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DISTORTED GEOMETRIES AT CARBON[1]

KENNETH B. WIBERG and G. BARNEY ELLISON
Department of Chemistry, Yale University, New Haven, Conn. 06520

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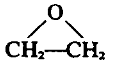
Abstract—The changes in energy resulting from deforming methane have been calculated. Tetrahedral geometry does not have the lowest electronic energy, but does have the smallest nuclear repulsion energy. The latter plays a major role in determining the changes in energy when methane is deformed. Some properties of small ring compounds are considered from the standpoint of bond angle deformation.

Although the tetrahedral C atom is at the core of organic structural theory, very few saturated compounds do indeed have pure tetrahedral geometry. This geometry is found only with highly symmetrical compounds such as methane, carbon tetrachloride and neopentane. Even in such simple and familiar compounds such as ethane, methyl chloride and methylene chloride there are significant deviations from the tetrahedral angle of 109·47° (Table 1).

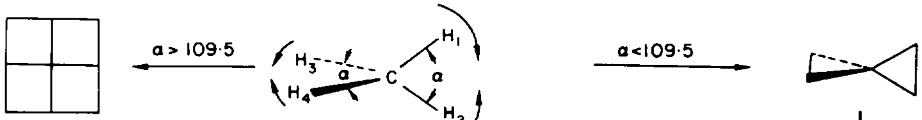
Some compounds, notably cyclopropane and cyclobutane derivatives, have bond angles which deviate markedly from tetrahedral. Such distortion leads to interesting changes in both physical and chemical properties and this has stimulated many investigations of these compounds. In order to put the problem in perspective, it seems helpful first to consider the modes of deformation for the bond angles in the simplest of organic compounds, methane.

If we consider the vibrations of methane, we may recognize two symmetry coordinates which involve the bond angles, a doubly degenerate (E) symmetric bend and a triply degenerate (F_2) antisymmetric bend:[2]

Table 1. H–C–H bond angles[a]

Compound	Angle
CH_3F	110·4
CH_3Cl	110·5
CH_3Br	111·2
CH_3I	111·8
CH_2F_2	111·9
CH_2Cl_2	112·0
CH_2I_2	114·7
CH_3OH	109·1
CH_3SH	109·8
CH_3CHO	108·3
 $\overset{O}{CH_2\text{—}CH_2}$	116·3

[a] The data were taken from *Interatomic Distances*, Special Publication No. 11. The Chemical Society, London (1958)



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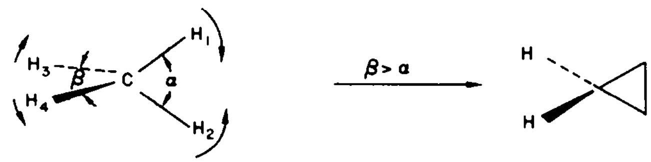
Symmetric bend, $\Delta a_1 = \Delta a_2$

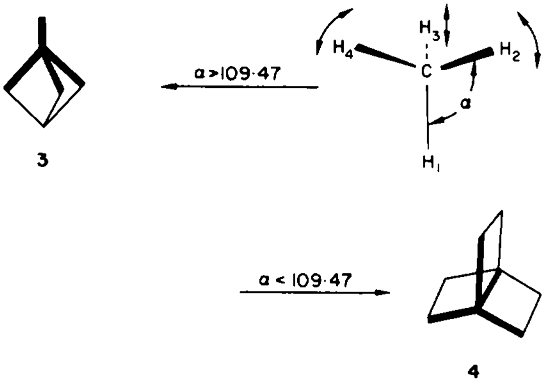


Antisymmetric bend, $\Delta a = -\Delta\beta$
Unsymmetric bend, $\Delta a \neq -\Delta\beta$

The symmetric bending mode leads to the type of distortion which is present in spiropentane (1)

($\alpha < 109{\cdot}5°$) and also that present in the still unknown tetracyclic compound, 2, variously known as "windowpane" or "fenestrane" ($\alpha > 109{\cdot}5°$). The antisymmetric mode requires that $\Delta\alpha = -\Delta\beta$ which is too restrictive for the present purpose. The unsymmetric mode, which requires only that β is greater than tetrahedral when α is less than tetrahedral, will be used as the second deformation mode. It leads to the type of distortion present in cyclopropane and cyclobutane in which the H–C–H angles are greater than tetrahedral.

