Ground States of Molecules. XXVI.[1] MINDO/3 Calculations for Hydrocarbons[2]

Richard C. Bingham, Michael J. S. Dewar,* and Donald H. Lo

Contribution from the Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712. *Received July 18, 1974*

Abstract: The MINDO/3 semiempirical SCF-MO method has been tested by calculations for a wide variety of hydrocarbons, for radicals and ions derived from them, and for several simple hydrocarbon reactions.

The preceding paper[1] described the development of an improved version (MINDO/3) of the MINDO[3-5] semiempirical SCF-MO method. Here we report the results of calculations for a wide variety of hydrocarbons, for ions and radicals derived from them, and for several simple reactions of hydrocarbons.

The calculations were carried out with the parameters listed in part XXV.[1] The geometry of each molecule was calculated by minimizing the energy with respect to all geometrical variables. Most of these calculations were carried out by the SIMPLEX method.[6] Here the computer time required becomes rather large for molecules with more than 15 atoms and increases with the degree of accuracy required. Thus while the calculated bond lengths and angles for small molecules are correct to ±0.001 Å and ±0.1°, those for the larger ones may be in error by as much as ±0.01 Å or 1°. Some of the calculations have been repeated by our variant[1,7] of the Davidon-Fletcher-Powell method which is much faster and much more reliable for large molecules. Since the errors in the earlier calculations proved to be much less than 1 kcal/mol in energy, and since errors of ±0.01 Å in bond lengths or of ±1° in angles are not chemically significant, we have not repeated all the earlier calculations.

The calculated heats of atomization were converted to heats of formation using the following values for the heats of formation of gaseous atoms at 25°: C, 170.89 kcal/mol; H, 51.102 kcal/mol. The results for a number of hydrocarbons of various types are compared with experiment in Table I while Table II shows a similar comparison of the calculated and observed molecular geometries.

The errors in Table I do not provide a fair indication of the general accuracy of MINDO/3 because the compounds treated are by no means a random sample. We deliberately concentrated on cases where the errors were large in the hope of tracking down their origin.

The compounds in Table I for which the error in ΔH_f is >10 kcal/mol seem to fall into four groups: (a) acetylene derivatives, ΔH_f too negative; (b) small ring compounds, ΔH_f too negative; (c) aromatic compounds, ΔH_f too positive; (d) compact, globular molecules, ΔH_f too positive. We suspect that these errors are inherent in the MINDO approximation in the sense that no choice of parameters can correct all of them simultaneously. MINDO/3 represents an optimum compromise in which the errors in general tend not to exceed 10 kcal/mol for compounds of any type. Although this is certainly not as good as one would wish, there do at least seem to be no classes of compounds for which MINDO/3 fails completely, as did MINDO/2. Note in particular that the calculated heat of atomization for H_2 agrees almost exactly with experiment. The error in MINDO/2 was huge and in MINDO/2′ still quite large.

The errors in the energies of aromatic compounds presumably depend on the values chosen for the π-resonance integrals. The same is probably also true for small ring compounds. All our parametrization studies seem to indicate that the two sets of compounds are interlaced, any improvement in the results for one being at the expense of a deterioration in those for the other.

The other errors probably arise from an overestimation of hydrogen-hydrogen nonbonded repulsions, due to an overestimation of the van der Waals radius of hydrogen. Thus the calculated heats of formation of cyclohexane and cyclohexene agree well with experiment; however, the calculated geometries of both are too flat. This is probably due to an overestimate of the axial hydrogen repulsions which of course can be relieved by flattening the molecule. In adamantane, where there are four sets of axial interactions, in cyclohexane moieties locked into the ideal diamantoid structure, MINDO/3 greatly overestimates the resulting repulsions with a consequent large error in ΔH_f. The negative deviations in acetylene probably arise from a combination of the two factors considered above.

It may be possible to overcome these problems by a different choice of parameters, in particular by a different choice of the functions f_2 and f_3 in the expressions[1] for the core resonance integrals and core-core repulsions. We can only say that we arrived at our present choice after trying several hundred possible combinations without any better results.

Geometries calculated by MINDO/3 (Table II) are in quite good general agreement with experiment, the errors in bond lengths being usually less than 0.02 Å and in bond angles less than 4°. Such errors are not of great chemical significance and attempts to reproduce geometries much more accurately than this are not of any real value. The only two consistent errors are the tendency to overestimate the flatness of rings, noted above, and a tendency to underestimate HCH bond angles in methylene groups. In our parametrization for MINDO/3 we adjusted the U_{ss} and U_{pp} values for carbon as explained in the preceding paper. We did not, however, realize at the time how large the optimum changes in these parameters could be. Subsequently we found that the fit for nitrogen compounds could be improved by allowing large variations in U_{ss} and U_{pp}. Changes in these parameters have little effect on calculated heats of atomization but they do influence bond angles. The barrier to inversion in ammonia was in particular sensitive to their choice. It is possible that similar changes in the U_{ss} and U_{pp} values for carbon might lead to an improvement in HCH bond angles and it might also improve calculations for small rings. Since this is uncertain, since a change in the CH parameters would involve a complete reparametrization for all the other elements, and since MINDO/3 in its present form has shown itself to be a useful tool in the study of chemical reactivity, we are publishing the present version as it stands.

Table I also compares observed first ionization potentials with the MINDO/3 values, calculated using Koopmans'

Theorem. The agreement is again quite good, the average error being *ca.* 0.3 eV. The higher ionization potentials are less satisfactory, MINDO/3 tending, like its predecessors, to give spurious high-lying σ levels.[8]

Table III compares calculated and observed dipole moments. MINDO/3 gives no spuriously large values; on the contrary, the calculated values, particularly for alkyl-substituted olefines, are too small. This suggests that MINDO/3 does not allow sufficiently for changes in the electronegativity of hybrid carbon AOs with their s content. This again could be due to the use of an insufficient separation between U_{ss} and U_{pp}. The errors are in any case small in an absolute sense.

Comparison with Alternative Procedures

The results in Tables I-III show that MINDO/3 is clearly superior to the earlier versions of MINDO since there are no longer large systematic deviations for specific classes of molecules. This is true in particular of small ring compounds, an important consideration since one of the most promising regions for chemically useful calculations of reaction paths lies in the area of thermal rearrangements, most of which are liable to involve cyclic intermediates. The results are very much superior to those of other semiempirical treatments that have been suggested. In particular, none of the latter cope satisfactorily with small rings and most of them lead to huge errors in calculated heats of atomization. This of course is not surprising since these methods have not been parametrized to reproduce heats of atomization in a general way. They have been parametrized either to mimic the results of *ab initio* calculations or to fit data for diatomic and triatomic molecules. Since approximate treatments based on CNDO or INDO are probably incapable of an accuracy much greater than MINDO/3, parametrization for small molecules only gives good results for them at the expense of a catastrophe in larger systems.

