

Non-Least-Motion Potential Surfaces. The Dimerization of Methylenes and Nitroso Compounds

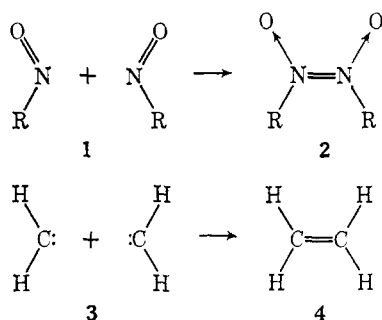
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Abstract: For two classes of facile dimerizations, those of methylenes and of nitroso compounds, it is shown that the least-motion geometry of approach, with the two monomers coplanar, is a high energy one. Non-least-motion reaction paths are computed for the reactions of CH_2 with CH_2 , and of HNO with HNO . The molecules approach each other so that a σ lone pair of one monomer impinges on the π system of the other. Similar non-least-motion reaction paths are anticipated for the interconversions of benzofurazan oxides and *o*-dinitrosobenzenes.

We discuss in this contribution two simple dimerizations, $1 \rightarrow 2$ and $3 \rightarrow 4$, whose computed reaction paths turned out not to be as simple as one might have thought.



The first reaction, the dimerization of nitroso compounds, is a well-known and facile process. Most organic nitroso compounds in fact exist as colorless or pale yellow dimers in the solid state, and as green or blue monomers in the liquid or vapor.¹ The kinetics of the fragmentation of the dimer to monomers have been studied²⁻⁵ for several derivatives. Typical activation energies are in the range of 20–25 kcal/mol. Activation parameters for the reverse reaction, dimerization, are less well known. A direct measurement of the rate of nitrosocyclohexane dimerization⁶ yielded an activation energy of 7.7 kcal/mol; an indirect estimate^{6c} of an activation energy of 8–10 kcal/mol for the dimerization of 3-methyl-3-nitrosobutan-2-one was derived. It is clear that dimerization is a facile process.

Monomeric nitroso compounds are typically bent molecules, with RNO angles in the range of 105–125°.⁷

(1) The following reviews summarize our knowledge of nitroso chemistry: (a) B. G. Gowenlock and W. Lüttke, *Quart. Rev.*, **12**, 321 (1958); (b) J. H. Boyer in "The Chemistry of the Nitro and Nitroso Groups," Part I, H. Feuer, Ed., John Wiley and Sons, Inc., New York, N. Y., 1968, p 215; (c) P. A. S. Smith, "Open-Chain Nitrogen Compounds," Vol. 2, W. A. Benjamin, Inc., New York, N. Y., 1966, Chapter 13.

(2) E. Bamberger and R. Seligman, *Chem. Ber.*, **36**, 685 (1903).

(3) K. D. Anderson and D. L. Hammick, *J. Chem. Soc.*, **30** (1935).

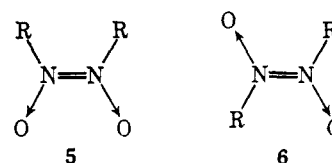
(4) J. R. Schwartz, *J. Amer. Chem. Soc.*, **79**, 4353 (1957).

(5) (a) B. G. Gowenlock, J. Trotman, and L. Batt, Special Publication No. 10, The Chemical Society, London, 1957, p 75; (b) L. Batt and B. Gowenlock, *Trans. Faraday Soc.*, **56**, 1023 (1960); (c) L. Batt and B. Gowenlock, *J. Chem. Soc.*, 376 (1960).

(6) E. J. Burrell, Jr., *J. Phys. Chem.*, **66**, 401 (1962).

(7) (a) HNO : J. L. Bancroft, J. M. Hollas, and D. A. Ramsay, *Can. J. Phys.*, **40**, 322 (1962); F. W. Dalby, *ibid.*, **36**, 1336 (1958); (b) FNO : D. W. Magnuson, *J. Chem. Phys.*, **19**, 1071 (1951); J. R. Durig and R. C. Lord, *Spectrochim. Acta*, **19**, 421 (1963); (c) ClNO : D. J. Millen and J. Pannel, *J. Chem. Soc.*, 1322 (1961); (d) BrNO : J. A. Ketelaar

Virtually all the dimeric nitroso compounds which are known possess the di-N-oxide structure **2**.^{1,2} The molecules are planar³ and exhibit geometrical isomerism, existing often as interconvertible *cis-trans* isomer pairs (**5**, **6**).⁹



The second reaction we will be concerned with, the dimerization of methylenes, is a less well established process. In virtually every reaction which produces methylenes, the formally dimeric ethylenes are present in sizable yields.¹⁰ The dimerization is exothermic by at least 150 kcal/mol.^{10a} Nevertheless methylene is so reactive that in most cases it seems to attack the substrate from which it was generated (which is usually present in significant concentration) before it can meet up with another methylene. This has been clearly demonstrated in the case of the ketene precursor,¹¹ where the ethylene is formed overwhelmingly by the reaction



