

ducing beams of stable or metastable molecules that would be difficult, if not impossible, to obtain by other methods. The potential to generate an essentially unlimited number of different neutral species can be an impetus for other experiments using beam techniques. In particular the technique may open up possibilities to obtain absorption spectra of metastables, using laser excitation with detection of photofragments. Beam studies using laser-excited alkali-metal target atoms<sup>44</sup> may provide information on Rydberg states of unstable molecules formed by resonant electron transfer. A possible example is the reaction



The  $^2T_2$  state of  $\text{NH}_4$  may then radiate to the  $^2A_1$

(44) V. S. Kushawaha, C. E. Burkhardt, and J. J. Leventhal, *Phys. Rev. Lett.*, **45**, 1686 (1980).

(45) D. P. de Bruijn and J. Los, *Rev. Sci. Instrum.*, **53**, 1020 (1982).

ground state or dissociate with conversion of internal energy to fragment kinetic energy.

In its present form the technique is limited in deriving structural information that may be contained in beam profiles. An interesting technical advance in beam detection is the development of an array detector (channel plate) by de Bruijn and Los,<sup>45</sup> using the time of flight coincidence method of Meierjohann and Vogler.<sup>15</sup> The increased resolution in beam profiles offered by their technique may reveal structural information masked by the isotropic scattering profile in  $I(\theta)$ .

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## The Barrier to Internal Rotation in Ethane

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Rotation about single bonds is discussed in many chemistry textbooks and has important consequences in molecular structure and dynamics.<sup>1</sup> Since ethane is the simplest molecule containing a carbon-carbon single bond, it is the prototype molecule for internal rotation in a large number of molecules and has therefore been the most frequently studied molecule in internal rotation studies.

The existence of a barrier to internal rotation in ethane was established in the 1930's, and in subsequent years the rotational barriers in a large number of molecules have been measured. The discussion of the origin of these barriers in terms of interactions between atoms or bonds began even before any experimental values had been obtained, and it is curious that even after a considerable number of rotational barriers had been measured, little progress had been made in understanding their origin. It was not until the 1960's, when moderate-sized (by the standards of the 1980's) digital computers could be applied to theoretical calculations, that firm conclusions could be drawn concerning the fundamental interactions involved.

During the later 1870's it was pointed out that the lack of rotational isomers of molecules such as  $\text{CH}_2\text{-ClCH}_2\text{Cl}$  meant that rotation about CC single bonds is practically free.<sup>2</sup> Subsequently there was some discussion as to whether a small hindering potential existed or not, but no evidence on this question was obtained for some time.<sup>2</sup>

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In the 1930's difficulties were found in the statistical mechanical treatment of the thermodynamic data for ethane, and the existence of an internal rotation barrier was one of several suggestions as to the source of these difficulties. The discrepancies were resolved in 1936 by Kemp and Pitzer, who showed that the third law entropy of ethane, in combination with other thermodynamic data, required the existence of a barrier of approximately 3 kcal/mol.<sup>3</sup> In 1951 this method of determining rotational barriers was reviewed by Pitzer, and, on the basis of the available data, a revised value of  $2.875 \pm 0.125$  kcal/mol was given for ethane.<sup>4</sup>

Since the 1930's a number of other methods of measuring rotational barriers have been developed, and these were reviewed by Wilson in 1959.<sup>5</sup> Microwave spectroscopy, one of the more extensively used techniques, is not directly applicable to ethane because the molecule lacks a dipole moment. By the use of infrared spectroscopic data, however, Smith was able to show in 1949 that the staggered conformation of ethane is the lower energy one,<sup>6</sup> as had been expected. A new value of the barrier itself was not obtained in this study because transitions between the internal rotation (torsional) energy levels in ethane are forbidden by infrared selection rules. Nevertheless, Weiss and Leroi, in 1968, were able to find these transitions by carrying out a

(1) W. G. Dauben and K. S. Pitzer in "Steric Effects in Organic Chemistry", M. S. Newman, Ed., Wiley, New York, 1956.

(2) W. J. Orville-Thomas in "Internal Rotation in Molecules", W. J. Orville-Thomas, Ed., Wiley, New York, 1974.

