An *Ab Initio* Molecular Orbital Study of the Hydrogen, Lithium, and Fluorine Derivatives of Nitric Oxide

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Abstract: An *ab initio* molecular orbital study, using a Gaussian basis, has been carried out on the hydrogen, lithium, and fluorine derivatives of nitric oxide. The connectedness and molecular geometries of the hydrogen and fluorine species were found to be in agreement with experiment; the results for the lithium derivative were somewhat at variance with the only previous experimental study. Mulliken population analyses and electron density maps are also presented and discussed.

The advent of the large computer has provided the opportunity for chemists to initiate *ab initio* molecular orbital studies of a wide range of compounds. It would appear that these calculations, which can be expected to yield relatively realistic molecular geometries[1] and charge distributions,[2] will have their greatest value in the study of molecules which have not yet been completely characterized and which can be prepared only under rather specialized laboratory conditions. We present herein such a study of several derivatives of nitric oxide; this work will also provide a foundation for future calculations on several related and novel compounds.

Method

A double-precision Fortran IV version of the POLYATOM[3,4] system, which utilizes a Gaussian basis to obtain an iterative solution to Roothaan's equations,[5] was adopted for our computations. The normalized Gaussian functions are of the form

$$G = Nr^l \exp(-\alpha r^2) Y_l^m(\theta, \phi) \tag{1}$$

where N is the normalization coefficient; the $Y_l^m(\theta, \phi)$ are normalized spherical harmonics; and α is the orbital exponent. We employed the exponents given by Whitman and Hornback[6] for the first-row elements, excluding hydrogen and lithium; the hydrogen exponents were those suggested by Reeves,[7] while the lithium exponents were a truncation of the set given by Huzinaga.[8]

Our strategy of calculation followed the standard procedure of initially assuming a set of hopefully realistic bond lengths and angles; each of these parameters was successively varied, while holding the others constant, until an energy minimum was located. The position of this minimum was taken as the equilibrium value of the bond length or angle, and the final configuration was assumed to be the equilibrium geometry of the molecule. Implicit in this procedure are the

(1) K. F. Freed, *Chem. Phys. Lett.*, **2**, 255 (1968).
(2) G. G. Hall, *Phil. Mag.*, **6**, 249 (1961).
(3) I. G. Csizmadia, M. C. Harrison, J. W. Moskowitz, and B. T. Sutcliffe, *Theor. Chim. Acta*, **6**, 191, 217 (1966).
(4) POLYATOM Program Set for Nonempirical Molecular Calculations; QCPE 47.1, Quantum Chemistry Program Exchange, Indiana University.
(5) C. C. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).
(6) D. R. Whitman and G. J. Hornback, *J. Chem. Phys.*, **51**, 398 (1969).
(7) C. M. Reeves, *ibid.*, **39**, 1 (1963).
(8) S. Huzinaga, *ibid.*, **42**, 1293 (1965).

assumptions that the initial set of geometrical parameters correspond to a point in the local vicinity of the absolute minimum of the potential energy surface, and that the equilibrium value of a parameter can be located independently of the values of the other lengths and angles. These assumptions are forced upon us not by their intrinsic attractiveness but by brutal practicality. They could be avoided by constructing a complete potential energy surface; however, except for the simplest of molecules, the construction of such a surface would require such copious amounts of computer time as to make the cost of the study prohibitive.

Results and Discussion

The calculated geometries and energies are listed in Table I. Although first prepared in 1933,[9] the hydro-

Table I. The Calculated Molecular Geometries and Energies

X(NO)	Bond angle, deg	$R(X-N)$ or $R(X-O)$, Å	$R(N-O)$, Å	E, au
HNO	110	1.04	1.21	−129.58137
HON	112	0.99	1.32	−129.54264
LiNO	68	1.82	1.32	−136.12798
LiON	81	1.68	1.33	−136.12835
FNO	109	1.50	1.24	−227.62356
FON	113	1.55	1.27	−227.54910

gen derivative of nitric oxide was first observed spectroscopically by Dalby[10] in 1958. He concluded that the connectedness was HNO with a bond angle of 108.5° and bond lengths $R(N-H) = 1.062$ and $R(N-O) = 1.211$ Å. A subsequent study by Brown and Pimentel[11] indicated that a bond angle of 110° was more appropriate; they reported bond lengths basically in agreement with Dalby's results. In a test of the unrestricted Hartree-Fock method, Salotto and Burnelle[12] computed a ground-state angle of 110.4° and found that $R(N-H) = 1.038$ and $R(N-O) = 1.321$ Å; they also reported an energy, calculated by Roothaan's method,[5] of −129.5880 au. Our results for HNO, which were obtained with a 7s + 3p basis set on each of nitrogen and oxygen and three s-type Gaussians on

