THE ILLUMINATION OF MOLECULAR BEHAVIOR BY ELECTRON WAVES

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ABSTRACT

Aspects of vapor-phase electron diffraction are discussed, singling out the seminal contributions of Yonezo Morino in collaboration with San-ichiro Mizushima and others. Recent developments leading to a precision approaching 0.0002 Å are sketched, explaining why accuracy tends to fall short of this by one or two orders of magnitude, even if experimental intensities are error-free. The role of electron diffraction in studies of rotational isomerism is then outlined, with emphasis on hydrocarbon systems, to illustrate how experimental results have led to improved understanding, useful predictive procedures, and a new approach to probe the dynamics of internal rotation.

INTRODUCTION

Although I never knew Professor San-ichiro Mizushima, a stroke of good fortune a quarter of a century ago brought me into close contact with his junior collaborator, Professor Yonezo Morino. Morino's influence changed the face of structural chemistry and the lives of many of us who shared his aims. One of his favorite tools for studying rotational isomerism at the time was electron diffraction, a technique undergoing rapid development. Gas-phase electron diffraction was at first a rather rough and ready, quick, somewhat subjective method for studying molecular structure. New instrumentation and greatly increased rigor in the interpretation of electron diffraction patterns, aided by the evolution of computer technology, was beginning to alter research in the field profoundly, however. During Professor Morino's involvement with electron diffraction, precision increased from about 0.02 Å (magnitude of atomic vibrational motions) to perhaps 0.0002 Å (magnitude of nuclear diameters). Because his research was at the center of this revolution it seems appropriate first to sketch a few of the more important advances indelibly bearing his personal stamp.

Although Professor Morino's research program ultimately broadened to encompass a wide range of fundamental problems in molecular science, his early collaborations were focused upon the topic of this seminar, rotational isomerism. He was one of the true pioneers in this flourishing field. He himself has described for us (ref.1) the discovery of dichloroethane's two conformers. His
investigations of dipole moments and Raman spectra, coupled with thermodynamic inferences, gave compelling evidence about the conformational equilibria of a variety of molecules in liquid, solid, and vapor phases (ref. 2). Despite the power of such a multipronged approach it is clear that the methods mentioned are all quite indirect. Not only do they require an imaginative application of theory to connect the experimental observations with a coherent picture of molecular behavior, they leave the nature of the conformers incompletely defined. What the researcher aspires to is a direct view of the structural forms adopted by his subject molecules. Such a direct view could be provided by means of electron diffraction (ref. 3). Electron diffraction registers interference features for each internuclear distance present in an ensemble of free molecules. The spectrum of internuclear distances readily derived from the diffraction pattern allows one to see directly,* for example, the Cl-...Cl separations corresponding to both the anti and gauche rotamers of ClCH₂CH₂Cl as well as the other internuclear distances, and to reconstruct bond angles and dihedral angles, and approximate ratios of rotamers. It is easy to understand why Dr. Morino found electron diffraction so attractive, in principle.

In practice the method presented challenging difficulties that had to be solved before truly quantitative results could be obtained. For one thing, molecules vibrate. Molecules offer no set of sharp, unique internuclear distances for the experimenter to record. Unless he takes explicitly into account the indeterminacies in atomic positions, substantial even at zero Kelvin, he cannot interpret the structure with precision. Professor Morino's prior expertise in vibrational spectroscopy proved to be of immense value in the field of diffraction. One of his important contributions was to show us systematically how to calculate amplitudes of atomic vibrations from spectroscopic information (refs. 4-7). As diffraction measurements became more accurate, he inverted this approach. For molecules of some complexity, vibrational spectra are insufficient to provide a full characterization of the quadratic force field. Morino showed (refs. 9-10) that combined diffraction-spectroscopic measurements afforded significantly more complete information about potential energy surfaces than did fundamental frequencies alone. Recognizing the synergism of combined analyses, Morino went on to demonstrate the great value of combining electron diffraction and spectroscopy also in structure studies (refs. 11, 12).

