SOME SYSTEMATIC ERRORS IN MINDO/3 CALCULATIONS

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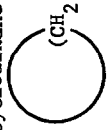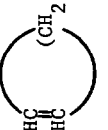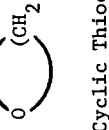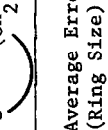
In their detailed description and evaluation of the MINDO/3 method Bingham, Dewar, and Lo[1] pointed out some types of compounds which gave calculated heats of formation which were poorly correlated with experimental values. They specifically identified acetylene derivatives, small ring compounds, aromatic compounds, and compact, globular molecules as types for which the error in ΔH_f often exceeded 10 kcal/mol. Dewar and Thiel[2] developed the MNDO method to overcome the problems inherent in the MINDO/3 method. The new approach was shown to give improved accuracy with some problem types but it was claimed that four-membered rings and branched compounds remained as problem cases.

Our interest in cyclic halonium ions[3,4] and in the equilibria between cyclic halonium ions and haloalkyl carbocations[4] led us to calculate the energies of cyclic chloronium ions and their isomeric open chain carbocations.[5-8] Because we subscribed to the view[1,2] that MINDO/3 calculations of the energies of small rings poorly correlated with experimental values, we calculated a variety of cyclic structures to see if the ring size errors were systematic and could possibly be systematically removed. Knowing that a branching error[5] would complicate the data analysis, we chose to calculate only unsubstituted ring systems. A comparison of calculated[9] and experimental heats of formation is shown in Table I. Geometries of the previously unreported structures are given in Table II.

We believe that the series of molecules in Table I is representative of the success of the method in calculating heats of formation for unsubstituted cyclic compounds. To our surprise the small rings were not uniquely calculated to be too stable. In fact the data show that four- and seven-membered rings have the largest average errors while six-membered rings have the smallest. Three- and five-membered rings have similar average errors.

Table I. Comparison of MINDO/3 Calculated and Observed Heats of Formation of Cyclic Systems (kcal/mol, gas phase, 25°)

Ring Size, n =	3			4			5			6			7			Average Errors (Type System)
Ring System	calcd	obsd[a]	(error)	calcd	obsd[a]	(error)	calcd	obsd[a]	(error)	calcd	obsd[a]	(error)	calcd	obsd[a]	(error)	
Cycloalkane $(CH_2)_n$	8.5[b,c]	12.7	(-4.2)	-8.1[b,c]	6.8	(-14.9)	-27.9[b,c]	-18.4	(-9.5)	-36.6[b,c]	-29.5	(-7.1)	-41.2[d]	-28.2	(-13.0)	-9.7 ± 4.3[e]
Cycloalkene HC=HC $(CH_2)_{n-2}$	59.4[b,c]	66.2	(-6.8)	33.0[b,c]	37.4	(-4.4)	5.6[b,c]	8.2	(-2.6)	-0.1[b,c]	-1.1	(1.0)	-15.8[d]	-2.2	(-13.6)	-5.2 ± 5.5[e]
Cyclic Ether O $(CH_2)_{n-1}$	-26.5[c,d]	-12.6	(-13.9)	-40.7[d]	-19.3	(-21.4)	-61.2[d]	-44.0	(-17.2)	-67.6[d]	-53.4	(-14.2)	-69.2[d]	-53[f]	(-13)	-15.9 ± 3.4[e]
Cyclic Thioether S $(CH_2)_{n-1}$	-2.1[d]	19.7	(-21.8)	-11.6[d]	14.6	(-26.2)	-30.1[c,d]	-8.1	(-22.0)	-38.1[d]	-15.1	(-23.0)	-42.6[d]	-15.7	(-26.9)	-24.0 ± 2.4[e]
Average Errors: (Ring Size)	-11.7 ± 7.9[e]			-16.7 ± 9.4[e]			-12.8 ± 8.5[e]			-10.8 ± 10.2[e]			-16.6 ± 6.9[e]			

Table II. Minimized Geometries Calculated by MINDO/3[a,b]

