Bent Bonds in Organic Compounds

KENNETH B. WIBERG

Department of Chemistry, Yale University, New Haven, Connecticut 06520

Introduction

The bonds in organic compounds are usually taken as a linear path between the two bonded nuclei. However, it is not obvious that this should always be the case, and experimental X-ray data sometimes indicate that the deformation density[1] related to the formation of a bond is not centered on the conventional depiction of the bond. It is clear that a precise definition of a bond is needed. An intuitively reasonable and physically precise definition is the path of maximum charge density between the pair of bonded atoms.[2] This path may be determined experimentally from X-ray data, or theoretically from the result of accurate ab initio calculations. In most cases, the bond path will be nearly collinear with the line of centers, but there are many interesting cases in which it is not.[3] They will be the subject of this Account.

Cyclopropane and Related Compounds

The first suggestion of bent bonds appeared in an unusual context. In 1913, a paper by Beesley and Thorpe reported the preparation of a bicyclobutane and a tricyclobutane via elimination reactions carried out under vigorous conditions (Scheme 1).[4] It is now known that even if the compounds had been formed, they would not have survived the workup conditions that were described. Bicyclobutanes undergo acid-catalyzed C−C bond cleavage at pH values as high as 4.[5] A reinvestigation of the work found it to not be reproducible.[6] These efforts were carried out before NMR spectroscopy and modern methods of chromatography became available, and so the identity of the products formed have not been determined, but they are probably lactones or similar compounds.[7]

Woodward managed to locate Beesley in Mexico working for an oil company. He informed Woodward that he had not done the work, and had been sent by Thorpe to the war because "he did not have the proper academic frame of mind".[4] It is now clear that the report is fraudulent. Nevertheless, it caught Ingold's attention in his early scientific years, and he wrote an interesting addendum to the paper suggesting that the bonds in tricyclobutane (tetrahedrane) should lie along the surface of a sphere onto which the carbons are inscribed in order to minimize angle strain.[8]

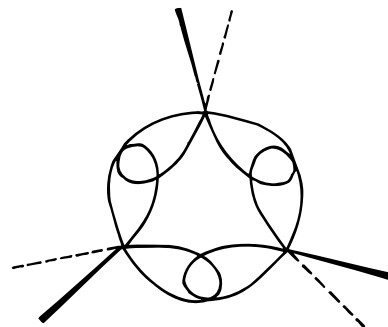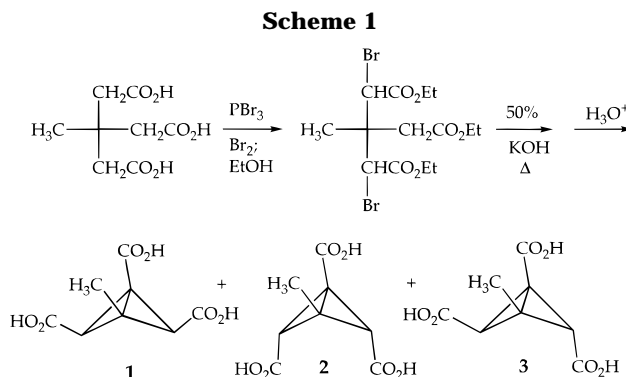The first theoretical studies of bent bonds were reported by Förster[9] and by Coulson and Moffitt[10] in

Kenneth B. Wiberg was born in Brooklyn, NY, in 1927. He obtained a B.S. from the Massachusetts Institute of Technology (1948) and a Ph.D. from Columbia University (1950). He was a member of the faculty at the University of Washington from 1950 to 1961, and then moved to Yale University where he is now the Eugene Higgins Professor of Chemistry. His research interests include small-ring chemistry, spectroscopic studies, and the application of ab initio MO theory to problems in organic chemistry.

Figure 1. Coulson−Moffit model for cyclopropane.

Scheme 1

studies of cyclopropane. This molecule presents the problem that the apparent C−C−C bond angles are 60° whereas the smallest angle that could be formed from s and p orbitals is 90° (i.e., pure p). Even here, the bonds would be expected to be rather weak. Coulson and Moffitt showed that the use of orbitals having relatively high p character would lead to a bent bond description for cyclopropane (Figure 1). The

(1) The deformation density is defined as the difference in electron density between the compound in question and that of a set of spherically symmetrical "proatoms" that are placed at the corresponding nuclear positions. It shows where electron density shifts in forming bonds: Dunitz, J. *X-Ray Analysis and the Structures of Organic Compounds*; Cornell University Press: Ithaca, NY, 1979.

(2) Bader, R. F. W. *Atoms in Molecules. A Quantum Theory*; Clarendon Press: Oxford, 1990.

