Conformational Analysis. LXIX. An Improved Force Field for the Calculation of the Structures and Energies of Hydrocarbons[1,2]

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Abstract: An improved force field is presented which allows the structures and energies of a wide range of hydrocarbons to be calculated by the molecular mechanics method (Westheimer method) with a higher degree of accuracy and reliability than was previously possible. A method for calculating strain energies in organic molecules is presented, and the origin of strain in cyclohexane, decalin, adamantane, etc., is discussed.

Previous work by several groups has shown that it is possible to calculate with a moderate degree of accuracy the structures and energies of saturated hydrocarbons, and other compounds as well, by a semiempirical method referred to as the "molecular mechanics" or "Westheimer" method.[4,5] A mechanical model is developed for each molecule, on which the calculations can be carried out precisely. By suitable parameterization, the mechanical model can be made to display the desired features of an actual molecule within certain limitations. Lifson,[6] for example, has chosen to calculate vibrational spectra of a set of polymethylene compounds, and the parameterization was chosen so as to reproduce the spectra as well as the details of the method allowed. Boyd[7] has included not only vibrational spectra, but also thermodynamic functions, in his objectives and has succeeded reasonably well. Bartell[8] has carried out calculations similar to ours, and has aimed primarily toward determining structures. Kitaigorodsky[9] and his group have been studying benzenoid compounds from a similar point of view. A large number of other groups have made calculations directed toward a specific problem or group of problems,[10] and simplified methods for studying polymers[11] and peptides[12] have been developed.

The mechanical model that we use to represent the molecule is at present very crude in comparison to the complex elegance actually dictated by the Schroedinger equation for the electronic wave function. We obviously cannot expect our present model to reproduce accurately *all* of the properties of a molecule, and have chosen to parameterize our model so as to fit (1) structure and (2) energy at 25°, and are prepared to sacrifice accuracy for other quantities to some extent as necessary. This approach is based on expediency. We need a reliable way to determine routinely structures and energies for use in other work. In the long run, the optimization as advocated by Lifson, including *all* available data and weighting it according to the properties under investigation, is obviously the approach to use.

Our last paper on the structures and energies of hydrocarbons[13] showed that with the force field then used it was possible to reproduce generally these quantities with a reasonable degree of accuracy; however, there were certain rather important items which were not calculated correctly, and it was found to be necessary to use a very unusual bending function. These problems have largely been overcome now, and the new force field is described in this paper. This force field is the basis of a series of papers to follow.

Discussion

Our earlier work was parameterized to fit the structures of the small molecules as they are obtained by

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microwave spectra. For larger systems of interest, almost all of the available experimental data comes from diffraction measurements, and because diffraction geometries are not identical with those obtained from microwave spectroscopy, we have chosen to reparameterize to fit the diffraction measurements. This change is rather small, however, amounting to approximately 0.006 Å in bond lengths on the average.[14] Bond angles have been kept the same as previously.

Deficiences in the Previous Force Field. In order to use the published force constants derived by valence force field treatments of vibrational spectra, it was necessary earlier to use an empirical bending function which approximated the usual Hooke's law function for small displacements, and to be frankly empirical for large displacements. It was mentioned at the time that an alternative was to use smaller force constants. As was pointed out earlier by several workers,[6,8,10f] the force constants obtained by vibrational analysis depend upon the rest of the force field, and particularly on the magnitude of the van der Waals interactions between the atoms; the published values are typically the limiting case where van der Waals interaction is neglected, except with a Urey–Bradley field, where geminal interactions are allowed for. If the van der Waals interactions of the order of magnitude discussed here are taken into account, then one must in fact use much smaller force constants to fit the observed vibrational spectra, as has been explicitly shown by Boyd.[7] Hence, in the present work we have taken a Hooke's law bending function as a first approximation, and reduced the numerical values of the force constants. (The next approximation was to add a cubic (anharmonic) term, *vide infra.*) Our present force constant can be considered as purely empirical quantities analogous to those obtained from vibrational spectra, except ours are chosen to yield good geometries, rather than good spectra.

Another worrisome problem in the earlier work[13] was that the spacing calculated for the hexane crystal was somewhat too large. This spacing indicated that the balance of forces in hydrocarbons would generally tend to hold intermolecular hydrogen atoms further apart than desirable, and this would be expected to lead to difficulty in molecules like cyclodecane, where the geometry[15] requires that the hydrogens be held rather closely together. The calculated A spacing of the hexane crystal in our earlier work was 4.39 Å, *vs.* 4.17 for the experimental value.[16] Similarly, larger values for the B and C spacings were calculated than observed.

Our earlier calculations on small rings (cyclobutane, norbornane) produced bond lengths which were too short by a few hundredths of an ångström. The reason for this result was that van der Waals interactions were not included between atoms bound to a common atom due to our lack of any quantitative knowledge about van der Waals interactions at short distances. The neglect of these latter interactions was partially accounted for by the arbitrary bending function, but, for example, no van der Waals interactions between the carbons in cyclobutane were counted, and only two such interactions were considered in norbornane. The result was that these molecules tended to collapse, and the calculated bond lengths were much too short.

Another problem was that for the medium ring compounds, particularly cyclodecane, the calculated bond angles were much too large (117.3–121.8°), the experimental values being about 2–3° smaller.

Finally, as more and better data have become available[17] on bicyclic and polycyclic systems, we have found that our energies for these classes of compounds were not very well calculated. These data showed that our calculated energies for norbornane, adamantane, and bicyclo[2.2.2]octane were considerably lower than are observed experimentally.

The Improved Force Field. It became clear that two rather fundamental changes in our mechanical model should be made to correct the aforementioned problems. One of these concerns the position of the hydrogen atom. As is well known, the electron density corresponding to a hydrogen atom bonded to another atom is not accurately centered at the hydrogen nucleus itself, since the overlap of the atomic wave functions leads to some of this density being shifted inward between the two atoms bound together. There are various ways which come to mind to allow for this computationally, the simplest of which seems to be to treat the hydrogen as still being spherical, but to offset the center of electron density slightly from the nucleus. The center of electron density is used for the van der Waals interaction calculations, and the position of the nucleus for other properties. Recent studies by Williams[18] have indicated that to understand the packing of molecules and crystals, such an offset of electron density is indeed necessary, and he recommends an offset value in the range of 10% of the bond length. In the present calculations, carbon atoms of the sp^3 variety are still treated as being spherical with their electron density centered at the nucleus. After some trial and error, we decided to offset the electron density of the hydrogen atom by 8%, so that the electron cloud of this atom is positioned 0.92 of the distance from the other atom along the X–H bond, this fraction being used to position the center of the hydrogen electron density when it is attached to any atom X. With this correction, the crystal spacing in hexane came out much better; the calculated A value in hexane is now 4.24 Å, and the heat of sublimation is calculated to be 11.5 kcal/mol. (These values are based on extrapolations from cubes of chains containing up to 9 for the spacing and up to 3375 for the heat, as described earlier.)

The next item considered was the tendency of the calculated bond lengths in small rings to be too short. Physically, the bond lengths in these compounds are actually longer than calculated by our earlier model in part because of what we want to call the van der Waals interaction between very close nonbonded atoms. For

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[17] R. H. Boyd has communicated privately to us the gas phase (25°) heat of formation of norbornane (−12.4 kcal/mol) and bicyclo-[2.2.2]octane (−23.8 kcal/mol). Also see S. Chang, D. McNally, S. Shary-Tehrany, M. J. Hickey, and R. H. Boyd, *J. Amer. Chem. Soc.*, **92**, 3109 (1970).

[18] (a) D. E. Williams, *J. Chem. Phys.*, **43**, 4424 (1965); (b) see also R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

reasons outlined earlier, we do not wish to include these very close interactions as such explicitly. Alternative solutions to the problem have been suggested by spectroscopists, who frequently use a Urey–Bradley field, in which the desired interactions are included with the aid of additional parameters, or by adding interaction constants (stretch–stretch, stretch–bend, etc.) to the valence force field.[19a] We have looked particularly at the stretch–bend interaction.

We noted that the bond length in cyclohexane is 1.528 Å, and this is the smallest value found among the cyclanes. The values increase with decreasing ring size, 1.546 for cyclopentane,[19b] and 1.548 for cyclobutane,[19c] and also for cyclononane and cyclodecane. Thus we see that as the angle bends, the bond stretches. However, to fit these data with a stretch–bend interaction of the usual sort $E_{\text{str–bend}} = k_{l\theta}(\theta - \theta_0)(l - l_0)$ requires $k_{l\theta}$ to have a different sign for angle opening from that of angle closing (the term $(l - l_0)$ is positive in all the calculations herein); the sign of $k_{l\theta}$ then would depend on to which class the compound belonged. For computational simplicity, we have used the absolute values of the displacements $(|\theta - \theta_0|)$ and taken $k_{l\theta}$ always to be negative. The force constant $k_{l\theta}$ was chosen empirically to give cyclobutane a correct bond length. It was only necessary to choose a single constant for stretching the C–C bond and bending the CCC angle to solve this bond length problem. However, when this was done, the imbalance between CCC stretch–bend interaction and the corresponding quantity for the C–C bond and CCH angle was such that in normal alkanes, the interior bonds stretched much more than did the end ones, and the C–C bond length to a methyl group was too short. This problem was rectified by reducing the CCC stretch–bend constant somewhat and by also adding a CCH stretch–bend constant, so as to keep bond lengths between primary and secondary carbons simultaneously consistent with the experiment.

