Variations of molecular geometry from electron diffraction

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Abstract - Gas-phase electron diffraction is one of the principal
tools for the determination of accurate molecular geometry. Re-
cently, research efforts have focused on the determination of
structural changes in series of compounds or even during some
chemical happenings rather than on the study of individual struc-
tures. Internal rotation, substituent effects, the transition
from vapor to crystal phase, and the formation of new bonds are
among the chemical changes whose structural consequences are
being examined. The study of unstable molecules and reaction
products is facilitated by combined electron diffraction/quadrupole
mass spectrometric experiments.

INTRODUCTION: MOLECULAR GEOMETRY AND CHEMICAL CHANGES

Molecular geometry

Molecular geometry means the relative positions of the atomic nuclei in the molecule
(see, eg, ref. 1). The most convenient characterization of the molecular geometry
for a chemist is by bond lengths, bond angles, and torsional angles. These are the
so-called internal coordinates and they are especially convenient to use when
changes of physical and chemical properties are to be correlated with structural
variations in diverse series of compounds. A statement is attributed to Linus
Pauling according to which the most important property of a chemical bond is its
length, ie, the distance between the two nuclei of its constituting atoms. Obvi-
ously, this statement does not merely refer to bond length only, but to molecular
geometry in general. In this connection, Roald Hoffman stated the following
(ref. 2), "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
property of the molecule."

Molecular geometry is only part of our modern definition of molecular structure.
The other part is the electron density distribution. Chemical changes are strongly
correlated with changes in the electron density distribution which, in turn, accom-
pany changes in the nuclear configuration.

The so-called equilibrium geometry characterizes the molecule in the minimum posi-
tion of its minimum in the potential energy function. Thus the equilibrium molec-
ular geometry refers to a hypothetical motionless molecule which does not even
exist in reality. On the other hand, it is an extremely important model correspond-
ing to the most stable structure at the energy minimum, and thus has unambiguous
physical meaning. The more rigid a molecule, the closer this model approximates
its real structure.

The validity and even usefulness of the rigid geometry model has been questioned during the past decade following studies of large amplitude motions and especially fluxional behavior of some systems. Indeed, the applicability of the rigid geometry model diminishes with increasing relative nuclear displacements in a molecule. A similar problem arises when structural information from different physical (and computational) techniques are to be compared (ref. 3). Quantum chemical calculations provide the equilibrium geometry whereas the various experimental physical methods yield geometries averaged over motion. There may be different kinds of average structure depending on the nature of interaction utilized in the physical technique and on the time period of this interaction. The outcome of this averaging, however, depends not only on the time scale of interaction employed in a physical technique but also on the life time of the structure under investigation, and the final result is determined by the relationship of these two.

The possible differences thus arising are often called operational effects. They are taken much more seriously today than they were a decade or two ago. The fact of the matter is that such operational effects may be considerably greater than the "experimental error" of a modern structure determination. The expression "experimental error" here implies not only the experimental error of the mesurements but also uncertainties in theory and analysis.

This raises the question of the accuracy limits in structure determination that remain meaningful in following changes in chemical behavior. No single length or angle value could constitute a comprehensive answer to this question, but it is safe to say that today's best attainable accuracies, amounting to a few thousandths of an angstrom and a few tenths of a degree, may well carry chemical meaning.

Structure and chemical change

Knowledge of molecular geometry has always been considered important in chemistry, primarily for understanding the nature of the chemical bond and generally of the forces keeping a molecule, an ion, a crystal, or any chemical system together. As for its practical importance, opinions have varied including extreme ones ascribing the elucidation of molecular geometry to satisfying aesthetic curiosity rather than to hard-core chemical research.

It was recognized early that molecular size plays a decisive role in molecular interactions and increasing attention has been paid to molecular geometry in the investigation of the mechanism of chemical reactions. However, it has always been a limiting factor that most information on molecular geometry is available for stable and nonreacting molecules, ie, molecules to which nothing is happening.

Much recent research is, however, being directed to the structure of molecules undergoing changes. Incidentally, the modern interpretation of chemical change is broader than it used to be, and includes events such as the torsion of one stable conformer into another, the joining of a gaseous molecule into a crystal or the reverse, dimerization or the dissociation of a dimer into monomers, and the formation of a coordination linkage between a donor and an acceptor. One of the most intriguing problems is the determination of structural changes in molecules at the early stages of chemical reaction.

