correspond to an angular fluctuation of the phosphate of at least ±30°. This estimate is based on the minimum angular fluctuation required about the σ_{22} tensor axis, to provide the observed degree of averaging. If the axis of the fluctuation is not the σ_{22} axis, then the size of the fluctuation must be even larger. Since the features of the powder spectrum are not severely broadened as water is added, the motion must always be in the fast exchange limit, at a minimum frequency of ca. 10 kHz, and increasing in amplitude with additional water. The spectrum at 20 waters per nucleotide corresponds closely with that obtained for B-form DNA prepared by vapor-phase equilibration. The motions at this point may correspond to the approximately nanosecond time scale processes that are observed in solution and are attributed variously to strictly local[3,4] and a superposition of local and collective[8] motions. The line shape that occurs is consistent with a twisting motion about the long axis of the helix, assuming that σ_{22} is near the helix axis, expected from model compound studies. The angular fluctuation derived from the powder line shape is larger than that for the torsional modes derived from fluorescence measurements in solution. However, the NMR measurement is sensitive to slower motions than the optical measurements, and hence the amplitude will be larger if slow motions are present and their contribution is included in the total amplitude. Upon further addition of water, the averaging becomes even more drastic, with an essentially isotropically averaged line occurring by 33 waters per nucleotide. The relaxation behavior does not change significantly over this range, which indicates that the new motion is too slow to be efficient for relaxation, bracketing it to be in the range greater than ca. 10 kHz but less than 10 MHz. This motion is equivalent in effect to (and probably is the same as) the motion observed in B-form DNA upon raising the temperature. Opella et al.[7] did not observe averaging of the deuterium quadrupole coupling tensor of a base-attached hydrogen in the same sample for which the ^{31}P tensor averaging was observed. However, in a recent report[19] Valeutine and Opella concluded from partially averaged ^{15}N spectra that backbone motions also appear at the level of hydration of 5 water molecules per nucleotide. These motions must be internal since at this low level of hydration, tumbling of the DNA in the solvent would be extremely unlikely. The discrepancy between their ^{2}H and ^{15}N results remains unexplained, but given the low sensitivity of ^{2}H and the broad spectra observed, the initial partial averaging of the ^{2}H tensor could have been obscured by quadrupolar effects. It is clear from the findings reported here that hydration is essential to permit the type of internal motions in DNA which can be detected by NMR and that the amplitude of such motions increases with an increasing degree of hydration.

From the present work we have shown that several different kinds of motion occur in DNA at various levels of hydration. The measurements are thus far limited to ^{31}P and hence probe only the backbone of the DNA. Further measurements will be made on defined-sequence DNA with labels incorporated in various sites to further define the nature of these motions.

Acknowledgment. We thank Dr. M. Hogan for preparing the DNA used in these studies and for many helpful discussions on DNA dynamics. This research is funded by Grant GP23633, National Science Foundation Grant PCM 80-21899, and National Institutes of Health Grant RR00711.

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(19) Valeutine, K.; Opella, S. J. In "Conversation in Biomolecular Stereodynamics"; Sarma, R. H., Ed.; Abstracts No. 17, p 42, 1983.

Ground States of Molecules. 62.[1] MINDO/3 and MNDO Studies of Some Cheletropic Reactions

Michael J. S. Dewar* and Lek Chantranupong[2]

Contribution from the Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712. Received December 16, 1982. Revised Manuscript Received July 16, 1983

Abstract: MNDO and MINDO/3 calculations are reported for the reverse cheletropic eliminations of nitrogen from *N*-(3-pyrrolinyl)nitrene and of carbon monoxide from 4-cyclopentenone and from tricyclo[5.2.1.0^{2,6}]deca-3,8-diene-5,10-dione, and the reverse Diels–Alder elimination of nitrogen from 3,6-dihydropyridazine. All these reactions are predicted to take place via very unsymmetrical transition states in which one of the breaking bonds is almost intact, leading to biradical-like species which then dissociate.

Introduction

While the mechanisms of cheletropic reactions[3] have been extensively discussed[4,5] in terms of qualitative MO theory, no adequate quantitative calculations for such reactions seem as yet to have been published. In order to be of any real chemical value in such connections, the calculations must not only be carried out by a procedure of adequate accuracy and reliability, but also with full geometry optimization, using a derivative optimization method and without making any assumptions.[6] Transition states must also be characterized by the McIver–Komornicki[7] procedure of calculating force constants and transition vectors. These requirements make calculations by adequate ab initio procedures prohibitively expensive for any but the simplest organic molecules.[8]

Meaningful calculations for the larger systems of direct interest to organic chemists can therefore be carried out at present only by some semiempirical procedure, and the only ones with any real claim to adequate accuracy currently available are the parametric methods developed by our group, i.e., MINDO/3[9] and MNDO.[10]

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(1) For Part 60 in this series, see: Dewar, M. J. S.; Nelson, D. J. *J. Am. Chem. Soc.*, accepted for publication.

(2) Robert A. Welch Predoctoral Fellow.

(3) Woodward, R. B.; Hoffmann, R. "The Conservation of Orbital Symmetry"; Academic Press: New York, 1972.

(4) Dewar, M. J. S. *Angew. Chem.* **1971**, *83*, 859; *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 761.

(5) Dewar, M. J. S.; Dougherty, R. C. "The PMO Theory of Organic Chemistry"; Plenum Press: New York, 1975.

(6) Any assumptions concerning the geometry of the TS must be based on an assumed mechanism for the reaction. Any calculation making such assumptions will then tend to reproduce the assumed mechanism, right or wrong.

(7) McIver, J. W., Jr.; Komornicki, A. *J. Am. Chem. Soc.* **1972**, *94*, 2625; *Chem. Phys. Lett.* **1971**, *10*, 303.

(8) In order to obtain acceptable results, it is necessary to use a large basis set (of at least double-ζ quality) and to allow for electron correlation either by very extensive CI or some comparable procedure. See, e.g.: Komornicki, A.; Goddard, J. D.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1980**, *102*, 1763.

(9) Bingham, R. C.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 1285, 1294, 1302.

(10) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899, 4907.

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Comparative tests[11] have shown that the results they give are, in general, comparable with those from rather good ab initio calculations and far superior to ones using small basis sets (e.g., STO-3G). Since the cost of calculations by our procedures is less by at least three orders of magnitude than that by any comparable ab initio method, they can be applied to quite large molecules, using computers that are generally available.

No current procedure can be relied on a priori, all of them being essentially empirical so far as chemical applications are concerned. The results can be trusted only insofar as the method has been tested, by comparisons with experiment. MINDO/3 and MNDO have the advantage of having been tested more thoroughly than any other procedure, parametric or ab initio, so it is usually possible to foretell their performance in any given connection. We therefore decided to use them in a survey of cheletropic reactions. Here we report results for some simple reverse cheletropic reactions involving loss of N_2 or CO from partly conjugated rings.

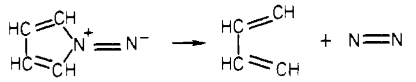
Procedure

The calculations were carried out using the standard MINDO/3[9] and MNDO[10] methods and parameters. Calculations for biradical-like, or potentially biradical-like, species were also carried out using the analogous spin-unrestricted treatments, UMINDO/3[12] and UMNDO.[13] Geometries were found by minimizing the energy with respect to all geometrical variables, no assumptions being made other than that of appropriate symmetry in deliberate calculations of symmetric structures. The minimizations were carried out by the Davidon–Fletcher–Powell[14] method, incorporated in our MOPAC computer programs.[15] Transition states were located approximately by the reaction coordinate method,[16] then refined by minimizing the norm of the gradient of the energy,[7] and characterized[7] by calculating force constants and transition vectors, as indicated above.

Results and Discussion

A. Conversion of *N*-(3-Pyrrolinyl)nitrene (1) to Butadiene (2).

The first reaction studied was the reverse cheletropic decomposition of *N*-(3-pyrrolinyl)nitrene (**1**) to form butadiene (**2**) and nitrogen.



1 **2**

(1)

While **1** itself is still unknown, saturated nitrenes are known to lose N_2 very readily, even below room temperature,[17] implying that the corresponding activation energies cannot be significantly greater than 20 kcal/mol. That for **1** is likely to be even less since it leads to a normal molecule rather than a biradical.