Although Professor Morino contributed many technical improvements, his main thrust was fundamental. His ideas were crucial in clarifying the very meaning of molecular structure in that shadowy limit where quantum indeterminacies in

*Just how directly the distances can be seen was only recognized recently (ref. 8) when it was realized that electron diffraction patterns constitute holograms. Suitably illuminated by laser radiation they directly produce an image displaying the internuclear distances!
atomic coordinates far exceed the error limits one wishes to work within in careful measurements of internuclear distances. While the major advances catalyzed by Morino greatly facilitated research on rotational isomerism, they went so deeply into structural chemistry in general that he found it irresistible to explore many other aspects, as well. These included beautiful studies of the structural consequences of conjugation in a variety of organic molecules, the stereochemistry of inorganic molecules, and vibronic coupling in Jahn-Teller molecules (ref.2). His perceptive modelling of molecular force fields opened the way to successful treatments of previously intractable problems (refs.2,16). Although his experimental program encompassed many more techniques than electron diffraction, these other approaches lie outside the scope of this paper.

It must not be overlooked that one of Professor Morino's most important contributions to structural chemistry was finding and training many creative scholars--far too many to name here. One of these, in particular, was instrumental in helping to complete the revolution in electron diffraction. He is our chairman, Professor Kozo Kuchitsu.

Having sketched in barest outline the character of Professor Morino's achievements in electron scattering, I now wish to chronicle in a more general way certain recent advances made in the field. These advances in understanding, owing much to Japan, illustrate the precision that is achievable today under the best of circumstances. They also illustrate various sources of error that users of structural data should be aware of. After this discussion of method I shall review, in perhaps too personal a way, research on rotational isomerism in hydrocarbons. Electron diffraction made early direct contributions and uncovered suggestive molecular features that helped to provoke the development of molecular mechanics. This development, in turn, stimulated fruitful quantum studies of internal rotation. Finally, advanced techniques of electron diffraction, combined with the technology of supersonic jets, have begun to probe dynamic aspects of rotational isomerization. All of these areas will be touched upon in the following.

ELECTRON DIFFRACTION METHOD
A warning about accuracy

Irrespective of whether they have any interest in the way electrons allow us to measure the dimensions of molecules, workers in the field of rotational isomerism are avid consumers of structural information (see ref.17). As Roald Hoffmann recently put it (ref.18), "there is no more basic enterprise in chemistry than the determination of the geometrical structure of a molecule. Such a determination, when it is well done, ends all speculation as to the structure
and provides us with the starting point for the understanding of every physical, chemical, and biological property of the molecule." As already mentioned, precision in electron diffraction analyses has increased during Morino's professional lifetime from 0.02Å to perhaps 0.0002Å, today, and similar precisions are attainable by some of the other techniques, as well. The trouble is that this precision is seldom if ever (for polyatomic molecules) matched by the true accuracy. Worse, unless one meticulously follows the guidelines developed by Morino and Kucnitsu (refs. 12-15,19), structures obtained by different techniques correspond to quite different vibrational averaging, and comparisons more delicate than, say, 0.02 - 0.002Å are unreliable. In the case of x-ray diffraction, even neglecting crystal packing influences, an interpretational rigor comparable to that attainable in electron diffraction and microwave spectroscopy has not yet been achieved, even for such simple examples as benzene or rock salt. To be sure, lattice parameters can be determined with considerable accuracy but the physical meaning in terms of, say, true equilibrium internuclear distances has not yet been fully analyzed.

One of today's most versatile and powerful (yet risky) techniques of conformational analysis, molecular mechanics, sidesteps the problem by being rather vague about the exact meaning of the structures produced. He who formulates such a field, however, as for example Lou Allinger (refs.20,21) to whom we all owe a great debt, soon recognizes what a headache it is to cope with the aforementioned problem. Because it is impossible to lay down easily applied, general, and accurate rules to cover this source of difficulty, it is wise to accept structure results with caution. It turns out, nevertheless, that some reasonably interesting molecular physics is involved in the factors impeding the improvement from 0.02 to 0.0002Å. Some of the points are briefly sketched below as they pertain to electron diffraction.

Diffraction of deBroglie waves

If incident electron waves were in reality scattered very weakly by well-separated, spherical scattering centers executing harmonic vibrations, the standard treatment of scattered electron intensities would be entirely adequate (refs.22,23). Analyses of diffraction patterns from such hypothetical molecules, measured by today's best procedures, would yield accuracies approaching 0.0001Å in favorable cases. In practice there are obstacles that make it difficult to achieve such accuracy. These obstacles are:

(a) Scattering potentials are not really weak.
(b) Atoms in molecules are not spherical.
(c) Molecular vibrations are not harmonic.