(3) Cf. Wiberg, K. B.; Murcko, M. A. *J. Mol. Struct.* **1988**, *169*, 355.

(4) Beesley, R. M.; Thorpe, J. F. *Proc. Chem. Soc.* **1913**, *29*, 346. Beesley, R. M.; Thorpe, J. F. *J. Chem. Soc.* **1920**, *117*, 591.

(5) Wiberg, K. B.; Lampman, G. M.; Ciula, R. P.; Connor, D. S.; Schertler, P.; Lavanish, J. *Tetrahedron* **1965**, *21*, 2749.

(6) Larson, H. O.; Woodward, R. B. *Chem. Ind.* **1959**, 193. Larson, H. O. Ph.D. Thesis, Harvard, 1950. The letter from Beesley to Woodward is reproduced in this thesis.

(7) It is interesting to note that cyclopropanes are often prepared by elimination of HX (Schlatter, M. J. *J. Am. Chem. Soc.* **1941**, *63*, 1733), and that the first bicyclobutane derivative was prepared by this method (Wiberg, K. B.; Cuila, R. P. *J. Am. Chem. Soc.* **1959**, *81*, 5261). It is quite possible that a bicyclobutane could be prepared from the dibromo triester using appropriate reaction conditions, but this does not appear to have been examined.

(8) Ingold, C. K. *J. Chem. Soc.* **1920**, *117*, 603.

(9) Förster, Th. *Z. Phys. Chem.* **1939**, *B43*, 58.

(10) Coulson, C. A.; Moffitt, W. E. *J. Chem. Phys.* **1947**, *15*, 151. *Philos. Mag.* **1949**, *40*, 1.

Table 1. Comparison of Ethylene, Cyclopropane and Cyclobutane Methylene Groups

parameter	ethylene	cyclopropane	cyclobutane
$r(CH)^a$	1.085	1.084	1.094
$\angle HCH$	117	114	109
$J(^{13}C-H)^b$	156	161	134
CH BDE^c	112	109	99

[a] The experimental data for cyclopropane and cyclobutane are not very precise, and the values given are taken from an MP2/6-31G* calculation. [b] Levy, G. C.; Lichter, R. L.; Neson, G. L. *Carbon-13 Nucelar Magnetic Resonance Spectroscopy*, 2nd ed.; Wiley: New York, 1980. [c] Reference 20.
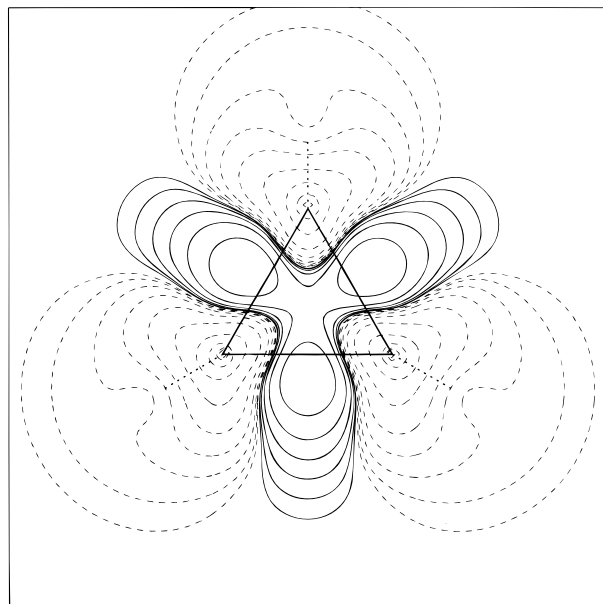

Figure 2. Deformation density plot for cyclopropane based on MP2/6-31G* wave functions. The solid contours indicate regions that gain electron density on bond formation, and dashed lines indicate regions that lose electron density.

resulting hybridization for the C−H bonds was close to sp², and in fact the properties of these bonds strongly resemble those of ethylene (Table 1).

A convincing demonstration that cyclopropane has bent bonds is found in X-ray crystallographic studies of cyclopropane derivatives.[11] Here, the deformation density is always found outside the line of centers between carbons. The same is found using the theoretically calculated deformation densities (Figure 2). As a result of the formation of bent bonds, the nominal C−C bond length is unusually short (1.512 Å).[12]

The bent bonds are responsible for many of the properties of cyclopropanes. They are readily cleaved by electrophiles, and in the case of protons, both edge- and corner-protonated ions have been considered as intermediates.[13] Protonated cyclopropanes have also been shown to be intermediates in some skeletal rearrangements of carbocations.[13]

