

Table I. Systems Studied and Heats of Formation of Monomer and Dimer

dimer system	MINDO/3	MINDO/3	ΔE , kcal/mol (ab initio)	$R_{x-x'}$, Å	
	ΔH_f for dimer	ΔH_f for monomers		ab initio	MIN- DO/3
(H ₂ O) ₂ , linear	-107.3	-107.2	-6.09 ^a	2.73 ^a	5.43
(H ₂ O) ₂ , bifurcated	-107.2	-107.2	-4.45 ^b	3.00 ^b	5.31
(H ₂ O) ₂ , cyclic	-107.2	-107.2	-4.0 ^b	2.90 ^b	5.62
NH ₃ →OH ₂	-62.9	-63.0	-5.89 ^c	2.91 ^c	6.68
			-5.8 ^d	3.12 ^d	
CH ₃ OH→OH ₂	-45.9	-103.7	-5.26 ^e	2.71 ^e	5.18
CH ₃ OH→NH ₃	-49.0	-59.5	-6.48 ^c	2.87 ^c	6.98

^a J. E. Del Bene and J. A. Pople, *J. Chem. Phys.*, **52**, 4858 (1970).

^b P. A. Kollman and L. C. Allen, *J. Am. Chem. Soc.*, **92**, 753 (1970).

^c J. E. Del Bene, *ibid.*, **95**, 5460 (1973). ^d P. A. Kollman and L. C. Allen, *ibid.*, **93**, 4991 (1971). ^e J. E. Del Bene, *J. Chem. Phys.*, **55**, 4633, (1971).

The conclusion is that MINDO/3 geometry optimization program² in its present form does not predict correct interatomic distances for heavy atoms connected by hydrogen bonds.

Acknowledgment. T.J.Z. and D.B. thank their respective institutions for summer grants which made possible this research. They also express their thanks to the Computing Center, State University of New York at Buffalo, for a generous allocation of computer time.

References and Notes

- R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, **97**, 1302 (1975). Note also the other papers in the series by these authors.
- Quantum Chemistry Program Exchange Program No. 279, 1973.

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Received March 20, 1978

Hydrogen Bonding in the MINDO/3 Approximation

Sir:

The MINDO/3 program has been heralded as being very reliable,¹ and, indeed, as we in our laboratories and others have found, it is a very good method for the calculation of the ground-state properties of large molecules. However, we recently uncovered a major shortcoming in the method, and we wish to warn the scientific community at large of this fact.

One of our recent studies involving the MINDO/3 method concerned the intermolecular interaction between carbonyl derivatives and water. We were surprised to find very little, if any, intermolecular interactions and as a check we decided to investigate the water dimer also to see whether MINDO/3 provides realistic results for such hydrogen-bonding problems.

We obtained the same results as those published by Dewar² for the minimization of both an isolated acetaldehyde and water units. For the water dimer, we chose the geometry given by Popkie et al.³ where the intermolecular angles α and β equal 0 and the oxygen-oxygen distance is fixed at 2.9475 Å (Figure 1). We obtained a heat of formation of -53.6 kcal/mol for the monomer and -99.7 kcal/mol for the dimer. This leads to a

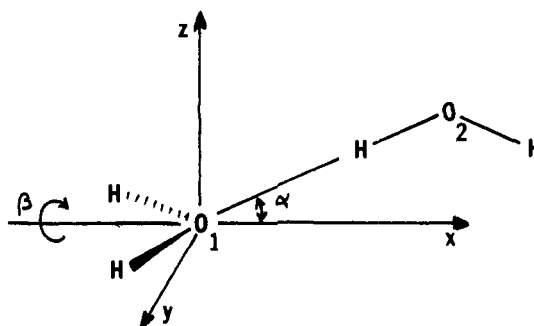


Figure 1. The geometry of a water dimer.

