 can be considered to exert a third-law reaction force on the five-carbon fragment tending to induce an inversion, according to Newtonian mechanics. To pursue this argument requires a rather drastic assumption that the single molecule of diazabicycloheptene can be considered free of collisions which might divert the reaction force, during the dissociation. Application of this assumption to slow chemical reactions occurring in the liquid phase is not very plausible; still the proposal bears examination because of the availability of data on the gas-phase reaction.

Let us consider that molecular nitrogen attains its root-mean-square gas velocity at 300°K upon dissociation, $(8RT/\pi M)^{1/2}$ according to kinetic theory, and that the acceleration to this velocity requires a single vibrational period, of roughly 10^{-12} sec. The impulsive force $F = \Delta(\text{momentum})/\Delta(\text{time})$ on the N_2 is then *ca.* 6.2×10^{-4} dyn. This force must match or exceed the force opposing the inversion; if the inversion barrier is 30 kcal/mol and the passage from bent to planar bicyclopentane requires a motion of roughly 1 Å, then the force opposing inversion, $F = -\Delta(\text{potential})/\Delta(\text{position})$, is on the order of 0.21 dyn. The impulsive force is far from adequate to induce inversion, unless the inversion barrier is reduced by some independent mechanism—presumably electronic—by at least 100-fold. Since a diradical five-carbon fragment, with a low barrier to inversion, enters much of the mechanistic speculation, it is appropriate to consider whether the impulse proposal is tenable for a molecule of this nature. It is quite likely that the Newtonian force of reaction is sufficient to surmount a very low barrier. The question remains whether one would observe a preference for the initially formed inverted species. In order for the inverted species to be stabilized, a substantial amount of energy must be transferred away from the five-carbon fragment by collisions. However, it is well known that small amounts of energy can be transferred much more efficiently than large amounts.[9] Therefore, we must conclude that collisions are much more likely to cause loss of the inverted configuration (a low energy process) than to efficiently carry away tens of kilocalories necessary to trap the initially formed inverted species. This conclusion applies regardless of the frequency of collision, so we are led to expect a statistical distribution of inverted and noninverted bicyclopentane insofar as the reaction dynamics influence this result. This conclusion supports the generalization that effects of reaction *dynamics* are frequently small relative to effects of the potential surface itself.

In order to account for the tendency of the five-carbon fragment to invert as nitrogen departs, we consider the antibonding component of the charge distribution of the dissociating species contributed by the former antisymmetric combination of the CN bond orbitals. Expressing that antisymmetric combination in the basis set provided by the independent fragments, we find that the antibonding π MO of cyclobutene corresponding closely to the CC π bond is the most important single representative of the antibonding component of the charge distribution. The introduction of an antibonding component of charge between the bridgehead carbons can be accomodated by a nuclear motion of the five-carbon system toward planarity, where the configuration maintaining antibonding between bridgehead carbons is the most stable single-determinant state. Since the ground state of the planar C_5 fragment and the ground state of N_2 are generated by the combination of concerted CN bond breaking and assumption of planarity by the C_5 species, the process is symmetry allowed, under thermal conditions. This is not to say that the reaction will be fast, since there is considerable contamination of the symmetry species of the set of orbitals occupied in the planar bicyclopentane, due to the marked CI.

If the planar C_5 fragment and N_2 were formed and separated, and the isolated planar C_5 sought out the more stable bent form, one would expect a 50:50 mixture of the possible bent species, after due allowance was made for thermodynamic equilibration. This is observed at low pressure; at high pressure, or in the liquid state, a net inversion is found. A possible explanation of this puzzle requires the assumption that N_2 is still interacting with the C_5 product when the latter has achieved its planar configuration. High pressure or a condensed phase would encourage N_2 to remain in the neighborhood of the five-carbon fragment. If N_2 can still interact with bicyclopentane, it exerts an attractive force on the antibonding component of the bridge-region charge distribution. The system can simultaneously seek out a stable bent form of bicyclopentane and accommodate the attraction of N_2 for the antibonding component by placing the antibonding component *below* the bridge, on the *nitrogen* side.