One other symmetrical mode of distortion is easily recognized. In this C_{3v} or umbrella mode, a 3-fold axis of symmetry is maintained



If the angle is increased over the tetrahedral value, the distortion is in a direction characteristic of bicyclic compounds such as bicyclo[1.1.1]-pentane (3). If the angle is decreased below 109·47°, the distortion is that required for the formation of the so-called "propellanes" such as tricyclo-[2.2.2.$0^{1,4}$] octane (4).

In order to learn more about the consequences of bond angle deformation, both with regard to energies and hybridization, we have carried out Hartree–Fock SCF calculations for several geometries of methane corresponding to each of these cases. Unless otherwise indicated, a minimal STO–3G basis set was used.[*][†]

The simplest is the symmetric bending mode since only one angle, α, need be specified, and since all bond lengths might reasonably be expected to be equal. The change in energy with α at the observed C–H bond length 1·0936 Å is shown in Fig 1. The nuclear repulsion is the Coulombic repulsion term for the five nuclear centers. Since the C–H bond lengths were constant, the C–H nuclear repulsion terms did not change during the angle deformation. Thus the changes in the repulsive energy are due only to the changes in H–H distances caused by the changes in angles. The electronic energy is the calculated electronic term, and the total energy is the sum of the two. The zero of energy was taken to correspond to tetrahedral methane.

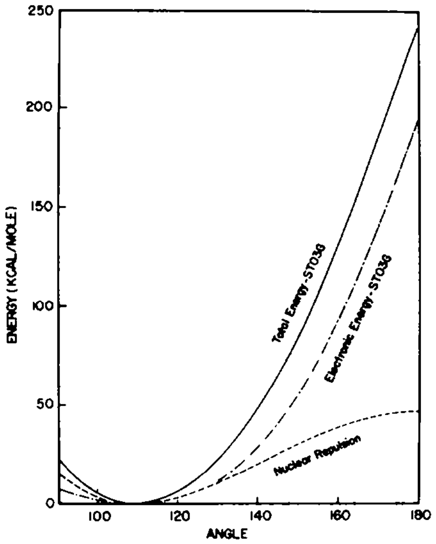


Fig 1. Effect of angle bending on the energy of methane for the symmetric mode. The electronic energies were calculated using the STO-3G basis set.

It can be seen that both the nuclear repulsion and the electronic energy increase as the angle deviates from tetrahedral. The increase in nuclear repulsion arises from the decrease in the H–H distances. The changes in electronic energy can be understood in terms of the zeroth order bonding molecular orbitals. Here, one HCH group is placed in the xz plane and the other is placed in the yz plane:

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\begin{aligned}
\psi_1 &= 1s,\ \mathrm{C}\\
\psi_2 &= 0{\cdot}35\ 1s,\ \mathrm{H}_1 + 0{\cdot}35\ 1s,\ \mathrm{H}_2 + 0{\cdot}35\ 1s,\ \mathrm{H}_3\\
&\quad + 0{\cdot}35\ 1s,\ \mathrm{H}_4 + 0{\cdot}71\ 2s,\ \mathrm{C}\\
\psi_3 &= 0{\cdot}50\ 1s,\ \mathrm{H}_1 - 0{\cdot}50\ 1s,\ \mathrm{H}_2 + 0{\cdot}71\ 2p_x,\ \mathrm{C}\\
\psi_4 &= 0{\cdot}50\ 1s,\ \mathrm{H}_3 - 0{\cdot}50\ 1s,\ \mathrm{H}_4 + 0{\cdot}71\ 2p_y,\ \mathrm{C}\\
\psi_5 &= 0{\cdot}35\ 1s,\ \mathrm{H}_1 + 0{\cdot}35\ 1s,\ \mathrm{H}_2 - 0{\cdot}35\ 1s,\ \mathrm{H}_3\\
&\quad - 0{\cdot}35\ 1s,\ \mathrm{H}_4 + 0{\cdot}71\ 2p_z,\ \mathrm{C}
\end{aligned}
$$

ψ_1 and ψ_2 are relatively unaffected by bond angle distortion since they involve only undirectional s-orbitals at carbon. In the tetrahedral geometry, ψ_3–ψ_5 are degenerate and are the highest occupied molecular orbitals.

When the angle is deformed toward 90°, the hydrogen orbitals will move out in the z direction and give better overlap with the p_z carbon orbital. As a result, ψ_5 will decrease in energy. At the same time, overlap with the p_x and p_y orbitals will decrease,

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[*] The calculations were carried out using POLYATOM-II obtained from the Quantum Chemistry Program Exchange. The coefficients for the STO-3G calculations were taken from Ref 3 and the details of our calculations will be presented elsewhere.

