

4d. In this connection our data³⁹ for the reaction of **21** with nitrous acid revealed only backside migration of Ph* (the asterisk denotes that the phenyl is labeled with carbon-14) with inversion at the migration terminus, a result we explained³⁹ by invoking ground-state control of product formation and restricted rotation about the C-C⁺ bond.

The cations formed during reaction of nitrous acid with the various substituted norbornylamines we investigated⁴⁷⁻⁵¹ undergo reactions which are not observed when cations of presumably identical structures are formed on solvolyses.⁵³ Further, their unusual character is preserved through one or several Wagner-Meerwein rearrangements or 6,2-hydride shifts. For example, endo attack by anion can occur *after* Wagner-Meerwein rearrangement (Charts VI and VII); even after five or six such consecutive shifts (Chart IX, cations A and B) complete nonclassical character has not yet been attained. Since a "hot" carbonium ion

(53) C. J. Collins and B. M. Benjamin, *J. Amer. Chem. Soc.*, **89**, 1652 (1967); **88**, 1558 (1966).

by definition⁹ undergoes no charge delocalization and *directly* produces only unrearranged product, then none of the cations designated in Charts VI-IX—except possibly those formed *directly* on decomposition of the diazonium ion—can be "hot" carbonium ions.

If these cations are neither "hot" nor nonclassical, the question as to how best to describe them still remains. We believe the answer to this question is to be found in ion-pairing phenomena, for the anion directly formed on decomposition of an aliphatic diazonium hydroxide (or acetate) not only is part of an ion pair but predominantly collapses²⁷ with the cation to yield product, quite in contrast to the situation which exists during solvolyses.⁵⁴ The "memory effects"³² observed in our work (Charts VII-IX) are explainable through ion pairs in which the two partners are differently oriented, depending upon the structure of the starting material.

(54) S. Winstein, E. Clippinger, A. H. Fainberg, and G. C. Robinson, *ibid.*, **76**, 2597 (1954); S. Winstein and A. H. Fainberg, *ibid.*, **80**, 459 (1958).

Narcissistic Reactions: Synchronism vs. Nonsynchronism in Automerizations and Enantiomerizations

LIONEL SALEM

Laboratoire de Chimie Théorique,† Université de Paris-Sud, Centre d'Orsay, 91-Orsay, France

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Reactions Which Are Equivalent to Pure Reflection

The year 1970 may mark the beginning of an era in which the very concept of organic reaction will undergo a profound change. There are indications that the beautiful mechanistic schemes used by organic chemists to interpret organic reactions will slowly be supplemented and may eventually be replaced by a detailed picture of the dynamic behavior of the reacting species on a complex potential energy surface. Extremely small, but often highly instructive, fragments of potential energy surfaces for some elementary organic reactions have already been calculated both by semi-empirical¹ and by *ab initio*² methods. In the coming

years one can confidently predict the total resolution of several organic transition states and of the potential surfaces surrounding them as well as preliminary calculations of the dynamical pathways on these surfaces.

Major difficulties in these quantum-mechanical calculations are the many dimensions of the potential surface (30 for as small a molecule as cyclobutane) and the awkward fact that, unlike reactant or product, the transition state is not an absolute energy minimum on the surface. Thus *any* simplifying feature in the search for the transition state—even for a restricted class of reactions—should be extremely precious. We shall investigate a family of reactions where two types of pathways, synchronous and nonsynchronous, can be distinguished, and where for one of these (synchronous) an extremely useful constraint is imposed on the reaction midpoint. This family includes all reactions which are equivalent to pure reflection.

Organic chemists have long been aware—probably

† The Laboratoire de Chimie Théorique is also part of the Laboratoire de Physico-Chimie des Rayonnements associated with the CNRS.

(1) (a) M. V. Basilevsky, *Dokl. Akad. Nauk SSSR*, **172**, 881 (1967); (b) M. Simonetta, G. Favini, C. Mariani, and R. Gramaccioni, *J. Amer. Chem. Soc.*, **90**, 1280 (1968); (c) R. Hoffmann, *ibid.*, **90**, 1475 (1968); R. Hoffmann, S. Swaminathan, B. G. Odell, and R. Gleiter, *ibid.*, **92**, 7091 (1970); R. Hoffmann, C. C. Wan, and V. Neagu, *Mol. Phys.*, **19**, 113 (1970); (d) A. M. Wooley and M. S. Child, *ibid.*, **19**, 625 (1970); (e) M. J. S. Dewar, E. Haselbach, and M. Shanshal, *J. Amer. Chem. Soc.*, **92**, 3505 (1970); (f) R. Bonaccorsi, E. Scrocco, and J. Tomasi, *J. Chem. Phys.*, **52**, 5270 (1970); (g) W. Th. A. M. van der Lugt and L. J. Oosterhoff, *Chem. Commun.*, 1235 (1968); *J. Amer. Chem. Soc.*, **91**, 6042 (1969).

