port. We are also grateful to Miss Patricia Eyring for drawing the spectra.

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Received March 30, 1970

Narcissistic Reactions

Sir:

In this communication a class of reactions is defined and its elementary properties are studied. A reaction is defined as *narcissistic* if reactant(s) and product(s) are mirror images with respect to a fixed plane and if the image of the reactant(s) undergoes the reverse "reaction" to the image of the product(s). (The mirror plane need not be a plane of symmetry for the starting system.)[1] Such reactions include the great majority of automerizations
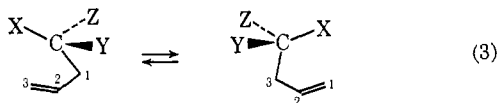
$$A \rightleftarrows A \qquad (1)$$

where A is achiral, and of interconversions

$$F \rightleftarrows \text{F} \qquad (2)$$

where F is chiral[2] and F is its enantiomer. The spontaneous racemization of an optically active species is almost always a narcissistic reaction; however the automerization $F \rightleftarrows F$ is not narcissistic.

There are innumerable examples of narcissistic reactions. Particularly interesting cases for our purposes are (a) the 1–3 suprafacial sigmatropic shift with inversion of configuration at the migrating center[3] (eq 3)
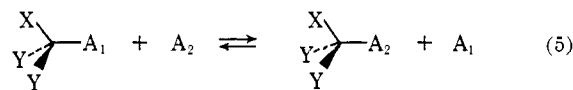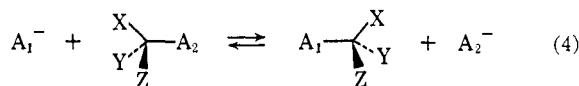

$$ (3) $$

(the 1–5 transposition, with retention of configuration, although also allowed by orbital symmetry,[3] is not narcissistic; however if the asymmetric center is re-

placed by a hydrogen atom, it becomes narcissistic); (b) the substitution reactions (examples of bimolecular narcissistic reactions) (eq 4 and 5); (c) the geometric

$$ (4) $$

$$ (5) $$

isomerization of cyclopropane[4] (eq 6).

$$ (6) $$

The potential energy surface for narcissistic reactions has the important property of being divided into two enantiomeric moieties. To each point on the surface, which represents a certain structure of the reactant, corresponds a point representing the image structure. There are also a number of points which coincide with their image point and hence possess reflection symmetry—for instance, points where all the atoms are forced into the fixed mirror plane.

Consider now the trajectory which converts the reactant into the image system, and the enantiomeric trajectory which brings the reverse reaction. At halfway these two trajectories might be expected to meet at one of these symmetric points, which would be the reaction midpoint. The two trajectories would then coincide, the first half of one being the second half of the other. However such a property is by no means ensured, because the trajectories can also remain distinct, equivalent, enantiomeric entities throughout. Burwell and Pearson have shown[5] that such a two-path mechanism is perfectly compatible with the principle of microscopic reversibility. The question thus arises as to the conditions under which a narcissistic reaction goes through a symmetric midpoint.

The coordinates which contribute to the reaction coordinate can be divided into two categories according to their symmetry with respect to the mirror plane: (1) "antisymmetric" coordinates, whose value inverts from some value a, *e.g.*, to $-a$ with intermediate value 0. Our definition of narcissistic reactions requires that there be at least one coordinate which is antisymmetric with respect to the mirror plane.[1b] A change of sign in all the antisymmetric coordinates is equivalent to reflection in the mirror plane. Configurations in which all antisymmetric coordinates are zero possess reflection symmetry. (2) The second category consists of "symmetric" coordinates which start from a certain value b and end up with the same value b, with *any* intermediate value c (for instance, transient stretching of a bond during the reaction). Now if the reaction coordinate involves only one antisymmetric coordinate, this coordinate