The main question of course is how well MINDO/3 compares with *ab initio* SCF methods. It has been rather commonly assumed in recent years that while existing *ab initio* methods give very poor estimates of heats of atomization, due to large changes in correlation energy when atoms combine, they do nevertheless give good estimates of heats of reactions, provided that the reactants and products contain similar numbers of bonds. The basis for this belief comes partly from the success of *ab initio* methods in predicting conformational effects in small molecules, *e.g.*, conformation equilibria, barriers to rotation about single bonds (as in ethane), barriers to inversion (as in ammonia), and partly from the work of Pople, *et al.*, on the calculation of bond separation energies.[9,10] Both these situations are, however, concerned with comparisons of systems whose classical structures contain exactly the same bonds. As Pople, *et al.*, remark[10] the agreement becomes less satisfactory when the types of bonds in the reactants and products differ, even when their total number remains the same. Comparisons of the latter kind are of course of much greater chemical significance, hardly any chemical reactions conforming to the former condition if bonds are formed and broken during their course. Since MINDO/3 is parametrized to give an optimum compromise for systems of all kinds, it is less satisfactory than *ab initio* SCF methods for problems of the first type. Thus the calculated barrier to rotation in ethane (0.9 kcal/mol) is too low. On the other hand published data seem to indicate that comparisons of structures with different types of bonding are reproduced better by MINDO/3. It is difficult to find many examples because so few *ab initio* SCF calculations have been reported with any kind of geometry optimization, for any but very simple molecules. Table IV shows the superiority of MINDO/3 in a few cases. Note the very large error in the STO-3G value of ΔH for the trimerization of acetylene to benzene.

Radicals and Carbonium Ions

Table V compares calculated and observed heats of formation for a number of hydrocarbon radicals and Table VI those for analogous carbonium ions. The agreement is about as good as for the hydrocarbons themselves. This is an important point because it has often been stated in print that semiempirical methods cannot give satisfactory results for ions, using parameters derived from neutral molecules. This is clearly not true.

Heats of Hydrogenation and Strain Energies

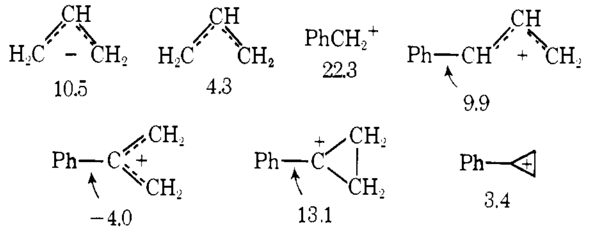
Table VII compares calculated and observed heats of hydrogenation for a number of unsaturated hydrocarbons. The agreement is quite reasonable. This is a property which seems to be reproduced very poorly by *ab initio* methods. Thus the calculated heats of hydrogenation of ethylene and acetylene to ethane, all geometries being optimized, are respectively 72.0 and 134.9 kcal/mol with STO-3G and 42.0 and 94.7 kcal/mol with 4-31G.

Barriers to Rotation

Table VIII compares calculated and observed barriers to rotation in a number of hydrocarbons and carbonium ions. These were calculated by twisting the molecule about the bond or bonds in question and at each point optimizing the geometry with respect to all other geometrical variables.

The barriers to rotation about CC double bonds in olefines and cumulenes are very well reproduced. The agreement with experiment is much better than that given by any previous calculations, including MINDO/2. Note in particular the very good prediction of the small difference between the barriers for ethylene and 2-butene. The barriers for rotation about single bonds are, however, consistently too low. This is exactly the converse of the situation with *ab initio* SCF calculations which give very good estimates of the barriers to rotation about single bonds but values that are far too high for rotation about double bonds.[11]

We have also calculated barriers to rotation in some additional ions and in the allyl radical with the following results (barrier height in kcal/mol):



Note the *negative* value for 2-phenylallyl cation. This implies that the stable conformation is predicted to be one in which the ring is orthogonal to the allyl moiety; *cf.* the similar situation in singlet trimethylenemethane.[12]

Conformational Equilibria

While MINDO/3 underestimates the barriers to rotation about single bonds, it often gives good estimates of the relative energies of the conformers separated by such barriers. Some examples are given in Table IX. The situation is less satisfactory for conformers involving rotation about a single bond linking two conjugated carbon atoms, presumably as a result of the underestimation of conjugation energies by MINDO/3. Thus while MINDO/3 does correctly predict the more stable conformer of 1,3-butadiene to be trans planar, it predicts much too small an energy difference (0.4 kcal/mol) between it and the less stable one and much too

Table I. Calculated and Observed Heats of Formation (ΔH_f) and Vertical Ionization Potentials for Hydrocarbons

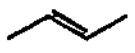
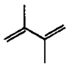
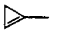
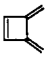
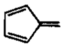
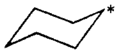
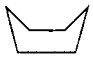
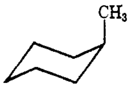
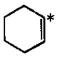
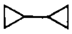
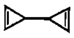
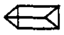
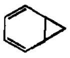
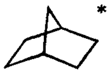
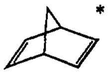
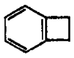
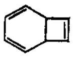
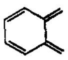
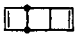
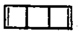
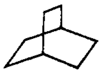
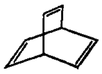
Compd[a]	ΔH_f, kcal/mol Calcd	Obsd[b]	Error	Vertical ionization potential, eV Calcd	Obsd	Error
H_2*	0.1	0	0.1	15.63	15.45	0.18
CH_4*	−6.3	−17.9	11.6	13.30	12.70	0.60
CH_3CH_3*	−19.8	−20.2	0.4	11.79	11.56	0.23
$H_2C{=}CH_2$*	19.2	12.4	6.8	10.42	10.51	−0.09
$HC{\equiv}CH$*	57.8	54.3	3.5	10.83	11.40	−0.57
$CH_3CH_2CH_3$*	−26.5	−24.8	−1.7	11.31	11.06	0.25
$CH_3CH{=}CH_2$*	6.5	4.9	1.6	9.85	9.69	0.16
$CH_3C{\equiv}CH$	35.0	44.3	−9.3			
$H_2C{=}C{=}CH_2$	42.0	45.9	−3.9	9.64	9.69	−0.05
$CH_3(CH_2)_2CH_3$ trans*	−30.4	−30.4	0.0	10.82	10.67	0.15
gauche	−29.5	−29.7	0.2			
$CH_3CH(CH_3)_2$*	−24.9	−32.4	7.5	10.97	10.69	0.28
$CH_3CH_2CH{=}CH_2$	1.0	−0.2	1.2	9.81	9.59	0.22
	−6.3	−3.0	−3.3	9.44	9.12	0.32
	−5.7	−1.9	−3.8	9.48	9.12	0.36
	2.5	−4.3	6.8	9.63	9.17	0.46
*	31.9	26.1	5.8	9.09	9.08	0.01
	32.6	28.1	4.5			
$H_2C{=}C{=}C{=}CH_2$	64.3			8.78		
$CH_3C{\equiv}CCH_3$	12.1	34.7	−22.6	10.79		
$HC{\equiv}C{-}CH{=}CH_2$*	61.7	72.8	−11.1	9.27		
$HC{\equiv}C{-}C{\equiv}CH$	91.1	113.0	+21.9	9.52	10.17	−0.65
	−36.1	−35.1	−1.0	10.82	10.37	0.45
$C(CH_3)_4$	−14.6	−40.3	25.7	10.93	10.40	0.53
	19.16	18.14	1.0	8.87	8.56	0.31
	20.1	19.1	1.0	8.88	8.59	0.29
$H_2C{=}C{=}C{=}C{=}CH_2$	107.2			8.01		
	30.6	10.8	19.8	8.97		
	21.6	20.1	1.5	9.68		
*	8.7	12.7	−4.0	10.33	10.06	0.27
*	59.4	66.2	−6.8	9.31	9.70	−0.39
	33.9	47.9	−14.0	9.59	9.4	0.2
	42.2	58.2	−16.0	9.04		
	−5.3			9.63		
	−2.0	1.3	−3.3	9.58		
	25.0	46.4	−21.4	8.79		
	83.2			9.22		
	−5.1	6.8	−11.9	10.26		
*	33.1	37.4	−4.3	9.56	9.43	0.13
	17.1	30.0	−12.9	9.64	9.19	0.45
	21.0	28.3	−7.3	9.24		
	9.8	19.8	−10.0	9.04		
	83.4			8.76		
	−27.9	−18.4	−9.5	11.08	11.59	−0.51
	5.6	8.2	−2.6	9.34	9.01	0.33
	41.7	39.4	2.3	8.81	8.58	0.63
	68.2	47.5	20.7	8.69		
	46.1			8.75		
*	−36.6	−29.5	−7.1	10.46	9.81	0.65
	−34.7			10.44		