Molecule	Geometry, Bond Lengths (A^i-B^j) in Å, Bond Angles ($A^i-B^j-C^k$) in Deg.
Cycloheptane:	$C^1C^2, 1.519$; $C^2C^3, 1.518$; $C^3C^4, 1.518$; $C^4C^5=C^5C^6=C^6C^7=C^1C^7=1.517$; $C^5C^7, 1.516$; $HC^1, 1.120, 1.122$; $C^2C^3C^4, 121.7$; $C^4C^5C^6, 121.5$; $HC^1C^2, 107.8$; $HC^2C^3, 107.7, 106.8$; $C^1C^2C^3C^4, 47.3$; $C^2C^3C^4C^5, 64.4$; $C^3C^4C^5C^6, 55.2$; $C^4C^5C^6C^7, 48.0$

Cycloheptene:
C^1C^2, 1·495; C^2C^3,1·519; C^3C^4,1·521; C^4C^5,1·517; C^5C^6,1·514; C^6C^7,1·492;C^1C^7,1·342; HC^2,
1·123,1·119; HC^3,1·122,1·120; $C^1C^2C^3$,120·5; $C^2C^3C^4$,119·2; $C^3C^4C^5$,115·2; $C^4C^5C^6$,123·3; HC^1C^2,111·6;
HC^2C^3,109·0,108·5; $C^1C^2C^3C^4$,50·4; $C^2C^3C^4C^5$,70·5; $C^3C^4C^5C^6$,61·7;$C^4C^5C^6C^7$,34·3

Oxetane
CO,1·389; $C^1C^2=C^2C^3$,1·513; HC^1,1·124; HC^2,1·113; HC^3,1·125; $C^1C^2C^3$,83·2; $C^2C^3C^4$,92·1; $HC^1C^2=HC^3C^2=$
117·8,117·6; HC^2C^3,117·5; $C^1C^2C^3C^4$,0·1

Oxolane:
CO,1·372; $C^2C^3=C^4C^5$,1·516; C^3C^4,1·523; $HC^2=HC^5$,1·128,1·127; C^3C^2O,107·9; $C^2C^3C^4=C^3C^4C^5$,
105; HC^2C^3,113·5; $HC^3C^4 = HC^4C^5$,112·4,112·3; HC^5C,113·6 113·4; C^4C^3C0,0·2; $C^2C^3C^4C^5$,0·3

Oxane:
C^1O,1·363; C^1C^2,1·514;$C^2C^3=C^3C^4$, 1·520; C^4C^5,1·515; C^5O,1·361; $HC^1 = HC^5$,1·133,1·128; HC^2,1·120,1·118;
HC^3,1·120,1·190; HC^4,1·119,1·118; C^2C^1O,115·4; $C^2C^3C^4$,115·6; $C^3C^4C^5$,114·5; $HC^1C^2=HC^5C^4$,
112·1,110·0; HC^3C^4,110·3,109·3; HC^4C^5,110·1,109·0; HC^4C^5,110·1,109·9; $C^1C^2C^3C^4$,31·2; $C^2C^3C^4C^5$,32·3;$C^3C^4C^5O$,
35·6

Oxepane:
C^1O,1·353; C^1C^2,1·515; C^2C^3,1·526; C^3C^4,1·522; C^4C^5,1·521; C^5C^6,1·516; C^6O,1·352; HC^1, 1·131;
$HC^2=HC^3$,1·120,1·119; HC^4,1·119; HC^5,1·121, 1·119; HC^6,1·135,1·130; C^2C^1O,116·4; $C^2C^3C^4$,115·3;
$C^3C^4C^5$,114·6; $C^4C^5C^6$,117·6; C^5C^6O,118·8; HC^1C^2,110·1,108·5; HC^2C^3,110·2,109·3; HC^3C^4,110·5,109·0;
HC^4C^5,110·3,109·5; HC^5C^6,109·6,108·7; HC^6C^5,110·6,108·8; $C^1C^2C^3C^4$,71·6; $C^2C^3C^4C^5$,64·6; $C^3C^4C^5C^6$,63·9;
$C^4C^5C^6O$,66·1

Thiirane:
$C^1S=C^2S$,1·791; C^1C^2,1·425; $HC^1=HC^2$,1·104; C^1C^2S,66·6; $HC^1C^2=HC^2C^1$,121·5

Thietane:
$C^1S=C^3S$,1·790; C^1C^2,1·500; C^1C^2,1·501; C^2C^3,1·119; HC^2,1·119; $C^1C^2C^3$,101·2; C^2C^3S,89·0;
$HC^2C^2=HC^3C^2$,116·8; $C^1C^2C^3S$,0·4.