[†] Several calculations have been reported for the effect of small deformations on the energy of methane.[4]

leading to an increase in energy for ψ_3 and ψ_4. When the angle is deformed in the other direction, the energy changes will be in the opposite sense. In the range 90–130°, the changes in energy largely cancel, leading to only a small net change in electronic energy. Even if it is somewhat in error as a result of the small 3G minimal basis set used in the calculations, the change in total energy is dominated by the nuclear repulsion which is calculated exactly.

When the angle increases from 130° to 180°, the calculated electronic energy rises rapidly.* In this range of α, the energy associated with ψ_3 and ψ_4 decreases only slightly. On the other hand, the energy of ψ_5 increases rapidly. It can be seen that when $\alpha = 180°$, ψ_5 represents a non-bonding situation.† The minimal basis set, which reproduces the properties of methane fairly well for the tetrahedral geometry, is no longer able to give bonding character to ψ_5. The basis set could be improved in two ways. First, *d* orbitals could be added at carbon. A $d_{x^2-y^2}$ orbital could lead to a bonding interaction with the four hydrogens placed at the corners of a square. Alternately, 2*p* orbitals could be added at hydrogen. The $2p_z$ orbitals would give a bonding interaction with the $2p_z$ orbital at carbon.

A larger basis set which included 3*d* functions on carbon and 2*p* functions on the hydrogens was used in order to try to obtain a better estimate of the electronic energy at large angles.‡ The results of the calculations are present in Fig 2. It can be seen that the larger basis set does effect a significant reduction in the electronic energy. As a result, the total energy at 180° drops from 241 kcal/mole to 160 kcal/mole using the more flexible basis set. It was interesting to note that the small amount of *d* character at carbon was calculated to decrease on going from tetrahedral to planar geometry suggesting that *d*-orbital stabilization is not of real importance for carbon–hydrogen bonds. On the other hand, the 2*p* character at hydrogen increased markedly on going from tetrahedral to planar geometry and this accounts for the drop in calculated energy.

At 140°, an angle which might accommodate compounds having structures such as 2, the total energy using the larger basis set is only 37 kcal/mol above that of tetrahedral methane. Thus, the preparation of such compounds may not be unreasonable. On the other hand, the racemization of an optically active methane derivative via a planar activated complex appears to have an unreasonably high activation energy. Bond dissociation would occur first.

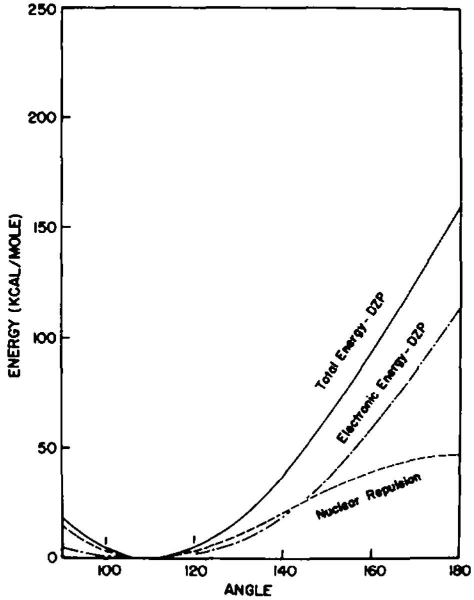

Fig 2. Effect of angle bending on the energy of methane for the symmetric mode. The electronic energies were calculated using a double zeta plus polarization (*d* orbitals on carbon and *p*-orbitals on hydrogen) basis set.

The unsymmetric bending mode leads to a quite different picture. Suppose $\alpha = 90°$. The MO which utilizes the 2*s* orbitals at carbon is calculated to be about 10 ev (~230 kcal/mol) lower in energy than the three MO's which utilize the 2*p* orbitals at carbon, and it does not have directional characteristics. As with the symmetric bending mode, it is relatively unaffected by bond angle deformation. In order to minimize the energies of the MO's formed using the 2*p* orbitals, one hydrogen may be placed at each of the p_x and p_y orbitals, and two at the p_z orbital. This predicts that when $\alpha = 90°$, the minimum electronic energy should be found when $\beta = 180°$.

