Self-Consistent Changes of Geometrical Parameters: Experiment and Theory

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It is well-known that the geometry of a molecule of any complexity can be unequivocally described by three types of parameters which are normally considered to be independent, i.e., internuclear distances (r), bond angles (α), and dihedral or torsional angles (τ).[1,2] In spite of the formal independence of these parameters in a properly chosen coordinate system, a change in one of them in a molecule may result in changes of others. This is readily illustrated in a quantum chemical calculation. Suppose an equilibrium structure is established for a molecule and the r_e, α_e, and τ_e parameters are found. Now, if the theorist changes one of the parameters by a small increment and fixes it, a subsequent refinement will invariably give slightly different values for all of the remaining parameters in the molecule, with the largest differences generally found in the near neighborhood of the imposed change.

A number of questions arise regarding the nature of such geometry interrelationships. For a given change of one type of parameter, say a bond distance, can we predict the changes (size and magnitude) induced in neighboring parameters? What is the general functional form of all the binary combinations, e.g., r/α, r/τ, and α/τ? How different are such changes for different molecules at the quantitative level? Are there qualitative differences?

It is not our intention to discuss these problems from the viewpoint of the relationships between intramolecular potential functions and structural trends, although such a presentation is logical, important, and interesting. Such a relationship has been known in principle for a long time, and it has been taken into account in force field analyses by including some specific cross terms, e.g., stretch/bend and torsion/stretch/bend constants. Rather, the purpose of this Account is to collect some relevant material to furnish a data base from which answers can be sought for the questions posed. There are two basic types of information available for this purpose, experimental and computational. The relevant experimental data consist of equilibrium or near-equilibrium geometric structures of a very large number of molecules amassed from X-ray diffraction of crystals, electron diffraction

from gases, microwave spectroscopy, and a variety of other techniques. These data are valuable because of their quantity, but the quality differs greatly and care must be exercised in their use. They are also limited, in general, to near-equilibrium geometries so that changes in a given parameter can be observed only by intercomparison between structures of different molecules. The computational data are more limited in quantity, but they have the advantage that, in a single molecule, the value of a given parameter can be constrained at a variety of values and the adjustments of the related parameters can be followed by their relaxation in a further refinement. Some results from the existing literature and some new results are summarized below.

Bond Length/Bond Angle Relationships

A search of the literature has revealed a number of isolated studies in which the relationship between a bond length and an adjacent bond angle is investigated. The range of this information is indicated in Table 1a, which shows both experimental and computational studies displayed in chronological order. Among the cases considered, two particular ones deserve comment. The first one, by Jorgensen, Schreiber, and co-workers,[6] refers to Si–O and C–O bond length/C–O–Si bond angle dependence. The authors have analyzed X-ray data for 127 silyl ether molecules and, in parallel, have performed ab initio calculations for some model systems that confirmed the established experimental correlations. Hoffmann and coworkers[9] have made an analogous study of transition-metal complexes with multiple metal–

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(3) Hargittai, I. *Z. Naturforsch, Teil A* **1979**, *34*, 755.
(4) (a) Irngartinger, H.; Jahn, R.; Rodewald, H.; Paik, Y. H.; Dowd, P. *J. Am. Chem. Soc.* **1987**, *109*, 6547. (b) Dowd, P.; Irngartinger, H. *Chem. Rev.* **1989**, *89*, 985.
(5) Schleyer, P. v. R.; Bremer, M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1226.
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(7) Davis, M. J.; Rankin, D. W. H.; Cradock, S. *J. Mol. Struct.* **1990**, *238*, 273.
(8) Rathna, A.; Chandrasekhar, J. *J. Mol. Struct. (THEOCHEM)* **1991**, *228*, 249.
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Table 1. "Bond Length/Bond Angle" Relationships Established Empirically (Based on Experimental Data Herein) and/or Theoretically[a]

relationship	empirical	theoretical	year	ref
	type			
a. Literature Data				
1. S=O/∠O=S=O	+9		1979	3
2. C−C/∠C−C−C	+(4)		1987	4
3. C−C/∠C−C−H		+(1)	1989	5
4. Si−O/∠C−O−Si	+(127)	+(1)	1990	6
5. C−O/∠C−O−Si	+(127)	+(1)	1990	6
6. P−F/∠F−P−F	+(25)		1990	7
7. C−C/∠C−C−C		+(20)	1991	8
8. A−A/∠A−A−X	+(350)	+(6)	1993	9
(A = Cr, Mo, W, Re, Rh)				
9. N−N/α_av[b]	+(11)	+(6)	1993	10
b. Present Data				
1. C−C/∠C−C−C	+(13)	+(1)	1991	13, 14
2. C−H/∠H−C−H	+(9)	+(1)	1992	14, 15
3. C−C/∠C−C−H		+(1)		16
C=C/∠C=C−H		+(1)		
C≡C/∠C≡C−H	+(10)	+(1)		
4. A−A/∠A−A−A		+(3)		17
A−H/∠H−A−H		+(3)		
(A = C, Si, Ge)				
5. A−X/∠X−A−X		+(22)	1992	18, 19
(A = C, Si, N, P, O, S)				
6. Si−O/∠C−O−Si	+(7)	+(1)	1992	20
Si−O/∠Si−O−Si	+(5)	+(1)		

[a] Every relationship established is shown by a plus (+), with the number of molecules investigated given in parentheses. [b] The average of the bond angles at nitrogen in sesquibicyclic hydrazines.

metal bonds in more than 350 compounds. We think that this approach is an effective one, and we attempt to follow their methodology in the present work.