(9) P. Harteck, *Ber.* **66**, 423 (1933).
(10) F. W. Dalby, *Can. J. Phys.*, **36**, 1336 (1958).
(11) H. W. Brown and G. C. Pimentel, *J. Chem. Phys.*, **29**, 883 (1958).
(12) A. W. Salotto and L. Burnelle, *ibid.*, **52**, 2936 (1970).
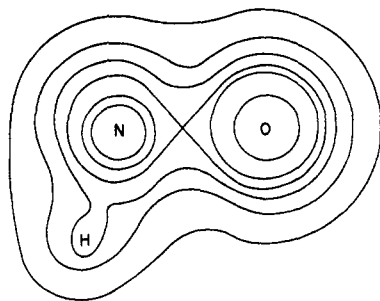
Figure 1. A map of the electron density in the molecular plane of HNO. The contours ranging out from the heavy nuclei are in the order 1.25, 0.65, 0.45, 0.27, 0.15, and 0.05.
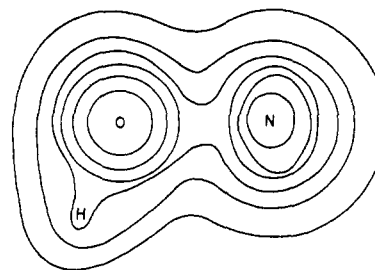

Figure 2. A map of the electron density in the molecular plane of HON. The contours ranging out from the heavy nuclei are in the order 1.25, 0.65, 0.45, 0.27, 0.15, and 0.05.

hydrogen, are essentially in agreement with the above experimental and computational studies.

We investigated the possibility of isomerism. It can be seen from Table I that HON is predicted to be less stable than HNO; the energy difference is 24.3 kcal/mol. In Tables II and III we present a Mulliken

Table II. Mulliken Population Analysis of HNO

| Orbital | Energy, au | Partial overlap populations | |
		H–N	N–O
1a	− 20.6693	0.000	0.002
2a	− 15.7186	0.001	0.001
3a	− 1.5496	0.018	0.566
4a	− 0.9963	0.347	−0.396
5a	− 0.7258	0.132	0.246
6a	− 0.6352	0.047	0.099
1b	− 0.5765	0.0	0.394
7a	− 0.4159	−0.017	−0.435
	Total overlap population	0.528	0.476

Gross atomic charges   H, 0.28; N, 0.01; O, −0.29

Table III. Mulliken Population Analysis of HON

| Orbital | Energy, au | Partial overlap populations | |
		H–O	N–O
1a	− 20.6824	0.001	0.001
2a	− 15.6650	0.000	0.000
3a	− 1.5001	0.103	0.357
4a	− 0.9808	0.250	−0.019
5a	− 0.7065	0.116	0.086
1b	− 0.5871	0.0	0.022
6a	− 0.5845	0.004	−0.130
7a	− 0.3868	0.033	−0.286
	Total overlap population	0.506	0.228

Gross atomic charges   H, 0.39; O, −0.50; N, 0.10

population analysis[13] for these isomers. Upon comparing the overlap populations of the molecular orbitals of HNO with those of HON, we see that the hydrogen-nitrogen bond of the former species is predicted to be of similar strength to the hydrogen–oxygen bond in HON. This, however, is not the case with regard to the nitrogen–oxygen bonds. Generally, the absolute value of the nitrogen–oxygen overlap population of an orbital of HNO is greater than the contribution from the corresponding orbital of HON. Of particular note are the 1b orbitals whose overlap populations are a measure of the π-electron density in the respective nitrogen–oxygen bond regions. In HNO the 1b

(13) R. S. Mulliken, *J. Chem. Phys.*, 23, 1833 (1955).

population is 0.392 while in HON it is only 0.022. The net result, reflected in the total overlap populations, is a stronger nitrogen-oxygen interaction in HNO than in HON.