(3) J. D. Kemp and K. S. Pitzer, *J. Chem. Phys.*, **4**, 749 (1936); *J. Am. Chem. Soc.*, **59**, 276 (1937).

(4) K. S. Pitzer, *Discuss. Faraday Soc.*, **10**, 66 (1951).

(5) E. B. Wilson, Jr., *Adv. Chem. Phys.*, **2**, 367 (1959); *Proc. Natl. Acad. Sci. U.S.A.*, **43**, 816 (1957). See also R. A. Pethrick and E. Wyn-Jones, *Q. Rev., Chem. Soc.*, **23**, 301 (1969).

(6) L. G. Smith, *J. Chem. Phys.*, **17**, 139 (1949).

high-pressure, long-path-length experiment, and they obtained a barrier value of  $2.928 \pm 0.028$  kcal/mol.<sup>7</sup> Recently Hirota et al. were able to obtain source-modulated microwave spectra of isotopically substituted ethanes such as  $\text{CH}_3\text{CHD}_2$ . From the barrier values obtained for these molecules, they estimated a barrier value of  $2.90 \pm 0.03$  kcal/mol for  $\text{C}_2\text{H}_6$  itself.<sup>8</sup>

### Precomputer Theoretical Work

Quantum mechanical calculations of the ethane rotational barrier were attempted even before it had been measured.<sup>9,10</sup> The approach generally adopted then and later is to use approximate electronic wave functions to calculate the energies of both the staggered and eclipsed forms of the molecule and then obtain the barrier value by taking the difference of these energies. The errors in the individual energies are expected to be much larger than the barrier, but most of this error is also expected to cancel out in taking the difference.<sup>11,12</sup>

The original calculations were carried out with standard valence-bond (VB) wave functions. These were constructed from a minimal set of atomic orbitals, hybridized on the carbon atoms. Since the orbitals on one atom are not orthogonal to orbitals on another atom, the energy expression is quite complex, involving terms with various numbers of overlap and other integrals. The procedure used was the standard one at the time of neglecting all terms except the VB coulomb and single exchange terms.<sup>13</sup> When this is done, the calculated barrier value is low by about a factor of 10.<sup>5</sup>

In retrospect it is clear that in these calculations the baby was being thrown out with the bath. The wave function itself was sufficiently accurate, but the integrals discarded were not small enough to neglect and should have been retained in evaluating the energies. Unfortunately it was not possible with the desk calculators of that time to evaluate all of these integrals in a reliable, accurate way. Instead, futile efforts were made to find out if improving the wave function would give a better result. This was done in particular by including 3d and 4f character in the hybrid orbitals both to allow for increased electron density in the bond regions and for noncylindrical character in the CC bond.<sup>14,15</sup>

The simplest force that could give rise to the barrier is the electrostatic force between the charge distributions of the CH bonds at each end of the molecule. Several attempts were made to evaluate the CH bond dipole moments, quadrupole moments, etc., and then calculate the barrier from electrostatics.<sup>16,17</sup> These calculations proved to be inconclusive due to difficulties in obtaining values for the bond moments and to the uncertain convergence of the expansions used for the energy.<sup>5</sup>

(7) S. Weiss and G. E. Leroi, *J. Chem. Phys.*, **48**, 962 (1968). Error limits from ref 8.

(8) E. Hirota, S. Saito, and Y. Endo, *J. Chem. Phys.*, **71**, 1183 (1979).

(9) H. Eyring, *J. Am. Chem. Soc.*, **54**, 3191 (1932).

(10) W. G. Penney, *Proc. R. Soc. London, Ser. A*, **144**, 166 (1934).

(11) P. O. Löwdin, *Adv. Chem. Phys.*, **2**, 207 (1959).

(12) H. F. Schaefer, III "The Electronic Structure of Atoms and Molecules", Addison-Wesley, Reading, MA, 1972.

(13) C. A. Coulson, "Valence", Oxford, 1961, Chapter 7.

(14) E. Gorin, J. Walter, and H. Eyring, *J. Am. Chem. Soc.*, **61**, 1876 (1939).

(15) L. Pauling, *Proc. Natl. Acad. Sci. U.S.A.*, **44**, 211 (1958).

(16) E. N. Lassette and L. B. Dean, Jr., *J. Chem. Phys.*, **17**, 317 (1949).

