Molecular Structure by Diffraction Methods

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Molecular Structure by Diffraction Methods

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up to September 1977

Senior Reporters

L. E. Sutton, *Chemical Crystallography Laboratory, University of Oxford*
M. R. Truter, *Molecular Structures Department,*
Rothamsted Experimental Station, Harpenden, Herts.

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Introduction

This volume differs from its predecessors in not being divided into three parts, an indication of a change of emphasis. While the first chapter is devoted specifically to results from electron diffraction, the next two deal with conformational energies of discrete molecules and the use of this information to predict crystal structures. Effects on molecules of packing are discussed in Chapter 7, 'Intermolecular Interaction' (other than hydrogen bonding). Hydrogen bonding is mentioned in nearly all the other chapters, and covered explicitly in Chapter 5 which is on the results of neutron diffraction.

For the results of X-ray diffraction measurements coverage has changed in that 'molecular' is interpreted more widely to include macromolecules; these were previously represented by proteins, a chapter (10) on which is still included, but now, in addition, there are chapters on mono-, oligo-, and polysaccharides (8), on nucleic acids and their constituents (9), and on silicates and related compounds (6). In the new topics covered Reporters have been able, where necessary, to include background information on technique as well as results. All Reporters have written critical accounts with emphasis on correlation and interpretation, *i.e.*, the things which are not provided by straightforward retrieval facts. Most chapters cover the literature to October 1977.

At the urging of its author, a major change in the organization of the chapter on results from electron diffraction studies has been made. The aims are to provide a more precise self-indexing of compounds and to give more technical information about the individual determinations of structure. At the same time, the progress of investigations in various groups of compounds is indicated. The results given are for the greater part from papers published in the period August 1976 to July 1977 inclusive (see the end of Section 2 of Chapter 1). This chapter also emphasizes an interestingly controversial matter, *viz.* the proper use of structural information derived from so-called '*ab initio*' and 'molecular mechanics' calculations about which we have commented previously in general terms. The growing importance to the discussion of structure of 'molecular mechanics' calculations has been recognized by including two chapters on this subject, covering rather different aspects. These provide a more theoretical complement to, *e.g.*, the massive collection of facts about conformation that was presented in Volume 5, and to much other information too.

The decision to select some topics has been made easier by the existence of good sources of information which are described in Chapter 4. Of particular importance is the Cambridge Crystallographic Data Centre (mentioned by so many of the Reporters in this and previous volumes); their files contain checked results from three-dimensional X-ray or neutron diffraction determinations on compounds that contain at least one organic carbon atom (but not too many such atoms, macromolecules are excluded) and there are extremely good facilities available for retrieval

by chemists who may, or may not, be crystallographers. Results for small organic molecules can be readily located if the structural formula is known.

In small molecules the effects of improved technique are shown in the results reported here. Automatic diffractometers allow rapid collection of observations, the main limitation on precision being the quality of the crystal, while direct methods often (though still not invariably) provide the solution to the phase problem. One effect is the increase in the determinations of structures containing two or even more molecules in the asymmetric unit, giving particularly valuable results for conformational studies. The greater reliability of atomic positions means that variations in distances may be evidence, not of experimental error, but of real effects in bonding, *e.g.* Chapter 6 on 'Silicates' deals with the recent interest in the effect on the structure of cations which do not just fit into holes, and also with the rationalisation of Si—O distances and Si—O—Si angles. While valencies of less than 1 are a common concept in such electrostatic structures, the realisation that anomalous interatomic distances really do correspond to some bond valence between 0 and 1 within and between molecules, is discussed in Chapter 7, again broadening the concept of the 'molecule'. These two chapters represent the selection from Inorganic Chemistry which we have been able to cover in this volume. It has been necessary to omit coordination chemistry which is well served by the two Specialist Periodical Reports on Inorganic Chemistry and, for organic ligands, by the Cambridge Crystallographic Data Files.

In Chapter 8 the wealth of quantitative measurements on monosaccharides is summarised and correlated. The investigation of mono- and oligosaccharides to help to understand the biologically important polysaccharides is considered and the techniques in current use for diffraction studies of polysaccharides are evaluated.