Considering the broadening of what we include into the domain of chemical changes, the distinction between what is assigned to physical and chemical changes is becoming blurred. An example will illustrate the matter.

Structural differences in torsional isomers

It is generally accepted that there are differences in *both* the physical and chemical properties of *cis*-dichloroethene and *trans*-dichloroethene (Fig. 1). The geometrical isomers of 1,2-dichloroethene are two different chemical substances and they can be separated on the basis of their physical properties.

Consider now 1,2-dichloroethane and its two torsional isomers, ie, the gauche and anti conformers (Fig. 2). They cannot be separated on the basis of their physical properties, and are generally not considered to be two different chemical substances. Yet their molecular geometry as well as their reactivity are different. Incidentally, what is said about their identical physical properties is valid for some properties only. Thus, eg, the two torsional isomers greatly differ in their permanent electric dipole moment which is also a physical property.
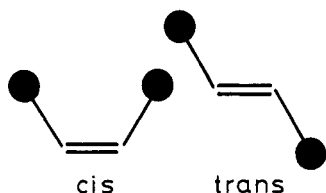

cis   trans

Fig. 1. Model of *cis-* and *trans-*
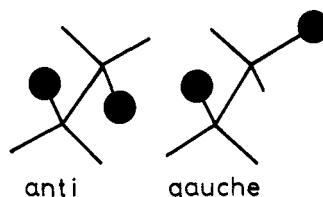   dichloroethene

anti   gauche

Fig. 2. Model of *anti-* and *gauche-*
   dichloroethane

The bond configurations of the gauche and anti conformers of 1,2-dichloroethane used to be considered the same. The general assumption was that their geometries differ in the torsional angles only. It is now known (ref. 4(a) and (b)), however, that there are other differences, including a 3° difference in the bond angle C-C-Cl which exceeds experimental error by a whole order of magnitude. There is a relaxation of the bond configurations during internal rotation and the emerging molecular geometry is the result of a compromise.

There are few physical methods for the elucidation of molecular geometry that satisfy the accuracy requirements allowing the discussion of structural changes accompanying chemical changes of the sort mentioned above. One of them is gas-phase electron diffraction.

MODERN GAS-PHASE ELECTRON DIFFRACTION

This technique of molecular structure determination is based on the phenomenon that a beam of fast electrons is scattered by the potential from the charge distribution of the molecule. The resulting interference pattern depends on the molecular geometry and many other properties.

Unique and precise experimental apparatuses, modern computational methods, understanding of the physical meaning of the determined parameters, and the combined application of this technique with other techniques all contributed to the recent developments in modern gas-phase electron diffraction (ref. 5). Its capabilities and the broadened area of its applications are characterized in the words of Jerome Karle (ref. 6):

"...As a result of the dedicated efforts in a relatively small number of laboratories, gas electron diffraction has served as a valuable tool in the investigation of molecular structure. Much information has been obtained concerning molecular configuration, bond distances and angles, internal motion including hindered rotation and barrier heights, preferred orientation in conformers and conjugation and aromaticity. Investigations have also concerned mixtures in equilibrium, including evaluation of thermodynamic quantities, free radicals, a wealth of high-temperature studies, clusters, isotope effects, and the joint use of other techniques such as laser excitation, microwave and mass spectrometry. We thus have the view of gas electron diffraction as a technique of wide application to many aspects of molecular structure and when it is combined with various spectroscopic techniques the value of both may be considerably enhanced. ..."

STRUCTURAL VARIATIONS

Substituent effects

Determination of the geometrical consequences of substitution in a series of com-
pounds may contribute to the understanding of intramolecular interactions and may
make possible the prediction of structural changes in compounds, not yet studied.
Substitution may take place at the central atom or at the ligands in the series.