A more realistic and detailed knowledge of the molecular charge distribution is found in a map of the total electron density, whose value at point **r** is given by

$$\rho(\mathbf{r}) = \Sigma_i N_i \phi_i^*(\mathbf{r}) \phi_i(\mathbf{r}) \qquad (2)$$

where N_i is the number of electrons in molecular orbital ϕ_i. Maps of the electron density in the molecular planes of HNO and HON are presented in Figures 1 and 2. We see that the gross description of the charge distributions given by the Mulliken population analysis is consistent with the electron-density maps. In particular, the charge distributions of the two isomers in the regions of their bound hydrogens are quite similar, while the distributions in the respective nitrogen–oxygen bond regions are a bit dissimilar. That is, in HON the 0.45 density contours are localized individually on oxygen and nitrogen while in HNO this contour essentially envelopes both of these nuclei; of course, these maps do not allow a comparison of the contributions of the respective π-electron densities which would occur perpendicular to the molecular plane. After combining the information gleaned from the density maps with that of the population analysis, it would appear that it is the difference in nitrogen-oxygen bonding that is responsible for the greater stability of HNO. This is consistent with the classical valence description of a double nitrogen–oxygen bond in HNO and only a single bond in HON.

Lithium nitroxide was first prepared by Asmussen[14] in 1957, while Andrews and Pimentel,[15] in the only other study of this compound, observed its infrared spectrum in 1966. Andrews and Pimentel's results favored, although not unequivocally, a connectedness of LiON with a bond angle of 100 ± 0°; their reported bond lengths were $R(\text{Li–O}) = 1.63$ and $R(\text{N–O}) = 1.30$ Å. Our results for LiON, which were computed with a basis set of six s-type Gaussians on lithium and 6s + 3p Gaussians on both nitrogen and oxygen, are partially at variance with the spectroscopic results. Although our distances are in good agreement with Andrews and Pimentel's values, our bond angle falls 9° outside their lower bound. Further, upon considering the possibility of isomerism, it was found that the energies of LiNO and LiON were virtually identical and an un-

(14) R. W. Asmussen, *Acta Chem. Scand.*, 11, 1435 (1957).

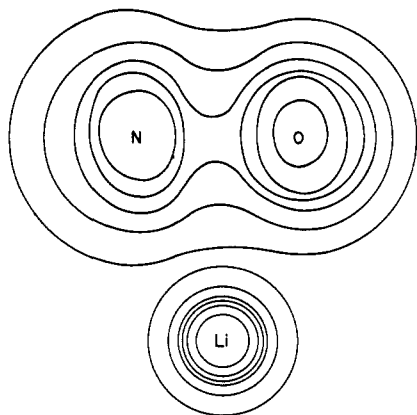(15) W. L. S. Andrews and G. C. Pimentel, *J. Chem. Phys.*, 44, 2361 (1966).

Figure 3. A map of the electron density in the molecular plane of LiNO. The contours range out from each nucleus in the order 1.25, 0.65, 0.45, 0.27, 0.15, and 0.05.
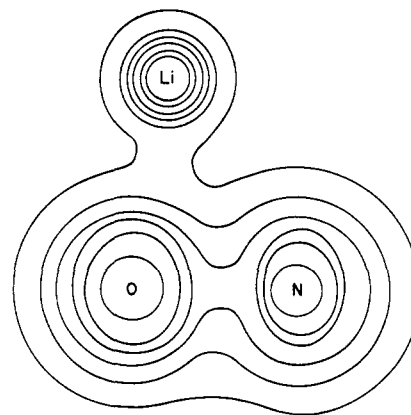

Figure 4. A map of the electron density in the molecular plane of LiON. The contours range out from each nucleus in the order 1.25, 0.65, 0.45, 0.27, 0.15, and 0.05.

ambiguous prediction of the relative stability of these isomers could not be made. It should be noted (see Figure 3) that we found the lithium nucleus in LiNO to be almost equidistant from the nitrogen and oxygen nuclei; thus, the statement that its connectedness is LiNO is not completely justifiable.