The molecules of nucleic acids and their constituents, Chapter 9, are, even more than monosaccharides, investigated for their relevance to the poorly-diffracting natural polymers. Some of the exciting advances described in Chapter 10 are in proteins which bind nucleic acids. Understanding of the principles of protein structure interacts with the solution of their crystal structures. The results are surveyed in groups classified by the biological action of the protein. A similar grouping, this time by pharmacological activity, is used for the final chapter on small organic molecules which have been selected on the basis of their pharmaceutical activity. The conformation and activity relationships are emphasised.

If space (and hence cost) were no object we would like to provide comprehensive coverage at the same level as that achieved on chosen topics. In future volumes we hope to treat other topics in depth and 'top-up' some of the present ones so that coverage would be comprehensive over a period of years.

Some Reporters had used nm or pm and others Å; all have been converted to Å for consistency and convenience (for SI purists $1\text{Å} \equiv 10^{-10}$ m so 1 nm $= 10^{-9}$ m $= 10$ Å, and 1 pm $= 10^{-12}$ m $= 0.01$ Å). We thank the Reporters who produced their articles on time and apologise to them and to our readers for delays caused by those who found the task more time-consuming than they had expected.

L. E. Sutton
M. R. Truter

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Electron Diffraction Determinations of Gas-phase Molecular Structures

BY L. SCHÄFER

1 Some Current Trends in Gas-phase Electron Diffraction Procedures

1977 marked the fiftieth anniversary of the first publication describing an electron diffraction experiment. To commemorate the event, the American Crystallographic Association called a special meeting.[1] The historical factors leading to the discovery of this phenomenon were reviewed in a special paper.[2]

To the critical observer of gas-phase electron diffraction (GED) as applied to structural chemistry, the record of this tool must appear somewhat mottled. The first successful structural studies of gaseous molecules by high-energy elastic electron scattering originally raised high hopes for a breakthrough in understanding the structure of matter. To some extent the technique has indeed contributed to such a development, but, like no other method of structural chemistry, GED combines quantitative precision with essential incompleteness because it gives only one-dimensional information. In addition to producing some very valuable and funda-mental structural insight, interpretations of electron diffraction data have, therefore, sometimes engendered strikingly misleading structural models.

In view of these characteristic imperfections, it is important to take note of a striking metamorphosis of current GED techniques. Very recently gradual im-provements of data analysis have produced a rather spectacular revolution of GED leading to a general enhancement of its versatility. It is now possible to supplement GED data with observables or their expectation values from other sources, by applying modes of analysis which were not known or not practical a decade or even a few years ago. The term 'electron diffraction' is, therefore, in a large number of current studies really the collective synonym for a matrix of complex and hybrid operations involving various consistently combined, different techniques. This development has had its main impact in two different areas, *viz.* in joint spectro-scopic–diffraction studies and, more recently, in hybrid theoretical–GED investigations.

In the former, rotational constants obtained from spectroscopy are incorporated into GED data analysis. Proper vibrational corrections are needed to make diffrac-tion and spectroscopy compatible. As a result of this joint application of different observables, it was often possible to determine very accurately the structural para-meters of molecules for which very little information could have been obtained by

[1] 'Proceedings of the Symposium Commemorating 50 Years of Electron Diffraction', *Trans. Amer. Cryst. Assoc.*, 1977, Vol. 13.
[2] K. Molière, *Naturwiss.*, 1977, **64**, 310.

either GED or spectroscopy alone. It is only about ten years ago that the first consistent joint study appeared which made use of the proper vibrational corrections and a least-squares scheme.[3]

In hybrid theoretical–GED investigations, calculated molecular parameters are incorporated into the data analysis in order to reduce the number of independent unknown variables. This has been done, for example, by optimizing the strain energies of model geometries employing molecular mechanics or quantum mechanical approximations. Thus in some cases, when several molecular models could be fitted to the same experimental diffraction pattern, their strain energies were used to discriminate against some of them. In other cases optimized molecular conformations were used as starting points for the least-squares analysis of the diffraction data. For relatively large molecules, the starting geometry can strongly bias the least-squares minimum, projecting in this manner the computational assumptions into the experimental results. With the continuing advancement of *ab initio* quantum mechanics, it seems now also possible to transfer calculated geometrical parameters (*e.g.* differences between nearly equal bond distances) directly, as constraints, into the least-squares scheme.