(2) (a) D. T. Clark and D. R. Armstrong, *Theor. Chim. Acta*, **13**, 365 (1969); (b) G. Berthier, D. J. David, and A. Veillard, *ibid.*, **14**, 329 (1969); (c) K. Hsu, R. J. Buenker, and S. D. Peyerimhoff, *J. Amer. Chem. Soc.*, **93**, 2117 (1971); (d) A. Devaquet and L. Salem, *Can. J. Chem.*, **49**, 977 (1971).

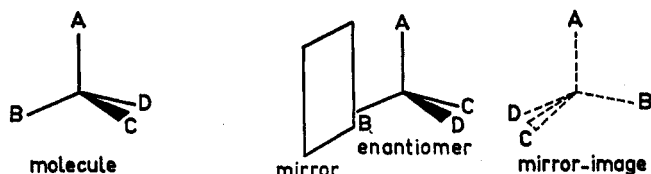


Figure 1. Molecule, enantiomer, and mirror image (the enantiomer cannot be obtained directly by reflecting the molecule in a mirror plane but can easily be brought into coincidence with any mirror image such as that shown).

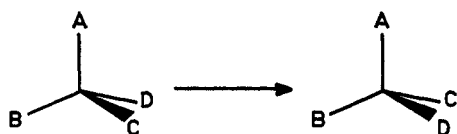


Figure 2. The enantiomerization process drawn in the conventional manner.

since the days of Pasteur—that a molecule and its enantiomer side by side can be considered as mirror images. In actual fact the enantiomer may not coincide directly with any mirror image and appropriate translation and/or rotation may be required to obtain this coincidence (see Figure 1). The relationship of enantiomers has received considerable attention in recent years with the development of a coherent theory of chirality.³ Less thought, perhaps, has been devoted to the pathways of the reactions which lead from molecules to their enantiomers or even to simpler, related automerizations. These reactions possess an apparently trivial but important property.

Although product and reactant are always written side by side for convenience (Figure 2), in the actual enantiomerization process the reactant and product constitute a single molecule occupying a given volume. If the reaction does not involve overall rotation or translation,⁴ the product enantiomer actually coincides with the image of the reactant molecule with respect to a fixed mirror plane. This plane appears clearly if we superpose the product (dotted lines) onto the reactant, as is shown in Figure 3. It is unique for the assumed reaction, which has interchanged the positions of C and D relative to the plane passing through A, B, and the center. Such a reaction is therefore equivalent to pure reflection in the fixed mirror plane.

Reactions which are equivalent to pure reflection are the central topic of this Account; a good deal can be said about their reaction pathways. Such reactions have been termed "narcissistic reactions."⁵ The position

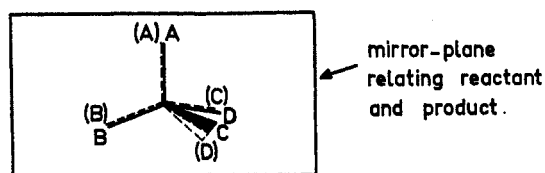


Figure 3. Reaction process drawn with reactant (full lines) and product (dotted lines) superimposed.

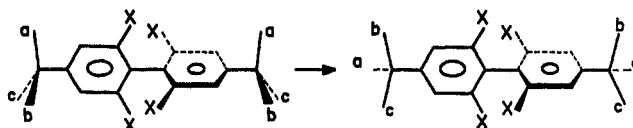


Figure 4. Enantiomerization which is not equivalent to pure reflection, and thus nonnarcissistic.

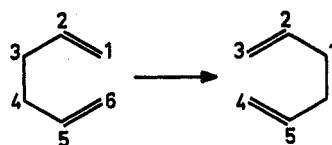


Figure 5. The Cope rearrangement is a typical narcissistic reaction. (The numbers of the atoms do not count in the mirroring process.)

and orientation of the unique mirror plane which relates reactants and products can generally be obtained by superposing product and reactants, as in Figure 3. Narcissistic reactions cover, but are not restricted to, the vast majority of enantiomerizations. Exceptions are those enantiomerizations where product and reactant are related by an S_n axis, such as in Figure 4.⁶ There the product enantiomer can be brought into coincidence with a mirror image of the reactant only via an overall rotation of 90° . The narcissistic family also includes a wide variety of automerizations. Some narcissistic automerizations to which we have paid particular attention are those suprafacial sigmatropic shifts which involve migration of an achiral center,⁷ the geometric isomerization of cyclopropane,⁸ and the Cope rearrangement. In the Cope rearrangement, for instance (Figure 5), product and reactant are clearly related by a vertical mirror plane crossing through atoms 2 and 5. Typical nonnarcissistic automerizations are antarafacial sigmatropic shifts of achiral migrating centers.