Our contributions are summarized in Table 1b. Our interest started from an attempt to sort systematically the C−C bond lengths found in various compounds[11,12] and to answer the question, Do C−C bond lengths depend on the size of the adjacent C−C−C bond angle?[13] We have found an interesting series of molecules studied by X-ray crystallography which exhibit gradual variations in bond angles around an sp³ carbon, with the ethane molecule serving as a standard:
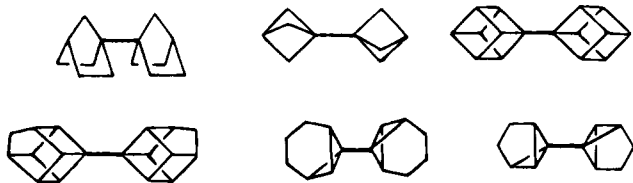
References for the individual molecules can be found in the publications cited in Table 1b.

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(13) Mastryukov, V. S. *J. Mol. Struct.* **1991**, *263*, 343.
(14) Mastryukov, V. S.; Schapin, I. Y. *Vestn. Mosk. Univ., Ser. 2: Khim.* **1991**, *32*, 569.
(15) Schapin, I. Y.; Mastryukov, V. S. *J. Mol. Struct.* **1992**, *268*, 307.
(16) Mastryukov, V. S.; Boggs, J. E. *Mol. Struct.* **1993**, *300*, 141.
(17) Mastryukov, V. S.; Samdal, S. *J. Mol. Struct.* **1992**, *268*, 395.
(18) Alcolea Palafox, M.; Boggs, J. E.; Mastryukov, V. S. *14th Austin Symp. Mol. Struct., Austin, TX, March 2−4,* **1992**, 76.
(19) Mastryukov, V. S.; Alcolea Palafox, M.; Boggs, J. E. *J. Mol. Struct. (THEOCHEM)* **1994**, *304*, 261.

Our initial analysis of these data was carried out in terms of the concept of orbital hybridization,[13] using cos² α as the independent variable, where α = ∠C₁−C₂−C₃, with C₁−C₂ being the bond in question. Later, however, we preferred the simplest description using the angle α itself as the variable, yielding the linear relationship

$$C{-}C = 2.0822 - 0.0049\alpha \qquad (\alpha = \angle C{-}C{-}C) \tag{1}$$

(Distances are always in angstroms and angles in degrees.)

(For a modification of eq 1, see ref 21.) We have previously noted a similar nonsensitivity of experimental data to the variable used in the correlation in a study of the ionization potentials (IP) of a family of oxygen heterocycles, $(CH_2)_nO$ ($n = 2, 3, 4$) as a function of bond angles.[22] All the correlations studied, which included use of α, cos α, cos(α/2), and ctg²(α/2) as variables, were shown to be statistically indistinguishable. This implies that the simplest version, IP = f(α), may be used.

Subsequently, we repeated[16] the computations on ethane done by Schleyer and Bremer[5] with a more complete basis set (6-31G*) and for a wider range of bond angles. We found the same type of dependence: the C−C bond length gradually decreases (with a certain curvature) while the C−C−H bond angle increases. The part of the angular range which is important in naturally occurring structures (110° ≤ ∠C−C−H ≤ 130°), however, looks quite linear with the corresponding numerical data as follows: C−C = 1.5347 Å at ∠C−C−H = 110°, 1.4854 Å at 120°, and 1.4515 Å at 130°. A straight line through these three points was obtained by least-squares and expressed by

$$C{-}C = 1.9897 - 0.00416\beta \qquad (\beta = \angle C{-}C{-}H) \tag{2}$$

Equation 1 was derived from experimental observations on many molecules while eq 2 came from computed distortions of a single molecule, yet lines corresponding to the two equations, shown in Figure 1, lie close to each other within experimental limits. This suggests that the C−C distance in hydrocarbons is dependent on the adjacent bond angle in a manner that does not depend on whether that angle connects to another carbon or to a hydrogen atom. Furthermore, it indicates the equivalence of data obtained by computations at distorted geometries and that obtained by comparison of many near-equilibrium experimental structures.