Such problems are not unique to vapor-phase electron diffraction. Factors
(b) and (c) are even more troublesome in X-ray crystallography. Microwave spectroscopy, offering measurements of far greater intrinsic precision than obtainable by any diffraction method, suffers seriously from (c) because it relies heavily on subtle differences between measurements from different isotopic species. What effect these factors have on diffraction analyses is briefly summarized below.

**Scattering by real atoms.** Because electrons are strongly attracted to nuclei, they speed up and shorten their wavelength during their encounters with atoms. The resultant complicated patterns of phase shifts had been neglected entirely until Schomaker and Glauber found that it makes molecules with heavy atoms look distorted, and showed how to treat the scattering by individual atoms in molecules (ref.24). Systematic residuals remained, however, that were finally traced to diffraction effects ensuing when one atom passes, as it were, through the shadow cast by another. Only recently has a tractable treatment been devised (refs.25,26). Left untreated, this disturbance has an influence on distances and mean amplitudes in the range of $10^{-2}$ - $10^{-3}$Å and effects are noticeable even in comparatively light molecules such as SF$_6$. Few structure analyses have been corrected for this effect.

**Asphericity of atoms.** Most diffraction analyses rely on the "independent atom model" implying that electron densities in molecules are simple sums of spherically averaged Hartree-Fock atomic densities. Effects of bond formation, ionicity, etc., that displace effective scattering centers, are neglected. Although the effects are implicitly understood, it took the special circumstances of a recent laser excitation study of SF$_6$ (ref.27) to provide the careful analyses of many dozens of control plates needed to demonstrate that residuals are reproducible and characteristic of the molecules, and not experimental noise. Such residuals may influence amplitudes of vibration and internuclear distances by several thousandths of an angstrom unit. While quantum calculations of electron densities in molecules have corroborated the effect, (ref.28) the routine correction of data is beyond current technology.

**Effects of anharmonic vibrations.** To a first approximation molecules are multidimensional harmonic oscillators. This means that each internuclear distance in a molecule can be represented by a distribution function that is very nearly Gaussian in shape. Correction for the "Morse anharmonicity" of covalent bonds has long been fairly well understood (refs.29,30). Only recently, however, have nonbonded distributions been analyzed even for such elementary cases as CF$_4$ and SF$_6$. Here, skewing of the nonbonded radial distribution peaks was greater than expected (refs.31,32) and confused distances by 0.01Å when molecules were hot. Later quantum calculations confirmed the anharmonic skewing (refs.33,34). For less rigid molecules the effect can be considerably greater (ref.35).
For no molecule exhibiting rotational isomerism have any of the above complicating factors been treated with full rigor. Uncertainties of several thousandths to several hundredths of an angstrom unit must be expected. As discussed in the next section, this does not prevent electron diffraction from being useful in conformational analysis.

ROTATIONAL ISOMERISM

Role of electron diffraction

Hundreds of compounds exhibiting rotational isomerism have been investigated by vapor-phase electron diffraction, the first being 1,2-dichloroethane by the method's founder, Wierl, in 1930 in his second paper (ref.36). It was only later that the method became sensitive enough to establish the structures of both conformers. An excellent summary of structural research and conformational analysis by diffraction and spectroscopy was published recently by Vilkov, Mastryukov, and Sadova (ref.17). These authors have made noteworthy contributions to the field, themselves, over the last three decades.

For the purposes of the present seminar I shall focus on a rather small area of research in order to illustrate some ideas that have been generated by diffraction investigations and introduce new techniques being developed for the future.