Table I (*Continued*)

	ΔH_f, kcal/mol			Vertical ionization potential, eV		
Compd[a]	Calcd	Obsd[b]	Error	Calcd	Obsd	Error
	−34.0	−37.0	3.0			
	−32.0					
 *	−0.1	−1.1	1.0	9.43	8.94	0.49
	28.8	19.8	9.0	9.22	9.25	−0.03
PhCH$_3$	23.5	12.0	11.5	9.06	8.82	0.24
	37.3	43.9	−6.6	8.47	8.40	0.07
	58.1	71.1	−13.0	8.08	8.21	−0.13
	49.8	51.9	−2.1	8.60		
 (trans)	23.8	30.9	−7.1	8.60		
	33.2	39.3	−6.1	8.52		
 (trans)	124.2			8.60		
	98.7			8.94		
	28.7	44.2	−15.5	9.65	9.45	0.20
	114.1			8.23		
	128.9			8.34		
	−0.9			9.56		
	65.4			8.62		
	117.0			8.46		
	47.5			8.36		
 *	8.4	−12.4	20.8	10.36	9.80	0.56
 *	84.5	59.7	24.8	9.04	8.62	0.42
	59.2			8.66		
	78.4			8.50		
	74.5			7.91		
	91.3			8.51		
 (anti)	120.2			8.80		
 (sÿn)	123.1			8.87		
	132.3			8.54		
	−10.1	−24.1	14.0	10.06	9.53	0.53
	56.1			8.20		
	99.0			9.10	8.24	0.86
Cubane	139.8	148.7	−8.9	9.20	8.74	0.46
Adamantane	2.2	−32.9	35.1			
Naphtalene	57.3	36.1	21.2			

[a] Compounds marked with asterisks were used in the parametrization. [b] J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds," Academic Press, New York, N. Y., 1970.