Similarly, the C−H distances measured by gas electron diffraction in nine cycloalkanes have been shown[14,15] to be correlated with the H−C−H bond

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(21) Schapin, I. Y.; Mastryukov, V. S. *Vestn. Mosk. Univ., Ser. 2: Khim.* **1992**, *33*, 235.
(22) Pupyshev, V. I.; Matryukov, V. S. *Zh. Fiz. Khim.* **1992**, *66*, 1922.
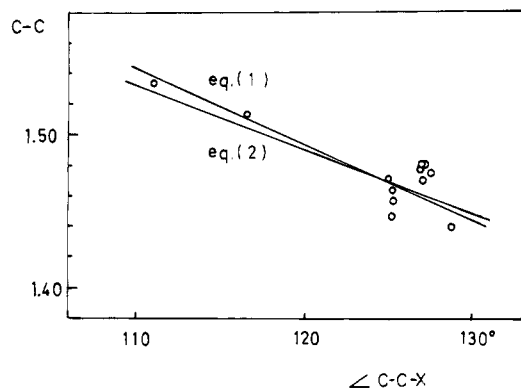(23) Wiberg, K. B.; Ellison, G. B.; Wendoloski, J. J. *Am. Chem. Soc.* **1976**, *98*, 1212.

Figure 1. Correlation of the C−C bond lengths with bond angles C−C−C (top) and with C−C−H bond angles (bottom). Equation 1 refers to the experimental data for molecules shown in the text. Equation 2 refers to the theoretical results for ethane.

Figure 2. The Si−Si and C−C bond lengths as functions of the corresponding bond angles in the Si_3H_8 and C_3H_8 molecules (ab initio results).

angles. The relationship can be described by

$$C-H = 1.2703 - 0.00146\gamma \qquad (\gamma = \angle H-C-H)$$
$$(3)$$

As in the case of C−C bond lengths, it proved possible to find an analogous expression from computational results, specifically, the data reported by Wiberg et al., who studied different deformations in the CH_4 molecule:[23]

$$C-H = 1.1818 - 0.0009\gamma \qquad (\gamma = \angle H-C-H)$$
$$(4)$$

One may note, however, that while the straight lines 3 and 4 are roughly parallel, they are shifted with respect to each other. This is not accidental, and the shift demonstrates the different physical meaning of C−H internuclear distances measured experimentally and predicted by quantum chemistry. While the electron diffraction experiment measures a vibrationally averaged distance denoted as r_g, the computed value refers to the vibrationless equilibrium state denoted as r_e. These distances are approximately related[1] by

$$r_e = r_g - (3/2) au^2 \qquad (5)$$

where a is the Morse constant and u is the mean amplitude of vibration. According to this equation, r_g should be larger than r_e, and this is the relationship found between eqs 3 and 4. From the slope of the straight lines 3 and 4, one may infer that an opening of the H−C−H bond angle by 1° produces a shortening of the C−H distance by 0.001 Å. The analogous change for C−C bonds with either the adjacent C−C−C or C−C−H angle is five times larger, as shown by eqs 1 and 2.

Most of the previous data was accumulated from saturated compounds. At the outset, it was not clear whether unsaturated compounds would follow the same pattern or present some new features. Accordingly, calculations were performed[16] for the $CH_2=CH_2$ and $CH\equiv CH$ molecules[16] for a series of different fixed C−C−H bond angles. The C=C and C≡C distances were found to behave in a manner analogous to the C−C distances, gradually shortening as the C−C−H bond angle increased in the range 90−180°. A quali-
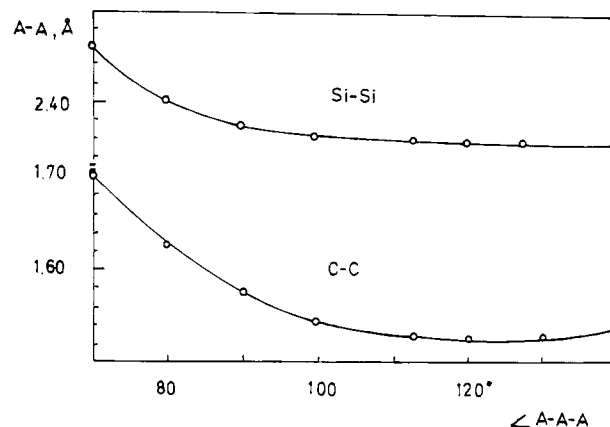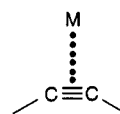
tative agreement with this finding exists for the complexes formed by acetylene and its derivatives with transition metals (see ref 24 and references therein). In these complexes, acetylene is no longer a linear molecule, being bent with a stretched C≡C bond,

in accord with our theoretical predictions.

The earlier computational studies of bond length/bond angle relationships for the C−H and C−C bonds used as a model the CH_4[23] and C_2H_6[5] molecules. We decided to find a model to investigate simultaneously both C−C/∠C−C−C and C−H/∠H−C−H relationships. It was also deemed of interest to extend these calculations to other elements of group 14. For this reason, the A_3H_8 molecules (A = C, Si, Ge) were selected and studied.[17] The A−H/∠H−A−H relationships found were in conformity with those already known for C−H and Si−H.[13-15] A new phenomenon was found, however, for the A−A/∠A−A−A relationship (see Figure 2). While the Si−Se and Ge−Ge distances (not shown in Figure 2) varied traditionally, the C−C/∠C−C−C relationship showed a minimum in the vicinity of a C−C−C bond angle of about 120°. Although the minimum itself was very shallow, its existence was a novelty not foreseen from previous studies. This difference from other r/α relationships provided further motivation for additional study.