Internal rotation in hydrocarbons

Studies of n-alkanes from C1 through C7 (refs.37,38) provide typical illustrations of the method and introduce some useful perspectives. Experimental radial distribution functions of n-heptane are shown in Fig. 1a (where internuclear distances corresponding to the three most important conformers are marked off) and Fig. 1b (exploded view of outer part, hydrogens deleted). Conformational equilibria were treated in terms of a free energy parameter ΔG° associated with each gauche kink introduced into a chain, in accordance with well-specified rules. Conformational populations govern areas of internuclear peaks in the radial distribution function and least squares refinements lead to optimum skeletal structure parameters as well as a value for ΔG°. If such a study had been carried out as a function of temperature, as were later beautiful studies of somewhat simpler molecules by Hedberg et al. (ref.39) among others, values of ΔH° and ΔS° could also have been established. Results of the n-alkane studies were rationalized in terms of the steric model of Fig. 2. It was assumed, in conformity with the traditional viewpoint, that the unfavorable 2Å gauche H···H repulsions singled out in the figure are responsible for the destabilization, ΔG°, and induce the illustrated chain perturbations ε, η, and ζ. Later work, as we shall see, showed this interpretation to be somewhat oversimplified.
Additional structural information from substituted ethylenes and carbonyl compounds obtained at about the same time (ref.40) provided suggestive evidence that not only were the somewhat remote nonbonded interactions shown in Fig. 2 of importance. Geminal (1-3) nonbonded interactions, previously virtually ignored, appeared to be particularly strong and crucial in governing bond angles in molecules.* If this were true, it was relatively simple to deduce

*An elementary model, assigning different "hard-sphere" geminal nonbonded radii to different atoms was originally found to be widely applicable to organic molecules (ref.40). Later it was shown to be of value for inorganic molecules as well (ref.41), and crystalline minerals (ref.42). Generalized to more realistic "soft-sphere" atoms, it became a Urey-Bradley variant of molecular mechanics (refs.43,44).
the effect of vibrations upon vibrationally averaged nonbonded forces. Since larger amplitudes imply larger forces, it was predicted (ref.45) that geminal C---H repulsions in C₂H₆ should exceed C---D repulsions in C₂D₆ and cause a secondary isotope effect of several thousandths of an angstrom unit on the C-C bond length. This effect was looked for by electron diffraction, and observed (ref.46) and later corroborated by ab initio molecular orbital calculations (refs.47,48). In the latter work the relevant cubic constants in the potential surface were derived and propagated into calculations of vibrational stress. It was confirmed that the cubic constants closely simulated the model of geminal nonbonded interactions (ref.47). Structural research, then, provided valuable clues about the character of intramolecular forces.

Emergence of molecular mechanics

As structural and conformational data on hydrocarbons accumulated it was very natural to ask whether the implications of steric influences could be formulated in a quantitative way and if so, whether the formulation could account for the new body of data. Such a formulation, of course, is now known as "Molecular Mechanics." Hendrickson (ref.49) had already made an important start in this direction, but his original analyses were somewhat inconsistent in the way geminal nonbonded interactions were handled. Such interactions, if included, must not be put in on top of conventional bond bending interactions because they constitute an important part of bond bending force constants. Instead, it is necessary, if explicitly incorporating geminal nonbonded interactions, to use a Urey-Bradley type of force field (ref.43). A mathematically equivalent field not explicitly incorporating nonbonded force constants can be fashioned by including certain combinations of stretch-bend and stretch-stretch interactions. A virtue of the Urey-Bradley approach, however, is that it can be extended very naturally with fairly well-understood factors to anharmonic terms. Such terms are absolutely essential if trends in structure and strain energy associated with changes in local environments of groups are to be accounted for without adding ad hoc parameters and changes in reference lengths, angles, etc.

The guiding principle in the first Urey-Bradley formulation of a model hydrocarbon force field, besides severe simplicity, was to apply to geminal, as well as to more remote interactions, some existing potential functions chosen to simulate intermolecular atom-atom interactions (ref.40). Once these H---H, C---H, and C---C functions had been adopted, conventional Urey-Bradley stretch and bend constants were assigned to make the model correspond closely with published hydrocarbon force fields inferred from vibrational spectra (ref.50). Many fewer potential parameters were incorporated into this modified Urey-
Bradley (MUB) field than in the later force fields of Lifson and Warshel (ref.51), Lifson and Ermer (ref.52), Allinger (refs.20,53), Schleyer (ref.54), and others, nor were the sparse parameters adjusted by least squares or extensive trial and error. Nevertheless, the MUB field (ref.43) was remarkably successful in accounting for trends in bond angles, bond lengths, conformations, and heats of formation. Despite its small number of empirical constants it seemed to capture much of the molecular physics. Typical illustrations of the trends in structure it yielded are shown in Figs. 3a and 3b. Note that the reference lengths for all C-H bonds were the same as were the reference values for all C-C bonds and all bond angles (taken as tetrahedral). Trends resulted solely from the local differences in nonbonded environments imposed by the universal set of H-H, C-H, and C-C functions. An updated version, MUB-2 (ref.44) introduced to test a hypothesis of Allinger (ref.55), was even somewhat better.