Table I. Dimer Orientations and Heats of Formation^a of Water Dimers^{b,c}

R_{OO} , Å	α	β	ΔH_F°
2.95	0	0	-99.7
2.85	0	0	-98.0
2.75	0	0	-96.0
2.6	0	0	-92.2
2.5	0	0	-88.9
2.95	30	0	-97.2
2.95	45	0	-98.3
2.95	52	0	-98.5
2.95	89	0	-98.2
2.95	0	90	-99.7

^a Kilocalories/mole. ^b Monomer heat of formation is -53.6 kcal/mol. ^c Molecule 1 is in the x - y plane. Molecule 2 is in the x - z plane. R_{OO} is the internuclear distance between the two oxygen atoms. α is the angle between the O₂-H₂ bond of molecule 2 and the x axis. β measures the rotation of molecule 1 around its principal axis (see Figure 1).

repulsion of 7.5 kcal/mol and contrasts with the value of -3.67-kcal/mol stabilization energy for the dimer calculated by these authors,³ -6.41 kcal/mol⁴ for STO/3G, -5.94 kcal/mol⁵ for CNDO/2, and -14.1 kcal/mol⁶ for the INDO method.

We then proceeded to minimize the distance between the two oxygen atoms in the hope that somewhere along this path we would find a minimum. We found the dimer to be unstable at all distances (Table I). Spot calculations at various intermolecular angles also failed to reveal any stable dimer structure. Although we have not made a thorough investigation of all the angular dependencies of the dimer to find a minimum, our preliminary findings show that MINDO/3 predicts a linear orientation of two water molecules to be repulsive, in contrast to the other semiempirical and ab initio techniques.

For the acetaldehyde-water pair we chose the geometry obtained by Del Bene⁷ from an STO/3G calculation (Figure 2). In contrast to a stabilization of 3.82 kcal/mol found by the

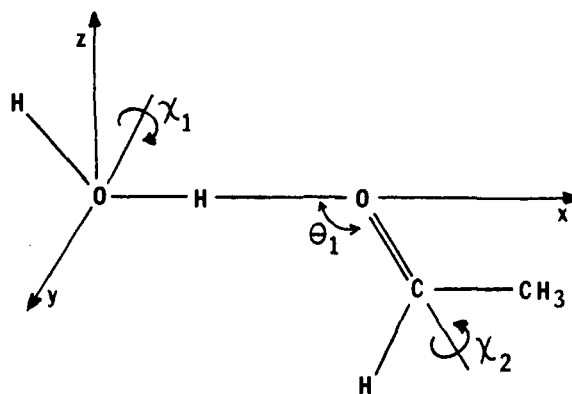


Figure 2. Geometry of the acetaldehyde-water pair.

Table II. Dimer Orientations and Heats of Formation of Water-Acetaldehyde Dimers^{a,b}

$R_{OO}, \text{\AA}$	θ_1, deg	χ_1, deg	χ_2, deg	ΔH_F° kcal/mol
2.85	119	0	0	-88.3
2.65	119	0	0	-83.8
2.45	119	0	0	-76.6
2.86	123	0	180	-87.8
∞				-97.2

^a Heat of formation of water is -53.6 kcal/mol and heat of formation of acetaldehyde is -43.6 kcal/mol. R_{OO} is the distance between the oxygen atom of water and the carbonyl oxygen. θ is the angle between the internuclear line (x axis) and the principal axis of acetaldehyde. χ_1 and χ_2 measure the rotation of the molecules about their principal axes (see Figure 2).

author, we obtained a repulsion of 8.9 kcal which could not be reduced by varying the geometry (Table II). These results lead us to conclude that the MINDO/3 method is not suitable for the evaluation of hydrogen bonding and casts a serious doubt on the credibility of the numerous calculations that have been made with this method on intermolecular complexes.

Acknowledgment. We thank the National Cancer Institute (Contract No. N01-CP-75927) and the National Science Foundation (Grant No. ENV 77-74061) for supporting our work.