Needless to say, the mirror plane which relates

narcissistic reaction. This reaction is equivalent to pure reflection with respect to the plane of the carbon atoms. However we also incorrectly stated that the reaction is narcissistic with respect to the vertical plane containing the migrating CH_2 group. We shall see further in this article that in this case no antisymmetric coordinate changes sign in the reaction (they are all zero to begin with), so that with respect to the vertical mirror plane the reaction is equivalent to pure overall rotation.

(6) Reference 3b, p 93.

(7) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

(8) (a) B. S. Rabinovitch, A. W. Schlag, and K. B. Wiberg, *J. Chem. Phys.*, **28**, 504 (1958). (b) For an application of the narcissistic concept to this reaction see L. Salem in "The Transition State," 21st Congress of the Société de Chimie Physique, Gordon and Breach, London, in press; Y. Jean, L. Salem, J. S. Wright, J. A. Horsley, C. Moser, and R. M. Stevens, *Nature (London)*, submitted for publication; *Pure Appl. Chem.*, in press.

(3) (a) R. S. Cahn, C. K. Ingold, and V. Prelog, *Experientia*, **12**, 81 (1956); V. Prelog and R. S. Cahn, *Chem. Brit.*, **4**, 382 (1968); (b) K. Mislow, "Introduction to Stereochemistry," W. A. Benjamin, New York, N. Y., 1966; (c) E. Ruch and I. Ugi, *Top. Stereochem.*, **4**, 99 (1969); (d) D. Arigoni and E. L. Eliel, *ibid.*, **4**, 127 (1969); (e) R. Bentley, "Molecular Asymmetry in Biology," Vol. I, Academic Press, New York, N. Y., 1969.

(4) Although in the actual dynamic process this may never be true, we restrict ourselves to the static process as described, e.g., by coordinate changes relative to a space-fixed set of Cartesian axes.

(5) L. Salem, J. Durup, C. Bergeron, D. Cazes, X. Chapuisat, and H. Kagan, *J. Amer. Chem. Soc.*, **92**, 4472 (1970). In this paper the geometric isomerization of cyclopropane was studied as a typical

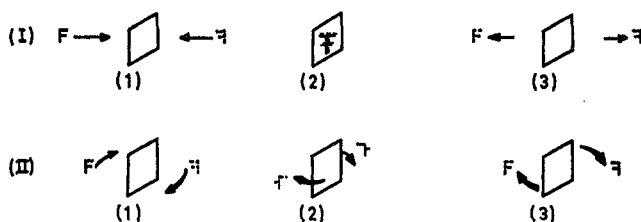


Figure 6. Illustration of the two fundamental pathway types for a narcissistic reaction. F represents the molecule and \bar{F} its image. (Although the symbol F is chiral only in two dimensions, the two entities in II (2) are assumed to be nonsuperimposable).

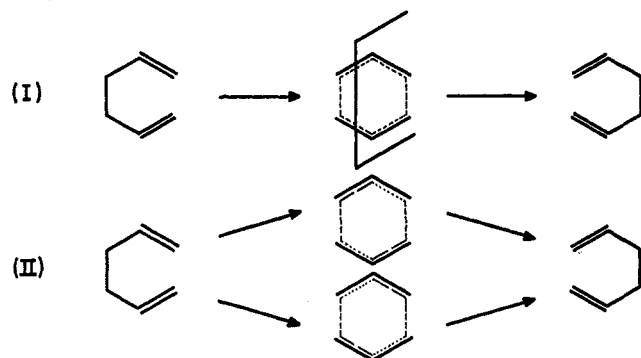


Figure 7. Illustration of the two different processes for the Cope rearrangement.

reactants and products need not be a plane of symmetry for the starting system. In certain cases the mirror plane may be identical with a symmetry plane in the reactant. The situation will then arise where the reaction is narcissistic with respect to *one* symmetry plane but not with respect any other symmetry plane in the reactant (see, further, the case of cyclopropane⁶).

Through the Mirror or Around the Mirror?

We must now answer the questions why we have singled out this particular class of reactions and what property makes them interesting and eventually conducive to a simplified potential energy surface search. The interesting feature is the analogy between the reaction and reflection in a mirror. A molecule must be transformed into the image of its initial self and simultaneously the initial image must be transformed into the image of the product, *i.e.*, the molecule itself. There are two distinct ways of achieving this transformation: (1) *via* a single pathway which "crosses" the mirror with the molecule and its image blending into a unique entity at halfway. At this halfway point the system is *achiral* with the mirror plane as plane of symmetry; (2) *via* two distinct pathways which go "around" the mirror, the molecule and its image tending toward each other's initial position without ever "meeting." The transformation of one into another is reached only at the final stage. This mechanism generally precludes an achiral system along the reaction pathway. Mislow was first to point out⁶ the possibility of totally chiral pathways in the interconversion of enantiomers (note, however, that, although neither path goes through an achiral geometry,

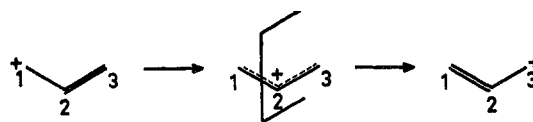


Figure 8. Automerization of the allyl cation.

other properties characteristic of chirality, such as optical activity, must vanish somewhere along both paths).