Table I shows the bond lengths, heats of formation (ΔH_f), first ionization energies (I_1), and dipole moments (μ) calculated for **1** by MINDO/3 and MNDO. Both methods predict **1** to have C_{2v} symmetry, as expected, and the geometries predicted by both are similar. MINDO/3 gave a much more negative value for ΔH_f, and a smaller one for μ, than MNDO. Since these differences are probably due to the tendency of MINDO/3 to overestimate the stabilities of molecules containing adjacent heteroatoms,[9] the MNDO values are more likely to be correct. The values for I_1 were calculated by using Koopmans' theorem. Here again the MNDO value is preferable because this is an area where MNDO excels.[10,18] No data are available for **1**, or for any derivative of **1**, for comparison with these predictions.

Table I. Calculated Properties of 3-Pyrroline

		MINDO/3	MNDO
bond lengths (Å)	N_1C_2	1.504	1.524
	C_2C_3	1.493	1.508
	C_3C_4	1.344	1.348
	N_1N_6	1.161	1.200
	C_2H	1.123	1.113
	C_3H	1.101	1.084
formal charge (e)	N_1	0.366	−0.029
	C_2	0.004	0.099
	C_3	−0.0024	−0.110
	N_6	−0.324	−0.282
	H_2	−0.010	0.040
	H_3	−0.010	0.085
ΔH_f (kcal/mol)		52.1	77.5
I_1 (eV)		7.85	8.75
μ (D)		2.75	3.88
symmetry		C_{2v}	C_{2v}

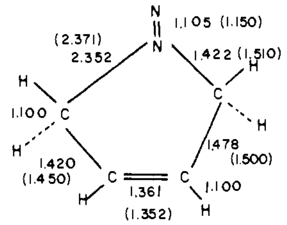


Figure 1. Geometries calculated by MINDO/3 (MNDO) for the transition state for thermolysis of **1**.

The calculated and observed heats of formation of the products ($\mathbf{2} + N_2$) are as follows:

$$\text{MINDO/3, 37.1; MNDO, 36.9; obsd,}^{19}\ 26.0\ \text{kcal/mol} \quad (2)$$

The heats of reaction (ΔH) for conversion of **1** to ($\mathbf{2} + N_2$) are then:

$$\text{MINDO/3, } -15.0\text{; MNDO, } -40.2\ \text{kcal/mol} \quad (3)$$

For reasons indicated above, the MNDO value is probably the better though in view of (2), even it may well be numerically too small by ca. 10 kcal/mol. The reaction is in any case extremely exothermic.

The course of the reaction was then studied by MINDO/3 and MNDO, taking the length of one breaking CN bond as the reaction coordinate. In each case the reaction took place in a concerted[20] manner, via a very unsymmetrical transition state (TS), whose calculated geometries are given in Figure 1. The calculated activation energies ($\Delta E^{\ddagger}$) were large (MINDO/3, 50.2; MNDO, 40.2 kcal/mol). We also studied the synchronous[20] conversion of **1** to ($\mathbf{2} + N_2$) by enforcing C_v symmetry. The corresponding values for the activation energy were even larger (MINDO/3, 55.4; MNDO, 43.4 kcal/mol), and the "transition states" were not even saddlepoints on the potential surfaces. Each of the corresponding Hessian (force constant) matrices had two negative eigenvalues.[7]

Even the true activation energies are, however, much too large,

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(11) Dewar, M. J. S.; Ford, G. P. *J. Am. Chem. Soc.* **1979**, *101*, 5558.

(12) Bischof, P. *J. Am. Chem. Soc.* **1976**, *98*, 6844.

(13) Dewar, M. J. S.; Olivella, S.; Rzepa, H. S. *Chem. Phys. Lett.* **1977**, *47*, 80. Dewar, M. J. S.; Rzepa, H. S. *J. Am. Chem. Soc.* **1978**, *100*, 784.

(14) See Fletcher, R.; Powell, M. J. D. *Comput. J.* **1963**, *6*, 163.

(15) Available from QCPE.

(16) The term "reaction coordinate" is used here in its original sense, i.e., an arbitrary geometrical variable that changes during a reaction and is used to follow the progress of the reaction. Recent use of this term to describe the normal coordinate in the TS, corresponding to the imaginary vibration, or the path of steepest descent from the TS, has caused unnecessary confusion. The former is much better described as the *transition coordinate* and the latter as the *minimum energy reaction path* (MERP).

(17) Schultz, P. G.; Dervan, P. B. *J. Am. Chem. Soc.* **1980**, *102*, 878.

(18) See, e.g.: (a) Dewar, M. J. S.; McKee, M. L. *J. Am. Chem. Soc.* **1977**, *99*, 5231; *Inorg. Chem.* **1978**, *17*, 1569; **1980**, *19*, 2662. (b) Dewar, M. J. S.; Ford, G. P.; Rzepa, H. S. *Chem. Phys. Lett.* **1977**, *50*, 262. (c) Dewar, M. J. S.; Rzepa, H. S. *J. Am. Chem. Soc.* **1978**, *100*, 58. (d) Cowley, A. H.; Dewar, M. J. S.; Lattman, M.; Mills, J. L.; McKee, M. L. *Ibid.* **1978**, *100*, 3349. (e) David, D. E.; Dewar, M. J. S. *Ibid.* **1980**, *102*, 7387. (f) Dewar, M. J. S.; Cabelli, D. E.; Cowley, A. H. *Ibid.* **1981**, *103*, 3286, 3290.

(19) Cox, J. D.; Pilcher, G. "Thermochemistry of Organic and Organometallic Compounds"; Academic Press: New York, 1970.

(20) The terminology used here, which we strongly recommend, is as follows: (a) a *concerted* reaction is one which takes place in a single kinetic step; (b) a *synchronous* reaction is a concerted one where all the bond-forming and -breaking processes have taken place to similar extents in the TS; (c) a *two-stage* reaction is nonsynchronous but concerted, some of the changes in bonding taking place mainly between the reactants and TS, the rest between the TS products; (d) a *two-step* process is one taking place in two distinct kinetic steps, via a stable intermediate.

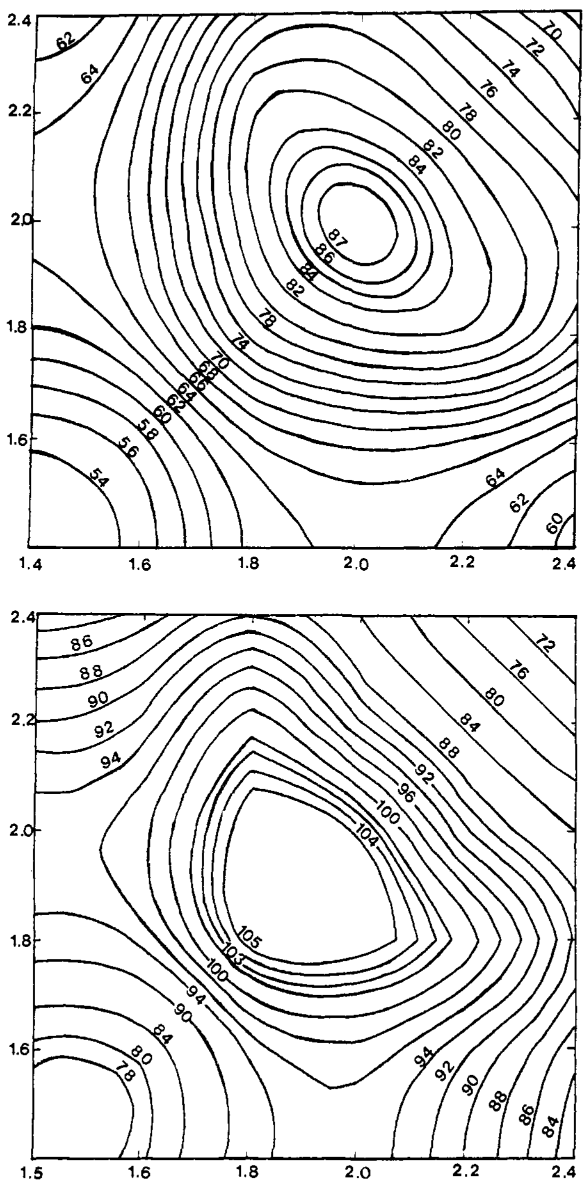


Figure 2. Contour maps representing projections of the potential energy surface for thermolysis of **1** in a plane defined by the lengths of the breaking CN bonds as coordinates: (a) MNDO, (b) MINDO/3. Contours (ΔH_f) in kcal/mol.