Table II. Calculated and Observed Molecular Geometries

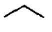
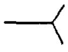
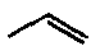
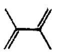
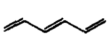
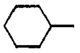
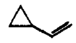
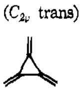
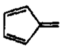
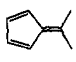
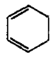
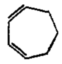
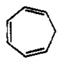
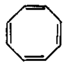
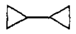
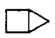
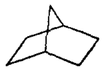
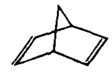
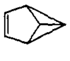
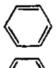
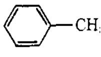
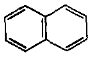
Molecule	Ref	Geometry, calcd (obsd), bond lengths (A^iB^j) in Å, bond angles ($A^iB^jC^k$) in deg[sss]
CH_3	*a*	CH, 1.102 (1.106)
H_3CCH_3	*b*	CC, 1.486 (1.532); CH, 1.108 (1.107); CCH, 112.8 (111.1)
	*c, d*	CC, 1.497 (1.526, 1.532); C^1H, 1.110 (1.071, 1.107); C^2H, 1.118 (1.096, 1.107); CCC, 119.6 (112.4, 112.0); HC^2H, 102.5 (106.1, 107.0)
	*e*	C^1C^2, 1.501 (1.539); C^2C^3, 1.524 (1.539); C^1H, 1.111 (1.100); C^2H, 1.121 (1.100); $C^1C^2C^3$, 119.5 (112.2); HC^1C^2, 113.2 (110.3); C^1C^2H, 108.8 (110.3)
	*f, g*	CC, 1.513 (1.525, 1.535); C^1H, 1.111 (1.092, 1.100); C^2H, 1.143 (1.108, 1.122); CCC, 103.8 (111.1, 110.8); HC^1C^2, 113.5 (109.4, 111.4)
	*h*	CC, 1.537 (1.539); CH 1.110 (1.120)
$H_2C{=}CH_3$	*i*	CC, 1.308 (1.336); CH, 1.098 (1.103); CCH, 124.8 (121.6)
	*j*	C^1C^2, 1.333 (1.336); C^2C^3, 1.480 (1.501); C^1H, 1.101 (1.091); C^2H, 1.114 (1.090); C^3H, 1.114 (1.090); CCC, 128.9 (124.3); HC^1C^2, 123.4 (120.5); HC^2C^3, 111.4 (116.7); HC^3H, 106.0 (107.7)
	*k*	C^1C^2, 1.339 (1.331); C^2C^3, 1.498 (1.505); C^1H, 1.101 (1.103); C^3H, 1.112 (1.113); $C^3C^2C^4$, 116.6 (112.0); HC^3C^2, 113.9 (110.4)
	*l*	C^1C^2, 1.464 (1.520); C^2C^3, 1.346 (1.339); C^1H, 1.111; C^2H, 1.103; CCC, 129.6 (123); HC^1C^2, 114.3; HC^2C^3, 117.9
		C^1C^2, 1.473; C^2C^3, 1.339; C^1H, 1.111; C^2H, 1.112; CCC, 134.3; HC^1C^2, 113.0; HC^2C^3, 114.8
$HC\equiv CH$	*m*	CC, 1.191 (1.205); CH, 1.076 (1.059)
$H_3CC\equiv CH$	*n*	C^1C^2, 1.206 (1.206); C^2C^3, 1.427 (1.459); C^1H, 1.071 (1.056); C^3H, 1.135 (1.105); HC^3C^2, 113.6 (110.2)
$H_3CC\equiv CCH_3$	*o*	C^1C^2, 1.433 (1.467); C^2C^3, 1.216 (1.213); CH, 1.105 (1.115); CCH, 112.7 (110.7)
	*p*	C^1C^2, 1.330 (1.342); C^2C^3, 1.464 (1.463); CH, 1.099 (1.093); CCC, 131.0 (123.6)
	*q*	C^1C^2, 1.350 (1.349); C^2C^3, 1.515 (1.491); C^2H^5, 1.500 (1.511); C^1H, 1.113 (1.111, 122.0); $C^3C^2C^5$, 119.6 (117.9)
	*r*	C^1C^2, 1.330 (1.337); C^2C^3, 1.462 (1.458); C^3C^4, 1.346 (1.368); CH, 1.100 (1.104); $C^1C^2C^3$, 130.9 (121.7); $C^2C^3C^4$, 130.8 (124.4)
cis-1,3,5-hexatriene	*s*	C^1C^2, 1.331 (1.336); C^2C^3, 1.463 (1.462); C^3C^4, 1.347 (1.362); CH, 1.099 (1.090); $C^1C^2C^3$, 130.7 (122.1); $C^2C^3C^4$, 133.6 (125.9)
$H_2C{=}C{=}CH_2$	*t*	CC, 1.311 (1.308), CH, 1.099 (1.087); HCC, 118.4 (118.2)
$H_2C{=}C{=}C{=}CH_2$	*u*	C^1C^2, 1.312 (1.318); C^2C^3, 1.295 (1.283); CH, 1.100; HCC, 124.7
$H_2C{=}C{=}C{=}C{=}CH_2$		C^1C^2, 1.304; C^2C^3, 1.291; CH, 1.097; HCC, 124.5
$H_2C{=}C{=}C{=}C{=}C{=}CH_2$		C^1C^2, 1.310; C^2C^3, 1.292; C^3C^4, 1.292; CH, 1.099; HCC, 123.6
$HC\equiv C{-}C\equiv CH$	*o*	C^1C^2, 1.397 (1.376); C^2C^3, 1.206 (1.217); CH, 1.077 (1.064)
	*v*	C^1C^2, 1.331 (1.341); C^2C^3, 1.437 (1.431); C^3C^4, 1.209 (1.208); C^1H, 1.102 (1.087); C^4H, 1.071 (1.062); $C^1C^2C^4$, 125.9 (123.1); $C^2C^3C^4$, 180 (177.9); HC^1C^2, 123.3 (120.6)
	*w*	CC, 1.504 (1.510); CH, 1.103 (1.089); HCH, 108.7 (115.1)
	*x, y*	CC, 1.525 (1.548); CH, 1.110 (1.104); CXC^2, 157.9 (153.0); HXC^2, 128.8 (122.1)
	*aa*	CC, 1.522 (1.546); CH, 1.111 (1.114)
	*bb, cc*	CC, 1.517 (1.528); CH, 1.123 (1.119); CCCC,[dd] 62.7 (55.9)
	*ee,*	CC, 1.529 (1.527); CH, 1.116 (1.116); $C^2C^1C^6$, 115.8 (111.3); $C^2C^1C^7$, 111.2 (110.1); $C^1C^2C^3C^4$[ad] 64.2 (55.3)
	*ff*	C^1C^2, 1.317 (1.300); C^1C^3, 1.481 (1.515); C^1H, 1.084 (1.070); C^3H, 1.114 (1.087); HC^1C^3, 153.1 (149.9); HCH, 105.2 (114.6)
		C^1C^2, 1.332; C^1C^3, 1.489; C^1C^4, 1.455; C^2H, 1.086; C^3H, 1.110; C^4H, 1.113; $C^2C^1C^4$, 151.4; HC^2C^1, 152.1; HC^3H, 107.3
		C^1C^2, 1.492; C^2C^3, 1.482; C^1C^4, 1.317; C^2H, 1.110; C^4H, 1.099; HC^4C^1, 124.4; HC^2C^1, 126.0
 (C_{2v} trans)	*gg*	CC(ring), 1.521 (1.522); C^1C^4, 1.490 (1.475); C^4C^5, 1.330 (1.334); CH, 1.105 (1.099); $C^1C^4C^5$, 127.2 (126.2); $C^2C^1C^4$, 134.7 (120.1); HC^5C^4, 122.7 (119.7)
	*hh, ii*	C^1C^2, 1.482 (1.453); C^1C^4, 1.321 (1.343); CH, 1.096 (1.108); HCC, 124.4 (121.8)
		C^1C^2, 1.472; C^2C^3, 1.331; C^1C^4, 1.337; $C^2C^1C^4$, 1.53.1; HC^2C^1, 150.4; HC^4C^1, 122.4
	*jj*	C^1C^2, 1.345 (1.342); C^1C^4, 1.512 (1.517); C^3C^4, 1.535 (1.566); C^1H, 1.099 (1.083); C^3H, 1.116 (1.094); $C^1C^2C^3$, 93.6 (94.2); HC^1C^2, 134.7 (133.5)
		C^1C^2, 1.362; C^1C^4, 1.520; C^1C^5, 1.479; C^2H, 1.093; C^3H, 1.114; C^5H, 1.109; $C^2C^1C^4$, 93.3; $C^2C^1C^5$, 136.3
	*kk*	C^1C^2, 1.357 (1.357); C^2C^3, 1.501 (1.488); C^3C^4, 1.536 (1.516); C^3C^5, 1.332 (1.335); CH, 1.098; HC^1C^2, 135.5 (131.5); $C^2C^1C^6$, 136.6 (135.7); HC^1C^2, 135.5 (131.5); HC^5C^3, 123.5 (121.5)
	*ll*	C^1C^2, 1.515 (1.509); C^2C^3, 1.352 (1.342); C^3C^4, 1.492 (1.469); C^1H, 1.116; C^2H, 1.103; C^3H 1.102; $C^2C^3C^4$, 109.2 (109.4); $C^2C^1C^5$, 103.6 (102.8)
	*mm*	C^1C^2, 1.509 (1.470); C^2C^3, 1.353 (1.355); C^1C^6, 1.339 (1.349); C^2H, 1.103 (1.078); C^3H, 1.107 (1.130); C^6H, 1.092 (1.080); $C^1C^2C^3$, 107.9 (107.7); $C^2C^1C^5$, 104.5 (106.6); HC^3C^2, 127.6 (126.4); HCH, 114.9 (117 ± 5)