These two possibilities are illustrated in Figure 6 for the enantiomerization of a chiral system F and in Figure 7 for the Cope rearrangement. In a given reaction it is by no means clear whether the system will prefer process I or process II. Even in the Cope rearrangement, although the concertedness⁷ would tend to give a "*préjugé favorable*" to process I,⁹ the concertedness could still be maintained if there was a slight lag between the formation of the two allylic systems.¹⁰ In Figure 7, the striking feature in process I is the *synchronism* in the behavior of the allylic moieties, in process II it is their *nonsynchronous* behavior. Thus the possible existence of a midpoint with reflection symmetry is intimately related to the mechanistic behavior of the reaction. This makes it worthwhile to seek out more specifically the conditions under which either type of process occurs.

Antisymmetric Coordinates

In order to ensure reflection in the mirror plane, some property of the reactant must change sign during the reaction. More precisely, some coordinate which contributes to the overall reaction coordinate must change from a value a , say, to a value $-a$. Now the ensemble reactant plus product has the mirror plane as plane of symmetry. One can therefore divide all the nuclear coordinates into combinations which are either *symmetric* or *antisymmetric* with respect to this plane.¹¹ Symmetric coordinates are unchanged by reflection in the mirror plane; however antisymmetric coordinates do change sign under reflection in the mirror plane. For instance, in the hypothetical interconversion of the two classical forms of the allyl cation (Figure 8), the difference $r_{12} - r_{23}$ in bond lengths is a typical antisymmetric coordinate which changes sign in the reaction. A coordinate such as $r_{12} + r_{23}$ is symmetric with respect to the mirror plane and has the same value at the beginning and at the end of the reaction. Its value may change during the course of the reaction, but this change says nothing of the extent to which the reactant has been transformed into its image. On the other hand, the *sign* of the antisymmetric coordinate is crucial in

(9) Authors have generally assumed, without too much justification, that the transition state in the Cope rearrangement has a plane of symmetry. See M. Simonetta, G. Favini, C. Mariani, and P. Gramaccioni, *J. Amer. Chem. Soc.*, **90**, 1280 (1968); A. Brown, M. J. S. Dewar, and W. Schoeller, *ibid.*, **92**, 5516 (1970).

(10) Note that, in this and in other reactions, even if the potential energy surface finally favors the single pathway mechanism (I), the energy increase for dual unsymmetrical pathways of type II may not always be so large as to preclude actual trajectories of type II.

(11) E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill, New York, N. Y., 1955, p 115 sqq.

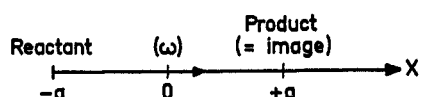


Figure 9. Reaction pathway in the case of one antisymmetric coordinate.

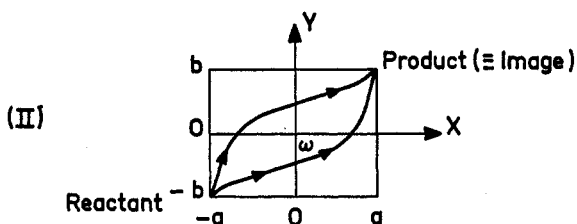
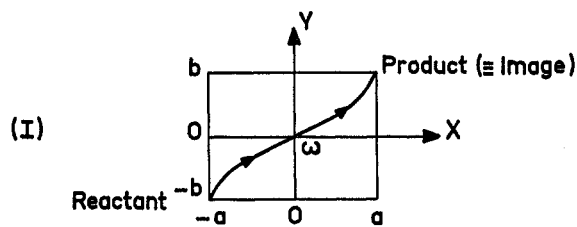


Figure 10. Reaction pathways in the case of two antisymmetric coordinates.

telling us whether the molecule has gone beyond the mirror plane or not. In particular it is zero at halfway, at which point, if no other antisymmetric coordinates are involved in the reaction, the mirror plane is also a plane of symmetry for the system.

Narcissistic reactions can now be defined more usefully as *reactions where reactant(s) and product(s) are mirror images with respect to a fixed plane*, with the restriction that *there be at least one nonzero antisymmetric coordinate which changes sign during the reaction*. In many cases of interest there are two antisymmetric coordinates which participate in the reaction coordinate: the pair $r_{23} - r_{12}$ and $r_{45} - r_{56}$ in the Cope rearrangement (Figure 5), the z coordinates of the migrating hydrogen atoms in the geometric isomerization of cyclopropane with respect to the xy CCC mirror plane,⁵ or the inversion angle at the pyramidal migrating center together with $r_{12} - r_{23}$ in the suprafacial 1,3 sigmatropic shift of an asymmetrically substituted carbon.⁵

Synchronism vs. Nonsynchronism

The behavior of a narcissistic reaction depends on the number of nonzero antisymmetric coordinates involved in the reaction process.