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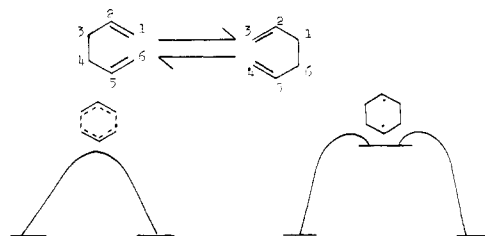
Received May 1, 1978

On the Mechanism of the Cope Rearrangement

Sir:

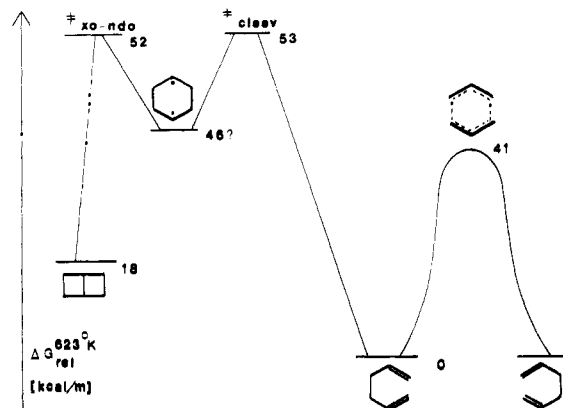
Despite intensive work,¹ the mechanism of the [3,3]-sigmatropic shift of 1,5-hexadienes remains unclear. At issue is whether it is a concerted process via a single transition state with partial bonding between C_1 and C_6 and between C_3 and C_4 or whether cyclohexane-1,4-diyl (a biradicaloid) is an intermediate.

The latter alternative, suggested by Grob^{2a} and by Doering,^{2b} is supported both theoretically by MINDO calculations³ and McIver's rules⁴ and experimentally by a constant multiplicative rate increase upon 2-phenyl and 2,5-diphenyl substitution.⁵ However, the experimental observations could equally well be due to a change in a single transition state toward a diyl-like species.



Unfortunately, the elegant stereochemical studies of Doering and Roth⁶ and of Hill⁷ are consistent with both alternatives; these results require a chair-like arrangement of six carbons in the lowest energy pathway. The single-stage concerted path should proceed suprafacially (or antarafacially) on both allylic moieties according to the orbital symmetry conservation principle,⁸ and secondary considerations favor the chair over the boat.⁸ On the other hand, the diyl is apparently generated in the thermal isomerization of bicyclo[2.2.0]hexanes (BCH) to 1,5-hexadienes, and the stereochemistry observed is consistent with least-motion cleavage of a chair-like cyclohexanediyl.^{9,10}

We wish to point out that, if the cyclohexanediyl is involved in the cleavage of BCH, as experiment and MINDO calculations suggest, then it is not accessible in the 3,3 shift of 1,5-hexadiene by 12 kcal/mol. Using Goldstein's values for the heats of formation and entropies of the relevant species at 250 °C,^{9c} BCH is 18 kcal/mol less stable (in free energy) than 1,5-hexadiene. The transition state for BCH cleavage, which is that for cleavage of the diyl, is 53 kcal/mol above 1,5-hexadiene. The low-energy 3,3-shift transition state is only 41 kcal/mol above 1,5-hexadiene.



The thermochemistry therefore indicates that the diyl, regardless of its stability, is insulated from the low-energy 3,3-shift energy surface by a kinetic barrier 12 kcal/mol above the actual transition state, which, by elimination, is that for the single-stage concerted route.

Evidence that the diyl is involved in the BCH cleavage comes from the work of Goldstein who demonstrated that exo-endo isomerization of 2,3,5,6-tetradeuterio-BCH occurs at the same rate as cleavage to 1,5-hexadiene.¹⁰ This geometric isomerization would appear to involve central bond rupture to a boat diyl which flips through the chair diyl to the boat again. The cleavage presumably proceeds from the chair diyl as even the MINDO calculations suggest.^{3a}

Just why the MINDO calculations lead to a prediction of inordinate stability for the diyl or why McIver's rules based