The equation which we use for calculating stretch–bend energy is

$$E_{\text{str–bend}} = k_{l\theta}(\Delta l_{\text{abc}})(\Delta\theta_{\text{abc}}) \qquad (1)$$

where $k_{l\theta}$ = stretch–bend force constant, $\Delta l_{\text{abc}} = [|(l_{\text{ab}} - l_{\text{ab}}{}^0)| + |(l_{\text{bc}} - l_{\text{bc}}{}^0)|]$, l_{ab} = bond length between atom a and atom b, $l_{\text{ab}}{}^0$ = "strainless" value (Table VI), $\Delta\theta_{\text{abc}} = [|\theta_{\text{abc}} - \theta_{\text{abc}}|]$, θ_{abc} = bond angle for atoms a, b, and c, $\theta_{\text{abc}}{}^0$ = "strainless" value (Table VI). The bond lengths calculated for cyclobutane, cyclopentane, and cyclohexane are 1.543, 1.534, and 1.530 Å.

Bending constants, as mentioned earlier, were chosen empirically. The ratios of the CCC to CCH to HCH constants were kept the same as have been found from valence force field treatments, but all values were reduced. Torsional parameters were chosen to fit the barriers in ethane and a few related molecules as previously described. For those compounds containing a cyclobutane ring (cyclobutane, bicyclo[1.1.1]pentane, cubane, etc.), it was found necessary to use a special CCCC torsional constant in order to account for the extra stability of the puckered form of cyclobutane over the planar one, and at the same time obtain a correct total energy. The parameters at this point had all been assigned in an internally consistent manner (Table VI, Appendix).

Finally, when the geometry of bicyclo[1.1.1]pentane was calculated, the secondary angles were found to be only about 70°, whereas the experimental value[20] for these angles is 73–75°. This molecule was by far the most strained with respect to angle deformation of any we had studied, and to keep the secondary angles from contracting so much, a cubic term was introduced into the bending function (Appendix). This term is quite small and makes no difference in strainless molecules, but does keep this molecule and those with similar deformations (such as bicyclo[2.1.1]hexane, etc.) from deforming quite so drastically.

The force field described above solves the principal problems with respect to geometry that we had experienced in our earlier work. As we had hoped, the bond angles in cyclodecane improved by about 1°, and there are various other small improvements as well. We regard the geometries calculated by this scheme now as being reasonably satisfactory, and for unstrained systems, the geometries seem to be within the accuracy we had originally set out to achieve (0.01 Å for bond lengths and 1° for bond angles) in all cases. For more strained molecules, we can for the most part still achieve this accuracy, although a few examples are outside of this limit.

There is also some question as to just what one wishes to duplicate for barriers to rotation that are determined spectroscopically. Initially the calculated barrier was taken as the energy difference between the minimum eclipsed and minimum staggered energies, allowing the molecule to relax in all degrees of freedom in each conformation. The barriers so calculated are always too small, however, for the following reasons. In calculating the minimum eclipsed energy of ethane, for example, the C–C bond stretches and the CCH angles become larger. It is felt that such changes, at least of the size calculated, do not approximate very well what occurs when the molecules undergoes a change in the *normal coordinate* assigned to rotation. Much of this stretching and bending is assigned to other normal coordinates that are so labeled. Another approximation would be to assume the molecule is acting more like a "rigid rotor." That is to say that bond lengths and bond angles do not change during rotation, only torsional angles do. The true situation appears to be somewhere in between. In addition, the spectroscopic barrier is the familiar cosine curve itself, as is our calculated barrier, while the actual molecule at 25° experiences a barrier from the torsional level (average) actually occupied. We have therefore calculated the barriers on the basis of complete relaxation, but have purposely made them come out a little low (about 0.2–0.5 kcal/mol) to compensate for these difficulties.

The general force field method, except for minor problems of transferability and truncation, is in prin-

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Table I. Heats of Formation

	Bond energies	Steric energy	Conf energy	Calcd ΔH	Exptl ΔH	Calcd − Exptl	Exptl error	Weight[a]	Ref[b]
Chain Series									
Methane	−17.88	0.00		−17.88	−17.89	0.01	0.08	10	
Ethane	−22.37	2.37		−20.00	−20.24	0.24	0.12	10	
Propane	−28.34	3.10		−25.24	−24.82	−0.42	0.14	9	
n-Butane	−34.31	4.46	0.28	−29.57	−30.15	0.58	0.18	9	
Isobutane	−34.31	2.13		−32.18	−32.15	−0.03	0.16	9	
n-Pentane	−40.28	4.37	0.56	−35.35	−35.00	−0.35	0.16	7	
Isopentane	−40.28	3.59	0.10	−36.59	−36.92	0.33	0.20	8	
Neopentane	−40.55	−0.37		−40.92	−40.27	−0.65	0.25	8	
n-Hexane	−46.25	4.99	0.90	−40.36	−39.96	−0.40	0.19	6	
2,3-Dimethylbutane	−46.25	2.93		−42.32	−42.49	0.17	0.24	7	
n-Heptane	−52.22	5.58	1.16	−45.48	−44.89	−0.59	0.19	4	
2,2,3-Trimethylbutane	−52.49	3.67		−48.82	−48.95	0.13	0.27	6	
n-Octane	−58.19	6.20	1.46	−50.53	−49.82	−0.71	0.20	2	
2,2,3,3-Tetramethylbutane	−58.73	4.99		−53.74	−53.99	0.25	0.46	6	
2,2,4-Trimethylpentane	−58.46	5.36		−53.11	−53.57	0.46	0.32	6	
3,3-Diethylpentane	−64.36	9.28		−55.08	−55.44	0.36	0.40		*e*
Ring Series									
Cyclobutane	−23.88	29.43		5.55	6.38	−0.83	0.10	2	*e*
Cyclopentane	−29.85	11.80		−18.05	−18.46	0.41	0.18	7	
Cyclohexane	−35.82	5.95		−29.87	−29.43	−0.44	0.17	8	
Cycloheptane	−41.79	13.41		−28.38	−28.34	−0.04	0.26	7	
Cyclooctane	−47.76	18.69		−29.07	−30.06	0.99	0.33	4	
Cyclononane	−53.73	23.65		−30.08	−31.80	1.72	0.38		
Cyclodecane	−59.70	24.40		−35.66	−36.29	0.63	1.0	3	*e*
Cyclododecane	−71.64	20.07		−51.58	−50.50	−1.08	2.0		*c*, *e*
Methylcyclohexane	−41.79	4.81	0.10	−36.88	−36.99	0.11	0.25	7	
1,1-Dimethylcyclohexane	−48.03	4.30		−43.73	−43.26	−0.47	0.46	6	
Fused Ring Series									
cis-Bicyclo[3.3.0]octane	−37.33	16.71		−20.61	−22.30	1.69	0.5		
trans-Bicyclo[3.3.0]octane	−37.33	21.97		−15.36	−15.90	0.54	0.6		
cis-Hydrindan	−43.40	13.45		−29.86	−30.41	0.55	0.47	4	
trans-Hydrindan	−43.30	12.23		−31.07	−31.45	0.38	0.50	4	
cis-Decalin	−49.27	8.38		−40.89	−40.38	−0.51	0.55		
trans-Decalin	−49.27	5.59		−43.68	−43.54	−0.14	0.55	5	
trans-syn-trans-Perhydroanthracene	−62.72	5.04		−57.68	−58.32	0.64	1.27	1	
trans-anti-trans-Perhydroanthracene	−62.72	10.90		−51.82	−52.93	1.11	1.47	1	
Polycyclic Series									
Bicyclo[1.1.1]pentane	−19.42	92.23		72.81					
Bicyclo[2.1.1]hexane	−25.39	44.64		19.25					
Cubane	−6.04	155.82		149.78	148.70	1.08	1.00	1	*f*
Bicyclo[2.2.2]octane	−37.33	13.22		−24.11	−23.80	−0.31	0.50	6	*d*, *e*
Bicyclo[3.3.1]nonane	−43.30	13.00		−30.29					
Adamantane	−38.84	5.06		−33.79	−33.0	−0.79	0.4	5	*e*
Bicyclo[3.2.1]octane	−37.33	13.24		−24.09					
1,3,5,7-Tetramethyladamantane	−63.80	−6.33		−70.13					
Diamantane ("Congressane")	−41.86	3.82		−38.04					
Binorbornane	−52.83	32.31		−20.52					
Biadamantane	−67.79	11.59		−56.20					
Norbornane	−31.36	17.95		−13.41	−12.40	−1.01	0.4		*d*, *e*
Homoadamantane	−44.81	17.28		−27.53					