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(1) (a) In this definition it should be understood that the reactant and product image are defined relative to a *single* space-fixed set of coordinate axes. This mirror plane is then *uniquely* defined within the reaction process. (It cannot be chosen arbitrarily as is done conventionally to create an image.) Under these conditions, the narcissistic definition covers all reactions which are equivalent to *pure reflection* (and, which therefore, as we shall see, may have a symmetry plane at halfway), while excluding those reactions which are equivalent to *reflection plus rotation*. The second part of the definition (in which reverse "reaction" does not necessarily imply reverse "trajectory") ensures that the reflection is not obtained *via* an overall translation or rotation of the displaced nuclei. (b) A typical nonnarcissistic reaction can be found in K. Mislow, "Introduction to Stereochemistry," W. A. Benjamin, New York, N. Y., 1966, p 93, in which the product system is not related to the reactant *via* a fixed mirror plane. Another case arises if the biphenyl group rotates by 90° (in the positive torsional direction, for example): there is a fixed mirror plane but the image of the reactant undergoes the *forward* (positive torsional direction) rather than the *reverse* (negative torsional direction) reaction. Similar exceptions will occur whenever antisymmetric coordinates are absent. See G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand, Princeton, N. J., 1945, pp 82–83.
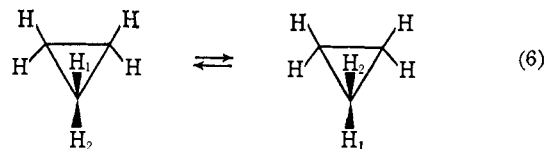
(2) For a review, see V. Prelog and R. S. Cahn, *Chem. Brit.*, **4**, 382 (1968).

(3) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 2511 (1965); (b) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 787 (1969).

(4) For recent chemical evidence see J. A. Berson and J. M. Balquist, *J. Amer. Chem. Soc.*, **90**, 7343 (1968); W. L. Carter and R. G. Bergman, *ibid.*, **90**, 7344 (1968).

(5) R. L. Burwell and R. G. Pearson, *J. Phys. Chem.*, **70**, 300 (1966). The two paths are followed equally by 50% of the reactants.

reaches zero at halfway and, in this trivial case, there is indeed a symmetric midpoint. We next consider the case of a narcissistic reaction involving two antisymmetric coordinates X and Y. In a two-dimensional plot the reactant has coordinates $(-a, -b)$, for example, and the product coordinates (a, b). The two-dimensional energy surface contains only one point with reflection symmetry, e.g., ω, with coordinates $X = 0$, $Y = 0$. Figure 1 now shows the two possible cases for narcissistic reaction paths in two dimensions. In the first case (1) there is a unique path which passes through ω. Along this path X and Y change in simultaneous fashion and, although each increment in X is accompanied by a different increment in Y, they also reach their halfway value 0 simultaneously. In case 2, however, there are two enantiomeric pathways, neither of which passes through ω. The main feature of each path is that one coordinate reaches its intermediate value 0 well in advance of the other; there is a time lag between X and Y throughout the entire reaction.

Hence path 1 corresponds to *synchronous* motion of strongly coupled coordinates, whereas path 2 corresponds to the *nonsynchronous* motion of weakly coupled coordinates. Strictly speaking, path 2 is "synchronous" in the sense that X and Y are always changing simultaneously. However we use the word "synchronous" here as implying *equal rates* of transformation for the various antisymmetric coordinates throughout the reaction. We also use the term "synchronous" rather than the term "concerted" since, even in a reaction with strongly coupled coordinates, ω can represent a secondary minimum (reaction intermediate). We can then make the general statement that *synchronous narcissistic reactions pass through a midpoint with reflection symmetry*. This is a defining statement rather than a theorem since we showed precisely that the passage through a symmetric midpoint was equivalent to a certain degree of synchroneity. Note that (a) the synchroneity holds relative to antisymmetric coordinates only; (b) the plane of symmetry at halfway is that which relates reactant to product; (c) the converse property also holds: a narcissistic reaction with a symmetric midpoint is synchronous as long as the plane of symmetry is of type b.

In practice each narcissistic reaction will have to be examined separately to see whether it appears to be synchronous and thus should possess a symmetrical midpoint. At the outset the very great majority of narcissistic reactions do appear to be synchronous. For instance spontaneous racemization often proceeds *via* a structure with reflection symmetry. Nonsynchronous narcissistic reactions are harder to come by. Mislow has made the important point[6] that racemization may proceed through intermediates which do not possess reflection symmetry. Most examples are reactions which occur in well-defined *sequential steps*. The simplest conceivable example is that of two independent chiral groups at the two ends of a lengthy chain, and which invert one after another. Both pathways are chiral and are related by a center of symmetry. This example, which corresponds to an extreme case of Figure 1 (2), in which the two paths would follow the edges of the surface, really constitutes two successive,