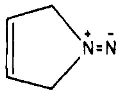
given that 1,1-diazenes decompose rapidly below room temperature.[17] Similar problems arose in a recent MINDO/3 study[21] of the Diels–Alder reaction between **2** and ethylene and were found to be due to biradical character in the intermediates. In order to study such species, specific allowance must be made[22] for the strong correlation between the "unpaired" electrons, either by introduction of configuration interaction (CI), by the "half-electron" (HE) method,[23] or by using a spin-unrestricted (UHF) treatment. Here we used the UHF versions of MINDO/3 (UMINDO/3) and MNDO (UMNDO) because they lead to variationally optimized wave functions. Derivatives of the energy can then be calculated very quickly, greatly reducing the time required for geometry optimizations and calculations of force constants.

Table II. Calculated Activation Parameters of 3,6-Dihydropyridazine

method	$\Delta H^{\ddagger}$ (kcal mol^{-1})	$\Delta S^{\ddagger}$ (eu)	log A
MNDO	47.14	8.60	15.26
MINDO/3	36.93	3.26	14.09
exptl	36.7 ± 0.5		15.53
	36.3 ± 0.2		15.58
	35.8 ± 0.4		15.19

When the calculations for $\mathbf{1} \rightarrow (\mathbf{2} + N_2)$ were repeated, using UMINDO/3 and UMNDO, very different results were obtained. Figure 2 shows projections of the potential surface, on the plane defined by the lengths of the breaking CN bonds as Cartesian coordinates, in the form of computer-drawn contour maps. Each point on each map corresponds to a geometry optimized with respect to the other variables. Here the reaction is predicted to be not only not synchronous[20] but not even concerted,[30] taking place in steps[20] via a biradical-like species (best represented by **5**) as a stable intermediate. The geometries calculated for **5**, and for the TS for its formation from **1**, are indicated in Figure 3, which also shows some of their other calculated properties.

The corresponding reaction profiles are shown in Figure 4. The rate-determining step in the overall conversion of **1** to ($\mathbf{2} + N_2$) is the initial ring opening to **5**, for which both procedures predict low activation energies (Table II). While no kinetic data are available for any derivative of 3-pyrroline itself, the decomposition of the dihydro derivative (**6**) of **3** has been studied.[17,24] This presumably involves loss of N_2 from **6** to give the biradical **7** which then fragments to isobutene (**8**), the final product. If we are right in thinking that the rate-determining step in the decomposition of **1** involves breaking of a CN bond to form **5**, rather than a synchronous breaking of both CN bonds, the same should also be the case for the less facile thermolysis of **6**, the rate-determining step being again the formation of a biradical-like intermediate **9**. If so, we might expect the decompositions of **1** and **6** to have similar entropies of activation and hence similar Arrhenius preexponential factors. The activation energy for **6** should, however, be somewhat larger than for **1** because the tertiary alkyl radical center in **9** should be less stabilized than the allyl one in **4**.



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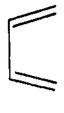

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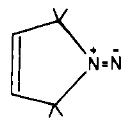

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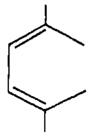

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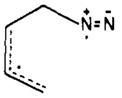

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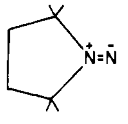

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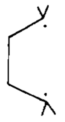

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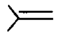

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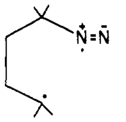

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The vibration frequencies of molecules can be calculated easily and effectively, using either MINDO/3[25] or MNDO.[26] Using

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(21) Dewar, M. J. S.; Olivella, S.; Rzepa, H. S. *J. Am. Chem. Soc.* **1978**, *100*, 5650.

(22) Dewar, M. J. S.; Doubleday, C. E. *J. Am. Chem. Soc.* **1978**, *100*, 4935.

(23) (a) Dewar, M. J. S.; Hashmall, J. A.; Venier, C. G. *J. Am. Chem. Soc.* **1968**, *90*, 1953. (b) Dewar, M. J. S.; Olivella, S. *J. Chem. Soc., Faraday Trans. 2* **1979**, *75*, 829.

(24) See: (a) Dervan, P. B.; Uyehara, T. *J. Am. Chem. Soc.* **1976**, *98*, 2003. (b) Hinsberg, W. D.; Dervan, P. B. *Ibid.* **1979**, *101*, 6142.

(25) Dewar, M. J. S.; Ford, G. P. *J. Am. Chem. Soc.* **1977**, *99*, 1685.

(26) Dewar, M. J. S.; Ford, G. P.; McKee, M. L.; Rzepa, H. S.; Thiel, W.; Yamaguchi, Y. *J. Mol. Struct.* **1978**, *43*, 135.

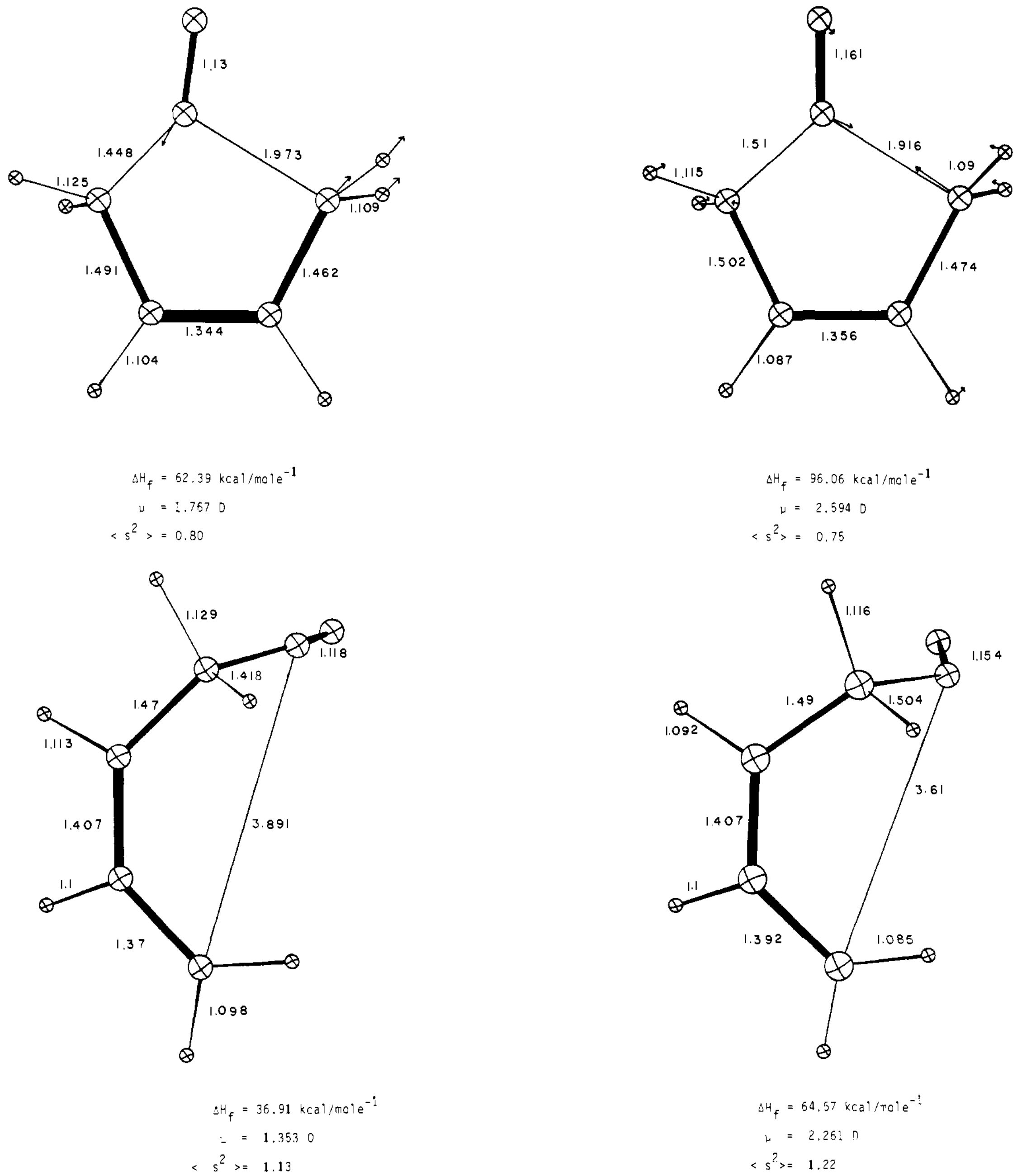

Figure 3. Geometries and other properties calculated for stationary points on the UHF potential surface for thermolysis of **1**: (a, b) the first transition state; (c, d) the intermediate. Transition vectors are indicated by arrows in the ORTEP plots for the transition states: (a, c) UMINDO/3; (b, d) UMNDO.