These qualitative remarks are supported by a series of SCF computations on the system bicyclopentane–nitrogen with N_2 at distances above and below the bridge of 3.5–7.5 Å. Even at quite long range, the arrangement of N_2 below the bridge is favored by 5–10 kcal. The electronic portion of the energy is responsible for this curious result, since the underbridge form is opposed strongly by nuclear- and core-repulsion energy terms. We conclude that the influence of the departing nitrogen is such to continue the inversion motion initiated by the symmetry conditions. The experimental data supplied by Roth and Martin[3a] are consistent with this proposal, since they observe that inversion is not marked at low pressure (where the escape of N_2 is not hindered by frequent collisions) but becomes apparent at higher pressure or in the liquid phase.

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(9) For example, inelastic cross sections for rotational energy transfer far exceed the inelastic cross sections for vibrational energy transfer: T. L. Cottrell and J. C. McCoubrey, "Molecular Energy Transfer in Gases," Butterworths, London, 1961.

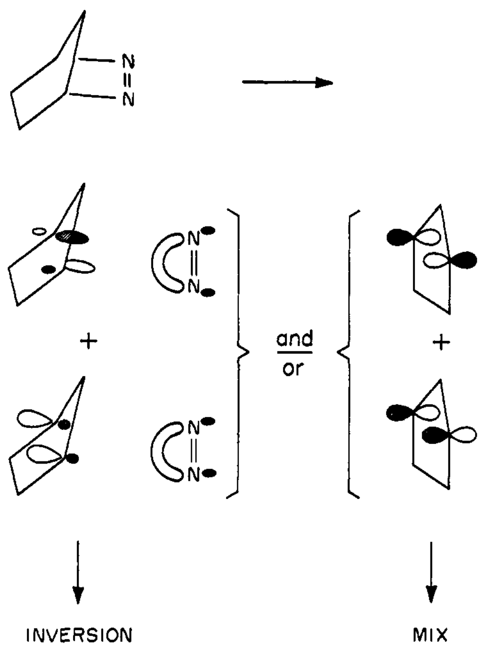

Figure 8. The observation of *net* but incomplete inversion of the C_5 fragment in the dissociation of 2,3-diazabicyclo[2.2.1]-2-heptene can be rationalized by the presumption that the departing N_2 exerts a small attractive force on the antisymmetric orbital localized at the bridge (see text).

While we have discerned a possible concerted path for the dissociation of 2,3-diazabicyclo[2.2.1]-2-heptene, it is not possible to rule out a competing nonconcerted path. To deal with this problem in a qualitative manner, we employ the transition density analysis of Salem and Wright.[10] In a few words, these authors propose that the easiest motion for any molecular system will have its largest amplitude in the region of the molecule where $\langle\psi_{\mathrm{HO}}|\psi_{\mathrm{LU}}\rangle$ is largest. Here ψ_{HO} means one of the highest energy occupied MO's, and ψ_{LU} means one of the lowest energy vacant MO's. There may be several contributions to the transition density which have comparable $(E_{\mathrm{LU}} - E_{\mathrm{HO}})^{-1}$ factors and amplitudes and which would, therefore, be of similar importance according to perturbation–theoretic criteria. In the present application we find two major contributions to the transition density (Figure 7). The first leads to an antisymmetric stretch of the two CN bonds, with negligible inversion. A large excursion in this mode would lead to a breaking of one CN bond at a time, clearly a nonconcerted dissociation. The second contribution to the transition density implies easy motion in a symmetric stretching of the CN bonds, accompanied by an inversion of the C_5 fragment. This motion is, of course, the proposed concerted dissociation–inversion (Figure 8). Since Salem and Wright's guide to low energy motion is useful mainly for qualitative argument, we can safely assume only that the two types of motion compete, without estimating which would dominate. However, the kinetic indication that both CN bonds break in the rate-determining step[3b] seems to favor the concerted process.