There is considerable evidence for the equilibrium between tetrafluoroethylene and two difluoromethylenes.

and K. J. Palmer, *J. Amer. Chem. Soc.*, **59**, 2629 (1937); T. L. Weatherly and Q. Williams, *J. Chem. Phys.*, **25**, 717 (1956); (e) HONO : L. D'Or and P. Tarte, *Bull. Soc. Roy. Sci. Liege*, **20**, 478 (1951); L. H. Jones, R. M. Badger, and G. E. Moore, *J. Chem. Phys.*, **19**, 1599 (1951); (f) CH_3ONO : F. Rogowski, *Chem. Ber.*, **75**, 244 (1942); (g) CF_3NO : M. I. Davis, J. E. Boggs, D. Coffey, Jr., and H. P. Hanson, *J. Phys. Chem.*, **69**, 3727 (1965); (h) nitrosobenzene: Y. Hanyu and J. E. Boggs, *J. Chem. Phys.*, **43**, 3454 (1965); (i) *p*-iodonitrosobenzene: M. S. Webster, *J. Chem. Soc.*, 2841 (1956).

(8) Crystal structures: (a) C. P. Fenimore, *J. Amer. Chem. Soc.*, **72**, 3226 (1950); (b) C. Darwin and D. C. Hodgkin, *Nature*, **166**, 827 (1950); (c) M. Van Meerse and G. Germain, *Bull. Soc. Chim. Belges*, **68**, 244 (1959); (d) G. Germain, P. Piret, and M. Van Meerse, *Acta Crystallogr.*, **16**, 109 (1963); (e) H. Dietrich and D. C. Hodgkin, *J. Chem. Soc.*, 3686 (1961).

(9) H. T. J. Chilton, B. G. Gowenlock, and J. Trotman, *Chem. Ind. (London)*, 538 (1955); B. G. Gowenlock and J. Trotman, *J. Chem. Soc.*, 4190 (1955); 1670 (1956); W. Lüttke, *Z. Electrochem.*, **61**, 976 (1956). The thermal *cis-trans* interconversion has been studied by A. U. Chaudhry and B. G. Gowenlock, *J. Chem. Soc.*, **B**, 1083 (1968).

(10) (a) H. M. Frey, *Progr. Reaction Kinetics*, **2**, 131 (1964); (b) W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964; (c) J. A. Bell, *Progr. Phys. Org. Chem.*, **2**, 1 (1964).

(11) G. B. Kistiakowsky and K. Sauer, *J. Amer. Chem. Soc.*, **78**, 5699 (1956); **80**, 1066 (1958).

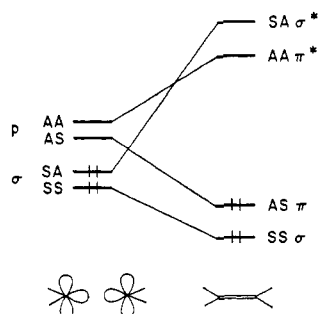
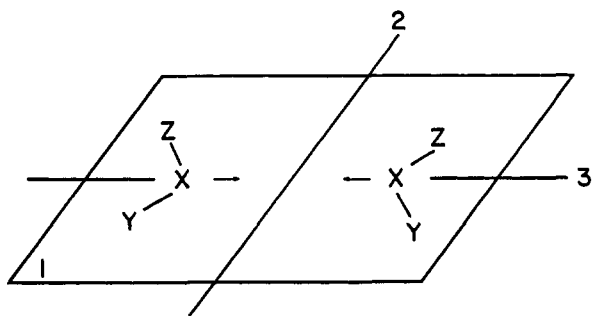


Figure 1. Level correlation diagram for the least-motion approach of two methylenes. Levels are classified according to the symmetry planes described in the text.

An activation energy of 1.2 kcal/mol for the recombination of difluoromethylenes has been measured.¹²

The Least-Motion Approach

Since products and reactants for both dimerizations are planar molecules, it is tempting to assume that in the many dimensional potential surfaces governing the dimerization or its reverse, the reaction path will be a least-motion one, *i.e.*, that both molecules will prefer to approach each other in a plane.



A level correlation diagram¹³ may easily be constructed for the methylene dimerization (Figure 1). The relevant orbitals for a bent methylene are an in-plane hybrid, σ , doubly occupied in the singlet, and an empty p orbital perpendicular to the methylene plane.^{10,14} The corresponding ethylene levels are a C-C σ bond, its unoccupied σ^* partner, as well as π and π^* levels. In the least-motion approach of D_{2h} symmetry, it suffices to classify these levels as being symmetric (S) or antisymmetric (A) with respect to plane 1, the plane of approach, and plane 2, a plane perpendicular to 1 and midway between the two methylene groups.