(17) L. Oosterhoff, *Discuss. Faraday Soc.*, **10**, 71 (1951).

Another suggested source of the barrier is the overlap (exchange) repulsion between the bonds or atoms at each end of the molecule, which is the principal component of steric repulsion, a more widely used but less precisely defined term. This repulsion is due to the overlap of filled electronic shells<sup>18</sup> and, like the electrostatic interactions, is described even by simple wave functions. Alternative attempts have been made to account for this interaction by using pairwise additive, parameterized potentials between nonbonded atoms. The functional forms of these potentials are less well-defined than the forms of electrostatic potentials but are usually chosen to have high inverse power or exponential dependences on the internuclear distances. The choice of parameters is made empirically and is not unique. Usually the resulting barrier values have been too low.<sup>5,19</sup>

Still another type of interaction is the London (dispersion) force, which, unlike the previous interactions, is not obtainable with simple wave functions. It is an attractive force and the potential has the well-known inverse sixth power form at long distances.<sup>18</sup> At the shorter distances of interest for ethane the form of the potential is not known.

Discussions of this early theoretical work are included in the reviews by Pitzer<sup>4</sup> and Wilson.<sup>5</sup>

### Computer-aided Theoretical Work

In the early 1960's it became apparent that the available digital computers could be used to evaluate the molecular integrals needed for calculations on molecules the size of ethane, and considerable effort was devoted to developing methods of computing these integrals<sup>20-23</sup> and of using symmetry to simplify the calculations.<sup>24,25</sup> Most calculations were done with molecular orbital (MO) wave functions because for many purposes they have the same level of accuracy as VB wave functions and yet have a considerably simpler energy expression.<sup>12,26</sup>

In 1963 a calculation was completed on ethane, using MO wave functions constructed from a minimal set of (Slater) atomic orbitals.<sup>27</sup> All integrals were computed and the resulting barrier value was 3.3 kcal/mol. This was quite encouraging but still subject to skepticism because at that time a number of similar calculations on smaller polyatomic molecules were known to contain errors,<sup>12,28</sup> primarily in the values of the molecular integrals.

Beginning in 1966, however, a number of similar calculations were carried out on ethane and yielded barrier values in the range of 2.5-3.7 kcal/mol, corroborating the original result.<sup>29,30</sup> Thus the barrier to

(18) K. S. Pitzer, "Quantum Chemistry", Prentice-Hall, 1953, especially sections 8v and 8w; *Adv. Chem. Phys.*, **2**, 59 (1959).

(19) E. A. Mason and M. M. Kreevoy, *J. Am. Chem. Soc.*, **77**, 5808 (1955).

(20) M. P. Barnett, *Methods Comput. Phys.*, **2**, 95 (1963).

(21) R. M. Pitzer, J. P. Wright, and M. P. Barnett, *QCPE*, **10**, 22-25 (1964).

(22) I. Shavitt and M. Karplus, *J. Chem. Phys.*, **36**, 550 (1962).

(23) I. Shavitt, *Methods Comput. Phys.*, **2**, 1 (1963).

(24) R. M. Pitzer, *J. Chem. Phys.*, **58**, 3111 (1973).

(25) N. W. Winter, W. C. Ermler, and R. M. Pitzer, *Chem. Phys. Lett.*, **19**, 179 (1973).

(26) C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).

(27) R. M. Pitzer and W. N. Lipscomb, *J. Chem. Phys.*, **39**, 1995 (1963).

(28) An exception of particular interest is J. M. Foster and S. F. Boys, *Rev. Mod. Phys.*, **32**, 305 (1960), predicting  $\text{CH}_2$  to have a nonlinear triplet ground state ( $^3B_1$ ).

internal rotation in ethane has turned out to be both obtainable from quite simple wave functions and insensitive to the details of the atomic orbital set used.<sup>30,31</sup>

Further refinements in calculations have involved the inclusion of 3d orbitals on the carbon atoms,<sup>32</sup> allowing the CC bond distance and CCH bond angles to change in going from staggered to eclipsed,<sup>32,33</sup> vibrational effects,<sup>33</sup> and use of configuration-interaction wave functions.<sup>32,34,35</sup> None of these has had a major effect on the calculated barrier values.