The most striking example of an interaction with an electron deficient center is found with the cyclopropylcarbinyl cations. Here, the preferred conformation is **A** ("bisected") in which the empty p orbital is aligned with the bent C−C bonds of the cyclopropane
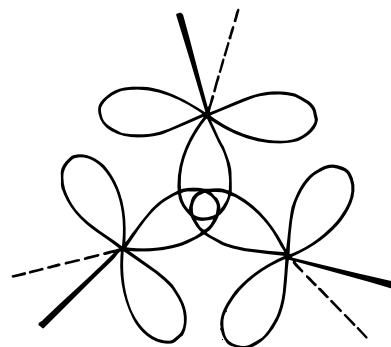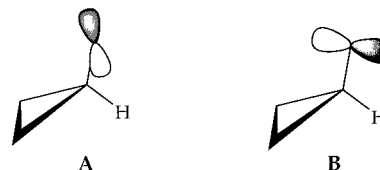
(11) Chalerabartin, P.; Seiler, P.; Dunitz, J. D.; Schuler, A.-D.; Szeimies, G. *J. Am. Chem. Soc.* **1981**, *103*, 7378. Boese, R.; Meibach, T.; deMeijere, A. *J. Am. Chem. Soc.* **1991**, *113*, 1743.
(12) Butcher, R. J.; Jones, W. J. *J. Mol. Spectrosc.* **1973**, *47*, 64.
(13) Saunders, M. *Acc. Chem. Res.* **1973**, *6*, 53.

Figure 3. Walsh orbitals for cyclopropane.

ring, and **B** is the rotational transition state.[14] In the

case of the cyclopropyldimethylcarbinyl cation, the rotational barrier has been measured to be 14 kcal/mol, indicating a very strong interaction.[15] Correspondingly, cyclopropylcarbinyl derivatives undergo rapid S_N1 solvolytic reactions.

These properties of the cyclopropyl compounds have also been attributed to interaction with the Walsh orbitals, as found in an alternative description of cyclopropane (Figure 3).[16] However, Honegger, Heilbronner, and Schmelzer have shown that the Walsh description cannot be transformed into the proper ground state description of cyclopropane via a unitary transformation, and therefore it does not correspond to the ground state of cyclopropane.[17]

Bent bonds have been found in a wide variety of cyclopropyl derivatives, and may be characterized by the bond path angle which is the angle between a pair of bond paths at the atom in question. Some of these data are summarized in Figure 4.[18] One of the unique observations is that the C−C bond emanating from the methylene groups of [1.1.1]propellane are slightly bent inward. The significance of this finding is not clear, but it has been suggested that bonding in the propellane is different from that of other cyclopropanes.[19]

Cyclobutanes

Cyclobutane has C−C bonds that are much closer to those of ordinary alkanes than those of cyclopropane. The angle between the bond paths at carbon are 96°, giving only a 7° deviation vs 19° for cyclopropane (Figure 4). Nevertheless, cyclobutane has about the same strain energy as cyclopropane. In addition,

(14) For a review on cyclopropylcarbinyl cations see: Wiberg, K. B.; Hess, B. A., Jr.; Ashe, A. J., III. In *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley: New York, 1972; Vol. 3.
(15) Kabakoff, D. S.; Namanworth, E. *J. Am. Chem. Soc.* **1970**, *92*, 3234.
(16) Walsh, A. D. *Nature* **1947**, *159*, 167, 712. *Trans. Faraday Soc.* **1949**, *45*, 179.
(17) Honegger, E.; Heilbronner, E.; Schmelzer, A. *Nouv. J. Chim.* **1982**, *6*, 519.
(18) Wiberg, K. B.; Bader, R. F. W.; Lau, C. D. H. *J. Am. Chem. Soc.* **1987**, *109*, 985, 1001.
(19) Jackson, J. E.; Allen, L. C. *J. Am. Chem. Soc.* **1984**, *106*, 591.
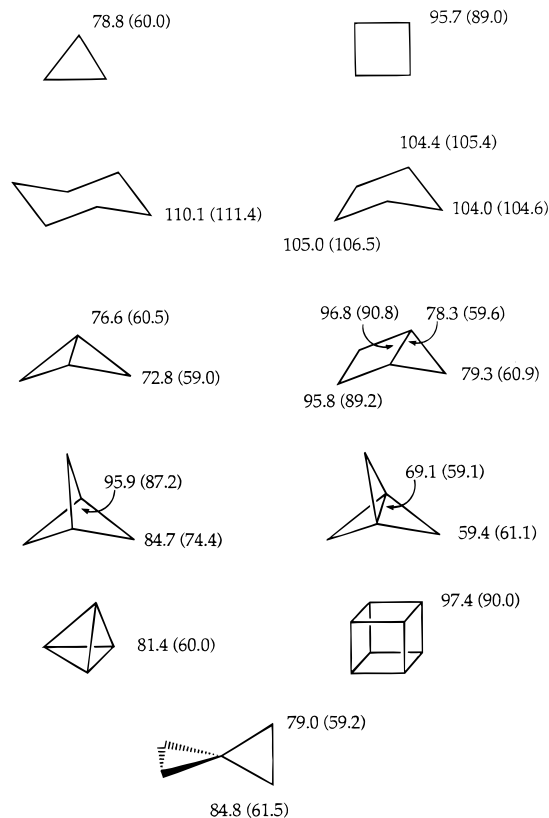
Figure 4. Bent bonds in cyclopropanes and cyclobutanes. The bond path angles are given, followed by the conventional angles in parentheses.