Similarly we construct a correlation diagram for the dimerization of two nitroso compounds (Figure 2). The relevant orbitals are, on the monomer side, the two N lone pairs, and the π and π^* levels of the two nitroso groups. On the product side, we include the new N-N σ bond and the four π levels, of which three are occupied, of the new ONNO π -electron system.¹⁵ Figure 2

(12) F. W. Dalby, *J. Chem. Phys.*, **41**, 2297 (1964); see also S. H. Bauer, K. C. Hou, and E. L. Resler, Jr., *Phys. Fluids, Suppl.*, **1**, 1 (1969).

(13) R. Hoffmann and R. B. Woodward, *J. Amer. Chem. Soc.*, **87**, 2046 (1965); R. B. Woodward and R. Hoffmann, *Angew. Chem.*, **81**, 797 (1969). Reprinted in book form by Academic Press, New York, N. Y., and Verlag Chemie, Weinheim/Bergstr., Germany.

(14) (a) R. Hoffmann, G. D. Zeiss, and G. W. Van Dine, *J. Amer. Chem. Soc.*, **90**, 1485 (1968); (b) R. Hoffmann, *ibid.*, **90**, 1475 (1968).

(15) As usual only the levels directly involved in the reaction are included in these correlation diagrams. See ref 13 for further details.

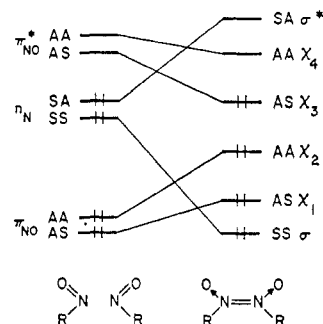


Figure 2. Level correlation diagram for the *cis* mode of dimerization of HNO. χ_1 - χ_4 are the π orbitals of the di-N-oxide.

is constructed for an approach leading to a *cis* dimer; accordingly levels are classified with respect to the same mirror planes used in the methylene case. The same correlation diagram would be obtained for an approach leading to a *trans* dimer, except that the second mirror plane would be replaced by a twofold axis.

The correlation diagrams of Figures 1 and 2 are characterized by a level crossing—they are orbital symmetry forbidden. The least-motion approach should be a high energy one. This is obvious if one recognizes that in each case the number of σ and π electrons is different on the reactant side from the product side. Thus two singlet methylenes possess between them four σ electrons and no π electrons, whereas the product ethylene has two of each kind. The nitroso monomers possess four π electrons and four σ , but the dimer has six π and two σ . Still another way of expressing the high energy character of this approach may be found in the realization that such an approach essentially forces two lone pairs onto each other, a patently repulsive situation resembling the approach of two helium atoms.

We should point out here that the result of Figure 2 was quite apparent to Lüttke and Gowenlock,^{1a,5,16} whose discussion of the dimerization is based on a state diagram which may be constructed from our level diagram. It was these workers' opinion that the forbidden reaction would proceed anyway, with a low activation energy as a result of the crossing in the correlation diagrams occurring in the region of small repulsion. A similar state diagram for the dimerization of CF_2 was constructed by Simons.¹⁷ Our experience, however, has been that whenever orbital symmetry control makes a given approach geometry, such as the least-motion one, forbidden, then there always exists another reaction path which is allowed, but which involves nuclear displacements which are *not* of the least-motion type. The orbital symmetry argument proscribes a certain approach geometry. It does not define which reaction path among the myriad other possibilities available will be followed. To establish the favored reaction path we resort to semiempirical molecular orbital calculations.

Thus though it is clear that the N lone pair must interact heavily with an in-plane O lone pair in a nitroso compound, we localize the lone pairs, and in the correlation diagram ignore the in-plane O lone pairs, whose number and symmetry properties do not change in the course of the reaction.

(16) W. Lüttke, *Angew. Chem.*, **68**, 417 (1956); **69**, 99 (1957); V. Keussler and W. Lüttke, *Z. Elektrochem.*, **63**, 614 (1959).

(17) J. P. Simons, *Nature*, **205**, 1308 (1965); *J. Chem. Soc.*, 5406 (1965).

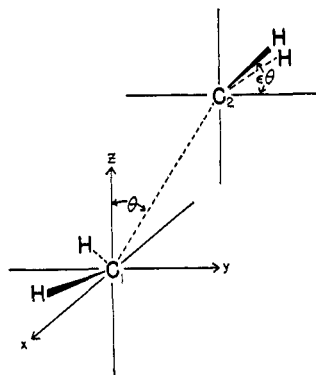


Figure 3. The coordinate system for the approach of two methylenes.

The Dimerization of Methylene

We used extended Hückel calculations^{14,18} in our exploration of the $\text{CH}_2 + \text{CH}_2$ potential surface. These calculations have numerous documented deficiencies, but they do seem to capture the essence of energetic changes in distortions within molecules or in potential surfaces of approaching molecules. They are the only calculations which we can do at present which allow, at computation times of *ca.* 1 sec per point, an examination of a potential surface in six dimensions.