### Important and Unimportant Interactions

From the calculations done since 1963 it is clear that very simple wave functions are adequate to describe the interactions giving rise to the internal rotation barrier in ethane but only if *no numerical or other approximations are made* in evaluating the energy expressions for these wave functions. It is only necessary to include a minimal set of atomic orbitals, namely, a 1s atomic orbital on each hydrogen atom and 1s, 2s, 2p<sub>x</sub>, 2p<sub>y</sub>, 2p<sub>z</sub> atomic orbitals on each carbon atom, clearly the smallest set of atomic orbitals possible for ethane. Furthermore, these atomic orbitals need only be combined in the simplest way (by linear combination) into molecular orbitals and the MO's need only be multiplied together in a single Slater determinant, the simplest type of many-electron wave function. Thus only the most basic type of wave function is needed; the energies and MO coefficients for such wave functions are most often obtained by the self-consistent-field (SCF-MO) method.<sup>26</sup> Part of the analysis of the interactions contributing to the rotational barrier is based on the well-understood limitations of these wave functions.

To begin with, effects that these wave functions are incapable of describing cannot be important. Since only atomic orbitals through 2p are necessary on carbon atoms, (1) *3d and 4f character in the carbon atom orbitals is not important*. Among other things this means that (2) *any noncylindrical character in the CC bond is not significant*. Since London forces are due to the correlated motion of electrons and the single determinant form of SCF-MO wave functions is incapable of describing this correlation,<sup>11</sup> (3) *London forces cannot be important with respect to the ethane rotational barrier*.

To determine the importance of electrostatic interactions between the ends of the molecule, calculations were carried out in 1968 in which the electronic charge distribution of each methyl group was kept rigid during internal rotation.<sup>36</sup> The atomic orbital set used was that of the 1963 calculation,<sup>27</sup> and the resulting barrier value was very small in magnitude and of the wrong sign.

(29) A. Veillard in "Internal Rotation in Molecules", W. J. Orville-Thomas, Ed., Wiley, New York, 1974.

(30) R. M. Pitzer, *J. Chem. Phys.*, **47**, 965 (1967).

(31) The only calculations for ethane since 1963 that have not given good agreement have been reported by M. Klessinger, *J. Chem. Phys.*, **53**, 225 (1970), and by C. T. Corcoran and F. Weinhold, *J. Chem. Phys.*, **72**, 2866 (1980). See also the discussion in ref 34 and in G. F. Musso, G. Vallini, and V. Magnasco, *J. Chem. Soc., Faraday Trans. 2*, **72**, 1021 (1976); **73**, 1238 (1977).

(32) P. W. Payne and L. C. Allen in "Methods of Electronic Structure Theory", H. F. Schaefer, III, Ed., Plenum, New York, 1977.

(33) B. Kirtman, W. E. Palke, and C. S. Ewig, *J. Chem. Phys.*, **64**, 1888 (1976); B. Kirtman and W. E. Palke, *Ibid.*, **67**, 5980 (1977).

(34) W. J. Hunt, P. J. Hay, and W. A. Goddard, III, *J. Chem. Phys.*, **57**, 738 (1972).

(35) B. Zurawski and W. Kutzelnigg, *Bull. Acad. Pol. Sci., Ser. Chim.*, **22**, 361, (1974).

Thus (4) *simple electrostatic interactions are not important in the ethane barrier*.<sup>36</sup>

The wave functions used in this electrostatic calculation, however, cannot satisfy the Pauli Exclusion Principle.<sup>37</sup> This is most easily understood by considering the wave function for one conformation as being made up of orthogonal, localized bond MO's. Upon rotation to the other conformation, the CH bond MO's at opposite ends of the molecule will no longer be orthogonal, and any method of making them orthogonal must change these bond MO's and therefore the charge distribution as well.<sup>38</sup> An MO wave function that obeys the Pauli principle must, in effect, have orthogonal MO's,<sup>26</sup> but clearly orthogonality cannot be maintained during internal rotation unless the MO's change, which is incompatible with rigidly rotating charge distributions.<sup>38</sup>