Figure 5. Structures of edge-protonated cyclopropanes and cyclobutanes based on 6-31G* wave functions. The distance from the carbons to the added proton is longer with cyclopropane than with cyclobutane because of the bent bonds.

it is not planar, but adopts a puckered conformation that has 88° conventional C—C—C bond angles. Whereas the C—C bonds of cyclopropane are shorter than normal as a result of the bent bonds, the C—C bonds of cyclobutane are longer than normal, probably as a result of cross-ring repulsion between the carbons.

The puckered conformation results from an effort to minimize torsional strain. The C—C bonds are eclipsed in the planar form, and the C—C—C—C dihedral angle is increased to 22° in the puckered form. If the eclipsing interaction is taken as 3 kcal/mol as in ethane, the decrease in torsional strain is about 0.9 kcal/mol per C—C bond.

Some of the properties of cyclobutane are compared with those of cyclopropane in Table 1. The [13]C—H NMR coupling constant for cyclobutane is close to that of an ordinary methylene group (125 Hz), and correspondingly the C—H bond dissociation[20] energy is much less than that for cyclopropane, and similar to that for propane (98 kcal/mol).

Two factors may be responsible for the longer than average C—C bond lengths in cyclobutane. It appears that the terminal atoms of a bond angle usually repel each other. This repulsion should be greater than found with the larger cycloalkanes because of the short 1—3 nonbonded distance. In addition, with ethane, rotation about the C—C bond from the staggered to the eclipsed conformation leads to only one significant structural change, an increase in the C—C bond length

by 0.014 Å,[21] and part of the increased C—C bond length in cyclobutane is probably due to the near-eclipsed conformation.

A major difference between cyclopropane and cyclobutane is found in their interaction with electrophiles. Whereas cyclopropane is readily cleaved by a variety of electrophilic reagents, cyclobutane is essentially inert, and in this way it behaves as an ordinary alkane. Again, this is related to the bending of the C—C bonds which is large in cyclopropane and small in cyclobutane. As a result, if an electrophile were to attack the C—C bond of cyclopropane, it could overlap the bent bond at a greater distance from the carbons than in the case of cyclobutane. This would minimize nuclear repulsion in the protonated species (Figure 5). In addition, the C—C bonds of cyclopropane are intrinsically weaker than those of cyclobutane, and more is to be gained by forming a bond to an electrophile. Both factors are probably involved.

An interesting feature of the structure of puckered cyclobutane is that the methylene groups are tilted inward,[22] whereas steric considerations would suggest that they should be tilted outward. Bartell and Anderson pointed out that the bent bonds in cyclobutane would lead to this inward tilt if the methylene groups adopted local C_{2v} symmetry.[23]

Ethylene: Bent C—C Bonds?

Pauling[24] and Slater[25] have described the double bond in ethylene in terms of two bent bonds, whereas Hückel[26] described it in terms of σ and π bonds. At the HF theoretical level, these two descriptions are equivalent for one can be transformed into the other

(20) The bond dissociation energies of cyclopropane and cyclobutane have not been measured. The values given are based on CBS-Q calculations that have been found to reproduce known C—H bond dissociation energies with an rms deviation of only ±1 kcal/mol: Ochterski, J.; Petersson, G.; Wiberg, K. B. *J. Am. Chem. Soc.* **1995**, *117*, 11299.
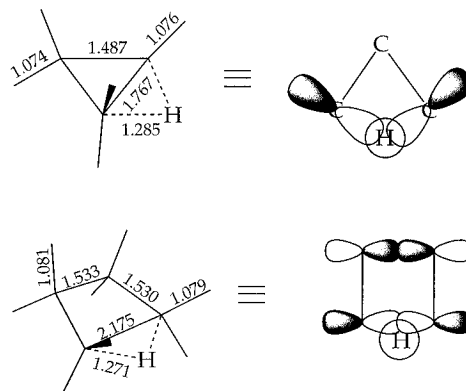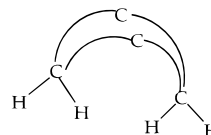
(21) Bader, R. F. W.; Cheeseman, J. R.; Laidig, K. E.; Wiberg, K. B.; Breneman, C. *J. Am. Chem. Soc.* **1990**, *112*, 6530.