To describe completely the configurations of a system with six atoms, 12 degrees of freedom are necessary. Since singlet methylenes are bent, and both the C-H distance and the HCH angle in the reactant methylenes and the product ethylene are similar, a reasonable assumption to make is that each CH_2 unit will change its geometry in only a minor way in the course of the reaction. Accordingly we carried through our calculations with fixed CH_2 units in an idealized geometry: C-H 1.10 Å, HCH angle 120° . The number of degrees of freedom is thus reduced to six. These degrees of freedom, describing the relative motion of two rigid bodies, may be conveniently chosen in the following manner. One methylene is arbitrarily fixed, symmetrically placed in the xy plane with the carbon at the origin (Figure 3). Three spherical coordinates R , θ , φ are used to locate the carbon atom of the second methylene relative to this invariant coordinate system. The orientation of the second methylene is fully specified by three Euler angles,¹⁹ $\epsilon\varphi$, $\epsilon\theta$, $\epsilon\psi$. Preliminary investigation of the potential surface showed that for any κ the second methylene preferred to symmetrically straddle the yz plane, *i.e.*, that the yz plane was the perpendicular bisecting plane of both methylenes. This allowed us to focus on three degrees of freedom: the carbon-carbon distance R , the spherical angle θ , and the Euler angle $\epsilon\theta$ (see Figure 3). In this notation $\theta = 90^\circ$, $\epsilon\theta = 0^\circ$ would correspond to a simply stretched ethylene.

For some values of R we computed the energy at intervals for all θ and $\epsilon\theta$. One such surface, at $R = 3.0$ Å, is shown in Figure 4. Symmetry properties may be used to reduce greatly the portion of the surface to be searched. The geometrical construction below shows

(18) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963); **40**, 2474, 2480, 2745 (1964); *Tetrahedron*, **22**, 521, 539 (1966). A hydrogen Slater exponent of 1.3 was used.

(19) For the definition of the Euler angles see H. Goldstein, "Classical Mechanics," Addison-Wesley Publishing Co., Reading, Pa., 1959, p 107.

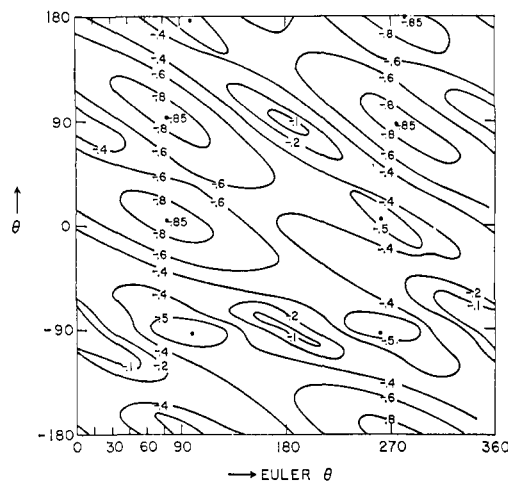
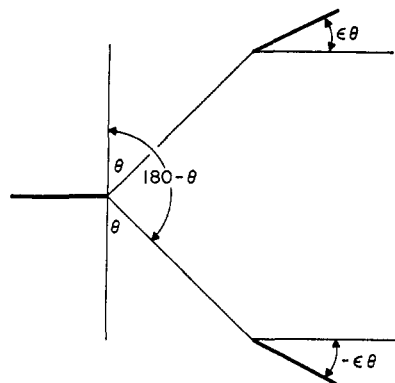


Figure 4. Contours of the energy (in eV) relative to an arbitrary energy zero, as a function of θ and $\epsilon\theta$ for two methylenes separated by 3.0 Å.

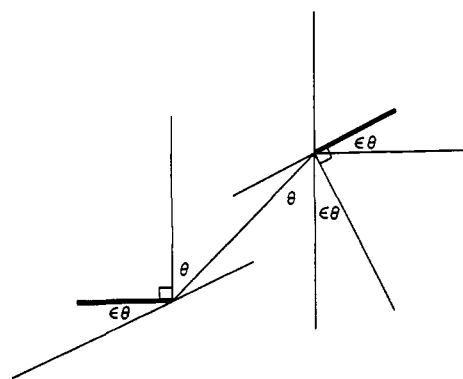
that symmetry imposes the following relations for identical points

$$E(\theta, \epsilon\theta) = E(180 - \theta, -\epsilon\theta)$$



Similarly switching the origin to the other methylene imposes the condition

$$E(\theta, \epsilon\theta) = E(\theta + \epsilon\theta, -\epsilon\theta)$$



These relations imply still another one, so that finally we have the constraints

$$E(\theta, \epsilon\theta) = E(180 - \theta, -\epsilon\theta) = E(\theta + \epsilon\theta, -\epsilon\theta) = E(180 - \theta - \epsilon\theta, \epsilon\theta)$$

Thus though there appear to be four distinct minima in the potential surface of Figure 4, at $(\theta, \epsilon\theta) = (6, 78)$, $(174, 282)$, $(84, 282)$, and $(96, 78)$, these belong, in fact,