The next step<sup>36</sup> was to perform calculations in which the wave function was allowed to change during internal rotation but only to the minimum extent necessary to preserve orthogonality and satisfy the Pauli principle. In this way the effect of the changes, during internal rotation, in the CH bond orbital overlaps across the molecule were included, but no further changes in electron density were permitted.<sup>39</sup> The resulting barrier value was 2.6 kcal/mol, showing that (5) *the principal interaction giving rise to the internal rotation barrier in ethane is the overlap (exchange) repulsion*,<sup>36</sup> and (6) *any changes in electronic structure other than those required by the changes in CH bond overlaps are of minor importance with respect to the barrier*.<sup>36</sup> Further calculations concerning the role of overlap repulsion have corroborated these simple conclusions and have provided more details concerning them.<sup>41-45</sup>

### Concluding Remarks

It is interesting that in determining the nature of the interaction responsible for the internal rotation barrier in ethane, the difficulty has not been one of a lack of suggested interactions to investigate but rather one of obtaining the computational power and techniques necessary to find out whether the suggestions are cor-

(36) O. J. Sovers, C. W. Kern, R. M. Pitzer, and M. Karplus, *J. Chem. Phys.*, **49**, 2592 (1968).

(37) These wave functions are simple (Hartree) products. In a sense, they partly satisfy the Pauli principle in that orbitals are no more than doubly occupied and almost orthogonal (overlap integrals less than 0.2).

(38) These statements must be modified if the orbitals are allowed to become complex. T. L. Gilbert, *Phys. Rev. B*, **12**, 2111 (1975), has shown how it is possible, by the use of complex phase factors, for orbitals to change and be orthonormal and yet not have their charge densities change. Permitting the orbitals to change in this way would put the primary energy changes into the kinetic energy terms but would presumably not give a value for the rotation barrier significantly different from the one obtained in ref 36 when the orbitals were kept real and only allowed to change enough to preserve orthogonality.

(39) Antisymmetrization (and renormalization) of MO wave functions in effect requires orthonormalization of the MO's and produces two changes in the energy expression: (1) MO exchange integrals appear, and (2) the kinetic energy, nuclear attraction, and MO coulomb integrals all change due to the orthogonality-required changes in the MO's. The second effect is the important one (ref 34) since exchange integrals between orthogonal, localized MO's are very small and so are their contributions to the barrier (ref 40). See also ref 45.

(40) R. M. Pitzer, *J. Chem. Phys.*, **41**, 2216 (1964).

(41) R. M. Stevens and M. Karplus, *J. Am. Chem. Soc.*, **94**, 5140 (1972).

(42) V. Magnasco and G. F. Musso, *J. Chem. Phys.*, **60**, 3754 (1974); G. F. Musso and V. Magnasco, *Chem. Phys. Lett.*, **23**, 79 (1973).

(43) P. A. Christiansen and W. E. Palke, *Chem. Phys. Lett.*, **31**, 462 (1975).

(44) P. A. Christiansen and W. E. Palke, *J. Chem. Phys.*, **67**, 57 (1977).

(45) K. Morokuma and H. Umeyama, *Chem. Phys. Lett.*, **49**, 333 (1977).

rect or not. As has already been mentioned, the overlap repulsion has been considered many times previously, but attempts to use VB wave functions<sup>5,8,9,14,15</sup> omitted difficult but important integrals, and the use of empirical potentials has been uncertain at best.<sup>5,19,46,47</sup> The type of calculation needed for studying the ethane barrier was essentially impossible in the 1930's, quite difficult in the early 1960's, but with the computers and computational techniques<sup>48,49</sup> developed by the 1980's, simple enough to be assigned as project in a quantum chemistry course.

Barriers to internal rotation have now been computed in numerous other molecules with use of SCF-MO and more elaborate types of wave functions, with generally good agreement with the experimental values where they are known.<sup>31</sup> In general it has been found that larger sets of atomic orbitals are needed for molecules whose atoms in the central bond contain lone pairs of electrons and that the effects of bond distance and bond angle relaxation during internal rotation may be important also. For example, in the hydrogen peroxide molecule it has been found that both a larger set of atomic orbitals and consideration of bond angle and bond length changes during rotation were needed<sup>50</sup> to obtain an accurate description of the internal rotation potential function, whose principal features in this case are the cis barrier, the trans barrier, and the minimum at a skew angle. In retrospect it seems that ethane, with no lone pairs of electrons and only one principal feature in its internal rotation potential function, the barrier height, is one of the simplest molecules to treat, despite the fact that it contains more atoms than some other molecules with internal rotation.