Approach of Alkenes to Bicyclo[2.1.0]pentane

It is experimentally established that alkenes and alkynes add to the bicyclopentane bridge from underneath and that addition is stepwise. The distribution of addition products reported by Gassman[2] indicates that addition follows the antisymmetric path referred to in the retroaddition in section IV. The underbridge addition is easily explained as deriving from the attraction of a double or triple bond of alkenes, alkynes, or nitrogen molecule for the antibonding component of the bridge charge distribution, which is located under the bridge. In other words, the formation of an S + A combination of CC bonds in the addition requires the introduction of an antisymmetric portion of the wave function; this is most easily accomplished where the bonding is weak.

Although the path followed by the addition of unsaturated hydrocarbons to bicyclopentane is not the same path followed by the retroaddition of nitrogen and bicyclopentane, this fact does not violate the principle of microscopic reversibility. First, the systems are different; second, although Gassman's data are easily interpreted to indicate stepwise addition, it does not rule out the possibility that both symmetric- and antisymmetric-path additions occur, if the symmetric-path addition is faster.

Summary

A concerted path for the decomposition of 2,3-diazabicyclo[2.2.1]-2-heptene to nitrogen and an inverted bicyclo[2.1.0]pentane is proposed and rationalized in the light of approximate MO theory. This concerted path and a stepwise path appear to be in competition. Experimental data do not rule out the concerted process for decomposition of diazabicycloheptene, but the path for addition of alkenes and alkynes to bicyclopentane is probably nonconcerted.

Details of Computations

Molecular orbital computations reported here were all based on the CNDO formalism. The program CNINDO written by Pople and Dobosh and distributed by the Quantum Chemistry Program Exchange[11] was used, after translation to Burroughs ALGOL by Peter W. Lert and C. T. Configuration interaction computations are based on an ALGOL coding of Cizek's formulation of CI matrix elements,[12] C. T. Density computations employed a simplified version of Rosenfeld's very general program[13] constructed by F. P. Billingsley, and contour plots were constructed with the aid of a plotter program by D. D. Shillady and F. P. Billingsley.

The geometries chosen were idealized; all CC bonds were assigned a length of 1.5 Å, and all CH bonds were assigned a length of 1.1 Å. (This sort of approximation can affect the computed energy considerably, but should have little effect on the qualitative features of the bonding stressed in this study.) The dihedral angle of bicyclopentane was taken to be 60°. The planar C_5 framework was assumed to be a regular pentagon, and the calculations describing the inversion barrier were made at geometries fixed by linear interpolation between the bent and planar forms.

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(10) L. Salem and J. S. Wright, *J. Amer. Chem. Soc.*, **91**, 5947 (1969).

(11) CNINDO by J. A. Pople and P. Dobosh, Quantum Chemistry Program Exchange, No. 91; Chemistry Department, Indiana University, Bloomington, Ind. 47001.

(12) J. Cizek, *Theor. Chim. Acta*, 6, 292 (1966).

(13) J. L. J. Rosenfeld, "Electron Distribution and Chemical Bonding," Technical Report 13, Institute of Theoretical Physics, University of Stockholm, Stockholm, Sweden, April 1963.

In the C_5N_2 species the N–N distance is 1.2 Å and the C–N distance is again 1.5 Å.

The representation of MO's of a molecule in terms of the MO's of independent fragments is a straightforward computation in the zero-differential overlap approximation. It should be noted that the MO's are determined for *isolated* fragments, but then translated so that the atomic orbitals in which the MO's are expressed are superimposed on corresponding AO's of the molecule in question. Under these conditions the expansion coefficients a_{ij} in the relation below are easy to evalulate. Here $\phi_{\mathrm{M}i}$ is the ith MO of the