(22) Meiboom, S.; Snyder, L. C. *J. Chem. Phys.* **1970**, *52*, 3857. Wright, J. S.; Salem, L. *J. Chem. Soc., Chem. Commun.* **1969**, 1370.

(23) Bartell, L. S.; Andersen, B. *J. Chem. Soc., Chem. Commun.* **1973**, 786.

(24) Pauling, L. *J. Am. Chem. Soc.* **1931**, *53*, 1367.

(25) Slater, J. C. *Phys. Rev.* **1931**, *37*, 481.

(26) Hückel, E. *Z. Phys.* **1930**, *60*, 423.

without a change in energy.[27] The question of which is the better description has been the subject of a number of valence-bond studies, with the more recent ones favoring the bent-bond description by a small amount.[28] A definitive answer to this question should make use of the best possible wave functions. In the work that has been done, which includes some electron correlation using a treatment related to GVB,[29] the calculated energies are only somewhat better than the HF limit (-78.063 H), and fall far short of a large basis set calculation with a good level of correction for electron correlation (QCISD/6-311+G(3df,2p) = -78.4642 H).

The natural orbitals from the latter calculation still retain the σ/π separation. There is at the present time no reason to think that a bent-bond description will give a lower energy. Although a conclusive statement cannot be made on the basis of the currently available information, it seems likely that we can continue to consider the σ/π and bent-bond descriptions of ethylene to be equivalent.

Bending Vibrations of Methane and the Sign of the C-H Bond Dipole

The sign of the C−H bond dipole in methane and other organic compounds has been the subject of much discussion.[30] In the case of methane, it centers around the dipole moments that are produced by the bending and stretching vibrations. These dipoles are directly related to the intensities of the infrared bands, the latter being proportional to the squares of the rate of change of the dipole moment with the change in atomic coordinates.

A study of the intensities of the infrared active antisymmetric stretching and bending modes of methane led to the following vibrationally induced dipoles:
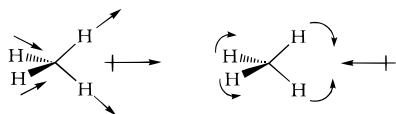

The stretching mode suggests a bond dipole with the sense C$^+$−H$^-$, whereas the bending mode suggests C$^-$−H$^+$. It has generally been assumed that the bending mode is relatively simple, and the stretching mode leads to a "charge flux" that leads to the apparent change in sign for the bond moment.[31] However, this view is incorrect.

Studies of bending modes by several groups have shown that there is incomplete orbital following in these modes.[32] Our studies have found that bending modes are characterized by the formation of bent bonds.[33] The bent bond provides the restoring force

for these modes. The reversed sign for the dipole formed in the bending mode results from the positively charged protons moving ahead of the overlap charge distribution, making it appear that the hydrogen was moving with a positive charge.

On the other hand, a calculation of the change in charge distribution for a methane C−H bond on stretching showed that the sign did not reverse in this process.[33] A comparison of a number of compounds such as ammonium ion, methane, and silane found that the stretching modes correctly indicated the sign of the bond moment.[33] Ab initio calculations lead to wave functions from which the charge distribution in a bond may, in principle, be calculated. However, it has not been so clear just how the calculation should be done.[34] The atoms in molecules approach (AIM)[2] using 6-31G** wave functions gives for methane a charge of -0.06 e per hydrogen, in accord with the conclusion from the dipole moment derivatives. Other methods such as the Mulliken population[35] and the natural population analysis[36] give the reversed sign. However, an analysis of the bond moment using the latter method agreed that the sign is C$^+$−H$^-$.[37]

The AIM populations at hydrogen decrease as the percents character in the bond increases, so that with acetylene, a reversed sign (C$^-$−H$^+$) is calculated. This is in good accord with the observed dipole moment derivative for the antisymmetric stretching mode:
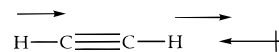
It is also possible to reverse the sign of the C−H dipole at a saturated carbon by an adjacent nonbonded negatively charged atom. In a study of cyclic lactones, evidence for a C−H···O stabilizing interaction was found, and an examination of the C−H group showed that the sign of the bond dipole had been reversed, leading to a hydrogen-bonding interaction.[38]

Substituted Methanes

Bent's rule states that electronegative atoms prefer to be bonded to orbitals having relatively high p character.[39] This rule has been found to have general applicability. Fluorine is the most electronegative of the elements, and in view of Bent's rule, one might expect a relatively small F−C−H bond angle in methyl fluoride. The increased p character in the C−F bond will lead to higher s character in the CH bonds. This should make the H−C−H bond angles change from the tetrahedral value of 109.5° to a larger value, on the way toward sp^2 (120°), thus reducing the F−C−H angle. However, the F−C−H angle is in fact 109°.[40] How can this be reconciled with the rule?