(1) There is only one antisymmetric coordinate (X) which contributes to the reaction. When X reaches the value 0 the mirror plane becomes a plane of symmetry for the system.¹² This midpoint, ω , *e.g.*, has reflection symmetry. Thus the reaction is necessarily of type I. The reaction path can be drawn as a line along the X -coordinate axis, in a one-dimensional diagram (Figure 9). Typical examples are the aforementioned de-

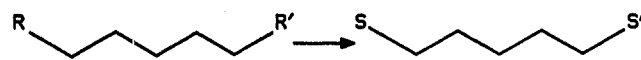


Figure 11. A likely nonsynchronous narcissistic reaction.

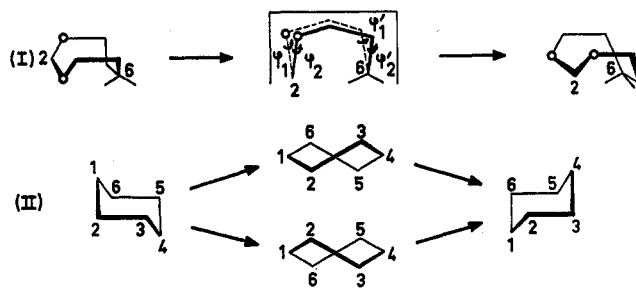


Figure 12. Narcissistic interconversions of medium-sized rings. In reaction I the (vertical) mirror plane is also a plane of symmetry at halfway; in case II the (horizontal) mirror plane is not a symmetry element at halfway.

generate rearrangement of the allyl cation (assuming the reaction to be limited to a change in the carbon-carbon skeleton) or the inversion of a tetrahedral chiral center.

(2) Two antisymmetric coordinates, X and Y , both change sign during the reaction, as in the Cope rearrangement. To study the behavior of the system along the reaction path, it is convenient to make a two-dimensional plot of the path in terms of X and Y . The two possibilities previously termed I and II now give rise to two different plots, shown in Figure 10. In these plots only one point, ω , with coordinates ($X = 0, Y = 0$), has the mirror plane as plane of symmetry.¹² In case I the single pathway goes through ω while in case II both pathways, although they interconvert reactant and image, avoid ω .

The behavior of the system in the two different cases can now be characterized in a more physical manner. In case I the coordinates X and Y change in a quasi-synchronous manner. There is never a great lag between the progress of X and Y because of the constraint that they reach their halfway value (zero) simultaneously. Such synchronous behavior is expected to be characteristic of strongly coupled coordinates. In case II the coordinate X lags significantly behind Y in the first half of the upper pathway, and X catches up only in the second half; the roles are reversed in the lower pathway. The two paths correspond to nonsynchronous motion of weakly coupled coordinates. An extreme case of such behavior would be the enantio-merization of two chiral centers at the termini of a long chain (Figure 11). The most likely pathway for such a reaction will consist in successive inversions of the termini R and R', corresponding to motion along the edges of the coordinate diagram in Figure 10.

The reader is encouraged to try and recognize, for narcissistic reactions with which he is familiar, whether the process is a synchronous or a nonsynchronous one. For example, Figure 12 shows two elementary interconversions of medium-sized rings, both of which are narcissistic, but with different behavior. The interconversion of two chiral boat conformations of 6,6-

(12) There may be other "accidental" planes of symmetry for the system either at the starting point or along the pathway. However, when all antisymmetric coordinates are zero, all nonzero coordinates must exist in combinations which are symmetric with respect to the mirror plane. Hence the latter is a symmetry plane for the system.

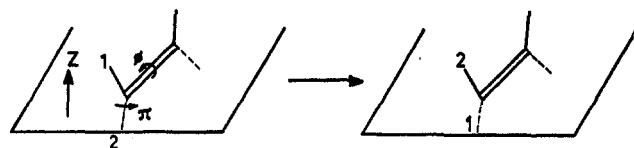
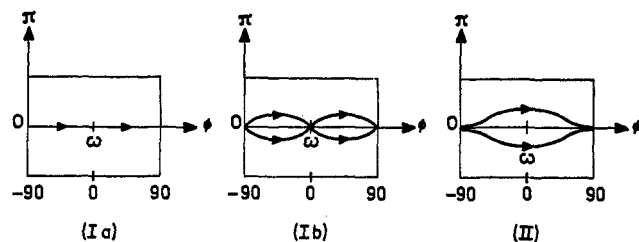


Figure 13. Twisting in ethylene and antisymmetric coordinates.