Ab initio self-consistent-field (SCF) studies with the 6-31G* basis sets have been carried out[18,19] for a series of molecules of general formulas AH_2X_2 (A = C, Si), AX_3 (A = N, P), and AX_2 (A = O, S). The ligands were H, CH_3, Cl, and F, and in total 22 molecules were studied. The results obtained may be summarized as follows. All the A−X/∠X−A−X relationships can be classified into two groups: those showing a traditional relationship characterized by a monotonic decrease in bond length with enlargement of the adjacent angle and those, which may be called nontraditional, showing a minimum in the curve. Schematically, both types of dependency are illustrated in Figure 3 for

(24) Hoffman, D. M.; Hoffmann, R.; Fisel, C. R. *J. Am. Chem. Soc.* **1982**, *104*, 3858.
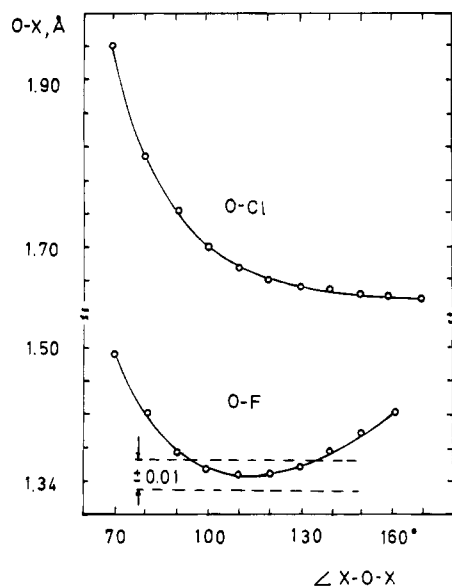
Figure 3. The O–Cl and O–F bond lengths as a function of the bond angle at oxygen in the OCl_2 and OF_2 molecules (ab initio results).

Table 2. Chemical Bonds Formed by a Central Atom from Group 14, 15, and 16 Elements[a]

14	15	16
C–H	N–H	O–H
C–Cl	N–Cl	O–C
C–F	N–Cl	O–Cl
	N–F	**O–F**
Si–H	P–H	S–H
Si–Cl	P–C	S–C
Si–F	P–Cl	S–Cl
	P–F	S–F

[a] Bold letters refer to those cases where the bond length/bond angle relationship has a minimum.

O–Cl and O–F bonds. The information obtained is summarized in Table 2, from which it can be seen that the numbers of traditional and nontraditional cases are nearly equal, at 10 and 12, respectively.

The previous study showed that the so-called non-traditional behavior cannot be considered to be a rare phenomenon since it occurred in more than 50% of the cases studied. The only difference was that the phenomenon was found with computational methods and no accompanying experimental evidence. A suitable system in which to look for such experimental confirmation would be the compilation[7] of P–F/∠F–P–F relationships cited in Table 1a from experimental data for 25 molecules. Using a least-squares method, we fit these data to a quadratic equation, yielding

$$P-F = 5.2886 - 0.073002\delta + 0.000358\delta^2$$
$$(\delta = \angle F-P-F) \quad (6)$$

We then applied the same type of polynomial to our own data on the PF_3 molecule to give

$$P-F = 2.4594 - 0.071736\delta + 0.000839\delta^2$$
$$(\delta = \angle F-P-F) \quad (7)$$

Graphical display of eqs 6 and 7 shows them[19] to be shifted with respect to one another in a way expected from the difference between the electron diffraction r_g parameters and the ab initio r_e values (see eq 5 above). The important feature of eqs 6 and 7 is that

they both have minima and that the positions of the minima are nearly identical at 101.9° and 103.4°, respectively, as found by differentiation. This, again, illustrates the qualitative equivalence of the two methods we have adopted to investigate bond length/bond angle relationship: the comparison of near-equilibrium experimental data on many molecules or computational structure refinement of model compounds with one parameter (in these cases a bond angle) constrained to assume a series of values.

We conclude this section by presenting two more empirical equations deduced for silyl ethers, eq 8, and disiloxanes, eq 9, studied by gas-phase electron diffraction.[20] Note that, for these bond parameters, the relationship is linear.

$$Si-O = 2.4839 - 0.00689\epsilon \quad (\epsilon = \angle Si-O-C)$$
$$(8)$$

$$Si-O = 1.9838 - 0.00244\zeta \quad (\zeta = \angle Si-O-Si)$$
$$(9)$$

Torsion Angle/Bond Length and Torsion Angle/Bond Angle Relationships

To our knowledge, there are no systematic empirical analyses of experimental studies relating the parameters in question, τ/r and τ/α. Partly, this lack can be explained by the fact that the changes of bond lengths and bond angles upon a change of torsional angle are not large and, therefore, not easily measurable. Gas electron diffraction, in particular, has great difficulty in measuring such small differences, and all conformational studies made by this method alone have been based on the assumption that conformers of a given molecule have structures identical except for a torsional angle.[1] On the other hand, it is well-known that solid-state methods are not entirely suitable for study of conformational phenomena because of the probable perturbation of torsional angles by crystal forces. Accordingly, such a powerful method as X-ray crystallography cannot shed light on this problem. Therefore, the only experimental technique which is likely to produce relevant information is microwave spectroscopy. Such studies would be very arduous, requiring analysis of the spectra of the different coexisting conformers of large numbers of isotopomers for a range of related molecules.