Thus, for example, the geometrical changes are of interest in series of sulfur de-
rivatives in which the ligands of sulfur are changed, or in which the same ligands
appear in analogous sulfides, sulfoxides and sulfones (ref. 7). Figures 3 and 4
show the variations in sulfur-carbon bond lengths (ref. 8), as well as similar
variations in selenium-carbon bond lengths (ref. 9) for sulfides and selenides, res-
pectively. Depending on the valence state of carbon, the changes in the S-C bond
lengths may exceed 0.1 A, going from an S-C≡ bonding situation to an S-$\overset{|}{C}$- bonding
situation. The two respective bond lengths are 1.671±0.002 and 1.806±0.002 A in
bis(methylthio)ethene, H_3C-S-C≡C-S-CH_3 (ref. 10). Note here that the two bond lengths
were determined in the same experiment and in the same molecule and, accordingly,
the bond length difference is known very accurately. Figure 3 also indicates some
spread of the bond lengths in the vertical direction for a given carbon valence
state amounting to around a hundredth of an angstrom. In the presence of more
electronegative ligands on carbon the S-C bond lengthens compared to an analogous
bonding environment in which these ligands are replaced by less electronegative
ones. The S-C bond length in trifluoromethyl mercaptan, CF_3SH, is 1.800±0.005 A
(ref. 11), but is 1.814±0.005 A in methyl mercaptan, CH_3SH, (ref. 12). The difference,
however, only slightly exceeds the combined error and the physical meaning of the
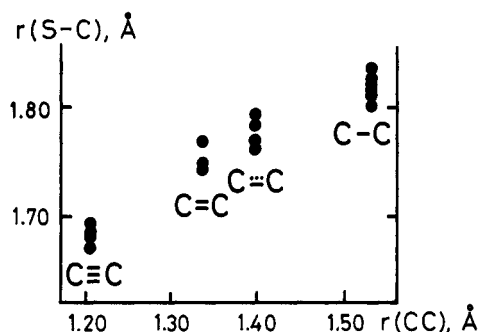two distance parameters is not the same.

Fig. 3. S-C bond lengths in sulfides
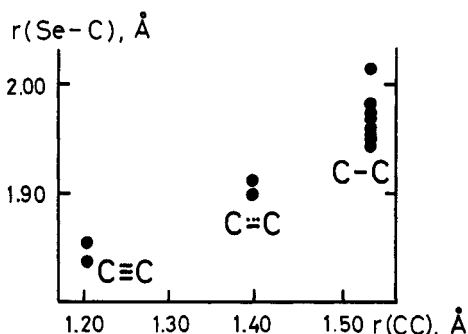at various carbon bonding situations

Fig. 4. Se-C bond lengths in selenides
at various carbon bonding situations

Sulfones show much greater variation of the S-C bond length with change of the
carbon ligands than do sulfides (ref. 13). The changes amount to almost a tenth of
an angstrom, as shown for two pairs of compounds below, using electron diffraction
data:

CH_3SO_2Cl	S-C	1.763±0.005 A	(ref. 14)
CF_3SO_2Cl	S-C	1.865±0.006 A	(ref. 15)

and

$(CH_3)_2SO_2$	S-C	1.771±0.004 A	(ref. 16)
$(CF_3)_2SO_2$	S-C	1.858±0.005 A	(ref. 17)

This bond lengthening upon CH_3/CF_3 substitution is due to the electron withdrawing
ability of the CF_3 group versus the electron releasing ability of the methyl group.
In spite of the intermediate nature of the CCl_3 group, the S-C bond of $(CCl_3)_2SO_2$
is the longest of all, viz. 1.894±0.005 A (ref. 18). However, the space requirement
of the bulky trichloromethyl groups apparently masks the electronic effects.

The shortest Cl...Cl nonbonded distance involving different CCl_3 groups is much smaller than twice the chlorine van der Waals radius (3.31 A vs 3.60 A). This is also in spite of the large CSC bond angle of 109.8±04° in $(CCl_3)_2SO_2$ as compared with the CSC bond angles in $(CH_3)_2SO_2$, 102°, and $(CF_3)_2SO_2$, 103°.

The strong sensitivity of S-C bond length in sulfones to the carbon ligands is accompanied by their conspicuous insensitivity to changes in the carbon valence state. This contrasts what was noted above for sulfides. Thus, eg. the S-C bonds have the same length in $(CH_3)_2SO_2$, viz. 1.771±0.004 A (ref. 16) and in $(C_6H_5)_2SO_2$, viz. 1.772±0.005 A (ref. 19). These two bond lengths have even been determined within the same molecule, viz. $C_6H_5SO_2CH_3$. Here however, the sulfur-carbon(methyl) bond appeared to be somewhat longer than the sulfur-carbon(phenyl) bond, but uncertainties were too large to reliably establish the difference (ref. 20).