Figure 14. Reaction paths for the twisting of ethylene; ϕ is the twist angle and π the pyramidalization angle.

dimethyldioxacyclooctanes¹³ (I) is assumed to pass *via* an intermediate conformation which has the mirror plane relating the two boat forms as plane of symmetry. The reaction is synchronous relative to the two antisymmetric coordinates $\phi_1 - \phi_2$ and $\phi'_1 - \phi'_2$. However the interconversion of the two chair forms of cyclohexane¹⁴ (II) *via* the twist-boat form, which is chiral (with only a C_2 axis), is a typical nonsynchronous narcissistic reaction. The same is true of the passage through the "boat" form, even though the latter has a (vertical) symmetry plane. The synchronous process would be a highly energetic one *via* a planar cyclohexane, with all six carbon atoms in the horizontal mirror plane.

A Word of Caution

It is sometimes convenient to replace a pair of antisymmetric coordinates X and Y by their combinations $X + Y$ and $X - Y$. This is particularly true if one of those combinations is zero at the start and at the end of the reaction. Since this coordinate also vanishes at ω (the eventual symmetric midpoint of the reaction), its departure from a zero value near the middle of the reaction path is a good measure of the nonsynchronism of the reaction. Thus, while one "primary" antisymmetric coordinate changes sign in the usual manner, this "secondary" coordinate goes from zero to zero with intermediate values which measure the departure from synchronism.

For example, in the 180° twisting of a methylene group in ethylene, the coordinates z_1 and z_2 of the migrating hydrogen atoms 1 and 2 are proper antisymmetric coordinates relative to the horizontal mirror plane (Figure 13). Now an equally appropriate pair of coordinates are: (1) The angle of twist, ϕ , around the CC bond. For a rigid CH_2 group, this twisting motion involves synchronous variation of the z coordinates of the two hydrogen atoms; (2) an angle π which measures the degree of pyramidalization of the CH_2 group as it rotates. Motion along the coordinate π (which is some

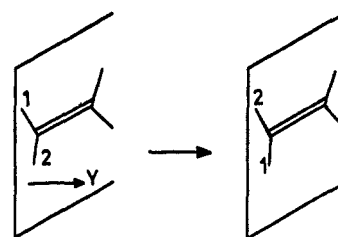


Figure 15. Relative to the molecular plane as mirror plane, the twisting of ethylene is not narcissistic.

varying mixture of internal coordinates: rocking, wagging, and H_1CH_2 angle bending) destroys the synchronism in the z behavior of H_1 and H_2 since pyramidalization destroys the molecular C_2 axis relating H_1 and H_2 . The angle π is therefore a measure of nonsynchronism of z_1 and z_2 .

Figure 14 then shows possible reaction pathways in a ϕ, π diagram. In case Ia the rotation occurs without any pyramidalization whatsoever. The reaction is synchronous (in z_1 and z_2) throughout. In case Ib, pyramidalization is fleetingly involved in the regions $-90^\circ < \phi < 0^\circ$ and $0^\circ < \phi < 90^\circ$. However, π is zero at halfway and the reaction pathway goes through ω . Again the reaction is very nearly synchronous in z_1 and z_2 . In case II, finally, the CH_2 group pyramidalizes throughout its rotation with a maximum folding near $\phi = 0^\circ$. The motion of the z coordinates is then nonsynchronous.¹⁵ This behavior could be expected for the rotation of the CF_2 group in $\text{CF}_2=\text{CH}_2$, since the $\cdot\text{CF}_3$ radical is known to be pyramidal.¹⁶

"Secondary" antisymmetric coordinates are therefore convenient measures of nonsynchronism in the basic antisymmetric coordinates. However, the previous example shows that one must be cautious in using the word "synchronous." The motion described in II, Figure 14, although it avoids ω and is nonsynchronous in z_1 and z_2 , appears to possess all the characteristics of "synchronism" relative to the motions of twisting (ϕ) and pyramidalization (π). It is therefore always necessary to specify for which pair of antisymmetric coordinates a given motion has synchronous behavior.

One should also beware of cases where *all* the antisymmetric coordinates involved in the reaction *are zero* both at the beginning and at the end of the reaction. *If such is the case, the reaction is not narcissistic.* A typical example would be the twisting of ethylene relative to its own molecular plane, which is a second mirror plane relating reactant and product (Figure 15). In this reaction the coordinates y_1 and y_2 , or their combinations $y_1 + y_2$ and $y_1 - y_2$, are antisymmetric with respect to the mirror plane and contribute to the reaction coordinate. However, both coordinates vary from 0 to 0 and there is *no antisymmetric coordinate which changes sign.* In our earlier definition⁵ we failed to notice that such a

(15) (a) Note that pathways Ib and II of Figure 14 are entirely equivalent to pathways I and II of Figure 10. (b) There are two equivalent pathways in Ib because of the C_2 axis relating H_1 and H_2 in ethylene.