The opposite situation is characteristic of theoretical chemistry, in which there is a long and distinguished history of studies of internal rotation, and the number of publications is very large. Many quantum chemical studies (we mention only a few of them[25-33] while more than 20 additional references can be found in our

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(30) Schleyer, P. v. R.; Kaupp, M.; Hampel, F.; Bremer, M.; Mislow, K. *J. Am. Chem. Soc.* **1992**, *114*, 6791.

(31) Gorse, D.; Cavagnat, D.; Pesquer, M.; Lapouge, C. *J. Phys. Chem.* **1993**, *97*, 4262.

(32) Liu, R.; Zhou, X. *J. Phys. Chem.* **1993**, *97*, 4413.

(33) Janoschek, R.; Csizmadia, I. G. *J. Mol. Struct.* **1993**, *300*, 637.

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papers[34,35]) find that treating internal rotation as a one-dimensional problem consisting of rotation of two rigid entities is a poor approximation and confirm the statement by Meyer and Wilson[36] that internal rotation "involves sizable deformations of the frame and/ or the top."

A great many of the existing quantum chemical studies of internal rotation concern rotation around C—C and C—X (X = O, N, S) bonds; therefore, it was decided to repeat some of them for consistency of methodology and to extend these studies to other types of linkages such as

B—B	C—C	N—N	O—O
	Si—Si	P—P	S—S
	Ge—Ge		

Hydrogen, chlorine, and fluorine acted as ligands in our studies, and a total of 24 molecules were analyzed.[34,35] This new material together with the literature data allowed us to formulate an approximate rule, which in turn allowed us to classify the limited experimental data available.[37]

Consider the simplest system, XA—AX,
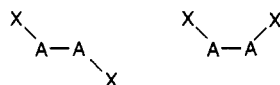
in which internal rotation is possible. It contains only three geometrical parameters that can change during internal rotation, and we will focus on the same three geometrical parameters in all other molecules. These are the central bond length A—A, the bond length A—X characteristic of the ligand, and the A—A—X bond angle. The convenience of this choice is that these three parameters are common to all molecules with the general formulas XA—AX, X_2A—AX_2, and X_3A—AX_3.[29-30]

Analysis of the available experimental microwave data[2a] revealed 11 molecules existing in two conformers, each being characterized by its complete substitution (r_s) structure. In each case, the structure of the more stable conformer was chosen as the reference from which to calculate the changes in the geometrical parameters during internal rotation. We are not interested in the absolute values, but rather in the changes. Thus information from experiment and from theory can be combined to obtain a complete characterization of structural variations during the internal motion, the equilibrium data coming from experiment and the pattern of intermediate structural changes from computation.

From the data described above, we can search for any general behavior that can be found in the pattern of changes of A—A and A—X bond lengths and of the A—A—X bond angle as the torsional angle is changed to convert the more stable to the less stable conformer. Unfortunately, we have been unable to find any such completely general patterns and could only settle for

Table 3. Geometrical Parameters of Two Different Conformers of 1-Butene and Ethylfluorosilane Studied by Microwave Spectroscopy

molecule	parameter	major conformer (1)	second conformer (2)	difference Δ_{2-1}	ref
$CH_2=CHCH_2CH_3$	C_2-C_3	1.493(8)	1.507(10)	+0.014	38
	$C_1=C_2$	1.342(9)	1.336(8)	−0.006	
	C_3-C_4	1.536(12)	1.536(6)	0.0	
	∠C=C—C	125.4(2)	126.7(4)	+1.3	
	∠C—C—C	112.1(2)	114.8(5)	+2.7	
$CH_3CH_2SiH_2F$	Si—C	1.847	1.853	+0.006	39
	Si—F	1.592	1.612	+0.020	
	C—C	1.534	1.534	0.0	
	∠C—C—Si	114° 11'	111° 50'	−2° 17'	
	∠C—Si—F	109° 31'	109° 30'	−0° 1'	

an approximate rule which was expected to be valid in most cases.[31] That rule stated, *In the most stable conformer, the A—A bond length is shorter and the A—A—X bond angle is smaller while the A—X bond length is longer than in the less stable conformer.* Later study suggested that the part of this rule concerning the ligand bond, A—X, shows the least reliable agreement with experiment, probably because this bond length normally varies only very slightly between different conformers. Most of the geometrical variation is exhibited by the central A—A bond and the adjacent angles.