[a] Weighting factor used in least-squares analysis. [b] All heats of formation without specific reference notation are taken from the compilation in D. R. Stull, E. F. Westrum, Jr., and G. C. Sinke, "The Chemical Thermodynamics of Organic Compounds," Wiley, New York, N. Y., 1969, Chapter 14. [c] See the discussion of the heat of formation of cyclododecane in the Appendix. [d] Reference 17. [e] Error in heat of formation data estimated by us. [f] B. B. Kybett, S. Carroll, P. Natalis, D. W. Bonnell, J. L. Margrave, and J. L. Franklin, *J. Amer. Chem. Soc.*, **88**, 626 (1966).

ciple capable of yielding quite a lot more structural, thermodynamic, and vibrational data than we are at present seeking. To obtain all of this information, one must either start from a Urey–Bradley force field (or else something equivalent, such as a valence force field with full interaction treatment), explicitly add the nongeminal van der Waals interactions (as Bartell, Boyd, and Lifson have done), then optimize the force constants with respect to structural, thermochemical, vibrational, and other data (Lifson has accurately optimized over a limited set of structural types, and Boyd has roughly optimized over a wider basis set), plus treat a wide variety of structural types (as herein), and include such other refinements (such as anharmonic and Coulombic terms) until the results are deemed sufficient. The force field developed in the present paper does not pursue this problem far enough to reproduce all of the experimental data that one might be interested in, but is shown to be adequate for the problem at hand; namely, prediction of structures and energies of saturated hydrocarbons at 25°, excluding only highly distorted molecules (more distorted than cyclobutane).

Heat of Formation Calculations. Our second major objective was to calculate accurately the heats of formation for hydrocarbons. The accuracy achieved in our earlier work was very good, but that was partly due to the fact that we had not studied a sufficiently varied set of compounds. Although the set used was large, it was deficient in certain types of structures. Thus, the bridged bicyclic and polycyclic compounds in particular (for which very limited experimental data were then available) were subsequently found not to give very good results. With the force field used earlier, we were able to calculate reasonable energies for molecules like cyclodecane, but at the expense of expanding the bond angles and distorting the geometries. In the present work, we have been able to improve the calculated angles substantially, and have still kept the calculated energies reasonable.

Our approach to the heat of formation problem was as follows. A set of 32 compounds was selected, and they are listed in Table I along with some other compounds we have studied. The compounds include simple aliphatic structures, many of which are highly branched, rings of many sizes up to C-12, fused systems such as decalins, hydrindans, norbornanes, etc., and finally a number of polycyclic systems such as adamantane, cubane, etc. Most of the accurate data available on heats of formation are for the aliphatic hydrocarbons. In order to obtain a representative cross section of all hydrocarbons, we have selected the list shown. This list includes just about all of the accurate data available on compounds other than the simple aliphatics, plus a balanced selection of the latter. (Inclusion of all the data on aliphatic compounds would unduly weight them with respect to other structural types.)

The approach used was then to evaluate the necessary heat of formation parameters (bond energies and correction terms for branching similarly to the method previously discussed) and to optimize simultaneously all parameters by the least-squares method. In our present heat of formation calculations we have included one more degree of freedom than previously reported,[13] namely a term for the contribution of a methyl group to the total bond energy. Our heat of formation method is based upon the methylene group as our basic unit of bond energy. Thus, for example, the heat of formation of monocyclic hydrocarbon requires, besides the steric energy, contributions only from the C–C and C–H bonds of methylene groups. The inclusion within the molecule of more or less branching requires further description in the form of small correction terms as a result of the perturbation of the methylene unit. The origin of these correction terms could arise from several sources. The rehybridization of the carbon atom in changing from a methylene group to, say, a methyl group may well be a primary source of these terms. In addition, van der Waals interactions between atoms bound to a common atom are not counted explicitly, and these are expected to change somewhat with the degree of substitution at a carbon. These correction terms allow these energy differences to be accounted for. Also, since our model calculates heats of formation at 25° (gas phase), the variations in zero point energy for the individual bonds may be of some significance (energies due to the admixture of less favorable conformations are separately allowed for)

$$\Delta H_f{}^\circ = \Delta H_{\text{steric}} + \Delta H_{\text{conf}} + \Delta H_{\text{bond}} + \Delta H_{1^\circ} + \Delta H_{3^\circ} + \Delta H_{4^\circ} \quad (2)$$

where ΔH_{steric} is the energy of the molecule as calculated by the program described, ΔH_{conf} is the conformational enthalpy contributions from other conformations coexisting at 25°, ΔH_{bond} is the sum of the enthalpy contributions from C–C ($\Delta H_{\text{C–C}}$) and C–H ($\Delta H_{\text{C–H}}$) bonds within the molecule, and ΔH_{1°, ΔH_{3°, and ΔH_{4° are correction terms for primary, tertiary, and quaternary carbons, respectively.

The only arbitrariness allowed in the above least-squares scheme was that we would weight in any desired manner the experimental values for the compounds used. We tried to give more weight to the compounds whose heats of formation were accurately known experimentally, and less weight to more highly strained compounds. This is a subjective matter. However, with the weights chosen, all of the parameters were evaluated and the results are given in Table II under General.

Table II. Parameters for Heats of Formation Calculation (kcal/mole)

	C—C	C—H	$\mathrm{C{-}\overset{H}{\underset{H}{C}}{-}H}$	$\mathrm{C{-}\overset{C}{\underset{C}{C}}{-}H}$	$\mathrm{C{-}\overset{C}{\underset{C}{C}}{-}C}$
General	+2.97	−4.47	+0.74	−0.74	−1.75
Strainless	3.75	−4.47	1.55	−3.31	−7.78

The experimental and calculated heats of formation for our selected balanced list of 32 compounds (those given nonzero weights) are given in Table I. The average experimental error reported for the 32 compounds is 0.39 kcal/mol. The average deviation of our values from the experimental ones is 0.46 kcal/mol. We can therefore calculate the heats of formation of this whole cross section of structural types with an accuracy quite close to that obtainable by experimental measurement[21] *on the average.* Some of our calculated values do not come up to this average, however, as indicated in Table I.

Results

The open chain series of aliphatic hydrocarbons has been studied previously in some detail and will not be considered here except in passing. On the whole, the heats of formation for these compounds are well calculated by the present method. Special effort was made to include compounds such as 2,2,3-trimethylbutane and 2,2,4-trimethylpentane which contain all of the degrees of branching (primary, tertiary, and quaternary carbon atoms). Conformational enthalpies resulting from the *n*-alkanes having several

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(21) Other recent approaches to the calculation of heats of formation for organic compounds include (a) S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rogers, R. Shaw, and R. Walsh, *Chem. Rev.*, **69**, 279 (1969); (b) A. I. Vitvitskii, *Theor. Exp. Chem.*, **3**, 44 (1969).

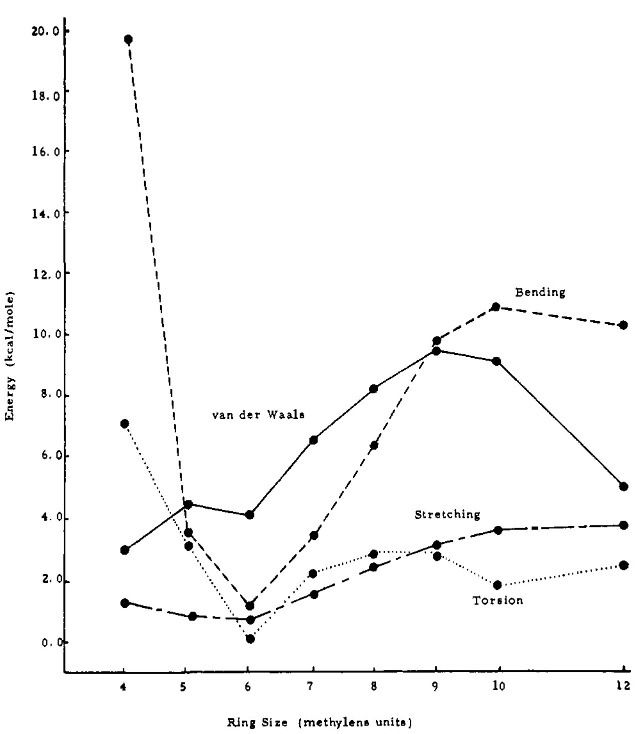

Figure 1. Contributions to the total steric energies in the C-4 to C-12 rings.

conformations coexisting at 25° have been estimated by considering the number of gauche interactions possible in the conformers of butane, calculating the total conformational enthalpy resulting from the equilibrium mixture at 25°, and extrapolating this result to the higher alkanes.