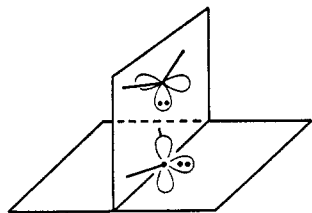


Figure 5. Optimum approach of two methylenes at large separation.

to one and the same geometry. At distances greater than 3 Å the approach geometry moves still closer to $\theta = 0^\circ$, $\epsilon\theta = 90^\circ$ (and its equivalent points (180, 270), (90, 270), (90, 90)). This arrangement of two methylenes is shown in Figure 5. The methylenes lie in perpendicular planes, and the approach may be described as the attack of a lone pair of the top methylene on the empty p orbital of the other methylene. It is accompanied by considerable electron transfer from the top to the bottom methylene. The repulsion of two lone pairs implicit in the least motion approach is avoided, and is replaced by a bonding electrophilic-nucleophilic interaction.

We next used a minimum-seeking program which for a given value of R searched for the values of θ and $\epsilon\theta$ which would minimize the energy. The optimum angles at selected R values are given in Table I. Each

Table I. The Angles θ and $\epsilon\theta$ Minimizing the Energy, at Indicated Carbon-Carbon Separation R^a

R , Å	θ	$\epsilon\theta$
<2.00	90	0
2.20	74	0
2.30	63	0
2.40	56	0
2.45	53	0
2.50	36	30
2.55	28	42
2.60	23	51
2.80	12	69
3.00	6	78
4.00	1	87

^a In each case $\varphi = 90^\circ$, $\epsilon\varphi = 0^\circ$, $\epsilon\psi = 0^\circ$.

of the entries in the table, listed as a two-dimensional minimum, was shown by us to be a minimum if all five angles are varied as well.

Ideally we would like to present a film showing the descent along the reaction path. For the moment we must be content with Figure 6, a superimposed series of snapshots of the approach of two methylenes. The view is from the side (see Figure 3); *i.e.*, both methylenes are projected on the yz plane.

As R decreases, the distant approach with $(\theta, \epsilon\theta) = (0, 90)$, of C_s symmetry, moves smoothly over to a C_{2h} geometry (50, 0), which then collapses to the D_{2h} ethylene (90, 0). C_{2h} symmetry would have been sufficient for converting a forbidden reaction into an allowed one. Though the molecule chooses a less symmetrical C_s structure for $R > 2.45$ Å, the potential surface is extremely flat over the entire range of angles between a C_{2h} geometry and the observed minimum.

There appear to be no other minima within our constraints.²⁰ Figure 4 showed at 3.0 Å some local minima

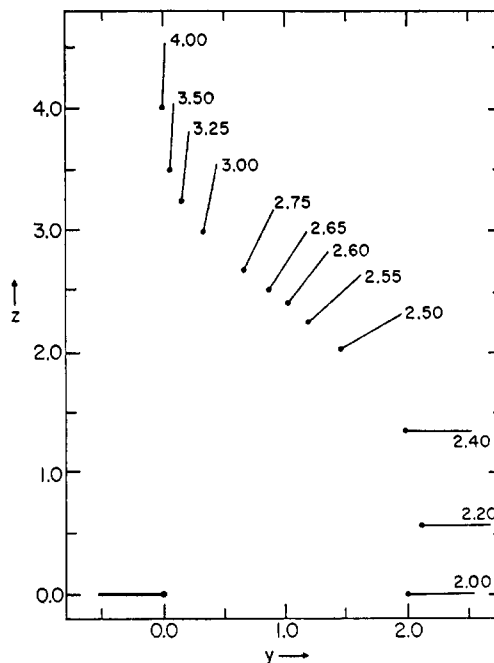


Figure 6. Projection of methylenes in a superimposed series of snapshots. The coordinate system is that of Figure 3. The methylene at lower left is fixed, while the other methylene is approaching it. The numbers accompanying each projection are C-C separations.

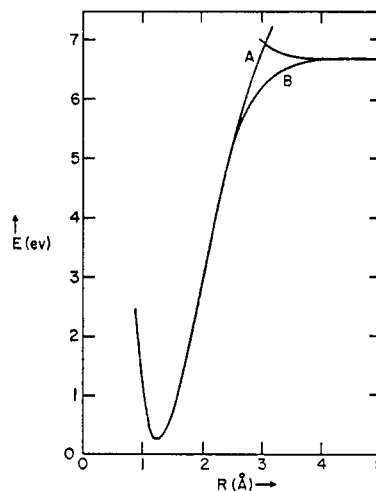


Figure 7. Energy along least-motion (A) approach of two methylenes, and the optimum reaction path (B) specified in Table I. The energy scale refers to an arbitrary energy zero. The horizontal scale is the C-C separation.

near $(-90, 90)$ and equivalent points, but these cease to be two-dimensional minima further in.