A detailed comparison of the above rule with available experimental data was made elsewhere,[37] and we will confine our discussion to two selected examples shown in Table 3 and to a summarizing statement. An inspection of the data collected in Table 3 helps one to see the magnitude of the effect and compare it with the experimental errors (unfortunately not always reported). Note that, even for microwave spectroscopy, the magnitude of the measured effect in about half the cases is less than the sum of the individual errors. Taking into account the experimental errors, one can see that the A—A bond length was found to be the shortest in the more stable conformer for all of the 11 cases, while there were two deviations from our approximate rule among the 22 cases (9%) for the A—A—X bond angle and 10 discrepancies among 24 cases (42%) for the A—X bond length.

Application of the above approximate rule may be extended to the case of a molecule existing as only one conformer but exhibiting vibrational torsional excitation. In such a case, departure from the minimum energy configuration frequently causes the same three consequences in the geometrical parameters. As an illustration, Iijima[40] studied the CH_3CD_3 molecule in its torsionally excited states and found that the C—C bond stretches and the C—C—H bond angle opens upon torsional excitation. There is no experimental information about changes in the C—H and C—D distances in this molecule. These observations are in accord with the calculations by Schleyer et al.,[30] who report the geometrical parameters for ethane and ethane-like molecules for staggered and eclipsed conformations at high levels of theory.

Concluding an examination of all the empirical relationships, one should consider the magnitude of the effects found. For this reason we give summarizing information in Table 4. For every relationship, the ranges of the variable parameters are presented

(34) Mastryukov, V. S.; Boggs, J. E.; Samdal, S. *J. Mol. Struct.* **1993**, *288*, 225.

(35) Mastryukov, V. S.; Boggs, J. E.; Samdal, S. *J. Mol. Struct. (THEOCHEM)* **1993**, *283*, 199.

(36) Meyer, R.; Wilson, E. B. *J. Chem. Phys.* **1970**, *53*, 3969.

(37) Mastryukov, V. S.; Khristenko, L. V.; Pentin, Y. A. *Zh. Obshch. Khim.*, in press.

(38) Kondo, S.; Hirota, E.; Morino, Y. *J. Mol. Spectrosc.* **1968**, *28*, 471.

(39) Hayashi, M.; Imachi, M.; Oyamada, M. *J. Mol. Struct.* **1981**, *74*, 97.

(40) Iijima, T. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 2311.

Table 4. Ranges of the Geometrical Parameter Change for Different Empirical Regularities[a]

relationship	Δr (Å)	$\Delta\alpha$ (deg)	ref
S=O/∠O=S=O	0.04	5	3
C–C/∠C–C–C	0.10	26	4
Si–O/∠C–O–S	0.20	40	6
C–O/∠C–O–Si	0.15	40	6
P–F/∠F–P–F	0.03	10	7
AA/∠AAA (A = Cr, Mo, W, Re, Rh)	0.14	6	9
N–N/α_{av}	0.05	5	10
C–C/∠C–C–C	0.10	18	13
C–H/∠H–C–H	0.02	10	15
Si–O/∠C–O–Si	0.10	12	20
Si–O/∠Si–O–Si	0.08	13	20
τ/r, α	0.03	7	37

[a] Individual ranges for each relationship were averaged (arithmetic mean) to give the following values. Relationship r/α: Δr_{av} = 0.09 Å and $\Delta\alpha_{av}$ = 17°. Relationship τ/r,α: Δr_{av} = 0.01 Å and $\Delta\alpha_{av}$ = 3°.

together with the corresponding average values. Comparison of these average values shows that, in the τ/r and τ/α relationships, the change in bond distance (0.01 Å) is about 1 order of magnitude less than the corresponding change (0.09 Å) for the r/α relationship. Similar differences of bond angles, 3° (τ/r,α) and 17° (r/α), amount to a ratio of approximately 6 times.

Discussion

We begin with a consideration of the bond length/bond angle relationship. Experimental material accumulated so far is based on approximately 500 and 55 molecules studied by X-ray crystallography and electron diffraction, respectively. The ab initio calculations are available for about 40 molecules. In total, 35 types of chemical bonds were analyzed, showing their dependence on adjacent bond angles. The most interesting question that arises concerns the existence of a model which can explain the phenomenon.

Model. In the stereochemistry of organic compounds there is the well-known Stoicheff's rule[41] showing a shortening of C–C bond distances influenced by adjacent multiple bonds. The material collected in this paper presents evidence that a similar shortening of the C–C bond length in a *saturated* system accompanies an increase in adjacent bond angle. It is of interest to compare the two generalizations. Stoicheff's rule was originally formulated in terms of the number of atoms linked to the bond in question. We took the basic molecules used by Stoicheff and calculated the average bond angles around the carbon atoms in order to reduce both kinds of data to the same scale. The relevant data are displayed in Table 5. Treatment by least-squares resulted in an empirical relation (eq 10),

$$C–C = 1.73988 - 0.0020\eta \qquad (\eta = \angle C–C–X_{av})$$
$$(10)$$

which is graphically represented in Figure 4 along with the straight line corresponding to eq 1 which gives the C–C distance as a function of ∠C–C–C. One can see that the bond length/bond angle relationship is characterized by a much stronger slope. We have no explanation for this phenomenon.