The barrier to rotation in butane has been calculated by us, and the results are listed in Table III. Hoyland[22] has carried out this calculation using an *ab initio* method. The comparison of the two different types of calculations indicates satisfactory agreement except, apparently, for the barrier corresponding to eclipsing the two methyl groups. Our number (4.55 kcal) is within the range of 4.4–6.1 kcal estimated by others.[23] Hoyland assumed (for calculational simplicity) the bond angles and bond lengths in the eclipsed forms would remain the same as in the ground state. The actual molecule will relax these various quantities, and hence Hoyland's energies are expected to be too high. Since our values are lower, there appears to be no disagreement.

Table III. Energy as a Function of Torsional Angle in Butane[a]

Angle, deg	This work	Hoyland[b] SCF
0	4.55	6.83
60	0.73	0.76
120	2.94	3.62
180	0.00	0.00

[a] 0° here refers to the conformation with eclipsing methyl groups, while Hoyland uses 0° to designate the anti conformation. [b] J. R. Hoyland, *J. Chem. Phys.*, 49, 2563 (1968).

In our calculations on ring compounds, we find that the total steric energy of the small, medium, and large rings reflects the various types of strain postulated by other workers.[24] The present calculations allow us to see how the strain energy is partitioned among the internal degrees of freedom. With respect to ring size, the steric energy per methylene unit of the rings (C-4 to C-12) passes through a minimum at cyclohexane and through a maximum in the region of cyclononane and cyclodecane (Table IV and Figure 1). The chemical results of this ring strain have been extensively studied.[24,25]

Table IV. Strain Energy of Carbocyclic Rings per CH_2 Group, Relative to Cyclohexane[a]

	Calcd[b]	Exptl[c]
Cyclobutane	6.5	6.5
Cyclopentane	1.4	1.2
Cyclohexane	0.0	0.0
Cycloheptane	0.9	0.9
Cyclooctane	1.4	1.2
Cyclononane	1.6	1.4
Cyclodecane	1.4	1.3
Cyclododecane	0.6	0.7

[a] Note that these strain energies are relative to cyclohexane, which itself is strained according to the definition used later on in this paper. These numbers are therefore not the same (on a per CH_2 group basis) as those in Table V, but are about 0.3 kcal/mol less. [b] The calculated strain energy is relative to cyclohexane, and is $(H_f/n - H_f°/6)$, where H_f is the calculated heat of formation, n is the number of methylene groups, and $H_f°/6$ are the corresponding quantities for cyclohexane. [c] The experimental values quoted are calculated from heat of combustion data and correspond to the expression $(H_c/n - 157.4)$ kcal/mol, where H_c/n is the heat of combustion per CH_2 group and the constant 157.4 is the ΔH_c of cyclohexane (assumed strainless), all for the gas phase.

In cyclobutane the major component of the steric energy is the bending energy. Using the bending function mentioned earlier, this energy contribution is two-thirds (19.5 kcal) of the total steric energy. We calculate that the nonplanar form is more stable than the planar one by 0.2 kcal. Minimum basis set *ab initio* calculations[26] lead to a value of 0.3 kcal/mol. Both of these values are small compared to the experimental value of 1.28 kcal/mol. We also calculate that one carbon of the cyclobutane ring is puckered out of the plane of the other three by 10.2°. This puckering is a result of angle bending in response to the eclipsed torsion residing in the planar form.[27] Although our calculated degree of puckering is appreciably less than found experimentally,[28] our calculated bond angles are only off about 1°. A 1° error in bond angle makes a very much larger error in dihedral angle.

In cyclopentane the envelope conformation is calculated to have the same energy as the half-chair, and a maximum torsional angle of 44°, consistent with spectroscopic evidence.[29a] All of the bond angles

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(22) See Table III, footnote *b*.

(23) (a) W. G. Dauben and K. S. Pitzer in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, p 8; (b) K. Ito, *J. Amer. Chem. Soc.*, 75, 2430 (1953).

(24) H. C. Brown and K. Ichikawa, *Tetrahedron*, 1, 221 (1957).

(25) For a review, see E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience, New York, N. Y., 1965, p 189.

(26) J. S. Wright and L. Salem, *Chem. Commun.*, 1370 (1969).

(27) K. B. Wiberg, J. E. Hiatt, and K. Hsieh, *J. Amer. Chem. Soc.*, 92, 544 (1970).

(28) (a) T. Ueda and T. Shimanouchi, *J. Chem. Phys.*, 49, 470 (1968); (b) S. Meiboom and L. C. Snyder, *ibid.*, 52, 3857 (1970).

(29) (a) J. R. Durig and D. W. Wertz, *J. Chem. Phys.*, 49, 2118 (1968); (b) K. S. Pitzer and W. E. Donath, *J. Amer. Chem. Soc.*, 81, 3213 (1959);

calculated for the cyclopentane conformations are within 0.5° of those given by Bartell. The major component energies of the steric energy in either conformer comprise a 1:1:1 ratio of van der Waals, bending, and torsional energies. The latter quantity, corresponding to 3.6 kcal of "Pitzer" strain energy, arises due to a number of gauche interactions which occur in this molecule.[29]

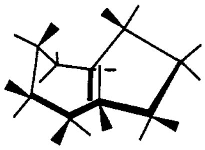
The geometry of cyclohexane is well known[30] and corresponds to a minimum of both torsional (Pitzer) and angle bending strain. The energy of the twist-boat conformation of this molecule has been estimated to be 5.3 kcal higher than the chair form;[31] the agreement between this value and the presently calculated one of 4.88 kcal is satisfactory. Similarly, the boat form has been estimated to be higher in energy than the chair by about 6.9 kcal[31] which corresponds to 6.7 kcal in our present calculations.

The X-ray structures of the derivatives of the C_8,[32] C_9,[33] C_{10},[15,34] and C_{12}[35] medium rings have been extensively investigated by Dunitz. In cycloheptane and the larger rings, definite trends in energies, bond lengths, and bond angles exist which lead to a maximum of ring strain (corresponding to Brown's "I-strain"[36]) in cyclononane. For example, we calculate that the C–C bond lengths in cyclohexane are 1.530 Å and increase steadily through the larger ring series to peak at cyclodecane with values of 1.540–1.548 Å. Calculated bond lengths also increase with decreasing ring size to 1.534 Å in cyclopentane and 1.543 Å in cyclobutane. Similarly, the CCC ring angles increase from 111.0° in cyclohexane to 117.6–120.3° in cyclodecane. Both the bond lengths and bond angles in cyclododecane decrease from the cyclodecane values with a corresponding decrease in steric energy. From our calculations, the major contributions to the strain inherent in the medium ring hydrocarbons is a concomitant increase in van der Waals and bending energies with ring size. The contributions to the steric energy in the C_4–C_{12} rings are plotted in Figure 1.

Hendrickson[31b] previously made a study similar to that plotted in Figure 1 for the rings from C-6 to C-10. Because he used a hydrogen van der Waals radius which was unrealistically small, his calculated van der Waals terms were small, and to account properly for the ethane barrier, his torsional terms had to be correspondingly larger. In general, his numbers are roughly proportional to ours, with the van der Waals and torsional terms being approximately one-half and twice as big, respectively. There are other differences. For example, we include stretching energy in the calculation, and we note the cross-ring van der Waals repulsions are a good deal larger in our calculation. Hendrickson's results for the medium rings appear to be very good.[31b] However, since the same parameters give very poor results in other cases (methylcyclohexane, cyclopentane) they are in fact not nearly as good as they appear from the medium ring data alone.

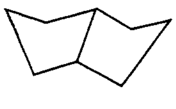
Previous conclusions concerning the medium ring compounds have been reinforced by the present study. The twist–chair conformation of cycloheptane is the lowest of several possible conformations as indicated by the extremely good calculation of its heat of formation. Similarly, the chair–boat conformation of cyclooctane is confirmed as the one having the lowest energy; the crown form of this molecule is calculated to be 1.8 kcal higher in steric energy.

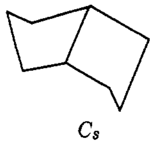
We have investigated several possible conformers of cyclononane and have found the one based on the X-ray diffraction work on cyclononylamine hydrobromide[32a] to have the lowest energy. This calculated energy is one of the poorest with respect to agreement with experiment, however. This conformation (A) does not possess symmetry. Hendrickson[37] has calculated a symmetrical conformation (D_3) as the lowest energy conformer. His assumption of an unrealistically small van der Waals radius for hydrogen appears responsible for this result. It is interesting to note that the van der Waals energy contribution to the steric energy in this conformation is the highest of all the ring compounds. Nonbonded H–H distances of the order of 2.20 Å are calculated for both cyclononane and cyclodecane.