Along this optimum path the energy varies as shown in Figure 7; *i.e.*, we compute no activation energy for this path. The same figure shows the energetic requirements of the least-motion pathway. Because of the small energy gap between σ and p , the forbidden approach does not have a large activation energy. Nevertheless our calculations indicate that at every point for $R > 2.5$ Å a D_{2h} geometry is unstable with respect to distortion to the C_s conformation along the optimum

(20) If these constraints are relaxed, *i.e.*, we were to return to 12 degrees of freedom, there would of course, be other potential wells, *e.g.*, $C_2H_2 + H_2$, $CH_3\dot{C}H$, $CH_3 + CH$, etc.

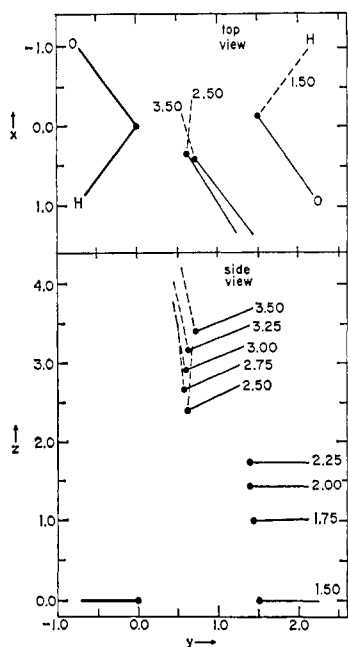


Figure 8. Two views of superimposed snapshots of an optimum *trans* approach of two HNO molecules. At bottom we have a side view (projection on yz plane) and at top a top view (projection on xy plane). The HNO at left is fixed. Solid line of descending HNO is the NO bond, toward us; dashed line is the NH bond, away from us. The labels on descending HNO are N-N separations. To avoid crowding only three of the nine snapshots shown at bottom are illustrated in the top projection.

reaction path. It should be noted that from Figure 1, as well as from our calculations, there is no barrier to the dimerization of two methylenes, both in the $(\sigma)^1(p)^1$ configuration. This configuration yields an excited singlet and the ground state triplet of methylene.^{10,13} Thus the least-motion formation of ethylene from two triplet methylenes is an allowed process, and will compete with the non-least-motion approach of two singlet methylenes which we have calculated.

We should remark here that the extent of motion exhibited by one methylene in Figure 6 is in some sense an artifact of the choice we made in freezing the position of the other methylene. In a center-of-mass coordinate system the relative motions would be more fairly treated.

The non-least-motion reaction path sets the two methylene fragments rotating relative to each other, as they separate. The consequent rotational excitation, relative to the lack of such along a least-motion path, could conceivably be used as an experimental criterion for non-least-motion processes.

The Dimerization of HNO

We chose to study the dimerization of HNO as a model for nitroso compound association. Two HNO units were frozen in their observed ground state geometry.^{7a} The orientation of the molecules and the choice of angular variables are identical with the methylene case. There exists here the further complication that there are two possible isomeric products—the *cis* and *trans* dimers **5** and **6**. There are two separate valleys, merging at infinite separation, which lead to the two products. We first explored each valley in two dimensions, varying θ and $\epsilon\theta$ as before, and then

proceeded to examine the computed pathway in five angular dimensions. In the case of methylene dimerization there was apparent a tendency to maintain a mirror plane of symmetry at large separations. Two HNO molecules placed in a geometry in which two methylenes have C_s symmetry now have only the trivial C_1 symmetry, and there should be no particular constraint keeping them to the specific orientation adopted by two methylenes. It is for this reason that we proceeded to examine a five-dimensional surface for every value of R .

The calculated optimum orientations for the approach of two HNO molecules leading to a *trans* dimer are listed in Table II. The spherical and Euler angles, while

Table II. Optimum Geometries for the *trans* Approach of Two HNO Molecules^a

$R, \text{\AA}$	θ	φ	$\epsilon\varphi$	$\epsilon\theta$	$\epsilon\psi$
3.50	14	60	34	78	-21
3.25	14	55	34	79	-21
3.00	14	54	33	78	-21
2.75	14	55	30	73	-20
2.50	16	61	25	67	-20
2.25	39	89	0	0	0
2.00	44	91	0	0	0
1.75	55	93	0	2	-1
1.50	90	95	0	0	0

^a For the specified N-N separation the optimum values of θ , φ , $\epsilon\varphi$, $\epsilon\theta$, $\epsilon\psi$ are listed.

specific, are not readily visualizable. Moreover they have an unavoidable redundancy built into them²¹ which makes for occasional discontinuities in angle variation not reflected by discontinuities in real orientation. We have found it advisable to plot out views of the molecule along the reaction coordinate. A series of side and plan views of snapshots of the HNO *trans* approach, similar to what we showed above for methylene, is illustrated in Figure 8. The following comments can be made on the basis of this figure, and a similar one not shown here, for the *cis* approach.