In other investigations, available force fields were used to derive mean amplitudes of vibration which are also, in principle, observables of the diffraction experiment. These theoretical amplitudes, or some of them, or amplitude differences calculated for a group of correlated distances, were then often used as constraints of the least-squares GED data refinement. Alternatively, the refined, experimental mean amplitudes of vibration for a particular model were compared with the theoretical ones.

The hybrid procedures mentioned are particularly satisfactory when the same force field is consistently applied to compute both the optimized geometries and the corresponding mean amplitudes. In such studies the optimum geometry and the force field which produced it are used together in the vibrational calculations, and calculated amplitudes and optimum geometry are used together in the least-squares scheme of the GED data analysis. The first consistent studies of this kind, which combined the experiences of many groups, used force fields derived from molecular mechanics in investigations of some relatively large cyclic hydrocarbons.[4,5] In several laboratories *ab initio* procedures are now applied in the same consistent way for relatively complicated systems, demonstrating the further advance of this technique. The co-operative effect achieved by these combined procedures has often made it possible to give a plausible description of the unperturbed conformational behaviour of relatively complicated molecules, for which no safe statement could have been made on the basis of any of the applied techniques alone. In some cases ambiguities existing in previous publications could be resolved in this way. In other cases, some older conclusions even had to be corrected. It is very pleasant to note the complementarity of theory and experiment in such studies. Whereas theoretical procedures need guidance and confirmation by experimental observation the conclusions obtained by them in turn significantly reflect upon proposed data interpretations in many specific cases.

[3] K. Kuchitsu, T. Fukuyama, and Y. Morino, *J. Mol. Structure*, 1968, **1**, 463.
[4] W. K. Schubert, J. F. Southern, and L. Schäfer, *J. Mol. Structure*, 1973, **16**, 403.
[5] R. L. Hilderbrandt, J. D. Wieser, and L. K. Montgomery, *J. Amer. Chem. Soc.*, 1973, **95**, 8598.

The optimism of the previous paragraphs must be qualified by a serious warning. Vapour-phase data of relatively complicated polyatomic molecules usually do not provide anything but circumstantial evidence for structural conclusions. In most cases the number of observables is smaller than the number of unknowns. There is a certain co-operative effect in consistently combining several different techniques, which makes the results of hybrid studies relatively reliable, but the quality of investigations of this kind depends profoundly on the quality of the applied techniques. Molecular mechanics calculations, for example, can in general provide satisfactory results when the conformational situation of a particular test case represents an interpolation with respect to the model systems which were used to define the empirical force field involved, but in extrapolative cases they have often led to disaster. Unfortunately, it is often not clear whether a particular model of interest represents an interpolative or an extrapolative situation. In quantum mechanical calculations when *ab initio* procedures are used, uncertainties can often arise from the choice of basis sets and because it is in most cases not possible to optimize molecular geometries fully by relaxing all relevant parameters. When semi-empirical procedures are applied, one has often the impression that an indefinite range of possible models may be derived by adjusting the empirical parameters. In computations of mean amplitudes of vibration, finally, the force fields applied are generally underdetermined or affected by uncertainties of spectroscopic assignments. Because of this long list of potential dangers, hybrid theoretical–GED procedures must be used with caution. The results of such studies can only be as good as investigators are careful. To make use of published GED results requires, therefore, more than the reading of the abstract of a paper.
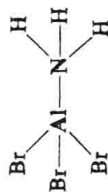
Many of the papers quoted in the following sections of this Report will demonstrate the changed methodology. Whenever possible, investigators are no longer satisfied merely to fit theoretical models to experimental radial distributions, as once was the conventional course, and indeed, the only practicable one. One has now the computional means to require, as a basic rule, that no GED study is concluded by a final molecular model which is energetically unstable, without giving special justification, and that no GED study is concluded, again without special justification, by a final theoretical model that reproduces experimental intensity only by using mean amplitudes of vibration which differ by orders of magnitude from calculated ones.