(41) Stoicheff, B. P. *Tetrahedron* **1962**, *17*, 135.

Table 5. C–C Bond Lengths and the Adjacent Bond Angles Together with Their Average Values for Molecules Related to Stoicheff's Rule[a]

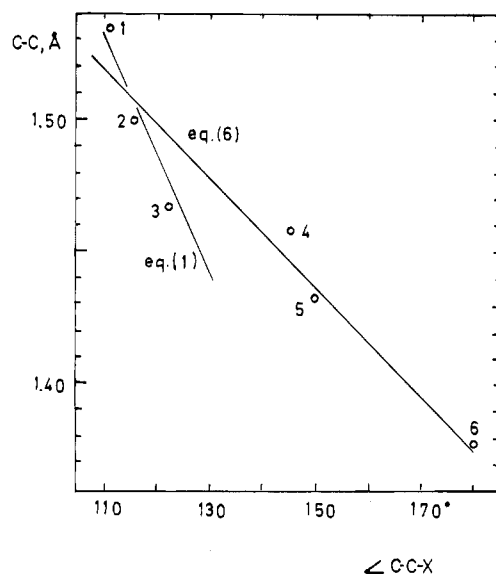| no.	molecule	C–C (Å)	∠CCC (deg)	∠CCH (deg)	∠CCX$_{av}$ (X = C, H)
1	CH_3CH_3	1.5351(1)		111.17(1)°	111.17(1)
2	$CH_3CH=CH_2$	1.501(4)	124.3(3)	116.7(5) 111.2(7)	115.85
3	$CH_2=CHCH=CH_2$	1.468(2)	124.3(1)	120.7(3)	122.5
4	$CH_3C\equiv CH$	1.4586(20)	180.0	111.17	145.6
5	$CH_2=CHC\equiv CH$	1.434(3)	123.1(5) 180.0	121.7(40)	149.58
6	$HC\equiv CC\equiv CH$	1.376(2)	180.0		180.0

[a] The geometrical data was taken from ref 2a.

Figure 4. C–C bond lengths as a function of the bond angles. The short line with a steeper slope refers to the deformation of angles only. The long line refers to Stoicheff's rule. The numbering of points is as follows: 1, ethane; 2, propylene; 3, butadiene; 4, methylacetylene; 5, vinylacetylene; 6, diacetylene. Further details are given in Table 5.

An inverse bond length/bond angle relationship was recognized in principle a long time ago. It was reflected by the inclusion of cross stretch/bend terms in both vibrational and molecular mechanics[42] force fields. Qualitatively, the model of nonbonded interactions that was invoked by Bartell[43] to explain Stoicheff's rule can also be applied to the present case because nonbonded distances change appreciably upon the deformation of bond angles. In parallel, the quantum chemical concept of hybridization gives a qualitatively correct explanation of the phenomenon: deformation of bond angles leads to a redistribution of s and p character, which in turn influences the bond lengths (see, e.g., ref 44).

At the same time, quantum mechanics permits a quantitative description of all the phenomena observed. Specifically investigated were some model cases such as the CH_4, C_2H_6, C_3H_8, etc. molecules. The results obtained were shown to be in conformity with the experimental relationships found for the families of molecules surveyed. This type of agreement between experiment and theory was observed several

(42) Burkert, U.; Allinger, N. L. *Molecular Mechanics*; ACS Monograph 177; American Chemical Society: Washington, 1982.
(43) Bartell, L. S. *J. Chem. Edu.* **1968**, *45*, 754.
(44) Gilardi, R.; Maggini, M.; Eaton, P. E. *J. Am. Chem. Soc.* **1988**, *110*, 7232.

times and cannot be considered a coincidence. Rather, it indicates a general observation when the deformation of bond angles is involved. It must be stressed also that this qualitative agreement exists regardless of the type of experimental technique involved, i.e., X-ray crystallography or electron diffraction. Note also that the different laboratory techniques refer to samples in different states of aggregation. It is to be remembered that a qualitatively new phenomenon, the existence of a minimum in the bond length/bond angle relationship, was predicted first from computational results for $C-C/\angle C-C-C$,[17] and only later was it verified[19] using structural data for PF_2X molecules.[7]

One might be concerned that the theoretical ab initio studies undertaken so far have used considerably smaller molecules than those studied in most experimental work, particularly that done by X-ray crystallography. Recently, however, Rathna and Chandrasekhar[8] have performed MNDO calculations that are free from this objection. The authors computed structures for considerably larger systems, 20 strained hydrocarbons of differing complexity, and found virtually the same phenomenon reported from experiment and from ab initio studies of smaller systems: "the reduction of bond length is...linearly related to the widening of bond angles".