Analogous sulfoxides have been investigated and the general observation is that the bonds in sulfoxides are always somewhat longer than the bonds of the corresponding sulfones (ref. 13).
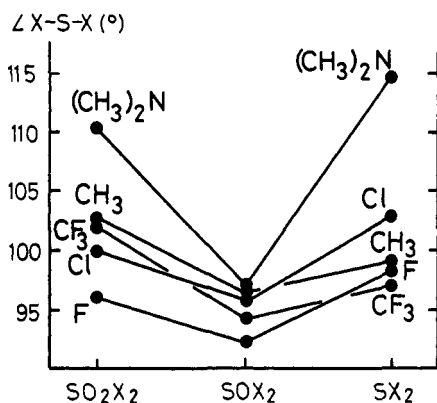

Fig. 5. Bond angles at sulfur in analogous sulfones, sulfoxides, and sulfides
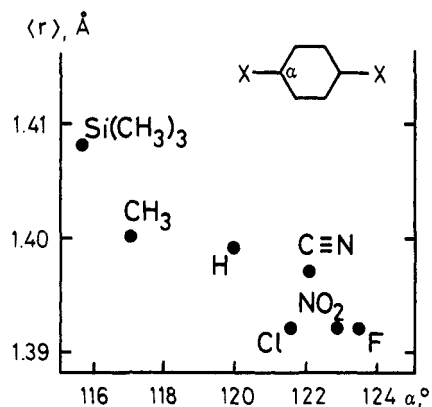
Fig. 6. The ipso angle and the mean bond length of the ring in para-disubstituted benzene derivatives

The bond angle variations (Fig. 5) in analogous series of sulfones/sulfoxides/sulfides have also attracted interest. For some time the observations seemed to be at variance with predictions (ref. 21) based on popular models, such as the valence shell electron pair repulsion (VSEPR) theory (ref. 22). The angular decrease in sulfoxides compared to sulfones was predicted to continue in the analogous sulfides. This was, however, not the case, except for the hydrides.

According to the VSEPR theory, the molecular shape is determined by all electron pairs in the valence shell of the central atom. The shape will correspond to the maximum distances among all electron pairs. Important limiting conditions augment this basic postulate. The valence shell is assumed to have spherical symmetry, and ligand sizes should be small relative to the size of the central atom. The first limiting condition excludes many structures with transition metal as central atom while the second excludes many structures with second period elements (Li to F) as central atom from the applicability of this theory. The theory should apply well to the structural chemistry of third and subsequent period main group elements.

Disagreements between observed angular variations and VSEPR predictions have been shown to be apparent and originate from improper application of the model rather than from its failure. The basic postulate considers both bonding pairs and lone pairs of electrons for predicting molecular shape, but usually only bond angle

variations are considered in judging the validity of these predictions (ref. 23).
Consider, eg, a valence shell with two bonds and two lone pairs. There will be
altogether six electron pair/electron pair interactions comprised of one bond/bond,
one lone pair/lone pair, and four bond/lone pair interactions. The electron pair
configuration, including the bond angle, will be least influenced by the single and
weakest bond/bond interaction in such a valence shell. Accordingly, the angles made
by the lone pairs will be important to consider for testing VSEPR predictions in
such a structure. Ab initio quantum chemical calculations for tetrahedral systems
were in perfect agreement with such a generalized applicability test (ref. 24). A
similar approach for testing the VSEPR model has been introduced for trigonal
bipyramidal configurations (ref. 25).

Investigation of the geometrical consequences of substitution in a series of com-
pounds may be useful in working out various empirical relationships between struc-
tural parameters and other physical and chemical characteristics. For example, the
large amount of experimental geometrical data on sulfones has been utilized for
predicting group electronegativities and vibrational frequencies (ref. 26).

Of the many available examples of substituent effects on molecular geometry we
mention here but one: the investigation of ring deformation in substituted benzene
derivatives. An early electron diffraction study of phenylsilane, $C_6H_5SiH_3$, by
Keidel and Bauer (ref. 27) has already raised this question. Subsequent observa-
tions of ring deformations were based mostly on X-ray crystallographic data leading
to valuable additivity relationships (refs. 28, 29). The application of electron
diffraction has proved to be especially successful for para-disubstituted deriva-
tives. The emerging pattern is illustrated in Fig. 6 (ref. 30) according to which
electronegative substituents somewhat compress the ring along the molecular axis,
while electropositive substituents somewhat elongate it (ref. 31). The most sensi-
tive parameter to the substitution is the ipso angle, ie, the ring angle adjacent to
the substituent. With accumulating data on the structure of substituted benzene
derivatives, the intriguing question whether these molecules undergo any appre-
ciable change when entering a crystal structure can also be investigated.