A

The geometries and energies of cyclodecane and cyclododecane have been calculated as before, but with improved correlation with experimental results. For cyclododecane, the heat of formation in the gas phase (25°) has been reestimated (for details, see Appendix). This quantity has been estimated previously,[6] but no details of the computation were reported.

In our studies of bridged compounds, we find that most of our earlier qualitative conclusions have been confirmed. Using the present force field, we find that the crown conformation (C_{2v}) for *cis*-bicyclo[3.3.0]-octane is slightly lower in energy than the twist one (C_2). (Both conformations contain cyclopentane rings in the envelope conformation.) The C_s conformation is of lower energy than C_{2v} by 0.1 kcal/mol. Allowing for the facts that the C_{2v} form has a symmetry number of 2, the C_s form should predominate over the C_{2v} by


C_{2v}


C_s

(c) H. J. Geise, C. Altona, and C. Romers, *Tetrahedron Lett.*, 1383 (1967); (d) for a quantum mechanical description of the interactions in cyclopentane, see D. O. Harris, G. G. Engerholm, C. A. Tolman, A. C. Luntz, R. A. Keller, H. Kim, and W. D. Gwinn, *J. Chem. Phys.*, **50**, 2438 (1969).

(30) See ref 25, Chapter 2.

(31) (a) J. B. Hendrickson, *J. Amer. Chem. Soc.*, **83**, 4537 (1961); (b) *ibid.*, **89**, 7036 (1967).

(32) (a) J. D. Dunitz and A. Mugnoli, *Chem. Commun.*, 166 (1966); (b) M. Dobler, J. D. Dunitz, and A. Mugnoli, *Helv. Chim. Acta*, **49**, 2492 (1966).

(33) (a) H. B. Bürgi and J. D. Dunitz, *ibid.*, **51**, 1514 (1968); (b) R. F. Bryan and J. D. Dunitz, *ibid.*, **43**, 3 (1960).

(34) (a) See ref 15; (b) E. Huber-Buser and J. D. Dunitz, *ibid.*, **43**, 760 (1960); (c) *ibid.*, **44**, 2027 (1961); (d) J. D. Dunitz and K. Venkatesan, *ibid.*, **44**, 2033 (1961); (e) J. D. Dunitz and H. P. Weber, *ibid.*, **47**, 951 (1964); (f) J. D. Dunitz and H. Eser, *ibid.*, **50**, 1565 (1967).

(35) J. D. Dunitz and H. M. M. Shearer, *ibid.*, **43**, 18 (1960).

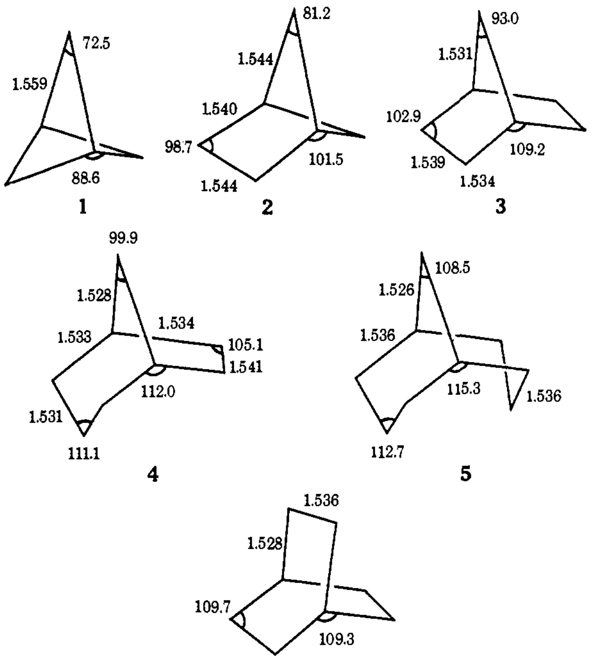
(36) H. C. Brown, R. S. Fletcher, and R. B. Johannesen, *J. Amer. Chem. Soc.*, **73**, 212 (1951).

(37) J. B. Hendrickson, *ibid.*, **89**, 7036, 7047 (1967).

at least 2:1 at room temperature, which is consistent with recent spectroscopic results.[38a] The calculation of the heat of formation of *cis*-bicyclo[3.3.0]octane is, however, one of our most serious problems, being in error by 1.7 kcal/mol.

We have extended these studies to a number of small bicyclic hydrocarbons. Bicyclo[1.1.1]pentane (**1**),[20] bicyclo[2.1.1]hexane (**2**),[38b] norbornane (**3**),[39] bicyclo[3.2.1]octane (**4**),[40] and bicyclo[3.3.1]nonane (**5**)[41] all possess a single carbon bridge between two other rings (see Chart I). The angle between the two bridging carbons in these compounds indicates the progression from the extremely strained[20a] four-membered ring in bicyclopentane (72.5°) to the relatively unstrained six-membered ring in bicyclononane (108.5°). The angle at the tertiary bridge carbons connecting the two rings reaches a near tetrahedral value in norbornane (the "strainless" value for this angle occurs in isobutane at 111.2°). In bicyclononane, this angle is expanded even further to 115.3° by the nonbonded repulsions of the two endo hydrogens at C-3 and C-7.[42] We calculate the distance between these two hydrogens to be 2.20 Å. Bicyclo[2.2.2]octane (**6**)[43] is calculated to have a tertiary angle of 109.3°.

Chart I



Schleyer[40] has measured by equilibrium studies the following relative enthalpies in the isomeric bicyclooctane series: bicyclo[3.2.1]octane (0.00), bicyclo[2.2.2]octane (0.06), *cis*-bicyclo[3.3.0]octane (+1.89). Our calculated heats of formation for these compounds (Table I) give relative values of 0.00, −0.03, and 3.47 kcal/mol. The calculated enthalpy for the latter compound again was too high. It is interesting to note in passing that the conformer of bicyclo[3.2.1]octane having a chair form of the cyclohexane ring is calculated to be more stable than the conformer containing the boat form by 6.74 kcal.

Bicyclo[3.3.1]nonane (**5**) has recently been studied experimentally as a hydroxylated derivative, and it was concluded somewhat indirectly that the energy of the double chair form was lower than that of the boat by about 2.5 kcal.[41c] Our calculations gave the chair to be of lower energy by 1.52 kcal/mol.

Strain Energy. We pointed out earlier that strain energy at 25° was in part composed of the enthalpy increase brought about by the presence of high-enthalpy conformations mixed in with the most stable conformations, and a correction to the experimental enthalpy which would be needed to reduce *n*-hexane, say, to a basis comparable with cyclohexane. Schleyer[44] has recently chosen to define the strain in a given molecule as the energy, after allowing for this conformational mixing, by which the molecule differs from that of an *n*-alkane, corrected for chain branching by incremental addition of terms obtained by comparison with isobutane and neopentane. With his definition, cyclohexane does not turn out to be strainless, but, rather, has a strain energy of 1.35 kcal/mol. We believe that a definition which allows cyclohexane to be strainless has some merit, but Schleyer's definition is of more general applicability and is accepted here in principle. In practice, since an experimental heat of combustion is needed to ascertain the strain of a given molecule by Schleyer's method, we use as our definition of "*strain energy*" the calculated heat of formation (eq 2) minus the heat of formation obtained for the *n*-alkane derivative of the same molecular formula, corrected for chain branching and functionalization (eq 3). Since experimental heat of formation data are available for relatively few organic compounds, and since the experimental measurements (including the syntheses) are laborious to carry out, it is a good deal easier in practice to use calculated heats of formation in place of experimental ones. Our strain energies differ slightly from Schleyer's, usually by only a few tenths of a kilocalorie. We have taken the anti conformation of the *n*-alkanes up to heptane as our "strainless" reference point plus isobutane and neopentane as strainless tertiary and quaternary carbon compounds. For any of this set of compounds, the "strainless" heat of formation ΔH_f^s can be written

$$\Delta H_f^s = \sum \Delta H_{C-C} + \sum \Delta H_{C-H} + \sum \Delta H_{1^\circ} + \sum \Delta H_{3^\circ} + \sum \Delta H_{4^\circ} \quad (3)$$

A set of "strainless" heat of formation parameters was deduced for the group as a whole (by a weighted least-squares method) which gave the parameters in Table II. For any saturated hydrocarbon, the corresponding

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(38) (a) R. Granger, L. Bardet, C. Sablayrolles, and J.-P. Girard, *C. R. Acad. Sci., Paris, Ser. C*, **270**, 1326 (1970); (b) G. Dallinga and L. H. Toneman, *Recl. Trav. Chim. Pays-Bas.*, **86**, 171 (1967). These authors report a value for the bridge angle in bicyclo[2.1.1]hexane of 84.5°; we calculate 81.2° for this angle.