1. The *trans* approach is best described as roughly similar to the methylene-methylene interaction. It begins at large R with an attack of one nitrogen lone pair onto the π system of the other, resembling nucleophilic attack on a carbonyl group. The initial stages of reaction are accompanied by some electron transfer from the impinging nitrogen to the other nitroso group. In contrast to the methylene case, the attacking nitroso group is somewhat twisted (see plan and side views) at large R . At $R \sim 2.5 \text{ \AA}$ the potential surface is very flat. For instance, only 0.02 eV in energy separates the observed 2.5 \AA minimum from one with angular parameters identical with those found for the 2.25- \AA geometry. In the region $1.50 < R < 2.50$ the optimum geometry is very much like that in the C_{2h} methylene interval, but small deviations in φ from 90° occur. Finally at $\sim 1.50 \text{ \AA}$ the flat product geometry is achieved.

2. For the *cis* approach we have also optimized all five angles at 0.25- \AA intervals of R . The angles and descent snapshots are very similar to the *trans* illustrations. In particular it is interesting to note that at

(21) E.g., if $\epsilon\theta = 0$ then the orientation $(\epsilon\varphi, \epsilon\theta, \epsilon\psi) = (\alpha, 0, 0)$ is identical with $(\alpha + x, 0, -x)$ for any x .

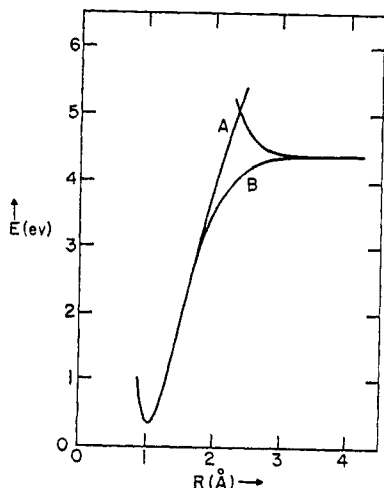
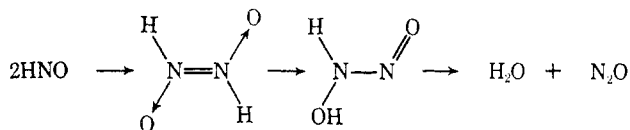


Figure 9. Energy along least motion (A) approach of two HNO molecules, and the optimum reaction path (B) specified in Table II. The energy scale refers to an arbitrary zero.

large R the direction of twist of the attacking HNO group is the same as in the *trans* case; *i.e.*, in the plan view of Figure 8, the H and O labels of the right-hand HNO need only be switched to obtain the best *cis* geometry. Though we do not as yet understand the reason for the twist, the above observation hints that the twist direction is tied up with the electronic structure of the attacked and not the attacking nitroso compound.

3. There is no activation energy for either *cis* or *trans* approach, and their energetic profiles are nearly identical. The *trans* approach potential energy curve is shown in Figure 9. For comparison the energetic requirements of the least-motion approach are shown in the same figure. The dimerization of the nitroso compounds which have been studied has a small but finite activation energy, as we noted at the beginning of this paper. Moreover the dimers are not as stable relative to the monomer as Figure 9 indicates. HNO itself is an extremely reactive species, with the end products of its dimerization being N_2O and H_2O .²² A possible nonconcerted mechanism for this reaction is



We believe that calculations on RNO dimerization, with R other than H, would yield a more thermoneutral dimerization and a small but nonzero activation energy for the reaction.

4. The two valleys leading to *cis* and *trans* dimers are distinct, with an activation energy for moving from one valley to the other at any finite separation.

5. The crystal structures of the nitrosomethane dimers^{3c,d} give a 0.09-Å difference in N-N bond length between the *cis* and *trans* dimers. The overlap populations we calculate at comparable distances indicate also longer N-N and N-O bond lengths for the *cis*

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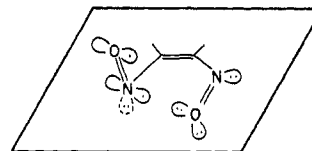
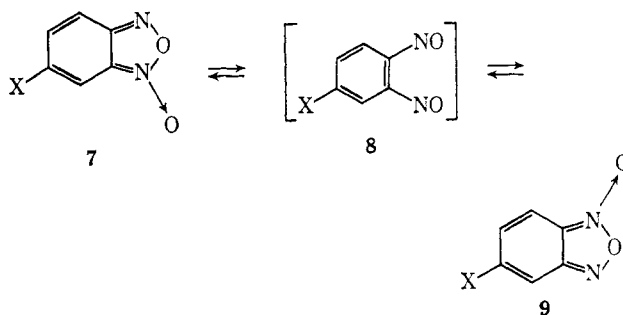


Figure 10. Probable transition state geometry for the isomerization of an *o*-dinitrosobenzene to a benzofurazan oxide structure.

dimer, but we estimate the difference to be a maximum of 0.02 Å.