(27) Newton, M. D.; Switkes, E.; Lipscomb, W. N. *J. Chem. Phys.* **1970**, *53*, 2645.

(28) Palke, W. E. *J. Am. Chem. Soc.* **1986**, *108*, 6543. Schulz, P. A.; Messmer, R. P. *J. Am. Chem. Soc.* **1993**, *115*, 10925, 10938.

(29) Hay, P. J.; Hunt, W. J.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1972**, *94*, 8293.

(30) Cf. Lazzeretti, P.; Zanasi, R.; Raynes, W. T. *J. Chem. Phys.* **1987**, *87*, 1681.

(31) Decius, J. C. *J. Mol. Spectrosc.* **1975**, *57*, 348. Decius, J. C.; Mast, G. B. *J. Mol. Spectrosc.* **1978**, *70*, 294. Mast, G. B.; Decius, J. C. *J. Mol. Spectrosc.* **1980**, *79*, 158.

(32) Nakatsuji, H. *J. Am. Chem. Soc.* **1974**, *96*, 24. Figeys, H. P.; Berckmans, D.; Geerlings, P. *J. Mol. Struct.* **1979**, *57*, 271.

(33) Wiberg, K. B.; Wendoloski, J. J. *J. Phys. Chem.* **1984**, *88*, 586.

(34) For a comparison of the charges calculated via a variety of methods, cf. Wiberg, K. B.; Rablen, P. R. *J. Comput. Chem.* **1993**, *14*, 1504.

(35) Mulliken, R. S. *J. Chem. Phys.* **1962**, *36*, 3428.

(36) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735. Reed, A. E.; Weinhold, F.; Curtiss, L. A. *Chem. Rev.* **1988**, *88*, 899.

(37) Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1986**, *84*, 2428.

(38) Wiberg, K. B.; Waldron, R. F.; Schulte, G.; Saunders, M. *J. Am. Chem. Soc.* **1991**, *113*, 971. Hydrogen bonds of this type have also been found in other cases: Cf. Koch, U.; Popelier, P. L. A. *J. Phys. Chem.* **1995**, *99*, 9747.

(39) Bent, H. A. *Chem. Rev.* **1961**, *61*, 275.

(40) Clark, W. W.; DeLucia, F. C. *J. Mol. Struct.* **1976**, *32*, 29.

Table 2. Bond Path Angles for Methyl Derivatives with C_{3v} Symmetry

compound	angle	bond path	conventional	$\Delta\alpha$
MeN_2^+	HCN	101.17	104.98	3.81
$MeNH_3^+$	HCN	104.71	108.10	3.39
MeCl	HCCl	105.73	108.45	2.72
MeF	HCF	106.68	109.17	2.49
MeNC	HCN	107.42	109.62	2.20
MeCN	HCC	108.26	109.79	1.53
MeC≡CH	HCC	109.43	110.61	1.18
MeMe	HCC	110.25	111.20	0.95
$MeSiH_3$	HCSi	110.54	111.12	0.76
MeNa	HCNa	110.82	111.69	0.87
MeS^-	HCS	111.11	112.07	1.01
MeO^-Li^+	HCO	111.20	112.55	1.35
MeMgH	HCMg	111.64	112.13	0.49
MeBeH	HCBe	112.77	112.07	−0.70
MeLi	HCLi	113.37	112.56	−1.81
MeO^-	HCO	116.77	116.52	−0.25

Here, it is useful to locate the bond paths, and to examine the angle between the C–H and C–F bond paths at the carbon.[41] This leads to an angle of 106°, as expected on the basis of the rule. In a molecule with short bond lengths such as methane there is repulsion between the atoms attached to the carbon. The F···H repulsion leads to the formation of bent C–H bonds, and the apparent 109° bond angle.
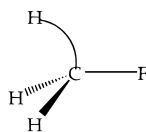
The bond paths have been examined for a number of methyl derivatives giving the data in Table 2.[41] The most electronegative substituent, N_2^+, leads to the smallest bond path angle, and inductively electron releasing substituents such as Li and O^- give relatively large bond path angles. The difference between the bond path and conventional angles may be attributed to steric interactions between the atoms attached to the central atom.