Table II (*Continued*)

Molecular	Ref	Geometry, calcd (obsd), bond lengths (A^iB^j) in Å, bond angles ($A^iB^jC^k$) in deg[sss]
	*nn*	C^1C^2, 1.510 (1 476); C^2C^3, 1.359 (1.340); C^3C^4, 1.477 (1.462); C^1C^6, 1.374 (1.347); C^6C^7, 1.499 (1.510); CH, 1.100 (1.100); $C^2C^3C^4$, 108.6 (109.0); $C^2C^1C^5$, 101.8 (107.0)
	*oo, pp*	C^1C^2, 1.353 (1.355); C^2C^3, 1.499 (1.504); C^3C^4, 1.530 (1.519); C^4C^5, 1.529 (1.550); CH, 1.104 (1.093)
	*qq*	C^1C^2, 1.351 (1.350); C^2C^3, 1.470 (1.468); C^4C^5, 1.505 (1.523); C^5C^6, 1.526 (1.534); C^1H, 1.106 (1.082); C^5H, 1.120 (1.096); $C^1C^2C^3$, 120.7 (120.1); $C^2C^1C^6$, 123.1 (120.1)
	*rr*	C^1C^2, 1.347 (1.347); C^2C^3, 1.461 (1.450); C^4C^5, 1.490 (1.509); C^5C^6, 1.524 (1.522); C^1H, 1.110 (1.092); C^5H, 1.121 (1.102); $C^1C^2C^3 = C^7C^1C^2$ = 130.1 (129.1); HC^2C^1, 116.8 (117.5), ξ,[ss] 63.6 (63.9)
	*tt*	C^1C^2, 1.346 (1.356); C^2C^3, 1.465 (1.446); C^3C^4, 1.347 (1.356); C^6C^7, 1.496 (1.505); C^1H, 1.109 (1.095); C^7H, 1.125 (1.106); $C^1C^2C^3$, 128.4 (127.2); $C^2C^3C^4$, 125.4 (119.8)
	*uu*	C^1C^2, 1.344 (1.340); C^2C^3, 1.466 (1.476); CH, 1.109 (1.100); HCC, 115.7 (117.6); θ,[vv] 148.3 (136.9)
		C^1C^2, 1.510; C^2C^3, 1.483; CH, 1.105
		C^1C^2, 1.497; C^2C^3, 1.313; CH, 1.082
	*vv*	C^1C^2, 1.537 (1.539); C^1C^3, 1.555 (1.497); C^2H, 1.106 (1.093); C^3H, 1.098 (1.071); C^2XC^4,[z] 130.5 (121.6), C^1C^3H, 131.5 (128.4); XC^4H(eq),[z] 125.1 (122.8); XC^4H(ax),[z] 128.5 (121.5)
 trans	*ww*	$C^1C^{1\prime}$, 1.506 (1.499); C^1C^2, 1.522 (1.507); C^2C^3, 1.488 (1.507); C^1H, 1.114 (1.103); C^3H, 1.105 (1.103); HC^1C^2, 113.1 (110.5)
	*xx*	CC, 1.541 (1.557); C^1H, 1.111 (1.108); C^2H, 1.107 (1.109); $C^1C^2C^3$, 73.0 (74.2)
	*zz*	C^1C^2, 1.520 (1.511); C^2C^3, 1.346 (1.341); C^1C^4, 1.583 (1.543); C^1C^5, 1.494 (1.533); C^1H, 1.103 (1.130); C^2H, 1.102 (1.089); C^5H, 1.107 (1.130); θ,[yy] 123.4 (114.5)
	*aaa*	C^1C^2, 1.522 (1.50); C^2C^3, 1.350 (1.32); C^1C^4, 1.591 (1.58); C^1H, 1.113 (1.09); C^2H, 1.098 (1.07); θ,[yy] 118.3 (115–124)
	*bbb*	C^1C^2, 1.530 (1.543); C^2C^3, 1.539 (1.622); C^1C^4, 1.562 (1.536); C^1C^5, 1.493 (1.507); C^1H, 1.102; C^2H, 1.104; C^5H, 1.114; (CH_{av}, 1.085); θ,[yy] 122.9 (112.7)
Prismane (D_{3h}) 		C^1C^2, 1.561; C^1C^5(Δ), 1.545; CH, 1.100; HC^1C^2, 131.5
Cubane (T) 	*rrr*	CC, 1.564 (1.551); CH, 1.107
	*ccc*	C^1C^2, 1.551 (1.556); C^2C^3, 1.536 (1.551); C^1C^7, 1.553 (1.559); CH, 1.115 (1.115); φ,[ddd] 115.7 (108.0)
	*eee, fff*	C^1C^2, 1.535 (1.538); C^2C^3, 1.358 (1.339); C^1C^7, 1.571 (1.573); C^1H, 1.108 (1.100); C^2H, 1.098 (1.098); C^7H, 1.118 (1.100); φ,[ddd] 117.7 (115.0)
	*ggg*	C^1C^2, 1.506 (1.531); C^2C^3, 1.358 (1.350); C^3C^4, 1.532 (1.531); C^1C^7, 1.568 (1.600); C^1C^8, 1.533 (1.530); C^4C^8, 1.566 (1.485)
	*xx*	C^1C^2, 1.496 (1.465); C^2C^3, 1.348 (1.346); C^3C^4, 1.527 (1.523); C^1C^7, 1.539 (1.542); C^1H, 1.114; C^2H, 1.103; C^3H, 1.103; C^4H, 1.130 (CH, 1.103); $Y^{hhh}C^4C^3$, 70.5 (72.5)
	*ppp*	C^1C^2, 1.532 (1.529); C^2C^3, 1.516 (1.503); C^3C^4, 1.320 (1.339); C^1C^6, 1.458 (1.452); C^1H, 1.098 (1.078); C^2H, 1.105 (1.082); C^3H, 1.099 (1.078); C^2C^3H, 122.8 (125.4); C^6C^1H, 121.7 (133.7); α,[qqq] 120.5 (106.0)
	*iii*	CC, 1.398 (1.397); CH, 1.102 (1.084)
	*jjj*	CC(ring), 1.413 (1.392); C^1C^7, 1.490 (1.51)
	*kkk*	C^1C^2, 1.382 (1.367); C^2C^3, 1.427 (1.414); C^1C^9, 1.447 (1.421); C^9C^{10}, 1.441 (1.419); CH, 1.105 (1.096)
CH_2, singet	*mmm*	CH, 1.121 (1.11); HCH, 100.2 (102.4)
Triplet	*nnn, ooo*	CH, 1.078 (1.078); HCH, 134.1 (136)