IMPACT OF CRYSTAL ENVIRONMENT

Although it has long been recognized that intermolecular interactions may influence
molecular geometry in the crystal as compared to the free molecule, it is only re-
cently that crystallographers have attempted to determine such differences. The
importance of knowledge of the impact of the crystal environment on molecular
structure is far from purely academic. The structure of biologically active mole-
cules is known from X-ray crystallographic studies but their activity is exercised
not in crystal but in solution where the intermolecular interactions present in the
crystal diminish or at least change.

That the possible gas/crystal molecular structure differences have previously been
generally ignored, originated from necessity. The data available for comparison
were seldom accurate enough to render such comparisons truly meaningful. Demand-
ing crystallographic research, however, in cooperation with gas-phase structure
studies and quantum chemical calculations, is aiming beyond the determination of
crystal molecular structure at uncovering the impact of crystal environment upon
molecular structure.

For the purpose of a meaningful comparison the results from all sources must be
free from the operational effects mentioned in the Introduction. If the geometries
determined in the gas and in the crystal still differ, after eliminating all opera-
tional effects, then these differences can be ascribed to consequences of intermo-
lecular interactions. The observation of such differences provides the best means
to investigate the impact of crystal environment on molecular geometry (ref. 32).
We will illustrate this with an example.

Table 1 presents the ipso angles in four para-disubstituted benzene derivatives in the gas and in the crystal. The gas/crystal differences range from half a degree to almost two degrees. In one case the ipso angle is larger in the crystal than in the gas, in the other three cases it is larger in the gas than in the crystal. Upon examining molecular packing in the crystals, it is possible to group the four cases into three kinds of interaction leading to gas/crystal differences. It must be stressed that there is no way to predict such differences unless the molecular packing in the crystal is known.

TABLE 1. The ipso angle in para-disubstituted benzene derivatives in the gas phase and in crystal

Compound	Ref.	Free molecule	Crystal molecule
p-$C_6H_4(CN)_2$	33	122.1±0.2	121.6±0.1
p-$C_6H_4(NC)_2$	34	121.7±0.2	122.2±0.3
p-$C_6H_4(NH_2)_2$	35	119.8±0.2	117.9±0.1
p-$C_6H_4(OH)_2$	36	120.7±0.2	119.7±0.1

It appears that the ring deformation decreases in the crystal of paradicyano benzene versus the free molecule because interactions between antiparallel cyano groups attenuate the deforming influence of the cyano groups in the layered crystal structure. The intermolecular distance between the cyano groups may be as short as 3.56 A. On the other hand, for para-diisocyanobenzene, interactions may occur between the isocyano group of one molecule and the benzene ring of another molecule in the crystal: the corresponding intermolecular distance is 3.45 A. This interaction enhances the deforming influence of the isocyano groups in the crystal.

The ipso angle decreases considerably for para-diaminobenzene in going from the free molecule to the crystal. The change was attributed to the formation of N-H...N hydrogen bonds, making the amino group a better π-donor in the crystal than in the gaseous phase. A similar interpretation, implying the influence of O-H...O hydrogen bonds in the crystal, has been suggested for the difference observed for para-dihydroxybenzene.

The relatively strong intraring interactions in the benzene ring make it rather insensitive to the influence of intermolecular interactions. It is only the capabilities of state-of-the-art structure analysis coupled with careful elimination of operational effects that allow the detection of these small differences in ring deformation.

Weaker intramolecular interactions are more susceptible to the influence of crystal environment than stronger intramolecular interactions. Coordination molecules (ref. 37) may thus be good targets for gas/crystal structure comparison. Coordination linkages, such as N-B, N-Si, and Zn-N have been observed to shorten considerably in crystal environment compared to the corresponding free molecules (Table 2).

TABLE 2. The length of coordination linkage in the gas phase and in the crystal

Compound	Bond	Coordination bond length (A)			
		Gas from electron diffr.	Ref.	Crystal from X-ray diffr.	Ref.
$(CH_3)_3N.BCl_3$	N-B	1.659±0.006	38	1.609±0.006	39
$N(CH_2CH_2O)_3SiCH_3$	N-Si	2.45±0.05	40	2.175±0.004	41
$[(CH_3)_2N(CH_2)_3]_2Zn$	N-Zn	2.392±0.015	42	2.307±0.004	42