Several aspects of the MUB fields deserve comment. First, the fields do show, as discussed above, that many molecular properties can be formally accounted for as steric consequences, provided anharmonic geminal nonbonded interactions are invoked. This is of some interest because few of the trends reproduced are normally considered to be steric. It is possible, of course, that what are better thought of as more specific interactions have somehow been smuggled into the model under the guise of "nonbonded interactions." Secondly, while the MUB type of field is particularly efficient in what it accomplishes per parameter invoked, it is computationally not an especially efficient field to use in calculations upon large molecules. Lastly, it exhibited one systematic deficiency in particular whose cure uncovered an unsuspected intramolecular interaction of...
general significance in rotational isomerism. This is discussed in the next paragraph.

When reliable differences in energy, $\Delta E_g$, between gauche and anti conformations became available, it was found that the MUB-2 results were systematically low by 1.5 kJ/mole for such prototype molecules as n-butane, 2-methyl butane, 2,3-dimethyl butane and 1/2(1-methylcyclohexane). The reason was soon found. In common with virtually all other model fields proposed for molecular mechanics, the MUB fields adopted simple 3-fold torsion functions to represent the "intrinsic," nonstercal barrier to rotation about single bonds. Using quite well balanced H--H, C--H, and C--C potential functions, the calculations of vicinal nonbonded interactions across the bond undergoing internal rotation gave a nearly null contribution to $\Delta E_g$. This left the H--H interaction identified in Fig. 2 as the principal contributor to $\Delta E_g$ in agreement with customary ideas. What is wrong with this is that, by minor flexing, the molecules can escape the full brunt of this interaction. The two most popular molecular mechanics fields of the time (refs.53,54) had both obtained fairly good results for $\Delta E_g$ but each had used physically implausible nonbonded potentials to achieve the result. In each case the mean of the H--H and C--C quite overwhelmed the C--H, contrary to conventional combining rules, and the vicinal nonbonded repulsions appreciably augmented the specific H--H repulsion of Fig. 2.

A way to come to terms with this fundamental problem in conformational analysis was soon suggested by several workers (refs.56,57). Intrinsic torsional components for <CCY fragments in substituted ethanes can be different for HCCC, hCCC, and CCCC. Moreover, symmetry does not exclude 1-fold and 2-fold components for any Xf combination. In a symmetrical molecule such as $X_3CCY_3$ the 1-fold and 2-fold contributions cancel, leaving a pure 3-fold torsional function. In unsymmetrical cases such as $XY_2CCXY_2$ and $XY_2CCX_2Y$ (referred to in the previous paragraph) the low-order barriers no longer cancel. Instead, they enter in a characteristic way identical for all the hydrocarbon cases referred to (ref. 56), and hence, can be represented by a single parameter (1.5 kJ/mole for MUB-2).

Molecular orbital analysis of restricted rotation

Is there any quantum mechanical basis for the invoking of low-order torsional potentials of substantially different magnitudes for the different cases just referred to? Indeed, what is the underlying quantum basis for restricted rotation in the first place, beginning with ethane itself? The answer to the first question fell into place when the second question was addressed by a new technique (ref. 58) due to Bruncck and Weinhold (BW). Now, internal rotation in ethane would seem to be a simple problem insomuch as quantum calculations at almost any level, from EHMO and IADO through Hartree-Fock and beyond, successfully reproduce the barrier. Moreover, many seemingly plausible interpretations of
the barrier have been proposed. Not long ago, however, Weinhold subjected these to searching scrutiny and found unsatisfactory aspects in several of the previous persuasive explanations. His own interpretation not only accounted for ethane but it very naturally led to a simple rationalization of considerable predictive power for preferred conformations in unsymmetrically substituted ethanes, amines, and alcohols. Readers interested in this subject could do no better than refer to Weinhold's publications (refs.58,59).