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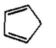
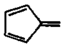
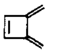
[a] L. S. Bartell, K Kuchitsu, and R. J. de Neui, *J. Chem. Phys.*, **35,** 1211 (1961). [b] L. S. Bartell, and H. K. Higginbotham, *ibid.*, **42,** 851 (1965). [c] D. R. Lide, Jr., *ibid.*, **33,** 1514 (1960). [d] T. Iijima, *Bull. Chem. Soc. Jap.*, **45,** 1291 (1972). [e] K. Kuchitsu, *ibid.*, **32,** 748 (1959). [f] D. R. Lide, Jr., *J. Chem. Phys.*, **33,** 1519 (1960). [g] R. L. Hilderbrandt and J. D. Wieser, *J. Mol. Struct.*, **15,** 27 (1973). [h] B. Beagley, D. P. Brown, and J. J. Monaghan, *ibid.*, **4,** 233 (1969). [i] L. S. Bartell, E. A. Roth, C. D. Hollowell, K. Kuchitsu, and J. E. Young, Jr., *J. Chem. Phys.*, **42,** 2683 (1965). [j] D. R. Lide, Jr., and D. Christensen, *ibid.*, **35,** 1374 (1961). [k] L. S. Bartell and R. A. Bonham, *ibid.*, **32,** 824 (1960). [l] B. P. Stoicheff, "Advances in Spectroscopy," E. W. Thompson, Ed., Interscience, New York, N.Y., 1959, p 148. [m] J. H. Callomon and B. P. Stoicheff, *Can. J. Phys.*, **35,** 373 (1957). [n] C. C. Costain, *J. Chem. Phys.*, **29,** 864 (1958). [o] M. Tanimoto, K. Kuchitsu, and Y. Morino, *Bull. Chem. Soc. Jap.*, **42,** 2519 (1969). [p] K. Kuchitsu, T. Fukuyama, and T. Morino, *J. Mol. Struct.*, **1,** 463 (1968). [q] C. F. Atens, L. Hedberg, and K. Hedberg, *J. Amer. Chem. Soc.*, **90,** 2463 (1968). [r] M. Traetteberg, *Acta Chem. Scand.*, **22,** 628 (1968). [s] M. Traetteberg, *ibid.*, **22,** 2294 (1968). [t] A. G. Maki and R. A. Toth, *J. Mol. Spectrosc.*, **17,** 136 (1965). [u] Unpublished work by A. Almenningen, O. Bastiansen, and M. Traetteberg, quoted by O. Bastiansen and M. Traetteberg, *Tetrahedron*, **17,** 147 (1962). [v] T. Fukuyama, K. Kuchitsu, and Y. Morino, *Bull. Chem. Soc. Jap.*, **42,** 379 (1969). [w] O. Bastiansen, F. N. Fritsch, and K. H. Medberg, *Acta Crystallogr.*, **17,** 538 (1964). [x] A. de Meijere, *Acta Chem. Scand.*, **20,** 1093 (1965). [y] S. Meiboom and L. C. Snyder, *J. Chem. Phys.*, **52,** 3857 (1970). [z] The molecule is folded about the line

Table II (*Continued*)

joining two carbon atoms; x is the midpoint of that line. [aa] W. J. Adams, G. J. Geise, and L. S. Bartell, *J. Amer. Chem. Soc.*, **92,** 5013 (1970). [bb] M. Davis and O. Hassel, *Acta Chem. Scand.*, **17,** 1181 (1963). [cc] H. J. Geise, H. R. Buys, and F. C. Mijlhoff, *J. Mol. Struct.*, **9,** 447 (1971). [dd] Dihedral angle. [ee] H. J. Geise, F. C. Mijlhoff, and C. Altona, *J. Mol. Struct.*, **13,** 211 (1972). [ff] P. H. Kasai, R. J. Myers, D. F. Eggers, Jr., and K. W. Wiberg, *J. Chem. Phys.*, **30,** 512 (1959). [gg] A. de Meijere and W. Lüttke, *Tetrahedron*, **25,** 2047 (1969). [hh] E. A. Dorko, J. L. Hencher, and S. H. Bauer, *ibid.*, **24,** 2425 (1968). [ii] V. H. Dietrich, *Acta Crystallogr., Sect. B*, **26,** 44 (1970). [jj] B. Bak, J. J. Led, L. Nygaard, J. Rastrup-Andersen, and S. O. Soerensen, *J. Mol. Struct.*, **3,** 369 (1969). [kk] A. Skanky, *Acta Chem. Scand.*, **22,** 3239 (1968). [ll] L. H. Scharpen and V. W. Laurie, *J. Chem. Phys.*, **43,** 2765 (1965). [mm] P. A. Brown, R. D. Brown, F. R. Burden, P. J. Domaille, and J. E. Kent, *J. Mol. Spectrosc.*, **43,** 401 (1972). [nn] J. F. Chiang and S. H. Bauer, *J. Amer. Chem. Soc.*, **92,** 261 (1970). [oo] J. F. Chiang and S. H. Bauer, *ibid.*, **91,** 1898 (1969). [pp] H. J. Geise and H. R. Buys, *Recl. Trav. Chim. Pays-Bas*, **89,** 1147 (1970). [qq] H. Oberhammer and S. H. Bauer, *J. Amer. Chem. Soc.*, **91,** 10 (1969). [rr] K. Hagen and M. Traetteberg, *Acta Chem. Scand.*, **26,** 3643 (1972). [ss] ξ is the angle between the planes $C^5C^6C^7$ and $C^1C^4C^5C^7$. [tt] M. Traetteberg, *ibid.*, **20,** 1724 (1966). [uu] Angle between adjacent C_4 planes tub geometry. [vv] K. W. Cox, M. D. Harmony, G. Nelson, and K. B. Wiberg, *J. Chem. Phys.*, **50,** 1976 (1969); **53,** 858 (1970). [ww] K. Hagen, G. Hagen, and M. Traetteberg, *Acta Chem. Scand.* **26,** 3649 (1972). [xx] A. Almenningen, B. Andersen, and B. A. Nyhus, *ibid.*, **25,** 1217 (1971). [yy] The carbon atoms lie in two planes; θ is the angle between the planes. [zz] J. F. Chiang, M. T. Kratus, A. L. Andreassen, and S. H. Bauer, *J. Chem. Soc., Faraday Trans. 2*, 1274 (1972). [aaa] Experimental geometry for hexafluoro derivative, H. M. Seig and B. Beagley, *Acta Chem. Scand.*, **23,** 1837 (1969); Z. Latajka, H. Ratajczak, W. J. Orville-Thomas, and E. Ratajczak, *J. Mol. Struct.*, **12,** 492 (1972). [bbb] R. D. Suenram and M. D. Harmony, *J. Chem. Phys.*, **56,** 3837 (1973). [ccc] J. F. Chiang, C. F. Wilcox, and S. H. Bauer, *J. Amer. Chem. Soc.*, **90,** 3149 (1968). [ddd] ϕ is the angle between the planes $C^1C^2C^3C^4$ and $C^1C^4C^5C^6$. [eee] Y. Morino, K. Kuchitsu, and A. Yokozeki, *Bull. Chem. Soc. Jap.*, **40,** 1557 (1967). [fff] G. Dallinga and L. H. Toneman, *Recl. Trav. Chim. Pays-Bas*, **87,** 805 (1968). [ggg] Y. C. Wang and S. H. Bauer, *J. Amer. Chem. Soc.*, **94,** 5651 (1972). [hhh] Y is the centroid of $C^1C^7C^8$, *i.e.*, a point on the threefold axis. [iii] L. Langseth and B. P. Stoicheff, *Can. J. Phys.*, **34,** 350 (1956). [jjj] F. A. Keidel and S. H. Bauer, *J. Chem. Phys.*, **25,** 1218 (1956). [kkk] D. W. J. Cruickshank and R. A. Sparks, *Proc. Roy. Soc., Ser. A*, **258,** 270 (1960). [lll] A. Almenningen, O. Bastiansen, and F. Byvik, *Acta Crystallogr.*, **14,** 1056 (1961). [mmm] G. Herzberg, *Proc. Roy. Soc., Ser. A*, **262,** 291 (1961). [nnn] G. Herzberg and J. W. C. Johns, *J. Chem. Phys.*, **54,** 2276 (1971). [ooo] E. Wasserman, V. J. Kuck, R. S. Hutton, and W. A. Yager, *J. Amer. Chem. Soc.*, **92,** 7491 (1970). [ppp] R. D. Suenram and M. D. Harmony, *ibid.*, **95,** 4906 (1973). [qqq] α is the dihedral angle of the four-member ring. [rrr] E. B. Fleischer, *J. Amer. Chem. Soc.*, **86,** 3889 (1964). [sss] Molecules numbered following IUPAC (1957) rules.