Tables IV and V present a population analysis for the lithium nitroxide isomers. We see that neither isomer

Table IV. Mulliken Population Analysis of LiNO

| Orbital | Energy, au | Partial overlap populations | | |
		Li–N	Li–O	N–O
1a	−20.5320	0.000	0.000	−0.001
2a	−15.5568	0.000	0.000	−0.001
3a	−2.4152	0.002	0.002	0.000
4a	−1.3253	0.013	0.020	0.525
5a	−0.7920	−0.006	0.003	−0.025
6a	−0.5366	0.016	0.022	0.307
7a	−0.4477	0.068	0.012	−0.014
1b	−0.4349	0.0	0.0	0.314
8a	−0.2640	0.004	−0.004	−0.539
Total overlap population		0.098	0.055	0.565
Gross atomic charges	Li, 0.82; N, −0.30; O, −0.51			

Table V. Mulliken Population Analysis of LiON

| Orbital | Energy, au | Partial overlap populations | | |
		Li–N	Li–O	N–O
1a	−20.5228	0.000	0.000	−0.001
2a	−15.5621	0.000	0.000	−0.001
3a	−2.4127	0.001	0.004	0.000
4a	−1.3135	0.015	0.023	0.503
5a	−0.7926	−0.009	0.009	−0.011
6a	−0.5309	0.017	0.013	0.296
7a	−0.4435	0.049	0.024	−0.008
1b	−0.4329	0.0	0.0	0.294
8a	−0.2629	0.028	−0.019	−0.509
Total overlap population		0.100	0.054	0.562
Gross atomic charges	Li, 0.81; O, −0.56; N, −0.24			

has a molecular orbital which is significantly lithium–nitrogen or lithium–oxygen bonding and, in contrast to the case of the hydrogen derivative, the nitrogen–oxygen overlap populations of corresponding orbitals of LiNO and LiON are approximately equivalent. The total overlap populations of both isomers reflect nitrogen–oxygen bonds of similar strengths and little

overlap between lithium and the nitric oxide group. In comparing the gross atomic charges of the lithium and the hydrogen isomers, it is observed that while HNO and HON have positively charged nitrogens and negatively charged oxygens, both of these centers possess rather large negative charges in the lithium derivatives. Also, the lithium atoms are assigned positive charges which are virtually twice as large as the charge on the hydrogen of the corresponding isomer. This apparent charge separation plus the slight overlap between lithium and the nitric oxide group suggests that the lithium isomers are ionic compounds.

The electron density maps for LiNO and LiON are given in Figures 3 and 4. As indicated by the population analysis, the charge densities in the nitrogen–oxygen bond regions are quite similar. It is also observed that both isomers have a significant amount of charge separation between the lithium and the nitric oxide group, which tends to confirm the suggestion that LiNO and LiON are ionic species. In a minor respect this result is reassuring. Our calculations predicted rather acute bond angles for both isomers, but if they are ionic, the molecular stability is not due to directional bonding but instead it is primarily electrostatic in origin; it is conceivable that an ionic molecule with an atomic cation attracted to a diatomic anion will have a resultant molecular geometry in which the nuclei lie on the corners of an acute triangle.

An assumption, perhaps unjustified, which we have made in the course of our calculations is that lithium nitroxide is a closed-shell molecule. If, as our results suggest, Li(NO) is ionic, then it will contain the anion NO⁻ as an approximately identifiable moiety. NO⁻ is isoelectronic with molecular oxygen and, from elementary molecular orbital theory, it could possibly exist in the triplet state. If this were true, it is conceivable that an ionic Li(NO) could instead be an open-shell molecule, thus invalidating our results. One piece of experimental evidence in our favor is Asmussen's[14] report that Li(NO) is diamagnetic.

It would appear that because of the partial disagreement of our results with the one spectroscopic study, the lack of an unambiguous indication of the connectedness of Li(NO), and the possibility that it is an open-shell molecule, this system would warrant further experimental and theoretical consideration.
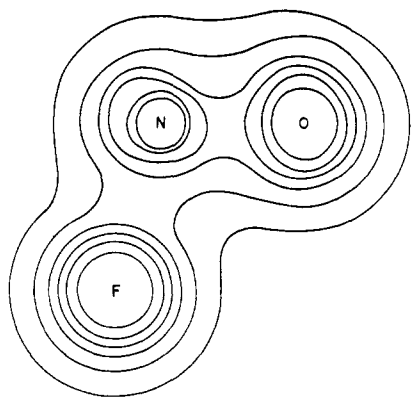
Figure 5. A map of the electron density in the molecular plane of FNO. The contours range out from each nucleus in the order 1.25, 0.65, 0.45, 0.27, 0.15, and 0.05.
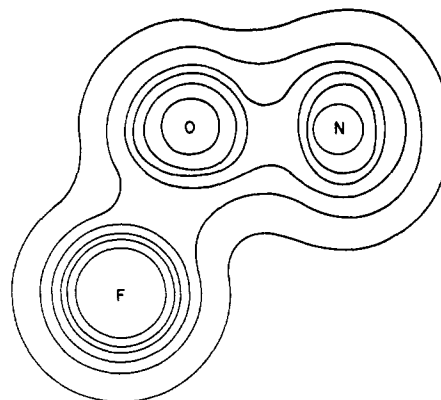

Figure 6. A map of the electron density in the molecular plane of FON. The contours range out from each nucleus in the order 1.25, 0.65, 0.45, 0.27, 0.15, and 0.05.