Thiane:
C^1S,1·782; C^1C^2,1·496; C^2C^3,1·517; C^3C^4,1·520; C^4C^5,1·497; C^5S,1·774; HC^1,1·112,1·110; HC^2,1·121;
HC^3, 1·120; HC^4,1·122,1·120; HC^5,1·113,1·112; $C^1C^2C^3$,118·0; $C^2C^3C^4$,118·4; $C^3C^4C^5$,117·4; C^4C^5,112·3;
HC^1C^2,113·6,112·3;HC^2C^3,109·1,108·8; C^3C^4C,108·7,108·8; HC^4C^5,108·9,108·7; HC^5C^4,113·6,112·5; $C^1C^2C^3C^4$,
51·8; $C^2C^3C^4C^5$,52·5; $C^3C^4C^5C$,42·3

Thiepane:
C^1S,1·781; C^1C^2,1·493; C^2C^3,1·520; C^3C^4,1·518: C^3C^4,1·520; C^4C^5,1·519; C^5C^6,1·494; C^6S,1·771; $HC^1=HC^6$,1·114,1·112;
HC^2,1·123,1·120; $HC^3=HC^4$,1·120; HC^1C^2,112·4,111·9; HC^2C^3,109·5,108·0; HC^3C^4,109·4,107·9; HC^4C^5,110·1,108·3; C^5C^6S,117·3; $C^1C^2C^3=C^2C^3C^4$,119·1; $C^3C^4C^5$,117·8; $C^4C^5C^6$,120·2;
HC^5,1·125,1·120; HC^5C^6,110·4,107·9; HC^6C^5,112·3,112·1; $C^1C^2C^3C^4$,78·1; $C^2C^3C^4C^5$,68·3; $C^3C^4C^5C^6$,71·3; $C^4C^5C^6S$,66·5
107·9;

Another point can clearly be made from these data; there is a significant functional group (or element) error which appears to be systematic.[10] For example, the average error in ΔH_f for cycloalkenes is less than that for the other type structures while the average error for the cyclic thioethers is the largest of the types compared. It is interesting to note that although the accuracy in calculating ΔH_f values for cyclic thioethers is poor, the precision is quite good as each value is within 3.0 kcal/mol of the average of the set.

It is our current view that the branching,[5] functional group, and ring size errors are systematic; therefore, comparison of ΔH_f values for isomeric structures of any type would seem to be justified provided the ΔH_f values are corrected for the systematic errors. Although the systematic functional group and ring size errors could be estimated from the data in Table I, the use of acyclic molecules for the correction of the functional group errors would be preferred. We are currently in the process of calculating the series of molecules which will allow an independent evaluation of these errors and will therefore postpone any discussion on our ability to correct for such errors to a later article.[11] Until the errors are completely catagorized, conclusions drawn from comparing MINDO/3 calculations on molecules of different ring sizes and from calculations of different functional groups should be qualified.

References
1. R. C. Bingham, M. J. S. Dewar, and D. H. Lo, J. Am. Chem. Soc., 97, 1285, 1294 (1975).
2. M. J. S. Dewar and W. Thiel, J. Am. Chem. Soc., 99, 4899, 4907 (1977).
3. S. P. McManus and D. W. Ware, Tetrahedron Lett., 4271 (1974).
4. S. P. McManus and P. E. Peterson, Tetrahedron Lett., 2753 (1975).
5. S. P. McManus and S. D. Worley, Tetrahedron Lett., 555 (1977).
6. S. D. Beatty, S. D. Worley, and S. P. McManus, J. Am. Chem. Soc., submitted for publication.
7. Our calculations of cyclic chloronium ions of various ring sizes (ref. 8) was inspired by a conversation with Professor Paul Peterson.
8. S. P. McManus, M. B. Smith, M. R. Smith, and S. D. Worley, to be published.
9. All calculated values are completely geometry optimized as described elsewhere (ref. 6). None of the values of Dewar (ref. 1) were assumed as they were in most cases found not to be minimum energy values, cf. See W. L. Jorgensen, J. Am. Chem. Soc., 99, 281 (1977).
10. This was not especially evident in Dewar's articles (ref. 1).
11. Some problems with MINDO/3 have previously been aired, e.g. see ref. 1; J. A. Pople, J. Am. Chem. Soc., 97, 5306 (1975); W. J. Hehre, ibid., 5308 (1975); M. J. S. Dewar, ibid., 6591 (1975); obviously, our simplistic approach does not offer a solution to all of the problems.