these, together with the calculated geometries, it is a simple matter to calculate partition functions and hence thermodynamic properties, in particular, entropies.[27] Calculations can moreover be carried out equally easily for transition states, leading to estimates of entropies of activation, and the results of a number of such calculations have been in good agreement with experiment.[27] Table II shows entropies of activation calculated in this way by MINDO/3 and MNDO for **1** → (**2** + N_2) and Arrhenius preexponential factors derived from them, together with the experimental values for the thermolysis of **6**. The agreement between the calculated and observed values of the preexponential factors is reasonable. The activation enthalpy calculated by MINDO/3 is less than that observed for **6**, as expected, but the MNDO value is greater. Clearly the latter is too large.

The dipole moments calculated for the TS for **1** → **5** are less than those for **1**. According to current theories of solvent effects, the reaction should then be faster in less polar solvents and presumably the same should be true also for thermolysis of **6**. The observed rates for the latter reaction in hexane were indeed greater than in either ether or THF. Thus the rate constants calculated from the Arrhenius parameters in Table II lead to estimated rate constants at 250 °C of 2.0×10^{-3} s^{-1} in hexane and 3.2×10^{-5} s^{-1} in THF.

B. Conversion of 3,6-Dihydropyridazine (10) to Butadiene. Most of the molecules adding to polyenes in the course of cheletropic reactions are ambident species[28] able to undergo 1,1 or 1,2 cycloaddition. This, for example, is true of N_2, which can formally add to butadiene (**2**) to form either **1** or 3,6-dihydropyridazine (**10**). Cheletropic reactions are therefore no different in kind from other cycloadditions, and it would be more systematic to class them as such, i.e., as (n + 1) cycloadditions. On this basis the conversions of **1** and **10** to (**2** + N_2) are analogous, the former being a reverse (n + 1) cycloaddition (reverse cheletropic reaction) while the latter is a reverse (n + 2) cycloaddition (reverse

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(27) Dewar, M. J. S.; Ford, G. P. *J. Am. Chem. Soc.* **1977**, *99*, 7822.

(28) E.g., SO_2 vs. -O—SO- or $N^+{=}N^-$ vs. -NN-.

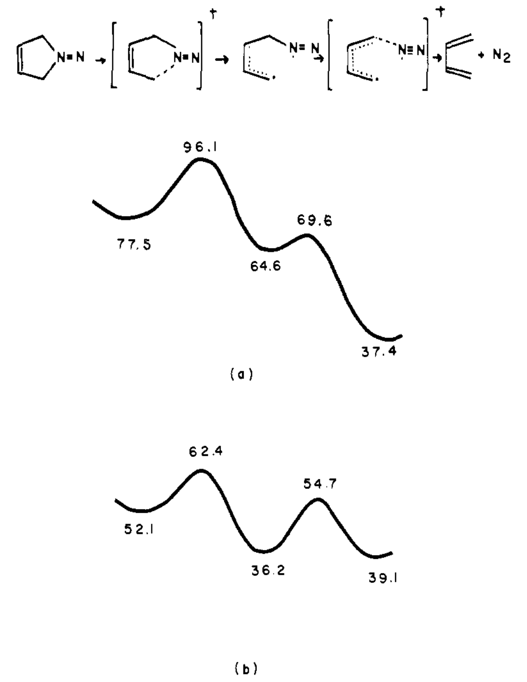

Figure 4. Reaction profiles for the thermolysis of **1**, calculated (a) by UMNDO; (b) by UMINDO/3.

Table III. Calculated Properties of 3,6-Dihydropyridazine (**10**)

	bond lengths (Å)				ΔH_f (kcal/mol)	I_1 (eV)	μ (D)
	N_1N_2	N_2C_3	C_3C_4	C_4C_5			
MINDO/3	1.174	1.460	1.494	1.347	17.7	8.00	1.49
MNDO	1.210	1.484	1.504	1.345	37.4	10.32	2.78

Diels–Alder reaction). In view of this analogy, it seemed to us a good idea to study the decomposition of **10** for comparison with that of **1**.

Table III shows the geometry and other properties calculated for **10** by MINDO/3 and MNDO. Here again the MINDO/3 value for ΔH_f is much less positive than the MNDO one, as anticipated in view of the systematic error in MINDO/3 for molecules containing adjacent heteroatoms.[9] As might be expected on this basis, both methods give comparable estimates for the difference between the heats of formation of **10** and **1**, i.e., 34.4 (MINDO/3) and 40.1 (MNDO) kcal/mol. Both methods predict **1** to be far less stable than **10**, as it undoubtedly must be. No experimental data are available[29] for **10** because it, like **1**, is still unknown.

Because of this extra stability, the conversion of **10** to (**2** + N_2) is no longer exothermic. MNDO predicts this reaction to be almost exactly thermoneutral while MINDO/3 predicts it to be endothermic by 19.7 kcal/mol. Here again, for reasons indicated above, MNDO is probably much closer to the truth.

The conversion of **10** to (**2** + N_2) was studied in the same way as that of **1**. Both MINDO/3 and MNDO predicted the reaction to take place, like that of **1**, via a very unsymmetrical TS, whose calculated energies and geometries are shown in Figure 5. The corresponding activation energies (MINDO/3, 50.7; MNDO, 75.1 kcal/mol) were, however, unreasonably large. This, of course, was not surprising in view of the analogy between the pyrolyses of **1** and **10**.

The calculations were accordingly repeated, using UMINDO/3 and UMNDO. As in the case of **1**, the heats of formation calculated for **10** were similar to those given by MINDO/3 and MNDO. Figure 6 shows the reaction profiles calculated by both methods for the thermolysis of **10**. Both were similar to the ones for **1** (Figure 5). Figure 7 shows the calculated geometries, etc., for the corresponding TS and intermediates. The latter were similar to the intermediates found in the reaction of **1**, the small differences in energy between them being due to their different conformations (cf. Figures 1 and 7). The TS for (**10** → **5**) and (**1** → **5**) did, however, differ significantly; cf. Figures 3a,b and 7a,b.

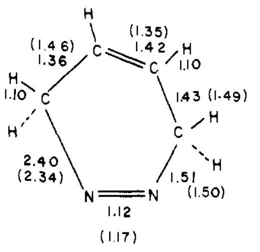

Figure 5. Geometries calculated by MINDO/3 (MNDO) for the transition state for thermolysis of **10**.