(39) G. Dallinga and L. H. Toneman, *Recl. Trav. Chim. Pays-Bas*, **87**, 795 (1968).

(40) P. von R. Schleyer, K. R. Blanchard, and C. D. Woody, *J. Amer. Chem. Soc.*, **85**, 1358 (1963).

(41) (a) M. Dobler and J. D. Dunitz, *Helv. Chim. Acta*, **47**, 695 (1964); (b) W. A. C. Brown, J. Martin, and G. A. Sim, *J. Chem. Soc.*, 1844 (1965); (c) E. N. Marvell and R. S. Knutson, *J. Org. Chem.*, **35**, 388 (1970).

(42) See, for example, the discussion by J. M. McEuen, R. P. Nelson, and R. G. Lawton, *ibid.*, **35**, 690 (1970).

(43) (a) A. F. Cameron, G. Ferguson, and D. G. Morris, *J. Chem. Soc. B* 1249 (1968); (b) O. Ermer and J. D. Dunitz, *Helv. Chim. Acta*, **52**, 1861 (1969). These authors find that bicyclo[2.2.2]octane exists essentially in the totally eclipsed (D_{3h}) state, with a difference in energy between the eclipsed and twist forms of no more than 0.1 kcal/mol. This is what the present calculations give also.

(44) P. v. R. Schleyer, J. E. Williams, and K. R. Blanchard, *J. Amer. Chem. Soc.*, **92**, 2377 (1970).

"strainless" heat of formation is readily calculated from these "strainless" values. The calculated heat of formation is then compared with that for a strainless hydrocarbon containing an equal number of C–C and C–H bonds, and primary, secondary, tertiary, and quaternary carbons. It is found that for most simple aliphatic compounds, the strain energy is small (Table V). For highly branched compounds, such as hexamethylethane, the strain is appreciable, and is a result of excessive van der Waals repulsions (from an analysis of the steric energy), plus the deformation energy incurred in an attempt to relieve these repulsions (Table V).

Table V. Strain Energies[a]

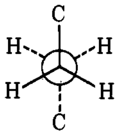
Compd	H_f^s (strainless)[a]	H_f° (calcd)	Strain energy
Methane	−17.89	−17.89	0.00
Ethane	−20.00	−20.24	−0.24
Propane	−25.19	−24.82	0.37
Butane	−30.11	−30.15	−0.04
Isobutane	−32.15	−32.15	−0.00
Pentane	−35.03	−35.00	0.03
Isopentane	−37.25	−36.92	0.33
Neopentane	−40.27	−40.27	−0.00
Hexane	−39.88	−39.96	−0.08
2,3-Dimethylbutane	−44.30	−42.49	1.81
Heptane	−44.82	−44.89	−0.07
Octane	−49.72	−49.82	−0.10
Hexamethylethane	−60.54	−53.99	6.55
Cyclobutane	−20.79	6.38	27.17
Methylcyclobutane	−27.74	−0.60	27.14
Cyclopentane	−25.99	−18.46	7.53
Cyclohexane	−31.18	−29.43	1.75
Methylcyclohexane	−38.04	−36.99	1.05
1,1-Dimethylcyclohexane	−46.26	−43.26	3.00
Cycloheptane	−36.38	−28.34	8.04
Cyclooctane	−41.58	−30.06	11.52
Cyclodecane	−51.97	−36.29	15.68
Cyclododecane	−62.36	−50.50	11.86
Norbornane	−30.30	−12.40	17.90
trans-Decalin	−45.89	−43.54	2.35
Bicyclo[2.2.2]octane	−35.49	−23.80	11.69
trans-syn-trans-Perhydroanthracene	−60.59	−58.32	2.27
trans-anti-trans-Perhydroanthracene	−60.59	−52.74	7.85
Cubane	−17.25	148.70	165.95
Adamantane	−39.81	−33.00	6.81
cis-Hydrindan	−40.69	−30.41	10.28
trans-Hydrindan	−40.49	−31.45	9.04
2,2,4-Trimethylpentane	−57.62	−53.57	4.05
2,2,3-Trimethylbutane	−52.42	−48.95	3.47
Cyclononane	−46.77	−31.80	14.97
cis-Bicyclo[3.3.0]octane	−35.49	−22.30	13.19
trans-Bicyclo[3.3.0]octane	−35.49	−15.90	19.59
Tetraethylmethane	−61.06	−55.44	5.62
Bicyclo[1.1.1]pentane	−19.88	−72.81	92.69
Bicyclo[2.1.1]hexane	−25.07	−19.25	44.32
Bicyclo[3.2.1]octane	−35.45	−26.95	8.50
Bicyclo[3.3.1]nonane	−40.64	−30.29	10.35
Diamantane ("Congressane")	−48.38	−38.04	10.34
1,3,5,7-Tetramethyladamantane	−72.20	−70.13	2.07
Homoadamantane	−44.95	−27.53	17.42
Binorbornane	−56.77	−20.52	36.25
Biadamantane	−75.77	−56.20	19.57

[a] The contribution allocated to the methylene group in Schleyer's scheme[41] has been further divided by us into separate C–C and C–H bond contributions (eq 3). This method was used only because it is consistent with our current method of calculating heats of formation at 25°, gas phase (eq 2). This extra parameter is essentially redundant.

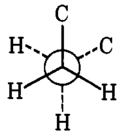
We calculate the strain energy of cyclohexane to be 1.75 kcal/mol (compared to Schleyer's value of 1.35 kcal/mol). This value is most interesting. Schleyer concludes "at least half of the strain in cyclohexane is due to repulsions, the bulk of them C···C. The analysis further indicates that the C···C repulsions of the type found in all chair-form cyclohexane rings are primarily responsible for the adamantane strain." Schleyer further states "only for those functions having a C···C van der Waals minimum at 3.60 Å or greater will the adamantane–decalin difference be of a reasonable magnitude."

Our calculations show that none of the above statements is necessarily true. We have used a van der Waals function with minimum at 3.00 Å for C···C interactions. Our calculations indicate that not only are the bulk of the repulsions in cyclohexane *not* of the C···C type, but that the latter terms correspond in fact to attractions. We do agree, however, that the most important cause of strain in adamantane is the same as in cyclohexane, and we can now look at the latter in detail.

To understand the strain in cyclohexane, we must compare it with an all anti hexamethylene segment (–$(CH_2)_6$–) and see just where the differences lie in terms of energy. We might do this by looking at the anti and gauche forms of *n*-butane. The latter is of higher energy in our calculations, because of three different kinds of terms. First, there are two hydrogens, one on each methyl, which are too close together and exert a repulsion of 0.2 kcal/mol on one another. Second, the bending, stretching, torsional, and van der Waals energies are all higher, by about 0.2 kcal total. This is because the molecule deforms in each available degree of freedom in an effort to minimize the H–H repulsions indicated. The remaining 0.3 kcal is the really interesting contribution, however, because this is the part of the energy that must lead to the strain in cyclohexane, where interactions analogous to the offending hydrogens in butane are absent. This energy difference is found to come from 1,4-interactions, such as between the vicinal hydrogens in ethane. In *anti*-butane (at the 2,3 bond) there are two such H–H interactions, and four C–H interactions. In *gauche*-butane there are three H–H interactions, two C–H and one C–C interaction. Our program gives the following approximate numerical values (kilocalories per mole) for these interactions: H–H, +0.42, C–H, −0.05, C–C, −0.13. Thus, the total energies for these interactions in *anti*- and *gauche*-butane are +0.64 and +1.01 kcal/mol, respectively, which accounts for 0.37 kcal/mol of energy in *gauche*-butane. Furthermore, in cyclohexane the H–H interactions are about 0.3 kcal/mol greater than in *anti*-hexamethylene for the same reason. This energy approximately accounts for the strain (1.75 kcal/mol) in cyclohexane. (The energy per methylene in cyclohexane is a little smaller than in hexamethylene with respect to bending and stretching.)



anti

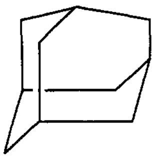


gauche

The strain in adamantane (**7**), compared to decalin, comes from the same basic source. In *anti-n*-butane there are ten H–H repulsions, in isobutane only six, and the decreased number of these repulsions accounts in part for the stability of branched chains relative to normal ones. In decalin there are 22 vicinal H–H interactions. For adamantane to have a strain similar to decalin, there would have to be eight fewer H–H interactions, because of the two additional tertiary centers. There are actually 24, a total of 10 *more* than needed to equal decalin in strain energy. The strain in adamantane is therefore largely due to an excessive number of H–H repulsions (and a decreased number of C–H and C–C repulsions), just as in cyclohexane.