Experimentally, FNO has been determined[16] to have a bond angle of 110.2°, a fluorine–nitrogen bond length of 1.52 Å, and a nitrogen–oxygen bond length of 1.13 Å. Peyerimhoff and Buenker[17] have made an *ab initio* study of this molecule with a basis set of Gaussian lobe functions. They calculated a bond angle of 111.1° and a fluorine–nitrogen bond length of 1.53 Å and assumed the experimental nitrogen–oxygen bond length. These investigators also reported an energy for the experimental geometry of FNO of −228.3800 au; Petrongolo, Scrocco, and Tomasi[18] obtained an energy of −227.7084 au using the same geometry and a minimal basis set of Slater-type orbitals. Our results were calculated with a 7s + 3p basis set centered on fluorine and a 5s + 2p set on each of nitrogen and oxygen.

Our calculated bond angle and fluorine–nitrogen bond length are in good agreement with experiment and Peyerimhoff and Buenker's values, while our nitrogen–oxygen bond length is ∼0.1 Å too long. The fact that the latter bond length is not in good agreement with experiment partially suggests that the portion of our basis set centered on nitrogen and oxygen is not completely adequate. Unfortunately, we were unable to expand the basis set because of the increased time and storage space that would have been required for the calculation.

Our study of FON predicts, in agreement with experiment, that it is not as stable as FNO. The difference in the calculated energies is 46.7 kcal/mol. The Mulliken population analyses are presented in Tables VI and VII. Somewhat analogous to the case of the hydrogen derivative, we find that the total overlap population of the fluorine–nitrogen bond in FNO is almost the same as the overlap population of the fluorine–oxygen bond in FON. There is also a difference in the nitrogen–oxygen overlap populations of the two isomers, with the bond predicted to be stronger in FNO than in FON. The difference between the nitrogen–oxygen overlap populations of the two fluorine isomers however is not as great as for the hydrogen isomers. This seems to be consistent with a calculated difference of only 0.03 Å in the nitrogen–

(16) C. V. Stephenson and E. A. Jones, *J. Chem. Phys.*, 20, 135 (1952).

(17) S. D. Peyerimhoff and R. J. Buenker, *Theor. Chim. Acta*, 9, 103 (1968).

(18) C. Petrongolo, E. Scrocco, and J. Tomasi, *J. Chem. Phys.*, 48, 407 (1968).

oxygen bond lengths for the former species and a 0.11 Å difference in the latter. In addition, the charge separations indicated by the gross atomic charges are not as extreme as that observed for Li(NO); in fact, after acknowledging the difference in electronegativity between fluorine and hydrogen, the charge separation in F(NO) is qualitatively similar to that in H(NO).

Table VI. Mulliken Population Analysis of FNO

		Partial overlap populations	
Orbital	Energy, au	F–N	N–O
1 a	−26.2989	0.000	0.000
2 a	−20.8683	0.000	−0.003
3 a	−15.9477	−0.001	−0.002
4 a	−1.6332	0.162	0.362
5 a	−1.5203	−0.002	0.238
6 a	−0.9766	0.006	−0.200
7 a	−0.7098	0.118	0.207
8 a	−0.6813	0.118	0.039
1 b	−0.6576	0.131	0.144
9 a	−0.5689	−0.080	0.054
2 b	−0.5474	−0.111	0.182
10a	−0.4575	−0.081	−0.183
Total overlap population		0.261	0.837

Gross atomic charges F, −0.30; N, 0.34; O, −0.04

Table VII. Mulliken Population Analysis of FON

		Partial overlap populations	
Orbital	Energy, au	F–O	N–O
1 a	−26.2856	0.000	0.000
2 a	−20.9811	0.000	−0.002
3 a	−15.8304	0.000	−0.002
4 a	−1.6338	0.148	0.317
5 a	−1.4714	−0.049	0.215
6 a	−0.9810	0.034	−0.107
7 a	−0.6873	0.148	0.186
1 b	−0.6732	0.094	0.150
8 a	−0.6482	0.085	−0.052
9 a	−0.5615	−0.081	0.033
2 b	−0.5557	−0.100	0.080
10a	−0.4011	−0.042	−0.099
Total overlap population		0.237	0.717

Gross atomic charges F, −0.29; O, 0.14; N, 0.15

These parallels between the overlap populations and the gross atomic charges of the fluorine and hydrogen derivatives indicate that the bonding in F(NO) more closely resembles that in H(NO) than in Li(NO).