The results of our calculations are shown in Fig 3. The electronic energy is, as expected, at a minimum at 180°. However, the nuclear repulsion is at a maximum at this angle, and is much larger than the electronic term. One might expect that as α is decreased, β would increase in order to minimize nuclear repulsion. However, this is not the case, and for $\alpha = 90°$ the minimum nuclear repulsion is found at $\beta = 106°$ (Fig 4). The minimum total energy is found at $\beta = 113°$. Thus, the dominant term in governing the geometry is nuclear repulsion. The electronic term only shifts the energy minimum to a slightly larger angle.

The equilibrium geometry for $\alpha = 90°$ utilizes bent bonds, and it may be noted that the value of β is similar to that for the H–C–H angle in cyclobutane (111°). This leads one to suspect that the geometry of cyclobutane is largely determined by

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*The energy of planar methane has been calculated to be 250 kcal/mol greater than that of tetrahedral methane using a minimal basis set.[5]

†The bonding in unsymmetrically substituted planar methanes have been discussed in Ref 6.

‡The coefficients for the double zeta plus polarization basis set were taken from Ref 7.

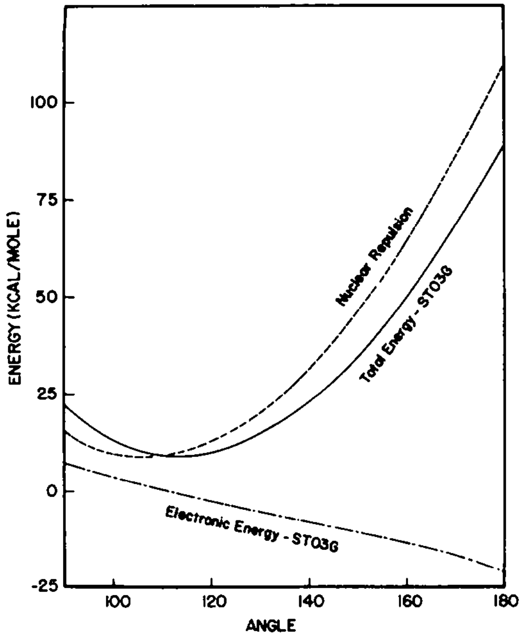

Fig 3. Effect on the opposite angle on the energy of methane when one angle is held at 90°.

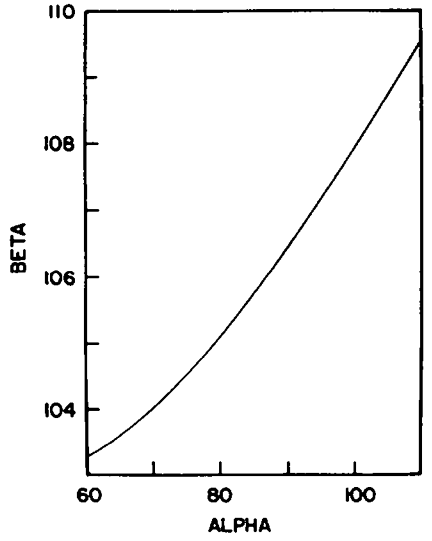

Fig 4. Relationship between the constrained angle (α) and the opposite angle (β) for minimum nuclear repulsion.

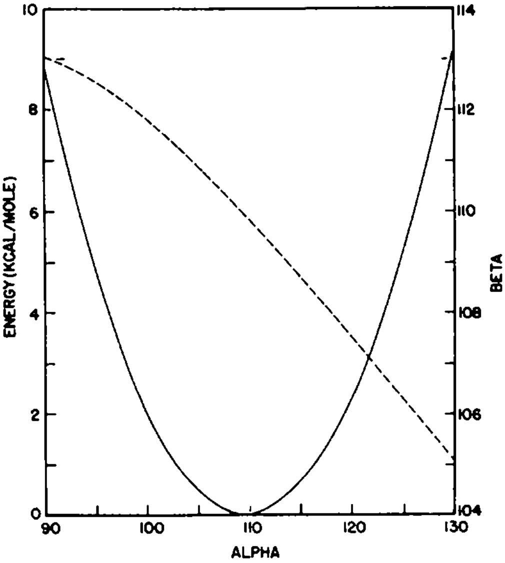

Fig 5. Effect of angle bending on the energy of methane for an unsymmetric mode. The values of β (dashed line) are those for the opposite angle which minimize the total energy for a given value of α. The solid line gives the corresponding energies. The energies were calculated using the STO-3G basis set.

nuclear repulsion. The effective nuclear charge of carbon is somewhat greater than that for hydrogen, but this is largely compensated by the greater C–C bond lengths.