(16) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **43**, 2704 (1965).

(13) J. Dale, private communication to the author, 1971.

(14) J. B. Hendrickson, *J. Amer. Chem. Soc.*, **89**, 7047 (1967).

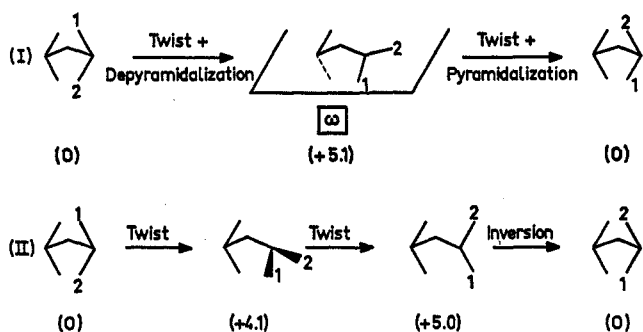


Figure 16. Comparison of types I and II processes for the geometrical isomerization of cyclopropane. (1) Rotation of a single methylene group (energies in kilocalories/mole).

case precludes pure reflection and that the reaction is then equivalent to an overall rotation. Indeed any labeling experiment of type $H_1 = D$, $H_2 = H$ designed to study the behavior of the reaction automatically destroys the vertical plane as mirror plane for the reaction; An analogous case is the geometrical isomerization of cyclopropane considered as a would-be narcissistic reaction relative to the vertical mirror plane which contains the migrating atoms. Relative to this plane the reaction is nonnarcissistic and equivalent to an overall rotation of the molecule.⁵ These examples emphasize the requirement that at least one antisymmetric coordinate change sign during the reaction and the considerable care which must be exercised in distinguishing between pure reflection and overall rotation.

General Consequences

We have demonstrated that the existence in a narcissistic reaction of a midpoint with reflection symmetry requires the reaction to be synchronous with respect to the antisymmetric coordinates. Conversely, an assumedly synchronous reaction involving strongly coupled antisymmetric coordinates is expected to have a symmetric midpoint. Thus, as mentioned previously, we have elucidated an intimate link between the type of reaction path—and therefore the mechanistic behavior of the reaction—and the symmetry of the reaction midpoint.

The requirement, under circumstances of strong coupling, that the reaction midpoint possess reflection symmetry is extremely useful for potential energy surface calculations. First, the transition state (or eventually a secondary minimum) of the reaction can be obtained by a conventional optimization.^{5,8b} It suffices to impose the mirror plane as plane of symmetry on the system: the reaction coordinate is automatically frozen out and one can minimize the energy relative to all the other coordinates. Secondly, the mechanistic picture of the reaction can often be clarified by comparing the situation with a symmetric midpoint constraint to that without constraint. Consider the geometrical isomerization of cyclopropane, for example. Using the face-to-face trimethylene diradical¹⁷ as starting point,

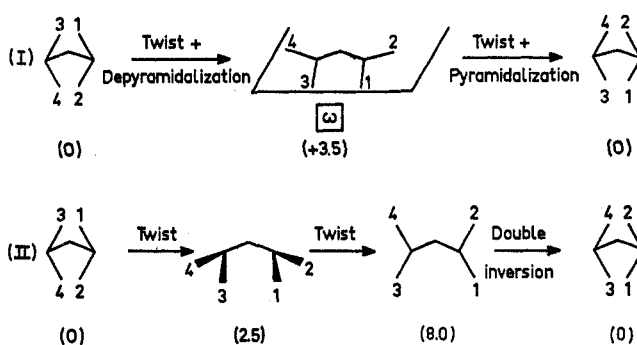


Figure 17. Comparison of types I and II processes for the geometrical isomerization of cyclopropane. (2) Concerted rotation of terminal methylene groups (energies in kilocalories/mole); the disrotatory case is shown.

simultaneous twist and pyramidal inversion are a prerequisite for a synchronous process. Type I and type II processes are then both allowed for rotation of a single terminal methylene group. This is shown in Figure 16; in each case the energy barrier is roughly the same. In the concerted rotation—whether conrotatory or disrotatory—of both terminal methylene groups, however, the type II process leads to an extremely high-energy face-to-face trimethylene¹⁷ with both terminal groups pyramidalized outward (Figure 17). Thus all concerted motions should proceed *via* the coplanar edge-to-edge trimethylene.

Implications for Electronic Theory

The electronic properties of the reactant molecule will of course determine its behavior in a narcissistic process. In the Cope rearrangement, for instance (Figure 7), nonsynchronous behavior (II) and synchronous behavior (I) have different implications on the electronic delocalization in the six-membered transition state. The effects which might favor chiral paths (II) with unsymmetrical allylic moieties may be as subtle as those which favor bond alternation in long polyenes.