Bond Angles in Ammonia and Water

Water and ammonia are prototypes of compounds having lone pairs. The bond angles in these compounds have received much discussion.[42] There are two ways in which the angles may be considered. In one, the lone pairs are counted as groups, and the central atoms are taken as four-coordinate with a normal hybridization of sp^3. The smaller than tetrahedral angles are then postulated to result from the greater repulsion between the lone pairs (which are more concentrated near the nucleus) than between the hydrogens themselves. The other way is to consider that stabilization of the lone pairs could best be effected by placing them in orbitals having high s character, resulting in orbitals with high p character for the hydrogens. The limiting angle in this case would be 90° which is considerably smaller than the observed angles. Here, repulsion between the hydrogens would in part lead to the observed angles.

(41) Wiberg, K. B.; Breneman, C. M. *J. Am. Chem. Soc.* **1990**, *112*, 8765.

(42) Cf. Gillespie, R. J. *J. Chem. Educ.* **1963**, *40*, 295; **1970**, *47*, 18.

Table 3. Structures and Bond Path Angles for Water And ammonia, MP2/6-311G(2df,2pd)

|	water	ammonia
$r(MH)_{obs}$, Å	0.958	1.012
$r(MH)_{calc}$, Å	0.957	1.010
$\angle HMH_{obs}$, deg	104.5	106.7
$\angle HMH_{calc}$, deg	104.2	107.1
$\angle HMH_{bond\ path}$, deg	101.7	105.5

Information bearing on the interactions in these molecules may be obtained by calculating the bond path angles using wave functions that correctly reproduce the observed angles. Calculations at the MP2/6-311+G(2df,2pd) level gave the results shown in Table 3. It can be seen that the bond point angles are smaller than the observed angles, indicating that H···H nonbonded repulsion is an important factor in determining the observed bond angles. The smaller bond path angle for water than for ammonia could result from the need to stabilize two lone pairs with s character in water whereas there is only one in ammonia.

Gauche Effect

It is known that the lowest energy conformer of 1,2-difluoroethane has the gauche arrangement, and that the anti conformation is higher in energy by 1 kcal/mol.[43] This is in contrast to 1,2-dichloroethane, which prefers the anti conformation.[44] Even here, the difference in energy is reduced to almost zero in polar solvents that stabilize the gauche form having a dipole moment over the anti form, which has a zero moment.[45] What is the origin of this preference for the gauche form?

The changes in energy on rotation about the C–C bond are similar to those found for *n*-butane (Figure 6).[46] The syn conformer of the difluoride has a higher energy because of the repulsion between the two C–F dipoles. The anti form of the difluoride appears to be less stabilized than in the case of butane. Is there a factor that would lead to destabilization of the anti conformer?

If one examines the bond paths, it is found that in the anti form the C–C bond paths are bent in opposite directions, whereas in the gauche form they are bent in essentially the same direction (cf. the dashed lines below).[47] This should lead to reduced overlap and a weaker C–C bond in the anti form as compared to the gauche form.
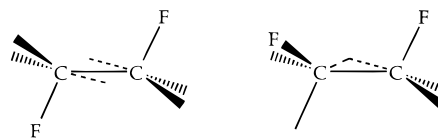
The same trend is found with the 1,2-difluoroethenes, where the cis isomer is more stable than the trans isomer. It has been found that in ab initio MO

(43) Durig, J. R.; Liu, J.; Little, T. S.; Kalaskinsky, V. F. *J. Phys. Chem.* **1992**, *96*, 8224.

(44) Tanabe, K. *Spectrochim. Acta* **1972**, *A28*, 407 and references therein.

(45) Wiberg, K. B.; Keith, T. A.; Frisch, M. J.; Murcko, M. *J. Phys. Chem.* **1995**, *99*, 9072.

(46) Wiberg, K. B.; Murcko, M. A. *J. Phys. Chem.* **1987**, *91*, 3616.