In observing these developments, the impression is conveyed that responsibly applied joint spectroscopic–GED and hybrid theoretical–GED procedures have created the effect of a quantum jump in the versatility of gas-phase electron diffraction that can be compared to the improvements which, in the earlier history of the field, were achieved by the invention of the rotating sector or by the first application of automated densitometry. It seems safe to predict that the hybrid techniques mentioned will be found to be increasingly useful.
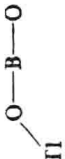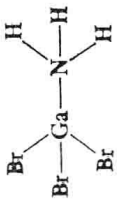
2 Structural Results from GED Studies of Individual Molecules

This Report departs from the conventions which have been followed in previous surveys of results. We present the structural results of the papers reviewed[6–88] by tabulating the significant geometrical parameters of each molecule. Each molecule is identified in the Table by its gross formula and by its name. The names given are those used in the original papers; if no names were used originally, the I.U.P.A.C.

Table *Results of gas-phase electron diffraction (GED) structure determinations*

Compound	Method	Results and Comments	Ref.
(a) Inorganic Molecules			
AlBr₃H₃N Aluminium bromide–ammonia complex	GED, vib. calc. T=191—204 °C	r_a(Al—N)=1.997(19) Å; r_a(Al—Br)=2.264(5) Å; ∠(BrAlBr)=115.7(3)°. C_{3v} symmetry with a staggered conformation was assumed. Mean amplitudes of vibration from spectroscopic calculations were used in the data analysis. Even though some of the bond distances are not resolved in the radial distribution curve, good estimates for individual bonds can be given from an analysis of non-bonded distances. The structure of the molecule is similar to that of the chlorine analogue.	6
Ar$_n$ Argon clusters	GED	Microaggregates are formed by homogeneous nucleation in the expansion of a free gas jet. The median number of atoms, n, in the aggregates can be varied by changing the gas density in the jet. Experiments are discussed, in which Ar aggregates are crossed by an electron beam to give photographic Debye–Scherrer-type diagrams. In the case $10 < n < 50$ the best agreement between theoretical and experimental curves is obtained when the model atoms form inter-locking icosahedra. At $n < 50$ these 'polyicosahedra' become unstable compared with large multilayered icosahedra. This transition seems to be much more due to the geometry and to the structure of the surface of the aggregates than to the interatomic forces. It is, therefore, possible that these results which were obtained for argon, can be extended to metals, using the same values of n.	7
AsBr₃ Arsenic tribromide	GED, MW, vib. calc. GED T(variable) =373, 466 K MW T=room temp.	From GED: at 373 K: r_a(As—Br)=2.3244(24) Å; r_a(Br···Br)=3.5518(49) Å; ∠(BrAsBr)=99.64(13)°; u(As—Br)=0.0564(24) Å; u(Br—Br) =0.1178(53) Å. at 466 K: r_a(As—Br)=2.3276(24) Å; r_a(Br···Br)=3.5554(61) Å; ∠(BrAsBr)=99.59(19)°; u(As—Br)=0.0610(26) Å; u(Br—Br) =0.1344(63) Å. From MW: r_z(As—Br)=2.324(3) Å; ∠(BrAsBr)=99.8(2)°.	8, 9

Compound	Method	Results	Ref.
AsH₉Si₃ Trisilylarsine (SiH₃)₃As	GED, vib. calc.	The two mean amplitude of vibration values u at each temperature of the GED study combined with observed vibrational frequencies were used to evaluate force constants for the molecule. The differences between the lower- and higher-temperature values of the distances and amplitudes are compared with the expected effect of temperature change on molecular vibration and rotation. Estimates are given for the anharmonicities of molecular vibration. $r_a^0(Si-As) = 2.353(3)$ Å; $\angle(SiAsSi) = 94.1°$; $\angle(AsSiH) = 108.2°$. The procedure applied is the same as that described for H₉PSi₃.	10
BO₂Tl Thallium metaborate O—B—O / Tl	GED $T = 1080$ K	$r_a(B-O) = 1.265(30)$ Å; $r_a(Tl-O) = 2.42(4)$ Å; the effective TlOB angle is given as 130(10)°. Composition of the vapour under the conditions of the experiment is given as 33(5)% Tl₂O and 67(5)% TlBO₂.	11
Br₃GaH₃N Gallium bromide–ammonia complex Br—Ga—N—H with Br, Br, H, H	GED $T = 215$ °C	$r_a(Ga-N) = 2.081(23)$ Å; $r_a(Ga-Br) = 2.288(5)$ Å; $\angle(BrGaBr) = 116.1(3)°$. C_{3v} symmetry with a staggered conformation was assumed. Mean amplitudes of vibration from spectroscopic calculations were used in the data analysis. Even though some of the bond distances are not resolved, good estimates for individual bonds can be given from non-bonded distances. The structure is similar to that of the chlorine analogue.	6
Br₃La Lanthanum tribromide	GED, vib. calc. $T = 1300(100)$ K	$r_g(La-Br) = 2.741(5)$ Å; $r_g(Br-Br) = 4.634(43)$ Å.	12