One general electronic property can be specified. At a symmetric midpoint, ω , the system must be stable with respect to any coordinate which does not contribute to the reaction coordinate. (This is true whether ω is a transition state or a secondary minimum corresponding to a reaction intermediate.) In particular, the symmetric midpoint ω must be stable with respect to distortions along secondary antisymmetric coordinates.¹⁸ For instance, in the twisting of ethylene, pathway Ia or Ib (Figure 14) will prevail only if the twisted system at 90° is stable with respect to the wagging motion which leads to pyramidalization (Figure 18). Hence the sign of the force constants at

pyramidalization and unfavorable outward pyramidalization by admixture of ionic character together with electron donation from the central CH_2 group into the outer lobes of the odd orbitals. All energies have been obtained in a minimal basis set SCF calculation.^{8b} It is important to realize that improved calculations may be seriously at variance with these, with significant changes in the location and geometry of the various energy extrema.

(18) If this were not the case, the secondary antisymmetric coordinate (for instance π , in the twisting of ethylene) would depart from zero. The reaction would not be synchronous and ω would not be its midpoint.

(17) Y. Jean and L. Salem, *Chem. Commun.*, 382 (1971). This paper attempts to explain the calculated favorable inward carbon



Figure 18. Antisymmetric distortion at a symmetric midpoint.

ω with respect to distortions along antisymmetric coordinates should be of paramount importance in determining the existence of a type I process.

The behavior of the energy near ω is not the only property to determine the synchronism or nonsynchronism of the reaction process. In Figure 17, although the edge-to-edge trimethylene diradical midpoint (3.5 kcal/mole) is unstable with respect to pyramidal folding of the two methylene groups (2.5 kcal/mole), a type I process is most likely. Here the overall energetics along the reaction paths have the last word. The final answer as to whether to expect a symmetric midpoint and synchronous behavior will always depend, ultimately, on the energetics of the potential energy surface and the dynamics on this surface. The outcome of future investigations of surfaces for various narcissistic reactions and observation of the trends in reaction paths is bound to lead to a more precise understanding of the electronic prerequisites for synchronous motion.

It should be possible, at least in principle, to distinguish experimentally between a type I process going through an achiral transition state and a type II process. The transition state ω for path I and the two transition states for paths II (Figure 10) behave like a meso compound *vs.* a racemic pair. Methods which distinguish between the latter can also be used to discriminate between the former; for instance, addition of a chiral solvent should affect differently the rates of path I and of *each* of paths II. The effect on mechanism I is expected to be different from the *average* effect on mechanism II with its two populated pathways. Also, in the event that one could observe the optical properties of the transients, the ultraviolet spectrum of ω in I has symmetry-forbidden bands which become weakly allowed in the transition states on paths II. Similarly, path I may lead through a nonpolar transition state while paths II go through polar situations.

Other Applications

The narcissistic concept can also be useful in revealing certain features of reaction mechanisms. Consider,



Figure 19. Solvent transfer in S_N2 reaction.

for instance, the S_N2 reaction $F^- + CH_3F \rightarrow FCH_3 + F^-$ illustrated in Figure 19. The assumption that the F^- ion is solvated tetrahedrally by four water molecules,¹⁹ while the fluorine atom in methyl fluoride has three water molecules surrounding it (in the direction of three sp^3 lone pairs²⁰), seems reasonable. The narcissistic nature of the reaction (same solvation in the products as in the reactants) then requires an *overall transfer of one solvent molecule* during the reaction. This transfer, which may actually occur *via* small displacements in a sequence of water molecules in the medium separating the two fluorine atoms, may well contribute to the activation energy of the reaction.

Also, we should point out that a plane of symmetry need not be the only type of symmetry element for the midpoint of a synchronous narcissistic reaction. Kagan and Balavoine²¹ have shown that if the reaction conserves a C_n axis perpendicular to the mirror plane relating reactant and product, the midpoint ω for a synchronous process has an S_n axis. Of course, ω is still *achiral*. If the reaction conserves a symmetry plane perpendicular to the mirror plane, a synchronous process will lead to a midpoint with a C_2 axis.

Finally it is possible to conceive of "quasinarcissistic" reactions, in which a substituent destroys the perfect mirror-image relationship between unsubstituted reactant and product. It seems that the presence of a substituent which does not participate in the primary reaction process should not modify the type of behavior (synchronous or nonsynchronous) adopted in the parent narcissistic reaction.

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(19) H. Lischka, T. Plessner, and P. Schuster, *Chem. Phys. Lett.*, **6**, 263 (1970).

(20) An alternative sp^2 hybridization of the fluorine atom would lead to a four-molecule solvation shell. This structure, which may actually be an intermediate in the process described above, would seem to give weaker solvation energies, particularly in the up and down π directions.

(21) H. Kagan and G. Balavoine, unpublished results.