COMBINED EXPERIMENT AND UNSTABLE SPECIES

The investigation of structural changes accompanying chemical changes necessitates careful control of the vapor composition in the electron diffraction experiment. This has been accomplished in a combined electron diffraction/quadrupole mass spectrometric experiment (ref. 43) outlined in Fig. 7.
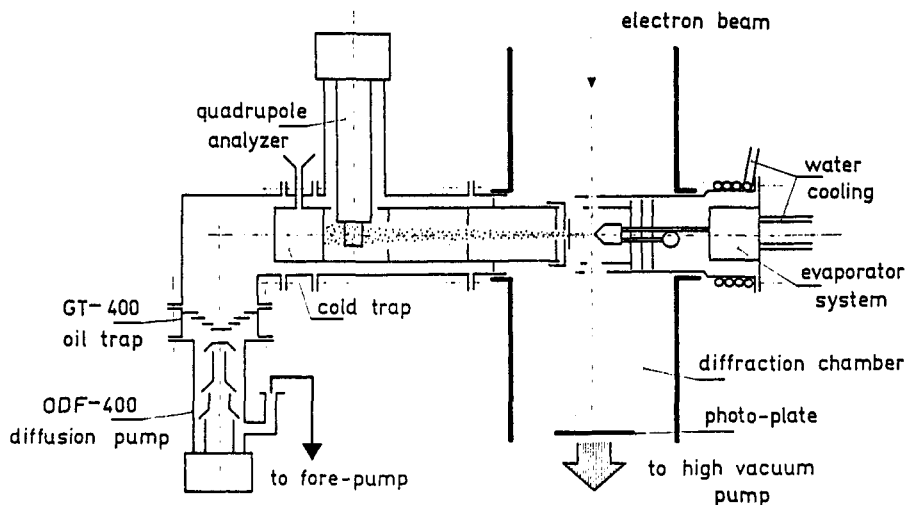

Fig. 7. Combined electron diffraction/quadrupole mass spectrometric experiment

Halogenated carbene analogs are important because of their reactivity, but this property has hindered their structure determination. Such unstable species, however, can be produced directly in the diffraction apparatus during the electron diffraction experiment. Solid/gas reactions have been utilized for this purpose under mass spectrometric control in the studies of $GeCl_2$ (ref. 44), $GeBr_2$ (ref. 45), $SiCl_2$ and $SiBr_2$ (ref. 46). Typical reactions carried out in a reactor nozzle system (ref. 47) of the electron diffraction experiment were the following:

$$Ge(s) \quad + \quad GeCl_4(g) \quad \xrightarrow{660\ ^oC} \quad 2\ GeCl_2(g)$$

$$Si(s) \quad + \quad Si_2Cl_6(g) \quad \xrightarrow{1200\ ^oC} \quad 3\ SiCl_2(g)$$
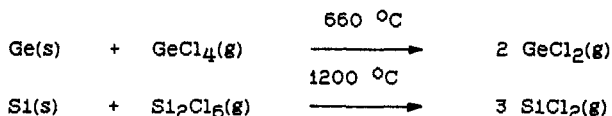
Table 3 presents the geometrical parameters obtained. The structures are highly bent. The variations among halogenated carbene analogs can well be interpreted by electron pair repulsions and nonbonded interactions (ref. 32). Indication of the presence of dimers and/or excited states in some of these experiments has prompted theoretical studies which also provided calculated geometries for the ground state monomers in good agreement with the experiment (ref. 48).

TABLE 3. Bond lengths and angles of some halogenated carbene analogs

$SiCl_2$	$SiBr_2$
2.089±0.004 A	2.249±0.005 A
103.1±0.6°	102.9±0.3°
ref. 46	ref. 46
$GeCl_2$	$SiBr_2$
2.186±0.004 A	2.337±0.013 A
100.4±0.4°	101.4±0.9°
ref. 44	ref. 45

Another recent study was aimed at elucidating the geometry of the allyl radical which was produced in a reactor nozzle during the diffraction experiment by pyrolysis of 1,5-hexadiene (ref. 49).

$$C_6H_{10} \xrightarrow{\quad 960\ ^{\circ}C \quad} 2\ C_3H_5$$
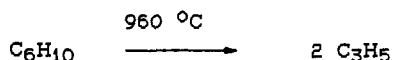
Knowledge of the allyl radical geometry may contribute to the understanding of the mechanism of propylene transformation through hydrogen migration (ref. 50). According to one of the supposed mechanisms, the allyl radical itself is the transition state in this transformation.

* * *

The above examples illustrate some of the potentials of modern gas-phase electron diffraction and the enhancement of its capabilities when applied with other techniques in a concerted way.

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