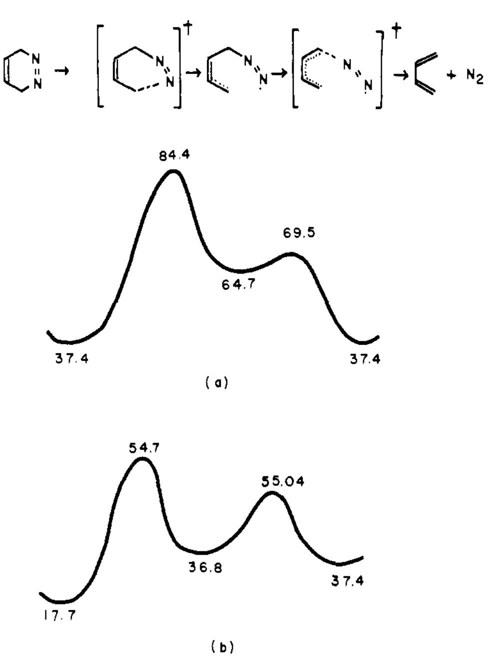

Figure 6. Reaction profiles for the thermolysis of **10**, calculated (a) by UMNDO; (b) UMINDO/3.

Table IV. Activation Parameters for Thermolysis of 10 and 11

method (compound)	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (eu)	log *A*
MNDO (**10**)	47.1	8.6	15.26
MINDO/3 (**10**)	36.9	3.3	14.09
exptl[29] (**11**)	36.7 ± 0.5		15.53
	36.3 ± 0.2		15.58
	35.8 ± 0.4		15.19

Here again experimental data are lacking, either for **10** or for any of its derivatives. Data are, however, available[29] for the thermal decomposition of 2,2,5,5-tetramethyl-2,3,4,5-tetrahydropyridazine (**11**) which bears the same relation to that of **10** that the pyrolysis of **6** does to that of **1**. Table IV compares activation parameters calculated for **10** with those observed for **11**. The parallel between them is similar to that between the values for **1** and **6**, suggesting that the MNDO value for $\Delta H^{\ddagger}$ is too large. The values for $\Delta S^{\ddagger}$, however, again agree quite well.

C. Conversion of 4-Cyclopentenone (12) to Butadiene (2). The third reaction studied was another reverse cheletropic process, i.e., the elimination of CO from 4-cyclopentenone (**12**) to form **2**. Since **12** is isoelectronic with **1**, and CO with N_2, the thermolyses of **1** and **12** might be expected to be analogous. Unlike **1**, **12** is a well-known compound, and a detailed kinetic study of its thermolysis has been reported.[30]

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[29] Engel, P. S.; Hayes, R. A.; Keifer, L.; Szilagyi, S.; Timberlake, J. W. *J. Am. Chem. Soc.* **1978**, *100*, 1876.

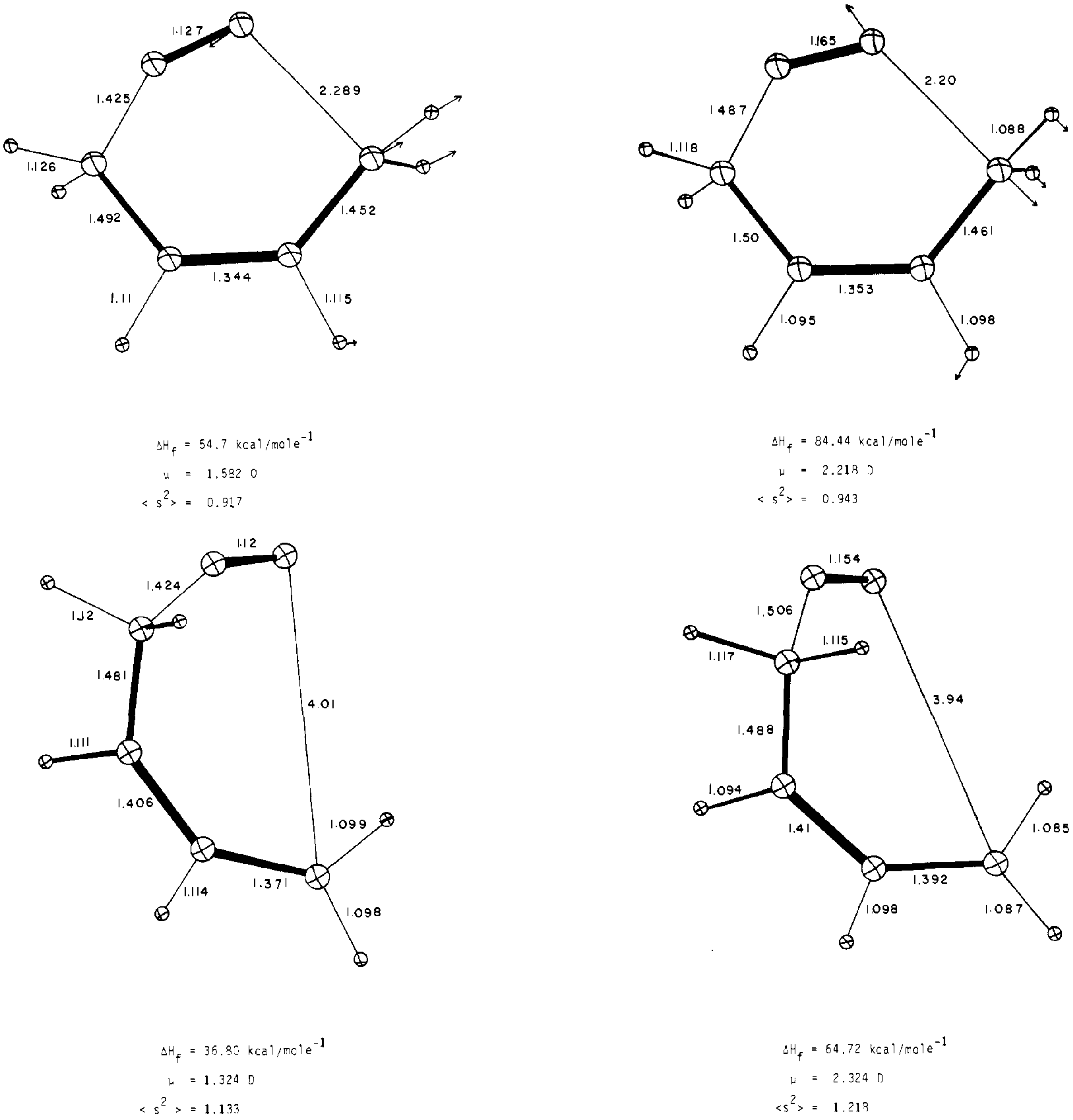

Figure 7. Geometries and other properties calculated for stationary points on the UHF surface for thermolysis of **10**: (a, b) the first transition state; (c, d) the intermediate. (a, c), UMINDO/3; (b, d) UMNDO. Transition vectors are indicated by arrows in the ORTEP plots for the transition states.

Table V compares the geometries calculated for **12** with experiment.[31] The three sets of values agree well. Table VI shows its other calculated properties. No experimental value of ΔH_f for **12** has been reported, but one can be estimated from the known heats of formation[19] of cyclopentene (**13**), cyclopentanone (**14**), and cyclopentane (**15**), on the reasonable assumption that the difference in ΔH_f between **12** and **13** is the same as that between **14** and **15**. The value found in this way (−19.4 kcal/mol) implies that the MINDO/3 and MNDO values are too negative by 5.7 and 7.3 kcal/mol, respectively, errors that are within their limits of accuracy. Indeed, both methods give energies for compounds containing five-membered rings that are systematically too negative by about this amount.[9,10] Note that the MINDO/3 and MNDO values for **12** agree closely. This confirms the explanation given above for the discrepancies between them in the case of **1**, **10**, and the related transition states, supporting the suggestion that the MNDO values there are to be preferred.

Table V. Calculated and Observed Geometries of 4-Cyclopentenone (12)

bond length (Å) or angle (deg)	MNDO	MINDO/3	exptl[31]
C_1O_6	1.220	1.201	1.210 ± 0.002
C_1C_2	1.543	1.534	1.524 ± 0.008
C_2C_3	1.512	1.504	1.509 ± 0.008
C_3C_4	1.350	1.348	1.338 ± 0.004
C_2H_7	1.110	1.115	1.086 ± 0.004
C_3H_9	1.080	1.101	1.079 ± 0.003
$C_5C_1C_2$	108.70	107.39	109.20 ± 1.0
$C_1C_2C_3$	103.13	104.35	103.13 ± 0.8
$C_2C_3C_4$	112.52	111.96	112.43 ± 0.3
$H_7C_2H_8$	107.38	103.45	107.30 ± 0.67
$C_3C_4H_{10}$	126.79	126.83	124.70 ± 0.27

Carbon monoxide is, unfortunately, a "bad" molecule for both MINDO/3 and MNDO, the errors in the calculated ΔH_f being +12.9 and +20.2 kcal/mol, respectively. Better estimates of the heats of reaction for **12** → (**2** + CO) can therefore be obtained by taking the experimental values of ΔH_f for CO rather than the calculated ones. Values of ΔH found in this way from the

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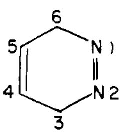
(30) Dolbier, D. R.; Frey, H. M. *J. Chem. Soc., Perkin Trans 2* **1974**, *14*, 1674.