The type of intramolecular force analysis applied to ethane here has also been applied to other molecules

(46) O. J. Sovers and M. Karplus, *J. Chem. Phys.*, **44**, 3033 (1966).

(47) M. L. Huggins in "Structural Chemistry and Molecular Biology", A. Rich and N. Davidson, Ed., Freeman, San Francisco, 1968.

(48) T. H. Dunning, Jr., and P. J. Hay in "Methods of Electronic Structure Theory", H. F. Schaefer, III, Ed., Plenum, New York, 1977.

(49) M. Dupuis, J. Rys, and H. F. King, *J. Chem. Phys.*, **65**, 111 (1976).

(50) T. H. Dunning, Jr., and N. W. Winter, *Chem. Phys. Lett.*, **11**, 194 (1971); *J. Chem. Phys.*, **63**, 1847 (1975). D. Cremer, *J. Chem. Phys.*, **69**, 4440 (1978).

such as methanol,<sup>44,45,51</sup> acetaldehyde,<sup>44</sup> hydrogen peroxide,<sup>44</sup> methylamine,<sup>45</sup> and butadiene.<sup>52</sup> The conclusions regarding the nature of the forces involved were essentially the same for all of these molecules, although in some cases there were additional complications. The hydrogen peroxide difficulties have already been mentioned; for butadiene a more complicated, correlated wave function was required for the cis portion of the potential although not in determining the barrier height from the lower (trans) minimum.

The nature of the intramolecular forces determining barriers can be probed in even more detail by studying the variation of barrier heights with vibrational excitation. This has been done both theoretically and experimentally for methylsilane,<sup>53</sup> and theoretically for  $\text{BH}_3\text{NH}_3$ .<sup>54</sup> Good agreement with spectroscopic values of the derivatives of barrier heights with respect to vibrational coordinates is obtained for methylsilane with SCF-MO wave functions but not with empirical non-bonded potential functions, again showing that these simple potential functions are generally not accurate enough to use in internal rotation problems. The study of vibrational motion in methylsilane also provided a value for the effect of the variation in zero-point energy on the internal rotation barrier.

Other points of view have been taken in attempts to understand internal rotational barriers, and extensive references to these may be found in the reviews by Dale,<sup>55</sup> by Lowe,<sup>56</sup> by Veillard,<sup>29</sup> and by Payne and Allen.<sup>32</sup>

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**Registry No.** Ethane, 74-84-0.

(51) C. W. Kern, R. M. Pitzer, and O. J. Sovers, *J. Chem. Phys.*, **60**, 3583 (1974).

(52) U. Pincelli, B. Cadioli, and B. Levy, *Chem. Phys. Lett.*, **13**, 249 (1972).

(53) C. S. Ewig, W. E. Palke, and B. Kirtman, *J. Chem. Phys.*, **60**, 2749 (1974).

(54) W. E. Palke, *J. Chem. Phys.*, **56**, 5308 (1972).

(55) J. Dale, *Tetrahedron*, **22**, 3373 (1966).

(56) J. P. Lowe, *Prog. Phys. Org. Chem.*, **6**, 1 (1968); *Science* **179**, 527 (1973).

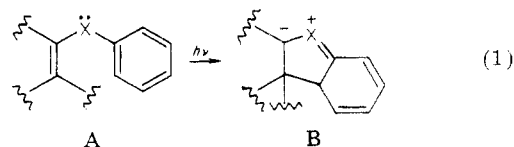
## Photochemical Six-Electron Heterocyclization Reactions

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The equation  $A \rightarrow B$  (eq 1) represents a photochemical six-electron cyclization. X is a heteroatom with an unshared electron pair available for participation in the electrocyclicization. The primary synthetic value of this



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reaction type is the formation of a carbon-carbon bond to an aromatic ring. From a methodological point of view, the heteroatom X functions as a connecting link, which allows the bonding centers to approach each other with the proper trajectory. We have suggested