The minimum total energies were determined as a function of β for a series of values of α giving the data presented in Fig 5. If we compare this deformation mode with the symmetric bend (Fig 1), the energies for the latter should be divided by two since two angles are constrained in the symmetric bend whereas only one angle is constrained in the unsymmetric bend. It can be seen that even with this factor taken into account, it is energetically more favorable to decrease α for the unsymmetric bend than for the symmetric bend. This is in good accord with the observation that spiropentane has a strain energy which is 8 kcal/mol greater than that for two cyclopropanes.[8]

The results of calculations on the umbrella mode are shown in Fig 6. It can be seen that the electronic energy is at a maximum at the tetrahedral angle. Surprisingly, the electronic energy decreases when α goes toward either 90° or 130°. This indicates that tetrahedral bonding is electronically less favorable than the less symmetrical arrangements. Tetrahedral geometry is, however, strongly favored by nuclear repulsion. Thus, the tetrahedral nature of carbon appears to be a result of nuclear repulsion rather than electronic terms.

The changes in energy with geometry are again largely determined by the changes in nuclear repulsion. Since the electronic terms are relatively small, it is unlikely that a larger basis set would significantly change the results. The energy changes are approximately symmetrical for positive and negative changes in α from tetrahedral. Therefore, the energy changes on going to bicyclic compounds on one hand, and propellanes on the other, should be similar for similar changes in angle.

In all of the deformation modes of methane, nuclear repulsion played a major role in determining

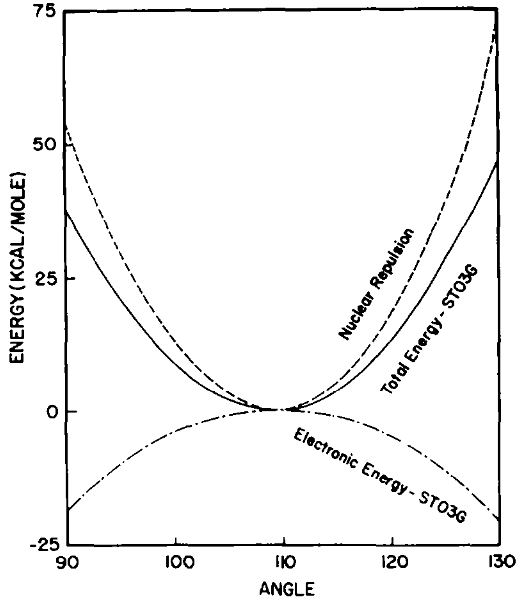

Fig 6. Effect of angle bending on the energy of methane for the C_{3v} or umbrella mode.

energies and geometries. It plays an important role in determining the geometries of many other acyclic compounds. For example, the barrier to internal rotation in ethane results mainly from the larger H–H nuclear repulsion in the eclipsed as compared to the staggered form of ethane.*

As indicated above, the molecules which possess significant bond angle deformation are mainly small ring compounds. Let us examine some groups of small ring compounds and see how their properties are related to the results of the calculations on methane.

Cyclopropane cannot directly be related to a methane having a 60° H–C–H angle because the latter cannot form a bond between the atoms which are moved close together. Thus, the energy of this highly deformed methane is calculated to be very large, mainly due to nuclear repulsion which cannot be compensated by electronic terms. It can be seen in Fig 4 that if methane were forced to have a 60° angle, the minimum nuclear repulsion would be found when the opposite angle is slightly over 103°. One might expect a similar effect in cyclopropane. Again it appears that the electronic energy terms lead to the increase in angle to the observed value of 115°.

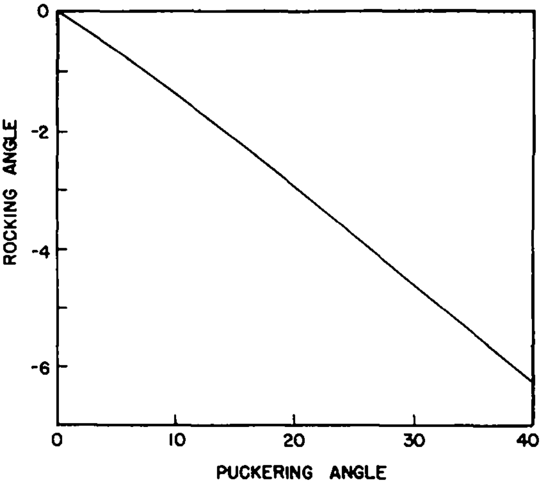

Fig 7. Relation between the methylene rocking angle and the ring puckering angle in cyclobutane for minimum nuclear repulsion. The negative angles correspond to the methylene group rocking away from each other.