(6) K. Mislow, "Introduction to Stereochemistry," W. A. Benjamin, New York, N. Y., 1966; p 86 gives a typical example.
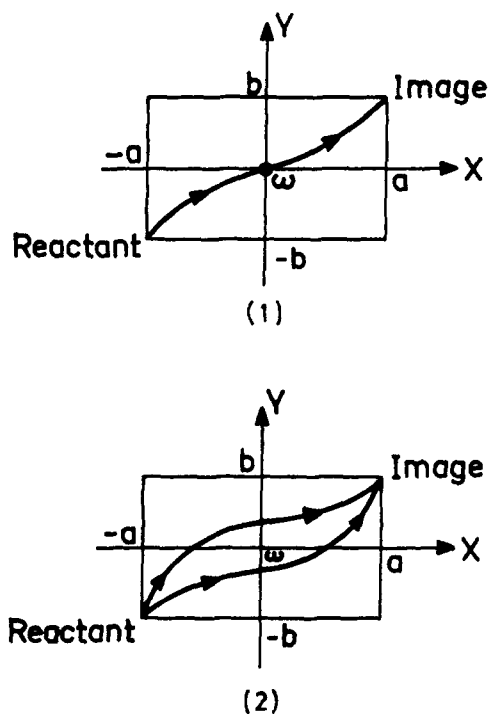
Y

b Image
-a
ω a X

Reactant -b

(1)

Y

b Image
-a
ω a X

Reactant -b

(2)

Figure 1.

nonnarcissistic reactions. A typical case with a path of type 2 may be the inversion of cyclohexane.[7]

We now turn toward an application of these results. Apart from the actual size of organic systems, the major difficulty in the search of transition states and intermediates lies in the very nature of these transients. The former are saddle points and the latter local minima on the potential energy surface. A calculation using a minimization procedure is certain, in the first case, and highly likely, in the second case, to lead directly to the reactants or the products. However, if the reaction coordinate can be *frozen out*, a minimization procedure can be safely carried out without risk of "falling off" the saddle point or missing the local minimum. The existence, in synchronous narcissistic reactions, of a plane of symmetry at the halfway point allows us to do just that.

Consider first reaction 3. If a vertical plane of symmetry is imposed on the system, optimization will lead unfailingly to the transition state. This example is somewhat trivial since the important features of the transition state are well known,[3] but it illustrates the method which we use for more complicated reactions.

Consider now reaction 6. Certainly the motions of the two migrating hydrogen atoms are very strongly coupled, both *via* their through-space interaction and *via* hybridization changes at the common adjacent carbon atom. Hence they should move synchronously. Under this reasonable assumption, what is the configuration midway through the reaction? The answer is obtained by looking first at the two parent reactions 7 and 8 (narcissistic interconversions of chiral cyclopro-

(7) (a) J. B. Hendrickson, *J. Amer. Chem. Soc.*, **83**, 4537 (1961); (b) N. L. Allinger, M. A. Miller, F. A. VanCatledge, and J. A. Hirsch, *ibid.*, **89**, 4345 (1967); (c) R. Bucourt and D. Hainaut, *Bull. Soc. Chim. Fr.*, 4562 (1967); (d) for a recent discussion of the inversion pathway for cyclohexene, see J. E. Anderson and J. D. Roberts, *J. Amer. Chem. Soc.*, **92**, 97 (1970), and references therein.
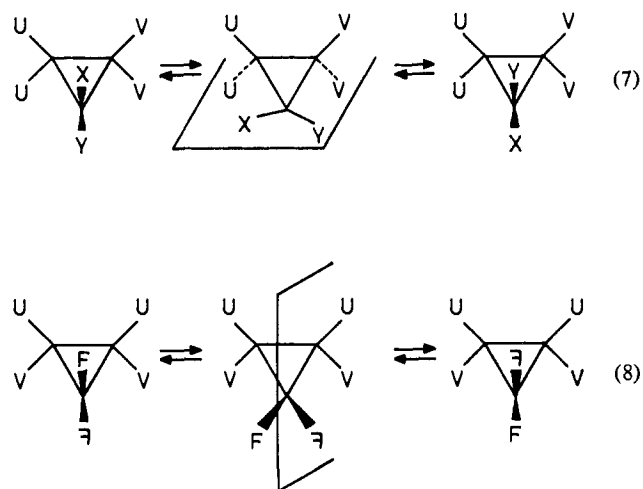
Figure 2.

Figure 3.

panes, Figure 2), in which the symmetry planes appear clearly. The distinctive feature between reactions 7 and 8 is a fixed horizontal symmetry plane in the former and a fixed vertical symmetry plane in the latter.