Table III. Calculated and Observed Dipole Moments for Hydrocarbons

Compd	Dipole moment, D Calcd	 Obsd[a]
$CH_3CH_2CH_3$	0.01	0.08
$(CH_3)_3CH$	0.03	0.13
$CH_3CH{=}CH_2$	0.03	0.35
	0.05	0.30
	0.81	0.46
	0.13	0.13[b]
	1.02	0.68[b]
	0.40	0.40[b]
	0.48	0.26[b]
	0.04	0.19[b]
	0.17	0.45
	0.44	1.1
	0.41	0.62[c]
	1.05	0.88[b]
$PhCH_3$	0.12	0.43

[a] Unless otherwise noted, the observed values are from A. L. McClellan, "Tables of Experimental Dipole Moments," W. H. Freeman, San Francisco, Calif., 1963. [b] R. D. Suenram and M. D. Harmony, *J. Amer. Chem. Soc.*, **94,** 5915 (1972), and references cited there. [c] A. Shanke, *Acta Chem. Scand.*, **22,** 3239 (1968).

Table V. Calculated and Observed Heats of Formation (ΔH_f) for Radicals

Radical	ΔH_f, kcal/mol Calcd	 Obsd[a]
$CH_3\cdot$	42.3	33.2
$CH_3CH_2\cdot$	21.9	25
$(CH_3)_2CH\cdot$	6.5	16.8
$(CH_3)_3C\cdot$	−0.9	4.5
$(CH_2CHCH_2)\cdot$	44.2	30,[a] 40[b]
$CH_2{=}\dot{C}H$	68.7	65,[a] 59.6[b]
$CH_3{-}\dot{C}{=}CH_2$	43.4	58
	76.4	70 ± 5[c]

[a] Values, unless otherwise stated, from J. L. Franklin, J. D. Dillard, H. M. Rosenstock, Y. T. Herron, K. Draxl, and F. M. Field, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, **No. 26** (1969). [b] F. P. Lossing, *Can. J. Chem.*, **49,** 357 (1971). [c] A. di Domenico. P. W. Harland, and J. L. Franklin, *J. Chem. Phys.*, **56,** 5299 (1972).

small an overall barrier to rotation (0.9 kcal/mol). This is, however, an improvement on a number of other semiempirical treatments, including MINDO/2 and MINDO/2′, which failed to predict the trans planar form to be the most stable. MINDO/3 predicts the less stable conformer to be gauche rather than cis, in agreement with a π SCF but not with a recent STO-3G study by Radom and Pople.[14]

The Cope Rearrangement

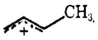
While MINDO/2 gave[16] a good qualitative account of the Cope rearrangement of 1,5-hexadiene (**1**) and a good

Table IV. Comparison of Calculated and Observed Heats of Reaction (ΔH)

Reaction	ΔH, kcal/mol (25°) MINDO/3	 Obsd	 STO-3G[a]	 4-31G[a]
$CH_3C{\equiv}CH \rightarrow CH_2{=}C{=}CH_2$	7.0	1.6	17.1	0.8
$H_2C{=}C{=}CH_2 \rightarrow$ 	17.4	20.2	12.9	34.8
$H_3C{-}CH{=}CH_2 \rightarrow$ 	2.1	7.8	−3.7	12.5
$3HC{\equiv}CH \rightarrow$ 	−144.6	−143.2	−209.8	−152.5[b]

[a] W. J. Hehre, R. Ditchfield, L. Radom, and J. A. Pople, *J. Amer. Chem. Soc.*, **92,** 4796 (1970). [b] Value for benzene calculated by D. A. Komornicki.

Table VI. Calculated and Observed Heats of Formation (ΔH_l) of Carbonium Ions

	ΔH_f, kcal/mol	
Carbonium ion	Calcd	Obsd[a]
CH_3^+	260.3	260
$CH_3CH_2^+$	214.6	219
$CH_3\overset{+}{C}HCH_3$	186.4	190
$CH_3CH_2\overset{+}{C}HCH_3$	176.1	183[b]
$(CH_3)_3C^+$	172.3	176
	222.2	216
	198.8	203
$PhCH_2^+$	220.4	216

[a] Unless otherwise noted, experimental values are from footnote *a* of Table V. [b] F. P. Lossing and G. P. Seneluk, *Can. J. Chem.*, **48**, 955 (1970); S.-L. Chang and J. L. Franklin, *J. Amer. Chem. Soc.*, **94**, 6347 (1972).