Roughly sketched, the quantum approach of BW is as follows. Atomic orbitals (AOs) are hybridized to direct tetrahedrally toward their partners in bonding and these hybrids are combined into bond orbitals (BOs, including bond and antibond pairs). The BOs then serve as basis orbitals in LCBO-MO calculations. As long as the full set of BOs is included, the molecular orbital computations yield precisely the same results as when the original set of AO's is adopted, of course. The value of the LCBO approach is that some of the basis functions can be excluded from the basis set and the resulting truncation is chemically meaningful. That is, it is feasible to suppress certain bonds or antibonds, or unneeded hybrids in cases in which not all the ordinary valences of an atom are saturated. This would be impossible to accomplish with a standard STO basis set, for example. Accompanying a truncation is a modification of the total calculated energy. This change is useful in diagnosing the source of various electronic interactions, as shown by BW.

The essential point of BW's analysis is that a stabilizing trans $\pi$-$\sigma^*$ bond-antibond mixing is ultimately responsible for the greater stability of the staggered conformations. Excluding the antibond orbitals from the basis set leads to nearly free rotation.

Brunck and Weinhold's approach makes it possible to follow the energetics of the individual torsional components $X_{CCY}$, discussed in the previous section, in molecular orbital computations. Substantial 1-fold and 2-fold components were indeed found (ref.60) and, moreover, they differed in HCCH, HCCC, and CCCC fragments in the manner forecast to be necessary to produce the "intrinsic" gauche destabilization $\Delta E_g$. Insufficient precision was available to yield a quantitative result for $\Delta E_g$, however. Although a full resolution of the problem of torsional potential energy in prototype cases has not yet been achieved, it appears that quantum theory can provide more than just the energy differences between rotational isomers that are usually studied. It promises to give decompositions into components that improve qualitative understanding, on the one hand, and provide ingredients to improve the predictive power of molecular mechanics, on the other.
FUTURE APPLICATIONS OF ELECTRON DIFFRACTION

For many years gas-phase electron diffraction served almost as an end in itself to provide structural information about molecules. Increasingly it is now being applied, instead, as an auxiliary tool to follow changes induced in molecules by various processes. Here the precision may be more important than the accuracy. The earliest major applications of this sort (see ref. 39) were to follow changes in populations of conformers as a function of temperature to measure thermodynamic quantities. Recently, systematic thermal changes in structure, vibrational amplitudes, and radial distribution peak shapes were used to study potential parameters, harmonic and anharmonic (refs. 31-33). It has been shown to be fruitful, with the aid of electron diffraction, to investigate the absorption of infrared laser radiation by jets of gas flowing from nozzles. By this means vibrationally excited molecular beams can be generated and characterized (ref. 61, 62). One promising new technique making use of diffraction in the field of rotational isomerism is the study of supersonic jets.

Because of the low temperatures that can be achieved in supersonic jets without inducing condensation, it is possible (under some conditions) to enrich greatly the low energy form of a mixture of rotamers. Examples are FCH₂CH₂F (monitored by spectroscopy after condensation into a matrix, ref. 63), and n-butane (monitored in the jet by electron diffraction, ref. 64). One potentially significant application would be to follow the kinetics of the transformation, say, from gauche to anti n-butane. Conventional investigations of this transformation by ultrasonic relaxation have nicely characterized the unimolecular kinetics (ref. 65) but have revealed nothing about the bimolecular activation step. In supersonic flows the activation step can easily be made to be rate limiting because the number of collisions experienced during cooling can be controlled to range from very few to enormous numbers. In rapid expansions the gauche is simply frozen into its potential minimum with no perceptible change in concentration. In slower expansions enrichment from 68% (at 300 K) to 90%, anti has been seen in preliminary work (ref. 64). Until effects of shock waves and skimmer interactions are thoroughly analyzed, it will be premature to carry out kinetic analyses.

CONCLUDING REMARKS

Historic and current roles of electron diffraction in research on internal rotation have been described. How the method evolved from the rather crude, qualitative tool that was inherited by Mizushima and Morino into one of considerable power and versatility has been recounted. Structural chemists will be forever indebted to these pioneers for their perceptive discoveries, their illuminating interpretations, and their distinguished leadership.
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REFERENCES

1. Y. Morino, contribution to this seminar.
2. H. Kimura, K. Kuchitsu and E. Hirota (Eds.), The Scientific Papers of Professor Yonezo Norino, Forty Years, Studies of Molecular Structure, a book published by the University of Tokyo, 1971.
18. R. Hoffmann, reference 17, foreward.
34. J. F. Stanton and L. S. Bartell, unpublished research.