An interesting phenomenon has been reported in a paper by Ogawa et al.,[45] who studied by X-ray diffraction the molecular structures of six (*E*)-stilbenes with different substituents on the benzene rings:
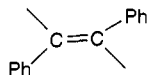
The authors found an inverse linear $C=C/\angle C-C-Ph$ relationship which qualitatively agrees with the conclusion established in this work. A more detailed analysis, however, reveals a strong quantitative discrepancy. The reported experimental data are in the range 1.343–1.283 Å for $C=C$ and 125.1–128.3° for $\angle C-C-Ph$. Our calculations for the ethylene molecule lead to

$$C=C = 1.4944 - 0.00143\theta \qquad (\theta = \angle C-C-H)$$

$$(11)$$

According to eq 11, the $C=C$ bond length seems to be more stiff, with a change in the above range of bond angles (125–128°) only from 1.315 to 1.311 Å. Ogawa et al. conclude that the phenomenon found in "the x-ray structures of these compounds is an artifact caused by dynamic averaging originating from the torsional vibration of the $C-Ph$ bonds, during which the movement of the benzene rings is restrained to be a minimum."

Concluding this section, we can say that the accumulated experimental data are generally accounted for either by Bartell's semiempirical model,[43] which is similar to molecular mechanics[42] or by rigorous quantum chemical computations.

Two Kinds of Bond Length/Bond Angle Relationships. As shown above, there are two kinds of bond length/bond angle relationships (see Figure 3 and text). The best documented is the inverse r/α rela-

(45) Ogawa, K.; Sano, T.; Yoshimura, S.; Takeuchi, Y.; Toriumi, K. *J. Am. Chem. Soc.* **1992,** *114,* 1041.

tionship. One cannot exclude the possibility that the linear dependence observed is a consequence of the range of bond angles found experimentally. Such a restriction can lead in some cases to a claim that *the distances do not depend on the bond angles*. This statement contradicts all the material presented above and therefore requires further discussion.

Let us examine the bottom part of Figure 3. One can see that the theoretical $O-F/\angle F-O-F$ relationship has a minimum. The smallest $O-F$ bond distance, 1.35 Å, is found for an $F-O-F$ bond angle of 110°. Typical experimental errors of ±0.01 Å are shown by dashed horizontal lines. An upper line intersects the $O-F/\angle F-O-F$ curve in two points, about 95° and 135°. This means that, for 135° > $\angle F-O-F$ > 95°, all the $O-F$ distances are indistinguishable within the limits of experimental error. Therefore, experimental uncertainties can mask a small but real $O-F/\angle F-O-F$ dependence which can be revealed only beyond the 95–135° interval.

After examination of the data presented in Table 2, one may infer that the appearance of curves having a minimum has a strong relation to the electronegativity of both the central atom and the ligands. Thus $A-H/\angle H-A-H$ relationships are mostly inverse linear while those of $A-F/\angle F-A-F$ mostly have a minimum. As far as the nature of the central atom is concerned, nitrogen never shows relationships with a minimum while sulfur always does. It is also important to note that the existence of a minimum does not necessarily occur only for single bonds because Hoffmann and co-workers[9] showed the phenomenon for multiple metal–metal bonds as well.

Torsion Angle/Bond Length or Torsion Angle/Bond Angle Relationships. The correlations of this type have little in common with the previous material. There are, however, several specific points we want to discuss briefly.

(1) Experimental data are scarce, and there is little hope that the situation will change in the near future. This is because the only technique which can be used for precision studies of related phenomena is microwave spectroscopy, which requires a large number of isotopomers for the complete determination of an r_s structure. The changes in the geometrical parameters r and α between different conformers with different torsion angles are 6–9 times less than the corresponding changes for the r/α relationships as may be seen from Table 4. Therefore the magnitude of the phenomenon in question is small and sometimes is marginally detectable even by microwave spectroscopy. Experiment and theory generally agree that changes in distances (central bond and adjacent bonds) for two different conformers amount to several hundredths of an angstrom, and the corresponding changes in bond angles can be several degrees in magnitude.

(2) Complete agreement between theory and experiment can hardly be expected simply because of differences between the systems treated experimentally and theoretically. For example, our theoretical studies were performed for saturated systems, while comparison sometimes had to be made with unsaturated molecules because of the scarcity of experimental data mentioned above.

(3) Comparison between theory and experiment does not explicitly provide evidence for the effect of the dihedral angle τ. Instead, another characteristics of

a molecule, i.e., its relative energy, becomes more important. The approximate rule discussed above has been formulated for molecules in which the energy difference between two conformers is on the order of 1 kcal/mol or more. When two conformers are close in energy (0.2–0.3 kcal/mol), the rule loses its sense, thus explaining some controversial cases.

(4) The approximate rule formulated in ref 37 and discussed above is in general accord with the structural consequences drawn from natural bond analysis

of internal rotation barriers developed by Weinhold and co-workers (see, e.g., ref 46).

The most general observation that can be drawn from the material presented above consists of the following obvious statement: The best description of molecular systems is obtained by combined use of several experimental techniques and theoretical methods. Active interaction between experiment and theory provides a better insight into the phenomena discussed in this review.

(46) Reed, A. E.; Weinhold, F. *Isr. J. Chem.* **1991**, *31*, 277.