Table VII. Calculated and Observed Heats of Hydrogenation (ΔH_h) of Unsaturated Hydrocarbons

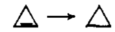
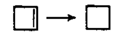
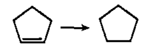
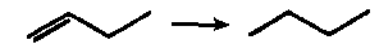
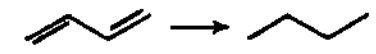
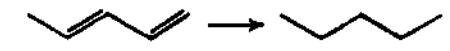
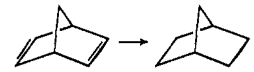
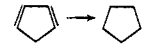
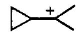
	ΔH_h, kcal/mol		
Reaction	Calcd	Obsd	Error
$H_2C{=}CH_2 \longrightarrow H_3CCH_3$	39.0	32.7	6.3
$HC{\equiv}CH \longrightarrow CH_3CH_3$	77.	74.6	3.0
$CH_3CH{=}CH_2 \longrightarrow CH_3CH_2CH_3$	33.0	29.7	3.3
	50.8	53.5	−2.7
	38.2	30.7	7.5
	33.5	26.7	6.8
	24.1	27.4	−3.3
	62.3	56.5	5.8
	55.3	53.2	2.1
	76.1	72.1	4.0
	69.6	50.4	19.2

Table VIII. Calculated and Observed Barriers to Rotation about CC Bonds

	Barrier to rotation, kcal/mol		
Compd	Calcd	Obsd	Error
$H_2C{=}CH_2$	63.9	65.0[a]	−1.1
$H_3CCH{=}CHCH_3$	60.4	62.8[b]	−2.4
$H_2C{=}C{=}CH_2$	46.9	47[c]	~0
$H_2C{=}C{=}C{=}CH_2$	37.7	~30[d]	?
$H_2C{=}C{=}C{=}C{=}CH_2$	30.4		
$H_2C{=}C{=}C{=}C{=}C{=}CH_2$	26.6	~20[d]	?
$H_3C{-}CH_3$	0.9	2.9	−2.0
	7.8	16[e]	−8.2
	11.5	17.1[f]	−6.6
	10.0	13.7[g]	−3.7

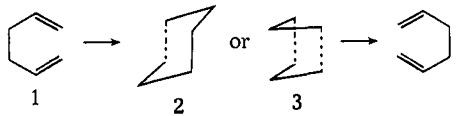
[a] B. S. Rabinovitch and F. S. Looney, *J. Chem. Phys.*, **23**, 2439 (1965). [b] B. S. Rabinovitch and K. W. Michel, *J. Amer. Chem. Soc.*, **81**, 5065 (1959). [c] Personal communication from Professor W. R. Roth. [d] Estimated from rates of cis,trans isomerization of tetrasubstituted derivatives: R. Kuhn, B. Schulz, and J. C. Joachim, *Angew. Chem.*, **78**, 449 (1966). [e] N. C. Deno, R. C. Haddon, and E. N. Novak, *J. Amer. Chem. Soc.*, **92**, 6691 (1970). [f] P. v. R. Schleyer, R. M. Su, M. Saunders, and J. C. Rosenfeld, *ibid.*, **91**, 5174 (1969). [g] D. S. Kabakoff and E. Namanworth, *ibid.*, **92**, 3234 (1970).

Table IX. Calculated and Observed Heats of Conformational Isomerization (ΔH_i)

	ΔH_i, kcal/mol		
Reaction	Calcd	Obsd[a]	Error
n-Butane, trans → gauche	0.8	0.7	0.1
2-Butene, trans → cis	0.5	1.1	−0.6
Methylcyclohexane, eg → ax	2.0	1.9	0.1
Piperylene, trans → cis	1.0	1.0	0
1,3-Butadiene, trans → cis	1.7	2.0	−0.3

[a] For references, see Table I.

estimate of the difference in activation energy between the "boat" and "chair" transition states,[17] the absolute activation energies were too low by *ca.* 10 kcal/mol. We have calculated the heats of formation of **1** and the symmetrical intermediates **2** and **3** by MINDO/3 with the following results (heats of formation in kcal/mol).



1 21.6

2 53.4

3 61.5

If **2** and **3** are the actual transition states, the calculated activation energies for the two paths are 31.8 and 39.9 kcal/mol, respectively, in good agreement with the experimental[18] values (33.5 and 44.7 kcal/mol). Recently, however, McIver[19] has shown that the symmetrical structures **2** and **3** are intermediates, not transition states. In the case of MINDO/2, calculations by them and here[20] show that the transition states lie about 2 kcal/mol above the symmetrical intermediates. Since the same is probably also true of MINDO/3, the agreement with experiment will probably be even better when detailed studies of the reaction path, now in progress,[20] are complete.

References and Notes

(1) Part XXV: R. C. Bingham, M. J. S. Dewar, and D. H. Lo, preceding paper in the series.

(2) This work was supported by the Air Force Office of Scientific Research through Contract F44620-71-C-0119 and by the Robert A. Welch Foundation through Grant F-126. The calculations were carried out using the CDC 6400/6600 computer at The University of Texas Computation Center.

(3) N. C. Baird and M. J. S. Dewar, *J. Chem. Phys.*, **50**, 3, 1262 (1969).

(4) M. J. S. Dewar and E. Haselbach, *J. Amer. Chem. Soc.*, **92**, 590 (1970).

(5) N. Bodor, M. J. S. Dewar, and D. H. Lo, *J. Amer. Chem. Soc.*, **94**, 5303 (1972).

(6) See J. A. Nelder and R. Mead, *Comput. J.*, **7**, 308 (1964). Our program was written by Dr. A. Brown.

(7) Unpublished work by H. W. Kollmar, D. H. Lo, H. Metiu, P. J. Student, and P. K. Weiner.

(8) See M. J. S. Dewar, E. Haselbach, and S. D. Worley, *Proc. Roy. Soc., Ser. A*, **315**, 431 (1970). Subsequent work has shown the error to be quite general.

(9) W. J. Hehre, R. Ditchfield, L. Radom, and J. A. Pople, *J. Amer. Chem. Soc.*, **92**, 4796 (1970); L. Radom, W. J. Hehre, and J. A. Pople, *ibid.*, **93**, 289 (1971).

(10) See L. Radom, W. A. Lathan, and J. A. Pople, *J. Amer. Chem. Soc.*, **93**, 5339 (1971).

(11) See L. Radom and J. A. Pople, *J. Amer. Chem. Soc.*, **93**, 289 (1971).

(12) M. J. S. Dewar and J. S. Wasson, *J. Amer. Chem. Soc.*, **93**, 3081 (1971).

(13) M. J. S. Dewar and A. J. Harget, *Proc. Roy. Soc., Ser. A*, **315**, 443 (1970).

(14) L. Radom and J. A. Pople, *J. Amer. Chem. Soc.*, **92**, 4786 (1970).

(16) A. Brown, M. J. S. Dewar, and W. Schoeller, *J. Amer. Chem. Soc.*, **92**, 5516 (1970).

(17) W. E. Doering and W. R. Roth, *Tetrahedron*, **18**, 67 (1962).

(18) M. J. Goldstein and M. S. Benzon, *J. Amer. Chem. Soc.*, **94**, 7147 (1972).

(19) J. W. McIver, Jr., *Accounts Chem. Res.*, **7**, 72 (1974).

(20) Unpublished work by L. E. Wade.