(31) Lewis, J. D.; Laane, J. *J. Mol. Spectrosc.* **1974**, *53*, 417.



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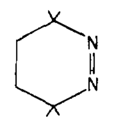

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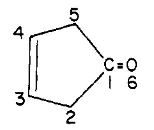

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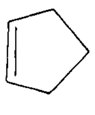

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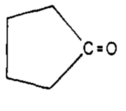

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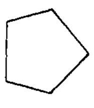

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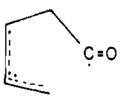

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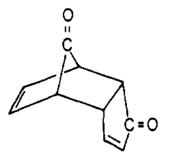


17

MINDO/3 and MNDO ΔH_f's for **12** and **2** are as follows:

$$\text{MINDO/3, 30.6; MNDO, 29.2; "experiment", } 19.0 \text{ kcal/mol} \quad (4)$$

The "experiment" value is derived from the above estimate of ΔH_f for **12** together with experimental values for **2** and CO. The values of ΔH, given by using theoretical values of ΔH_f throughout, are 43.5 and 49.4 kcal/mol, respectively.

The conversion of **12** to (**2** + CO) was studied in the same way as the previous reactions, taking the length of one breaking (CC) bond as the reaction coordinate. The calculations were first carried out using MINDO/3 and MNDO. Both procedures predicted the reaction to be concerted[20] but not synchronous,[20] taking place via a very unsymmetrical TS whose geometry and other calculated properties are shown in Figure 8. The corresponding activation energies were very large (MINDO/3, 69.7; MNDO, 83.3 kcal/mol) but less than those (79.6, 90.3 kcal/mol, respectively) calculated for a synchronous process by enforcing C_v symmetry. As in the case of **1**, the "TS" had moreover two negative force constants.

The activation energies found in this way are far larger than the experimental value (51.2 kcal/mol[30]), again in line with the analogous reaction of **1**. The calculations for **12** were therefore repeated, using UMINDO/3 and UMNDO, leading to the reaction profiles shown in Figure 9. As expected, these are similar to the ones found in the same way for thermolysis of **1** (Figure 5) and likewise predict a two-step[20] mechanism involving a biradicaloid (**16**) as a stable intermediate. Here the second TS, i.e., that for conversion of **16** to the products (**2** + CO), is predicted to be a little higher in energy than the first, but this is almost certainly due to the errors in the calculated ΔH_f for CO. Since these errors are specific for CO itself, they should not extend to other stable species on the potential surface. They should, however, tend to raise the energies of TS for reactions leading to CO. Therefore, there seems little doubt that the first transition state, i.e., that for **12** → **16**, corresponds to the rate-determining step. The structures and other properties calculated for this TS are shown in Figure 10.

Table VII compares the calculated and observed[30] activation parameters. The agreement is satisfactory.

The "experimental" value for the ΔH_f of **12** given in eq 3, together with the value of ΔH_f observed for the conversion of **12** to (**2** + CO), lead to an estimated value of 31.8 kcal/mol for the activation energy of the cheletropic addition of CO to **2** to form **12**. Since this is comparable with the values reported (27.5,[21] 34.3[21] kcal/mol) for the Diels–Alder reaction between **2** and ethylene, it should be possible to observe the formation of **12** from (**2** + CO) under suitable conditions.

Table VI. Properties Calculated for 4-Cyclopentenone (**12**)

		MINDO/3	MNDO
formal charges (e)	C_1	0.54	0.21
	C_2	0.04	0.02
	C_3	0.02	0.10
	O	−0.48	−0.27
	H_2	0.01	0.04
	H_3	0.02	0.08
ΔH_f (kcal/mol)		−25.1	−26.7
I_1 (eV)		9.54	10.17
μ (D)		2.96	2.49

Table VII. Activation Parameters for Thermolysis of 4-Cyclopentenone (**12**)

method	$\Delta E^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (eu)	$\log A$
MNDO	54.39	6.47	14.72
MINDO/3	51.74	2.78	13.90
exptl[30]	51.25 ± 0.2	5.62 ± 0.32	14.52 ± 0.07

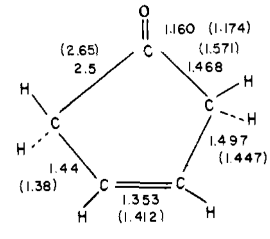
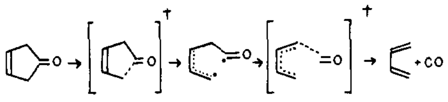


Figure 8. Geometries calculated by MINDO/3 (MNDO) for the transition state for thermolysis of **12**.



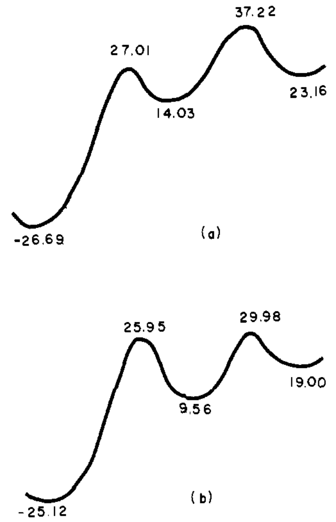


Figure 9. Reaction profiles for the thermolysis of **12**, calculated (a) by UMNDO; (b) by UMINDO/3.

D. Conversion of Tricyclo[5.2.1.0^{2,6}]deca-3,8-diene-5,10-dione (17) to 8,9-Dihydroindenone (18). The last reaction considered here has also been studied experimentally, i.e., the cheletropic decarbonylation of tricyclo[5.2.1.0^{2,6}]deca-3,8-diene-5,10-dione (**17**) to form 8,9-dihydroindenone (**18**). Figure 11 shows the geometries and other properties calculated for **17** by MINDO/3 and MNDO. No experimental data are available for comparison.

The heats of reaction (ΔH) for conversion of **17** to (**18** + CO), using both observed and calculated ΔH_f for CO, are as follows,