The H–C–H angle in cyclobutane was considered above. In this compound, it is believed that the methylene groups rock away from each other as the ring puckers.[10] This might be related to nuclear repulsion. In order to examine this possibility, the rocking angle which led to the minimum nuclear repulsion was calculated for several puckering angles giving the results shown in Fig 7. In this simple Coulombic sum, $\sum_{i<j} Z_iZ_j/r_{ij}$, it would be unrealistic to use $Z = 6$ for carbon since the nucleus is shielded by the electrons. Thus $Z = 1{\cdot}625$† was employed along with $Z = 1{\cdot}0$ for hydrogen. It can be seen that a small rocking angle does decrease nuclear repulsion. This conclusion is independent of the value of Z used for carbon since both the H–H and C–H nuclear repulsions decrease when the methylene groups are rocked away from each other.

In comparing the strain energies of cyclic and spiro-fused compounds, the ideal pair would be cyclobutane and [3.3] spiroheptane. Here, the difference in strain energy per small ring should be large enough to be easily determined and the angles are such that they could be compared with the results obtained for methane. Unfortunately, the strain energy of the spiroheptane is not known. The increase in strain in spiropentane over that in two cyclopropanes has been mentioned above. A rough estimate of the strain at the central carbon can be made by assuming that the methylene groups will have the same strain as in cyclopropane. This leads to a value of 26 kcal/mol which is considerably more than twice the 9 kcal/mol strain per carbon in cyclopropane.

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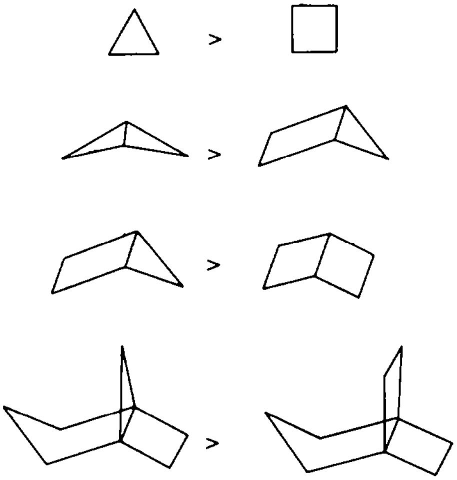
*The nuclear repulsion, assuming no changes in bond lengths or angle on rotation, is 5·1 kcal/mol greater for the eclipsed conformation of ethane than for the staggered conformation.[9] Since the barrier to rotation is 2·9 kcal/mol, the electronic energy is 2·2 kcal/mol less for the eclipsed form than for the staggered form.

†The value 1·625 is a commonly used Slater exponent for carbon and reflects the effective nuclear change.

One of the more general observations concerning small ring compounds is that cyclopropanes are much more reactive toward electrophiles than are cyclobutanes. In the following group of compounds, the molecule containing the cyclopropane ring is at least 10^6 times more reactive than the corresponding compound containing a cyclobutane ring:[11]



What is the major difference between cyclopropane and cyclobutane? Since the H–C–H angles in cyclopropane are not much larger than tetrahedral, the orbitals forming the C–C bonds must be strongly bent (the calculated interorbital angle is 104°).[12] On the other hand, the 90° internuclear angle in cyclobutane leads to only slightly bent bonds. As a result, electron density appears farther out from the line of C–C nuclear centers in cyclopropane than in cyclobutane. One attractive possibility for explaining the higher reactivity of cyclopropanes is that the electrophile may be able to achieve significant electronic interaction in cyclopropane at a larger distance from the carbons than in cyclobutane. This would result in a smaller nuclear repulsion in an edge protonated cyclopropane than in a protonated cyclobutane. It remains to be determined whether or not this explanation is viable.

Nuclear repulsion has not received much attention from chemists. The purpose of this essay is to point out cases in which nuclear repulsion is as important or more so than electronic terms in determining the energies and geometries of molecules. It appears that the simplest of organic compounds, methane, has its geometry determined by nuclear repulsion rather than by the electronic terms. The barrier to internal rotation in ethane arises largely from nuclear repulsion, and the geometries of many compounds such as ammonia may be accounted for by considering nuclear repulsion. Clearly, nuclear repulsion is a force which deserves more attention.

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