$$\phi_{\mathrm{M}i} = \sum_j \alpha_{ij}\omega_{\mathrm{F}j}$$

molecule and $\psi_{\mathrm{F}j}$ is the jth MO of the set of fragments: let $\alpha_{\mathrm{M}i} = \Sigma_\mu c_{i\mu}{}^{\mathrm{M}}\chi_\mu{}^{\mathrm{M}}$ and $\psi_{\mathrm{F}j} = \Sigma_\nu C_{j\nu}{}^{\mathrm{F}}\chi_\nu{}^{\mathrm{F}}$ where C's are expansion coefficients and χ_μ's are AO's; then

$$a_{ij} = \langle\phi_{\mathrm{M}i}|\psi_{\mathrm{F}j}\rangle = \sum_{\mu\nu} C_{i\mu}{}^{\mathrm{M}}C_{j\nu}{}^{\mathrm{F}}\langle\chi_\mu{}^{\mathrm{M}}|\chi_\nu{}^{\mathrm{F}}\rangle$$

Since $\{\chi_\mu{}^{\mathrm{M}}\} = \{\chi_\nu{}^{\mathrm{F}}\}$ according to the argument above, and the zero-differential-overlap approximation is applied

$$a_{ij} = \sum_\mu C_{i\mu}{}^{\mathrm{M}}C_{j\nu}{}^{\mathrm{F}}$$

The values of a indicate to what extent a fragment MO is populated in the course of molecule formation.

A portion of the projection matrix a is reproduced in Table I, for the cyclobutene–methylene/bicyclo[2.1.0]pentane system as corroboration of the schematic correlation diagram, Figure 5.

Axial–Equatorial Energy Difference in Cyclohexyl Fluoride from Rotational Transition Intensity Measurements

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Abstract: Relative intensities of rotational transitions of the axial and equatorial conformers of cyclohexyl fluoride were measured to determine the energy difference of 259 ± 28 cal/mol between the vibrational ground states. Partial power saturation of the transitions was used to increase the signal strength and to eliminate the dependence of the peak absorption coefficient on the transition line width. Differences in the rotational partition functions convert this energy difference to a free energy difference of 298 ± 28 cal/mol at 187°K. Differences in the vibrational partition functions can only be approximated but should be such that this free energy difference is reduced by 50 cal/mol or less. Within the combined error limits, the gas-phase free-energy difference is the same as that determined in solution by nmr: 276 ± 15 cal/mol from proton area ratio measurements in CS_2, 248 ± 12 cal/mol from fluorine area ratio measurements in $CClF_3$.

The equilibrium between the axial and equatorial conformers of cyclohexyl fluoride has been studied by electron diffraction,[1] nuclear magnetic resonance (nmr),[2–5] and microwave rotational spectroscopy.[6,7] For both conformers, the microwave study determined structural parameters and the magnitude and orientation of the dipole moment. Less definitive, however, was the value of 400 ± 300 cal/mol found for the conformational energy difference from rotational transition intensity measurements. The large error limit does not permit a critical comparison of this value to data obtained by other techniques. An uncertainty of this magnitude was most likely due to the stated[7] weak intensities. To allow a comparison of the microwave value of the energy difference to results from other methods, a more accurate study of transition intensities in cyclohexyl fluoride has been done and the conclusions are reported here. Particularly interesting is the fact that there is little if any difference in the conformational free-energy difference in the gas phase and in solution.

In the previous study,[7] the ratios of unsaturated peak intensity coefficients γ_0 were determined using the experimental procedure described by Esbitt and Wilson.[8] To extract the conformational energy difference from these data, it was necessary to assume that the line widths of the compared transitions were equal. In the present study, the approach used was that of Harrington[9,10] who introduced an intensity coefficient Γ and considered its properties, particularly its dependence on microwave power density. He found that under certain conditions of power saturation, the signal at a peak absorption frequency is directly proportional to the population density of the lower level of the transition. These conditions also yield a significant increase in signal strength over that obtained in measurements of γ_0. The latter measurements must be made at low power levels to ensure that the power-dependent coefficient γ has reached its limiting value γ_0. For a

(1) P. Andersen, *Acta Chem. Scand.*, **16**, 2337 (1962).

(2) A. J. Berlin and F. R. Jensen, *Chem. Ind. (London)*, 998 (1960).

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