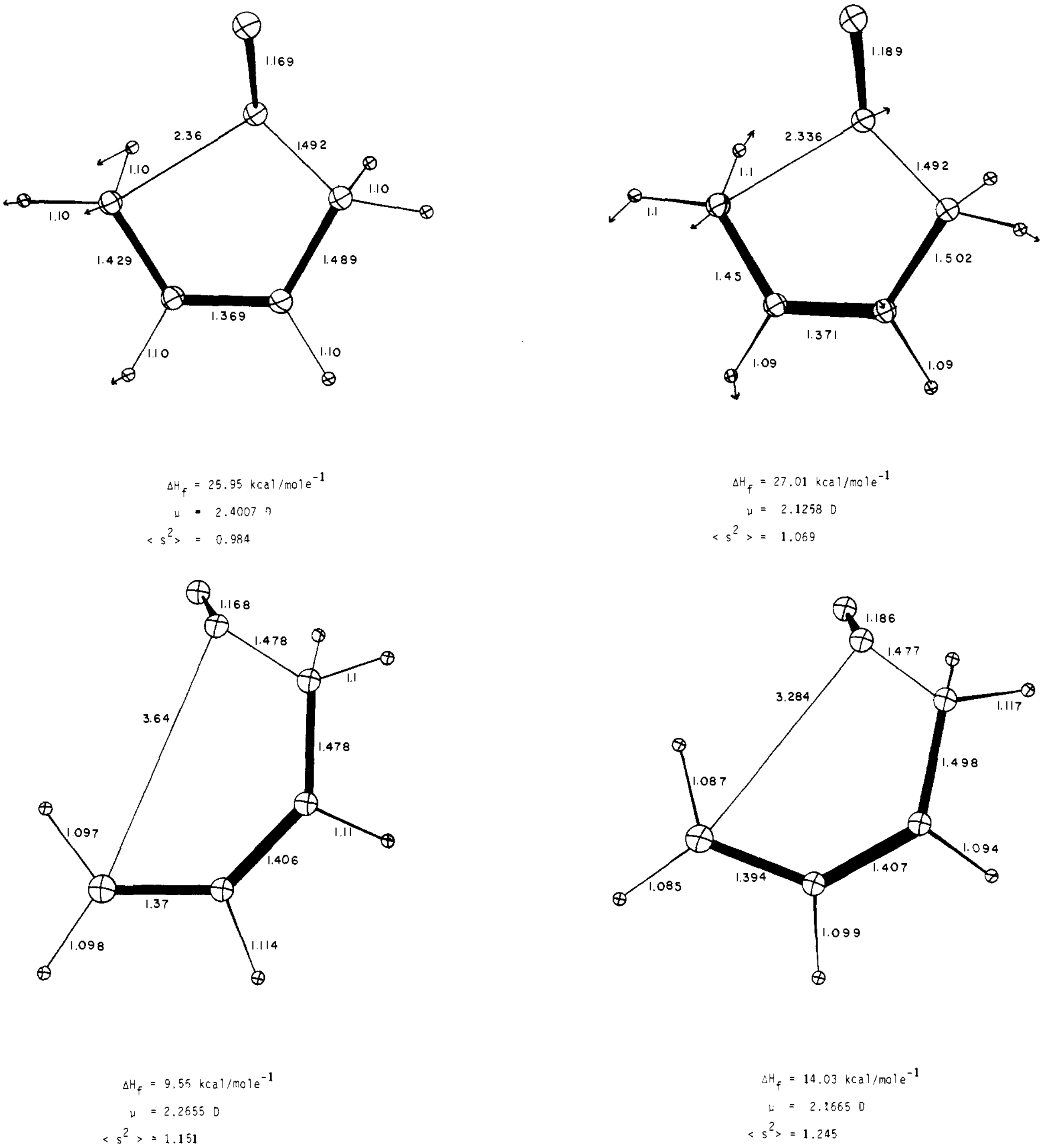


Figure 10. Geometries and other properties calculated for stationary points on the UHF potential surface for thermolysis of **12**: (a, b) the first transition state; (c, d) the intermediate. (a, c) UMINDO/3; (b, d) UMNDO. Transition vectors are indicated by arrows in the ORTEP plots for the transition states.

Table VIII. Calculated Activation Parameters of Tricyclo[5.2.1.0^{2,6}]deca-3,8-diene-5,10-dione

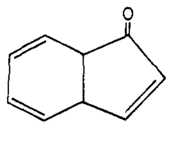
method	$\Delta H^{\ddagger}$ (kcal mol^{-1})	$\Delta S^{\ddagger}$ (eu)	log A
MNDO	33.85	2.64	13.91
MINDO/3	27.99	1.0	13.55
exptl	34.5 ± 0.8	9.8 ± 2.3	

the latter values being given in parentheses:

MINDO/3, −13.4 (−0.5); MNDO, −6.2 (+8.2) kcal/mol (5)

Since use of the experimental value for the ΔH_f of CO is clearly better, the reaction is probably exothermic.

The reaction was first studied using MINDO/3 and MNDO. Both methods predicted it to be concerted but not synchronous, taking place via a very unsymmetrical TS whose calculated structures and heats of formation are shown in Figure 12. The corresponding activation energies (MINDO/3, 39.4; MNDO, 54.0 kcal/mol) were again too large, the observed[32] value being 34.5 kcal/mol.



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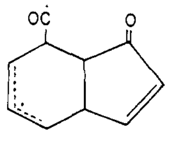

19

$CH_2=CH_2$

20

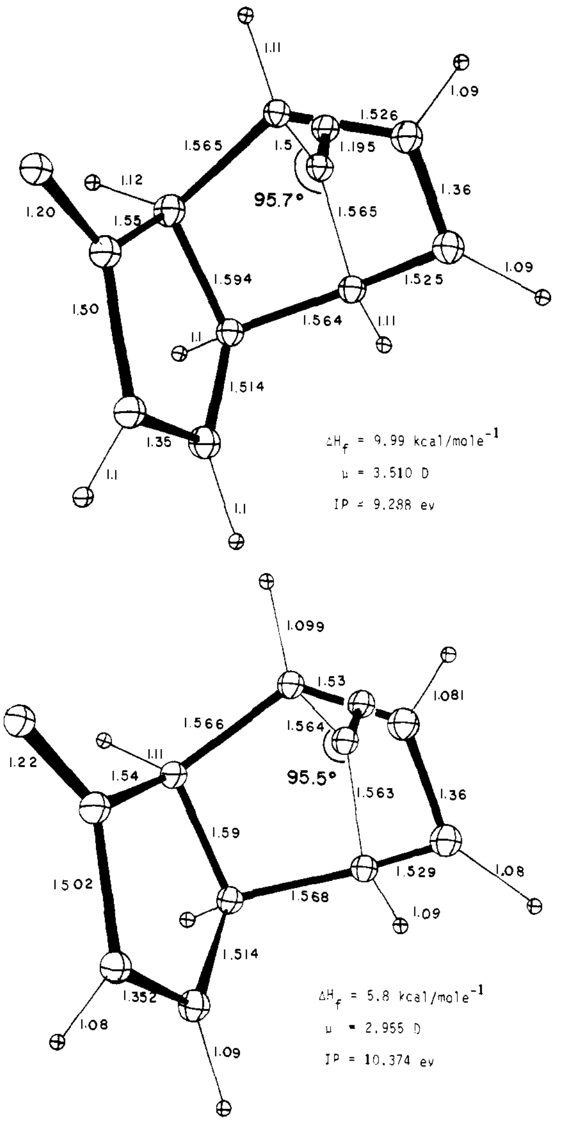

Figure 11. Bond lengths (Å), heats of formation (ΔH_f), first ionization potentials (I_1), and dipole moments (μ), calculated for tricyclo-[5.2.1.0^{2,6}]deca-3,8-diene-5,10-dione (**17**), by (a) MINDO/3; (b) MNDO.

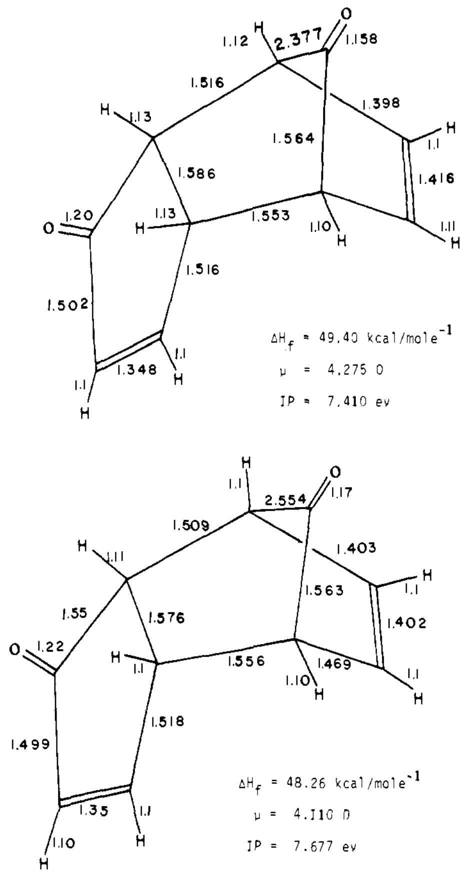

Figure 12. Geometries calculated for the transition state for thermolysis of **17**: (a) MINDO/3; (b) MNDO.