In cyclopropane itself there are three possibilities. (a) At halfway, both the vertical and horizontal planes are symmetry elements (Figure 3a). The migrating hydrogens are then further related by a horizontal C_2 axis, as in the starting molecule. One likely possibility then is that the C_2 axis has been maintained throughout the reaction, i.e., that the two atoms have migrated along symmetry-equivalent paths in a totally synchronous manner. The corresponding reaction path is sketched on the right-hand side of the figure, where the z (vertical) coordinates of the two atoms have been plotted.[8]

(b) At halfway the horizontal CCC plane is the symmetry element, as shown in Figure 3b.[9] The positions of the migrating atoms in this plane, however, are generally nonequivalent and their respective paths toward this point certainly different (although there is synchroneity in their motions), whence the dissymmetric trajectory shown on the right-hand side of the figure. Trajectories a and b both correspond to case 1 of Figure 1. (Note that there is a second equivalent pathway due to the presence of an additional symmetry element in the starting system.)

(c) Finally the system may have a vertical symmetry plane at halfway (Figure 3c). At this point the migrating atoms need not be in the plane of the carbons. Again the paths of the two atoms (till they reach the midpoint) are different, one being shorter than the other. Typical antisymmetric coordinates here are the polar angles defining the direction of H_3H_4 relative to an axis perpendicular to the symmetry plane.

That structure a, b, or c with the lowest energy will be the halfway point of the reaction provided also that the path leading to it has the lowest energy of the three corresponding paths.

We hope that this example illustrates how useful the general property of synchronous narcissistic reactions can be in limiting the number of degrees of freedom in the search of a reaction midpoint, and in allowing for the elucidation of a structure which should be close to, if not coincident with, the actual transition state. Work is now in progress on "frozen structures" of cyclopropane and other systems, with the total resolution of the transition states as ultimate purpose.

(8) J. Berson (private communication) has pointed out that H_3 and H_4 can exchange positions by remaining in the vertical plane of symmetry, in which case there is no C_2 axis in the intermediate stages and the reaction path is represented by a disymmetric trajectory similar to that of Figure 3b.

(9) The horizontal plane of symmetry can be course accommodate a second pair of hydrogen atoms, as in the intermediate proposed by R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 1475 (1968). If, however, two methylene groups are involved in the isomerization process, nonsynchronous pathways become possible and, although Hoffmann suggests a concerted mechanism, one is less certain that a structure with two in-plane methylene groups is a potential halfway point.
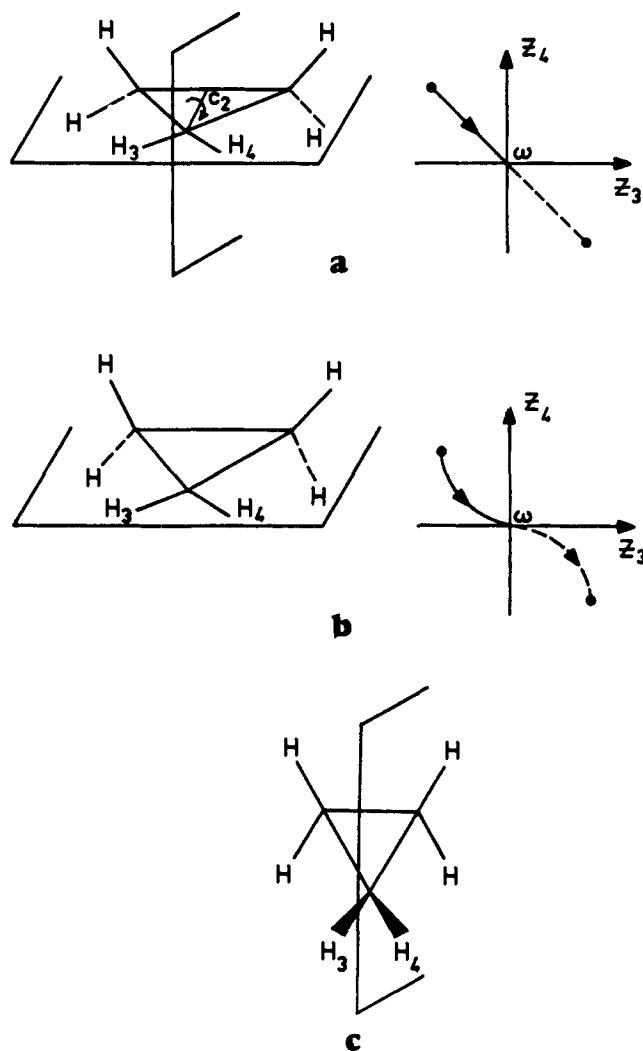
(10) Laboratoire de Chimie Théorique (also part of ref 11).

(11) Laboratoire Associé de Physico-Chimie des Rayonnements supported in part by the CNRS.

(12) Laboratoire de Synthèse Asymétrique.

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Received March 7, 1970