In line with the above conclusions, the tetramethyladamantane (**8**) should be much less strained than adamantane itself, because the vicinal H–H repulsions are entirely removed. The calculated $H_f°$ is −70.13 kcal/mol (not experimentally known), and indeed the strain energy calculates to be only 2.07 kcal/mol. Similarly, diamantane (**9**)[44–46] should be (and is, Table V) even more strained than adamantane due to the increased vicinal H–H interactions (30) and new tertiary centers (4).

Schleyer's conclusions quoted above are therefore not supported by our calculations. The experimental facts are well explained without requiring any C–C repulsions whatever.



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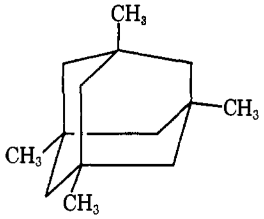

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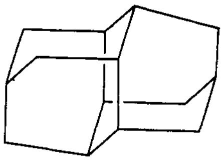


9

Another interesting problem exists which may be used to check the validity of our present force field, which is the central bond length calculated in sterically crowded molecules such as hexamethylethane. In our present scheme, the nonbonded interactions in this and other such molecules are severe enough to cause the crowded atoms to be pushed back away from those across the central bond.[8,47] We calculate the central bond length in hexamethylethane to be 1.568 Å, in reasonable agreement with the experimental number of 1.580 ± 0.006 Å,[48] obtained from electron diffraction data. Similarly, the central bond lengths in binorbornane and biadamantane are calculated to be 1.550 and 1.576 Å, respectively. These values may be compared with the experimental values[49] of 1.515 and 1.578 Å, respectively, obtained from X-ray data. For the latter, the agreement is good. For the former, we seriously question the experimental value (which may be affected by the problem of crystal dissorder), and believe our calculated value is a good deal more accurate. Note that the strain energy calculated for biadamantane is more than twice that of adamantane by 5.95 kcal/mol (Table V), while in binorbornane the corresponding number is only 0.45 kcal/mol. Thus, as suggested by Alden,[49] the interaction between the two adamantane units of biadamantane is very unfavorable, while the corresponding interaction in binorbornane is only very slightly so.

Appendix

We have estimated the heat of formation of cyclododecane (gas, 25°) as follows. The heat of combustion of solid cyclododecane has been found to be 1874.95 ± 0.31 kcal/mol.[50] This corresponds to a

Table VI. Energy Minimization Parameters[a]

van der Waals parameters for use in Hill equation

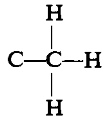
$$[E_v = -2.25\,\epsilon(r^*/r)^6 + 8.28(10)^5/\epsilon)\exp(-r/0.0736r^*)]$$

C, r^* = 1.50 Å; ϵ = 0.116 kcal/mol; H, r^* = 1.50 Å; ϵ = 0.060 kcal/mol

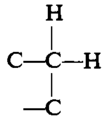
Natural bond lengths and stretching force constants

l_0(C–C) = 1.512 Å; k_l = 4.4 mdyn/Å; l_0(C–H) = 1.094 Å; k_l = 4.6 mdyn/Å

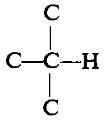
Natural bond angles and bending force constants


$\mathrm{C{-}\overset{H}{\underset{H}{C}}{-}H}$

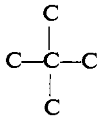
θ_0(C–C–H) = 107.8°
θ_0(H–C–H) = 111.2°


$\mathrm{C{-}\overset{H}{\underset{C}{C}}{-}H}$

θ_0(C–C–H) = 112.8°
θ_0(H–C–H) = 108.5°
θ_0(C–C–C) = 110.2°


$\mathrm{C{-}\overset{C}{\underset{C}{C}}{-}H}$

θ_0(C–C–H) = 108.4°
θ_0(C–C–C) = 110.6°


$\mathrm{C{-}\overset{C}{\underset{C}{C}}{-}C}$

θ_0(C–C–C) = 109.467°

k_θ(C–C–C) = 0.40 mdyn Å/rad²
k_θ(C–C–H) = 0.24 mdyn Å/rad²
k_θ(H–C–H) = 0.20 mdyn Å/rad²

Stretch–bend force constants

$k_{l\theta}$(C–C–C) = −0.09 mdyn/rad; $k_{l\theta}$(C–C–H) = −0.04 mdyn/rad (stretching of a C–H bond is neglected for calculation of a stretch–bend interaction); $k_{l\theta}$(H–C–H) = 0

Torsional parameters

V_0(Y–C–C–Z) = 0.50 (Y, Z any combination of H, C where the dihedral angle is between 0 ± 60° (zero outside that range) (except for cyclobutane rings, where V_0(C–C–C–C) = 1.00)

[a] Notation is identical with that used in ref 13.

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(45) See Table V, footnote *a*.

(46) I. L. Karle and J. Karle, *J. Amer. Chem. Soc.*, **87**, 918 (1965).

(47) Bartell has discussed a similar mechanism for explaining the lengthening of central C–C bonds in sterically crowded molecules: L. S. Bartell, *J. Chem. Phys.*, **32**, 827 (1960); (c) L. S. Bartell, *Tetrahedron*, **17**, 177 (1962).

(48) Taken from Figure 1 of ref 8.

(49) R. A. Alden, J. Kraut, and T. G. Traylor, *J. Amer. Chem. Soc.*, 90, 74 (1968).

(50) J. Coops, H. van Kamp, W. A. Lambregts, B. J. Visser, and H. Dekker, *Recl. Trav. Chim. Pays-Bas*, **79**, 1226 (1960).

crystalline heat of formation at 25° of −73.54 kcal/mol. Since the heat of sublimation at 25° for this compound is not known, we have chosen to estimate this quantity by using Bondi's value[51] of 2.03 kcal/mol per CH_2 group for the heat of sublimation of alkanes and cycloalkanes at their transition temperatures. This leads to an estimate of 24.36 kcal/mol for the heat of sublimation of cyclododecane at its transition temperature of 60.7°. The two unknown quantities at this point are the heat capacities of both the gaseous and crystalline hydrocarbon from the transition temperature to 25°. We estimate that these quantities are 0.2 and −1.5 kcal/mol, respectively. These values are subsequently combined with the above quantities to give a value of −50.5 ± 2 kcal/mol for the heat of formation (gas, 25°) of cyclododecane.

The bending function which we use in our present force field calculations is

$$E_\theta = (k_b/2)(\Delta\theta^2 + k_{\theta 3}\Delta\theta) \qquad (4)$$

where k_b is the bending constant in millidynes per ångström, $k_{\theta 3}$ = cubic force constant, and $\Delta\theta$ is the deviation from the natural angle. This function is illustrated in Figure 2.

Minimization Scheme. The scheme which we used previously for minimizing the energy was a steepest descent method, essentially that originally developed by Wiberg,[52] subsequently modified by us.[13] The improvement in energy with such a scheme is very fast when the geometry is far from the minimum of energy, but the improvement slows down drastically as one approaches the minimum, and the overall computation time is quite long. On the IBM 360/65, a molecule containing five or ten carbon atoms may require up to a few minutes of computation time, while a molecule the size of androstane (about 50 atoms counting hydrogens) may require more than 2 or 3 hr. We therefore gave some attention to reducing these long running times found with large molecules. Several other workers have studied this problem, and have devised various systems for carrying out the minimization efficiently.[6a,7a,8,12a,b,52] A strong feature of the Wiberg method is that it seems to be rather free from hangups. It is a brute-force method, but has proven to be a highly reliable method in our hands. We have developed another method, however, which deals with most molecules adequately and runs at least ten times faster than the Wiberg method. In comparison tests, using *n*-hexane as a test molecule, a program based on our new method is two to three times faster than that of Boyd.[7a,53] The running time required by this program increases approximately linearly with the number of atoms for small molecules, and this time gradually accelerates so that it is increasing approximately as the square of the number of atoms for large molecules. The method of Boyd involves a matrix diagonalization, for which the time required goes up approximately as a cube of the number of the atoms. Therefore our program is appreciably faster than Boyd's for small molecules, and this advantage probably increases with molecular size. There is probably at least one exception to this generalization, which can be exemplified with the boat form of cyclohexane. The twist–boat is of lower energy than the classical boat, and if one starts with the latter, it should go to the former. With our program it goes very slowly, because one really needs a cooperative motion of the ring atoms, and moving one atom at a time means a great many iterations are required. Boyd's method, which uses simultaneous equations, should have a definite advantage in such a case.