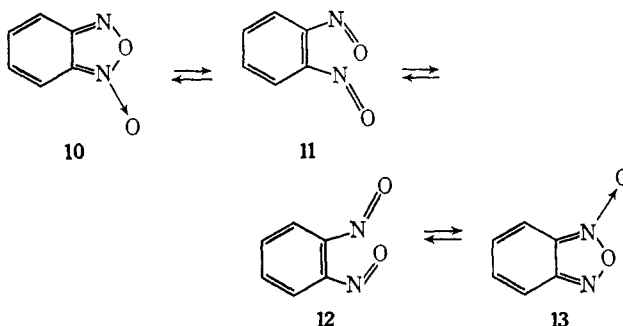
Isomerization of 1,2-Dinitroso Compounds

After a long period of structural controversy²³ benzofurazan oxides were found to possess structures such as 7 and 9, with low activation energies for equilibration of the two isomeric forms.²⁴ Some indirect evidence



for the intermediacy of *o*-dinitrosobenzenes such as 8 in this type of interconversion²⁵ as well as for the interconversion of dinitrosoalkenes in the similar isomerization of simple furazan oxides²⁶ has been presented.

A more detailed description of the isomerization process might be given by the sequence below. Here



there is again the tendency to assume that the interconversion of 10 and 11, or of 12 and 13, all planar molecules, would take place through simple bonding between N and O. This process, however, involves the same proximity of lone pairs (now on N of one nitroso group and O of the other) that discriminated against the

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least-motion dimerization of RNO. Or, again, molecule **10** possesses 12 π electrons, whereas **11** has only 10 such. A level crossing occurs in the simple closure.

The difficulties with the planar transition state are easily bypassed by rotating one nitroso group in **11** or **12** 90° out of planarity. This conformation is then prepared for a bonding interaction involving the oxygen lone pair and the low-lying nitroso group π^* level (see

Figure 10). The analogy with the nitroso compound dimerization is clear.

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Ab Initio Studies of the Electronic Structures of BH_3 , BH_2F , BHF_2 , and BF_3 ^{1a}

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Abstract: The electronic structures of the molecules BH_3 , BH_2F , BHF_2 , and BF_3 have been studied by the *ab initio* self-consistent field molecular orbital method. Of especial interest are changes of certain quantities through the series from no fluorination (BH_3) to complete fluorination (BF_3). These include essentially constant atomic charges for H and F atoms, linearly increasing total positive charge of the central B atom, increase of the $2p\pi$ -type population on B, increasing BF overlap—consisting of a balance between decreasing π overlap and increasing σ overlap, and linear increase of the orbital energy of the lowest unoccupied molecular orbital. Excluding the B $2p\pi$ from bonding yields directly a π energy of 27 kcal for BH_2F , and an estimated value of 59 kcal for BF_3 , based on the π overlap populations. The first ionization potential is examined for the series, and an explanation based on splitting of the degeneracy of the highest filled molecular orbital in BH_3 accounts for the decrease in the ionization potential upon initial fluorination. Consideration of calculated and experimental ionization potentials for BH_3 and BF_3 leads to an estimate of 11.8 and 13.6 eV for the first ionization potentials of BH_2F and BHF_2 . Comparisons of both inner-shell and valence-shell ionization potentials have also been made with the analogous series CH_4 to CHF_3 , based on *ab initio* calculations of Ha and Allen. The 1s binding energies of B and C correlate linearly with the Mulliken charge on the atom, and for multiple fluorination the changes in 1s binding energy are multiples of the change for a single fluorination.

The electronic structures of trigonally bonded boron compounds have been of interest for many years. In the simplest picture sp^2 hybrids of B are used for bonding with atoms (ligands) attached to B, and the empty $2p\pi$ atomic orbital of the B atom can accept electrons from the π orbitals (if there are any) of the attached atoms, with a corresponding increase in the strength of chemical bonding. Such concepts have been discussed both in the valence-bond² and the molecular orbital (MO) pictures.³ A general discussion of this family of molecules and the coordination compounds they form has been presented by Coyle and Stone.⁴ Several semiempirical calculations have been published about such systems recently,⁵⁻⁹ but non-

empirical studies exist only for BH_3 ^{10,11} and for BHF_2 .¹²

We chose to study the entire series BH_3 , BH_2F , BHF_2 , and BF_3 for obvious reasons. The successive substitution of F for H, with the corresponding changes in electronic structure, presented an interesting opportunity to study a *series* of well-related molecules. Since many chemical phenomena are of a relative nature, it is especially worthwhile to examine such a series.

This paper will first describe and summarize the calculations done. Then the valence-shell electronic structure will be analyzed. Finally, the changes in both the first (smallest) ionization potential and the binding energy of the B 1s electron through the series are considered. A comparison will be made of these results for the latter quantities with similar quantities for the series CH_4 to CHF_3 , as well as with available experimental results.

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