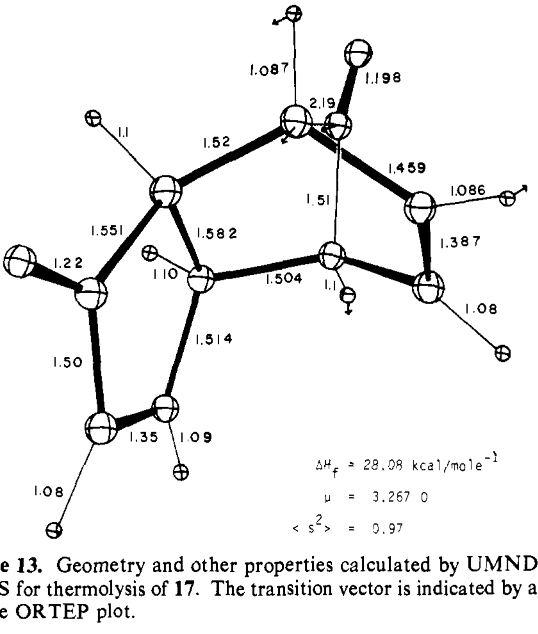

Figure 13. Geometry and other properties calculated by UMNDO for the TS for thermolysis of **17**. The transition vector is indicated by arrows on the ORTEP plot.

Reinvestigation of the reaction, using UMINDO/3 and UMNDO, led to results similar to those found in the three previous cases. Both procedures predicted the conversion of **17** to (**18** + CO) to be a two-step[20] process involving a biradicaloid (**19**) as a stable intermediate, formation of which is the rate-determining step. Figure 13 shows the structure calculated by MNDO for the corresponding TS. As in the case of **1**, the TS is very unsymmetrical, corresponding to breaking of one of the relevant C–C bonds while the other remains almost intact. The calculated activation parameters are compared with experiment[32] in Table VIII. The agreement is satisfactory.

Conclusions

The four reactions studied here are all predicted by both MINDO/3 and MNDO to take place in a nonsynchronous manner via very unsymmetrical transition states. Similar results were obtained in an earlier MINDO/3 study[21] of the Diels–Alder reaction between **2** and ethylene (**20**). A further point of resemblance between the reactions is that the transition states are all close to the adducts in structure, corresponding to situations where one of the relevant bonds is weakened but the other is almost intact. In the case of the Diels–Alder reaction of **2** with **20**, this corresponded to a mechanism which had not been previously considered, i.e., a two-step or two-stage process in which the transition state for the overall cycloaddition corresponds to ring closure of an intermediate biradical-like species. It had always been assumed that any such species would undergo cyclization without activation, so that the transition state for the overall reaction would have to correspond to the formation of the intermediate from the diene and the dienophile, not to the conversion of the intermediate to the final cyclohexene.

UMINDO/3 and UMNDO overestimate the stabilities of biradical-like species as a result of an overestimation of the

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[32] Baldwin, J. E. *Can. J. Chem.* **1966**, *44*, 2051.

correlation energy.[33] Since the error commonly amounts to 15–20 kcal/mol, the minima in the reaction profiles of Figures 3, 8, and 12 are probably not real. A similar situation arose in the case of the Diels–Alder reaction between **2** and **20**, as was pointed out at the time.[21] This error will naturally tend to make the transition states leading to such species too unsymmetric, but there are reasons for believing that the conclusions reached here concerning their structures are nevertheless essentially correct.

In the first place, very similar structures for the TS were predicted by the usual spin-unrestricted versions of MINDO/3 and MNDO (Figures 2, 7, 11, 15) although these grossly overestimate the energies of biradical-like species. This indeed is why these methods give activation energies that are far too large. There is, moreover, no indication of any systematic errors, either in MINDO/3 or in MNDO, that might be expected to make them overestimate the energy of a symmetrical TS relative to that of an analogous unsymmetrical one.[34] Both MINDO/3 and MNDO have indeed predicted symmetrical TS for several other pericyclic reactions.[37]

Secondly, the reasonable agreement between the calculated entropies of activation, both here and for the Diels–Alder reaction of **2** with **20**,[21] provide good support for the predicted TS structures.

And finally, McIver's rules[38] predict all these reactions to take place via transition states that are unsymmetrical. While these rules cannot indicate the extent to which symmetry is broken in any given case, and while their application to cycloaddition reactions is not completely rigorous,[39] they do nevertheless provide a strong indication that such processes cannot be synchronous.[20]

There seems, therefore, to be a strong indication that the cheletropic reactions considered here are not synchronous processes, as had been commonly assumed because they are "allowed" by the Woodward–Hoffman rules.[3] On the contrary, they seem to proceed via TS which are very unsymmetrical, one of the two breaking bonds being still almost intact while the other is weak.

Acknowledgment. This work was supported by the Air Force Office of Scientific Research (Grant AFOSR 79-0008) and the Robert A. Welch Foundation (Grant F-126). The calculations were carried out using a Digital Vax 11/780 computer provided by grants from the National Science Foundation (Grant CHE78-03213) and The University of Texas, and the Dual Cyber 170/750 computer at The University of Texas Computation Center.

Registry No. 1, 87494-91-5; **10**, 87494-92-6; **12**, 930-30-3; **17**, 826-65-3.

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[33] See, e.g.: Dewar, M. J. S.; McKee, M. L. *Pure Appl. Chem.* **1980**, *52*, 1432.

[34] For a refutation of claims to the contrary by Caramella et al.,[35] and of a much quoted ab initio study by Townshend et al.,[36] see ref 21.

[35] Caramella, P.; Houk, K. N.; Domelsmith, L. N. *J. Am. Chem. Soc.* **1977**, *99*, 4514.

[36] Townshend, R. E.; Ramunni, G.; Segal, G.; Hehre, W. J.; Salem, L. *J. Am. Chem. Soc.* **1976**, *98*, 2190.

[37] See, e.g.: Dewar, M. J. S.; Ford, G. P. *J. Am. Chem. Soc.* **1977**, *99*, 8343.

[38] McIver, J. W. *J. Am. Chem. Soc.* **1975**, *97*, 3632.

[39] In this case the argument rests on the assumption that off-diagonal force constants are always smaller than corresponding diagonal ones. While this is certainly true for stable molecules, it might not be for transition states.

Ground States of Molecules. 63. Reverse Cheletropic Reactions in Polycyclic Systems

Michael J. S. Dewar* and Lek Chantranupong[1]

Contribution from the Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712. *Received December 16, 1982. Revised Manuscript Received July 16, 1983*

Abstract: MINDO/3 and MNDO calculations are reported for the reverse cheletropic decarbonylations of 7-norbornenone, 7-norbornadienone, and *exo*- and *endo*-tricyclo[4.1.0.1^{2,5}]oct-3-en-8-one, and the reverse cheletropic denitrigenation of 1,4-cyclohexadien-2,5-ylene-1,1-diazene. The first four reactions are predicted to take place in a nonsynchronous manner via very unsymmetrical transition states while the last is synchronous, or almost synchronous.

Introduction

Our previous paper[2] reported MINDO/3[3] and MNDO[4] calculations for a number of reverse cheletropic reactions involving loss of CO or N_2 from unsaturated five-membered rings to form derivatives of 1,3-butadiene. Here we describe similar calculations for the reverse cheletropic loss of N_2 or CO from 7-norbornenone, the corresponding diazene, and various analogues containing additional structural features. Full details of the procedure used were given in the previous paper[2] and need not be repeated here.

Results and Discussion

The calculations for the individual compounds will first be considered in turn, the results being compared with experimental data when these are available. The final section discusses the collective implications of this work concerning the mechanisms of cheletropic reactions in general.

A. 7-Norbornenone (1). The first reaction studied was the thermolysis of 7-norbornenone (**1**) to 1,3-cyclohexadiene (**2**) and carbon monoxide (**3**).

Table I compares various properties calculated by MINDO/3 and MNDO for **1** with experimental values, where available. The agreement is acceptable. Since the energies calculated by MINDO/3 for norbornane and norbornadiene are much too positive,[3] whereas those from MNDO agree quite well with experiment,[4]

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[1] For part 60 see: Dewar, M. J. S.; Nelson, D. J. *J. Org. Chem.* **1982**, *47*, 2614.

[2] Dewar, M. J. S.; Chantranupong, L. *J. Am. Chem. Soc.*, preceding paper in this issue.

[3] Bingham, R. C.; Dewar, M, J. S.; Lo, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 1285, 1294, 1302.

[4] Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899, 4907.

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