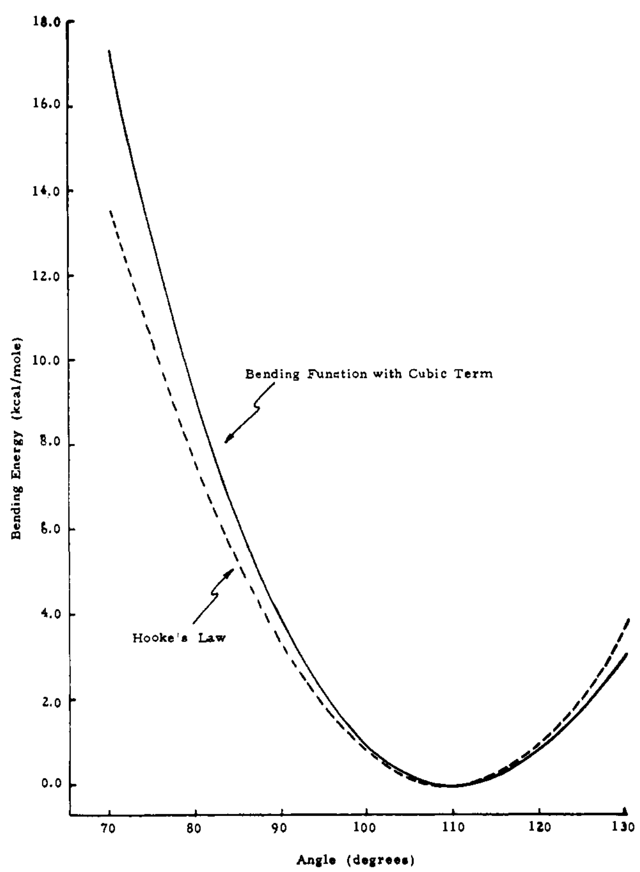

Figure 2. Bending energy for the quaternary CCC angle. The same function is used for other CCC angles, but the minimum is displaced to larger value of θ_0 as in Table VI.

The basis for our minimization scheme is as follows. It is assumed that the potential energy surface in the vicinity of the minimum energy for each atom can be approximated by the equation $E = Ax^2 + By^2 + Cz^2 + Dx + Ey + Fz + G$. The quantities xyz are the cartesian coordinates of the atom local energy, and the constants are to be determined. The energy of the molecule (in which electrostatic interactions are assumed negligible) is first written as $E_{\text{steric}} = \Sigma_{\text{bonds}} E_{\text{bond–stretch}} + \Sigma_{\text{angles}} E_{\text{bend}} + \Sigma_{\text{torsions}} E_{\text{torsion}} + \Sigma_{\text{VDW's}} E_{\text{VDW}} + \Sigma_{\text{str–bnd's}} E_{\text{str-bnd}}$, where the terms in order are the stretching energy for each bond, the bending energy for each bond angle, the torsional energy for each four-atom unit, the van der Waals energies between all atoms not bound to one another or to a common atom, and the stretch–bend interaction energies. For a given atom, the partial derivative of the energy with respect to each cartesian coordinate is taken (analytically). The atom is then moved in such a direction as to reduce the overall energy, the amount of motion being proportional to the partial derivative with respect to that coordinate (method of steepest descent). Once a given atom has been moved in the three co-

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(51) A. Bondi, *J. Chem. Eng. Data*, **8**, 371 (1963).

(52) K. B. Wiberg, *J. Amer. Chem. Soc.*, **87**, 1070 (1965).

(53) We are indebted to Professor Boyd for providing us with a copy of his energy minimization program.

ordinates, the partial derivatives at the new position are recalculated, and from the six partial derivatives for the two values of each coordinate, the constants in the energy equation (*A–F*) are calculated. The derivative of this equation is then set equal to zero, which gives the position of minimum energy, and the atom is placed at that point. The program then repeats the procedure for the next atom, and this process is continued until all atoms have had their positions of minimum energy calculated sequentially, and the atoms have been repositioned. The calculations are then repeated in their entirety, using the new set of coordinates as a starting point. This process is continued until the atomic motions are judged to be sufficiently small, and that it is not worthwhile to proceed. In practice, the allowable errors are usually on the order of 0.001 Å in each coordinate. Following the idea introduced originally by Wiberg, when a carbon atom is moved, the attached hydrogen atoms (or other attached atoms such as halogen) are moved along with it. The hydrogens are then allowed to seek their own minima holding the carbon constant.

Magnetic Nonequivalence in the Low-Temperature Nuclear Magnetic Resonance Spectra of *N*-Benzyl-*N*-methylhydroxylamine and *N*-Benzyl-*N*-methylchloramine[1]

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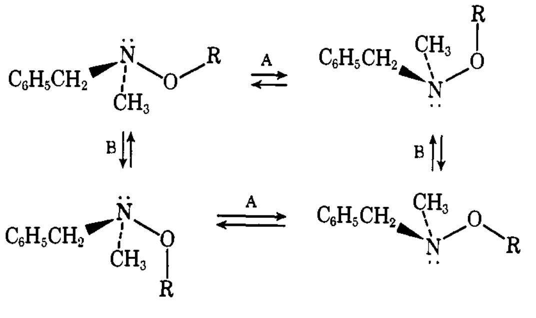
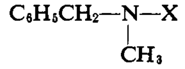
Abstract: Reinvestigation of the low-temperature nmr spectra of *N*-benzyl-*N*-methylhydroxylamine and *N*-benzyl-*N*-methylchloramine in acetone-d_6 at 100 MHz has revealed magnetic nonequivalence. The slow process with the *N*-chloro compound must be nitrogen inversion. The fact that, in acetone-d_6, *N*-benzyl-*N*-methylhydroxylamine undergoes degenerate racemization more slowly than *N*-benzyl-*O*,*N*-dimethylhydroxylamine supports the hypothesis that inversion of nitrogen is slower than the rate of rotation about the N–O bond in these compounds.

Since observation of magnetic nonequivalence in the low-temperature nmr spectra of some hydroxylamine derivatives[2] there has been controversy surrounding the nature of the measured rate process. In the case of cyclic hydroxylamines there appears to be general agreement that magnetic nonequivalence results from restricted pyramidal inversion at nitrogen;[3–5] however, in acyclic derivatives the possibility that the rate-determining step reflects a substantial barrier to rotation about the N–O bond must also be considered.[6–8]

Degenerate racemization of a benzylhydroxylamine requires both inversion at nitrogen (process A) and rotation about the N–O bond or its equivalent, inversion at oxygen (process B). If either A or B is slow on the nmr time scale, in principle, magnetic nonequivalence of the benzyl CH_2 protons will result. In fact, the observation of a small steric deceleration has been interpreted as evidence for a torsional barrier as the measured process.[8c]



We had previously reported[2a] that, although *N*-benzyl-*O*,*N*-dimethylhydroxylamine (**1**) exhibited magnetic nonequivalence of the benzyl hydrogens at readily accessible temperatures, neither *N*-benzyl-*N*-methylhydroxylamine (**2**) nor *N*-benzyl-*N*-methylchloramine (**3**) showed such nonequivalence. In light of the



$$C_6H_5CH_2\text{—}\underset{\substack{|\\ CH_3}}{N}\text{—}X$$

1, X = OCH_3
2, X = OH
3, X = Cl

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* Address correspondence to this author at Case Western Reserve University.

(1) Supported by the National Science Foundation.

(2) (a) D. L. Griffith and J. D. Roberts, *J. Amer. Chem. Soc.*, **87**, 4089 (1965); (b) R. E. Banks, M. G. Barlow, R. N. Hazeldine, and M. K. McCreath, *J. Chem. Soc.*, 9203 (1965).

(3) Oxaziridines: W. D. Emmons, *J. Amer. Chem. Soc.*, **79**, 5739 (1957); F. Montanari, I. Moretti, and G. Torre, *Chem. Commun.*, 1694 (1968).

(4) 1,2-Oxazetidines: J. Lee and K. G. Orrell, *Trans. Faraday Soc.*, **61**, 2342 (1965).

(5) Isoxazolidines and tetrahydro-1,2-oxazines: (a) F. G. Riddell, J. M. Lehn, and J. Wagner, *Chem. Commun.*, 1403 (1968); (b) D. L. Griffith and B. L. Olson, *ibid.*, 1682 (1968); (c) M. Raban, F. B. Jones, Jr., E. H. Carlson, E. Banucci, and N. A. LeBel, *J. Org. Chem.*, **35**, 1496 (1970).

(6) A. H. Cowley, M. J. S. Dewar, and W. R. Jackson, *J. Amer. Chem. Soc.*, **90**, 4185 (1968).

(7) J. M. Lehn and J. Wagner, *Chem. Commun.*, 1298 (1968).

(8) (a) M. Raban, F. B. Jones, Jr., and G. W. J. Kenney, Jr., *Tetrahedron Lett.*, 5055 (1968); (b) M. Raban, G. W. J. Kenney, Jr., and F. B. Jones, Jr., *J. Amer. Chem. Soc.*, **91**, 6677 (1969); (c) M. Raban and G. W. J. Kenney, Jr., *Tetrahedron Lett.*, 1295 (1969).