6 M. Hargittai, I. Hargittai, V. P. Spiridonov, and A. A. Ivanov, *J. Mol. Structure*, 1977, **39**, 225.

7 J. Farges, 'Proceedings of the International Meeting on Small Particles and Inorganic Clusters', Lyon-Villeurbanne, Sept. 1976.

8 S. Samdal, D. M. Barnhart, and K. Hedberg, *J. Mol. Structure*, 1976, **35**, 67.
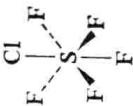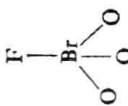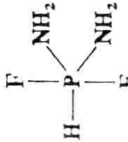
9 A. G. Robiette, *J. Mol. Structure*, 1976, **35**, 81

10 B. Beagley and A. R. Medwid, *J. Mol. Structure*, 1977, **38**, 239.

11 S. A. Komarov and Yu. S. Ezhov, *Zhur. strukt. Khim.*, 1976, **17**, 750.

12 N. I. Giricheva, E. Z. Zasorin, G. V. Girichev, K. S. Krasnov, and V. P. Spiridonov, *Izvest. Vyssh. Uchebn. Zaved., Khim. khim. Tekhnol.*, 1977, **20**, 284.

Table—*continued*

Compound	Method	Results and Comments	Ref.
ClF_5S Sulphur monochloropentafluoride	GED, MW, vib. calc., semi-empirical MO T=room temp.	$r_g(S–Cl)=2.047(3)$ Å; $r_g(S–F)$mean$=1.570(1)$ Å; $r_g(S–F_{eq})=1.566(3)$ Å; $r_g(S–F_{ax})=1.588(9)$ Å; $\angle(ClSF_{eq})=90.7(2)°$. A combined GED and MW study based on spectroscopically established C_{4v} symmetry. A harmonic force field was constructed to reproduce observed vibrational frequencies. An r_z-structure is given. Calculated mean amplitudes are in good agreement with those obtained from the diffraction data. Observed average moments of inertia are in good agreement with calculated ones. The experimental findings are discussed in the light of predictions of VSEPR theory and of semi-empirical MO calculations. A definitive resolution of the structure of this molecule by GED alone would not have been possible.	13
Cl_3Lu Lutetium trichloride	GED, vib. calc. T=1250(50) K	$r_g(Lu–Cl)=2.417(6)$ Å; $r_g(Cl\cdots Cl)=3.996(37)$ Å; $\angle(ClLuCl)=111.5(2.0)°$. A pyramidal configuration is proposed for the molecule.	14
$FBrO_3$ Perbromyl fluoride	GED, vib. calc. T=250 K	$r_g(Br–O)=1.582(1)$ Å; $r_g(Br–F)=1.708(10)$ Å. C_{3v} symmetry assumed. Vibrational amplitudes were fixed in the least-squares refinements at values calculated with force fields obtained from spectroscopic data. The given parameters are, therefore, highly correlated to the force-constant refinements. The data are consistent with two geometrical minima corresponding to a distorted tetrahedral structure and a more regular tetrahedron, respectively. r_α structures and estimates of r_α° and r_e geometries are also given.	15
$F_2H_5N_2P$ Diaminodifluorophosphorane	GED, CNDO/2 T=room temp.	An r_a structure which is not resolved in the RD curve is given. The experimental data can be reproduced by a trigonal-bipyramidal structure with axial fluorine atoms. CNDO/2 calculations incorporating experimental parameters suggest that the $P(NH_2)$ groups are planar and perpendicular to the equatorial plane of the trigonal bipyramid.	16