The electron density maps are presented in Figures 5 and 6. The overall charge distributions in the fluorine–nitrogen and fluorine–oxygen bond regions of FNO and FON are somewhat similar, as are the densities in the nitrogen–oxygen bond regions. From the electron density maps, it is also observed, as was pointed out by Peyerimhoff and Buenker[17] for FNO, that both isomers appear to be molecules in which the fluorine atoms and the nitric oxide group retain a large measure of their individual identities. Surmising from the similarity of the population analyses of the fluorine and hydrogen derivatives that the bonding in F(NO) is primarily covalent, this result is then suggestive of a rather weak bond between fluorine and nitric oxide in both isomeric configurations. Peyerimhoff and Buenker noted that such a bonding description of FNO is supported by its rather long fluorine–nitrogen bond length; we see that this description seems also to apply to FON, whose calculated fluorine–oxygen bond length is ~0.1 Å

longer than the anticipated value.[19] Parenthetically, it should be noted that Peyerimhoff and Buenker ascribed the molecular stability of FNO primarily to its highest occupied molecular orbital; however, our population analysis indicates that FNO's stability is due to a net contribution of several molecular orbitals and, in fact, the highest occupied orbital is predicted to be slightly fluorine–nitrogen antibonding. The same trend is observed for FON.

(19) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960, p 229.

Analysis of Qualitative Theories for Electrocyclic Transformations Based on the Results of *Ab Initio* Self-Consistent-Field and Configuration-Interaction Calculations

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Abstract: Analysis of the conservation of orbital symmetry principle of Woodward and Hoffmann shows it to rest upon the implied agreement between the *signs* of differences in total and certain critical orbital energies calculated for two different rotational modes of a given electrocyclic transformation; emphasis is placed on the fact that the theory does not require exact equality between the two energy differences. In addition, it is pointed out that evaluation of the pertinent energy quantities should be made over the respective minimum-energy reaction paths for each rotational mode; in the case of the cyclobutene–*cis*-butadiene transformation SCF and CI calculations indicate, for example, that the rotational phase of the reaction is initiated only after an expanded cyclobutene structure has been formed and then continues to completion before further significant increase in terminal CC bond distance occurs. Very good agreement is found to exist between differences in total and critical orbital energies for the dis- and conrotatory modes in the aforementioned C_4H_6 isomerization when evaluated over the indicated reaction paths, and *nowhere* in these calculations or those of Clark and Armstrong for $C_3H_5^*$ systems is a violation of the requirement for equal signs of the two types of energy differences found, thereby substantiating the validity of the assumptions of the conservation of orbital symmetry principle, at least for the thermochemical processes. A similar stepwise mechanism for the photochemically induced isomerization of cyclobutene and *cis*-butadiene is suggested by additional calculations, and it is pointed out that for the prerotation conformations of the lowest excited states of these systems orbital symmetry is conserved for *both* rotational modes; prediction of the preferred rotational mode in this case is thus shown to be based on a secondary effect introduced by taking account of the role of configuration interaction in the description of these processes. General circumstances for which the aforementioned qualitative theory may be expected to lead to incorrect predictions are also discussed.

In a previous paper[1] the potential surface involved in the thermochemically induced electrocyclic transformation between *cis*-butadiene and cyclobutene was investigated in detail by means of *ab initio* SCF and CI calculations employing a moderately large AO basis set. This work has indicated that the particular

isomerization reaction in question, and quite likely many others related to it, proceeds *via* a stepwise mechanism in which rotation of the methylene groups, in either the con- or the disrotatory mode, occurs only after an intermediate (not necessarily stable) structure with a partially destroyed ring of carbons has been formed. The key point in these findings is that the rotational phase of the reaction is not initiated until CC stretch (or contraction in the case of the open-chain isomer) deformation of the equilibrium form of the

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(1) K. Hsu, R. J. Buenker, and S. D. Peyerimhoff, *J. Amer. Chem. Soc.*, 93, 2117 (1971); hereafter referred to as part I.