(47) Wiberg, K. B.; Murcko, M. A.; Laidig, K. E.; McDougall, P. J. *J. Phys. Chem.* **1990**, *94*, 6956.
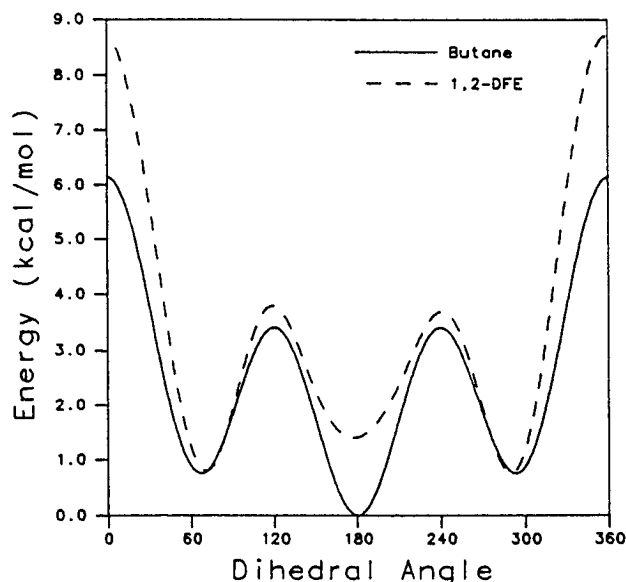
Figure 6. Rotational profiles for the C–C bonds of 1,2-difluoroethane and of *n*-butane. The energies of the gauche rotamers were arbitrarily set equal.

calculations the use of basis sets such as 6-31G* leads to the incorrect conclusion that the trans isomer is more stable than the cis isomer, and it is only by the addition of diffuse functions (+) that the correct relative energies are found. Then, one may ask what is the effect of the diffuse functions on the charge distribution that leads to the correct ordering? This question is easily answered by constructing maps of the charge density obtained using the 6-31+G* and 6-31G* basis sets, and examining the difference between them. The result is shown in Figure 7. It can be seen that the region that gains electron density on the addition of diffuse functions corresponds to a normal bent bond, whereas the corresponding region for the trans isomer is distorted in the direction suggested by the above bond path analysis.

The type of bond bending found with *anti*-1,2-difluoroethane also may be found in some organic compounds with trans-fused rings, such as *trans*-bicyclo[5.1.0]octane, and has been described as a twist–bent bond.[48]

Conclusions

Bent bonds are frequently found in organic compounds, and can result either from the formation of small rings or from nonbonded repulsion between the terminal atoms that form a bond. It is often possible to gain information about intramolecular interactions by examining the bond paths and bond path angles.

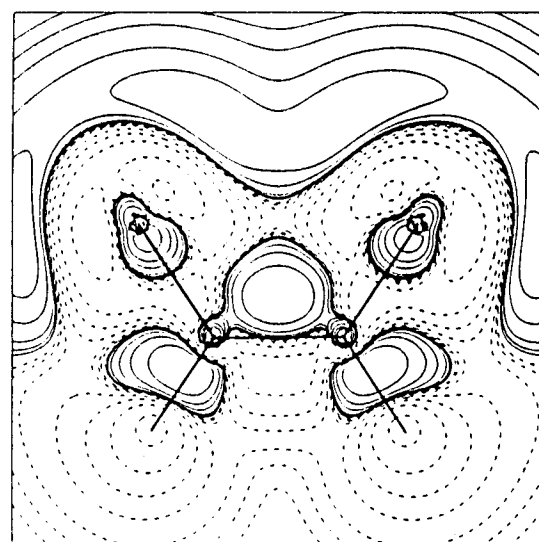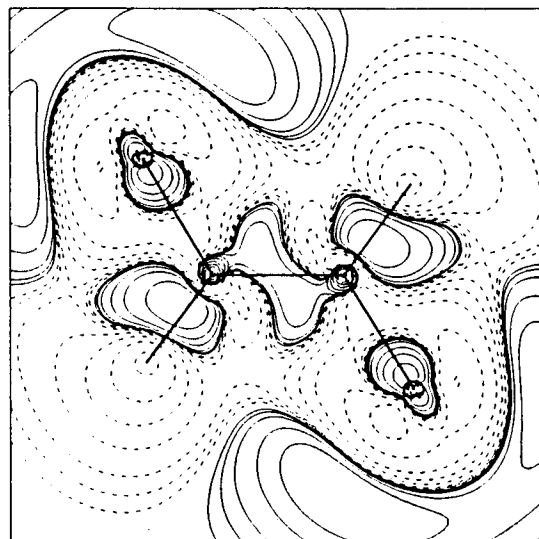(48) Dixon, D. A.; Gassman, P. G. *J. Am. Chem. Soc.* **1988**, *110*, 2309.

Figure 7. Difference between the electron density maps for *trans*-1,2-difluoroethene (top) using the 6-31+G* and 6-31G* basis sets, and for *cis*-1,2-difluoroethene (bottom) using the same basis sets. The solid contours indicate regions into which electron density has been moved via the addition of diffuse functions to the basis set.

The latter are readily derived from high-level ab initio calculations, and may also be derived from the charge density distribution maps that are obtained in X-ray structure determinations.