

## Meeting Report

### The Winter Meeting of the American Crystallographic Association, Albuquerque, 3-7 April 1972.

The Winter meeting of the ACA at the University of New Mexico and the Hilton Inn opened with a **symposium on Experimental and Theoretical Studies of the Electron Density in Crystals and Molecules** which will be published as Volume 8 of the *Transactions of the ACA*. The lectures brought together quantum chemists, interested in the *a priori* calculation of molecular properties, and the growing number of experimentalists who are attempting to determine accurate charge and spin densities by diffraction (X-ray, electron, and neutron) methods. Since the difference in density between the real molecule and a molecule composed of non-interacting atoms is small, great care must be exercised in both theoretical and experimental approaches.

The emphasis to date has been on the attempts to obtain agreement between theory and experiment for small molecules. Such attempts have led to an examination of the validity of various approximations in the theory and to the critical evaluation of experimental error. A number of models for the refinement of quantum mechanical parameters from the experimental data were suggested during the symposium. It appears that the purely theoretical approach may provide the most definitive results for organic molecules containing only a few atoms. For larger molecules, however, the experimental approach, when properly calibrated by comparison with theory, will probably provide most new information on complex systems. The importance of a comparison between data from neutron diffraction (scattering by nuclei) and from X-ray diffraction (scattering by electrons) in aiding this calibration (*D1*, *B3*)\*, and the beneficial effects of data collection at temperatures approaching 0°K (*D3*), were recognized.

The proceedings were enlivened by the display 'for the first time in public' of a real picture of the electron density associated with an atom (*A2*). The photograph was produced by laser illumination of a hologram obtained from an ap-

propriately modified electron diffraction pattern of argon gas. The interesting suggestion that a formalism relating the second-order density matrix to the X-ray structure factors might provide a new method of structure factor phase determination was made in a post-deadline paper (*B4*).

In the meeting itself **large-molecule** structural studies were reported (to 2 Å resolution) on a bacterial ferredoxin (*L2*), in which compact clusters of iron and sulphur atoms perform oxidation-reduction functions, and (to 2.5 Å resolution) on a flavodoxin (*L1*), in which similar biological functions are performed by a mononucleotide without the participation of a heavy metal. The clusters in the ferredoxin consist of two interpenetrating tetrahedra of iron and labile sulphur atoms respectively, plus four cysteine sulphur atoms coordinated to each iron atom. In the flavodoxin the flavin lies over a tyrosine residue. Another large structure reported on was alkaline phosphatase (*L7*) for which the electron density map at 7.7 Å resolution revealed the site of metal binding and the dimer structure.

There were several themes throughout the sessions on **organic structures**. Studies, such as that on the naturally occurring antileukemic agent, maytansine (*C4*),  $C_{34}H_{46}ClN_3O_{10}$ , revealed the previously unknown chemical formula of the molecule as well as its absolute configuration. In the same way, from other structural work the courses of reactions such as the photodimerization of 3-phenyl-2-cyclopentenone (*P9*) of the sorption of ammonia onto zeolites (*N11*) were ascertained.

Many structures, such as those of the alkaloids zygacine (*M8*), nupharidine (*M10*) and yohimbine (*M9*) were determined to reveal details of their **stereochemistries**. Peptides, such as Pro-Pro-Gly (*L3*) which is a part of a collagen model), and some nucleosides, including 2-thioisouridine (*L8*) and 6-thioguanosine (*L9*) (which were investigated to determine the effect of incorporation of sulphur) were described. The **relationship of the molecular and crystal structure to various biological, chemical and physical properties** was stressed in many reports. Such properties included antitumor, antibiotic and antimalarial activity, analgetic potency, non-reactivity of a double bond (due to steric effects), Cotton effect, n.m.r. vicinal proton coupling constants, and dichroism. In the latter example the yellow-

red dichroism of a lumiflavin naphthalene diol complex (*E11*) was correlated with its molecular packing.

The effect on the molecular packing of substitution in a molecule by, for example, sulphur or halogen, was investigated. An interesting study of **molecular packing** involved crystals of a 1:1 complex of deoxycholic acid and acetic acid (*M4*). These crystals were shown to contain acetic acid molecules, which are hydrogen bonded in the same way as in the crystal structure of acetic acid, and lie in tunnels between sheets of deoxycholic acid molecules. No hydrogen bonds, only van der Waals contacts, were found between guest and host molecules. Structures and conformations of several 'overcrowded' molecules such as tetranitrofluorene derivatives (*P4*) and 2-bromo- and 2-methylhexahelicene (*P3*), were described.

Several reviews of related structures were given, the most extensive of which dealt with the molecular packing of some 150 published structures of **steroids** (*M1*). The dominant feature is a tendency to form head-to-tail chains by hydrogen bonding. The conformation of the molecule influences the chain type. Estranes tend to form extended chains, androstanes form twisted chains, while pregnanes show helical packing with molecular shape bowed toward the  $\alpha$  side of the molecule. The relevant features will be included in Volume 1 of *Atlas of Steroid Structures* which should be available by the end of 1972.

The papers on **minerals** were concerned with **site occupancy and disorder**. In the zeolite, bikitaite (*F1*),  $LiAlSi_2O_6 \cdot H_2O$ , the lithium ion is tetrahedrally coordinated by three oxygen atoms and one water molecule, an unusual coordination in mineral structures. The occupancies of tetrahedral sites in orthopyroxenes (*F2*) and the iron occupancies of the octahedral sites in a titaniferous clinohumite (*F4*) were discussed. Disorder, such as that of carbonate groups in the layered structure of scawtite (*F3*),  $Ca_6Si_6O_{18} \cdot 2H_2O \cdot CaCO_3$ , was found.

In the sessions on **coordination compounds** several structures were described which gave important new evidence about the geometry of the attachment of ligands, such as nitrosyl groups (*H3*, *H4*, *H6*), to metals. By contrast, it was also made clear that sulphur dioxide was bound, not to the metal, but rather to the halogen in an iodo-platinum complex (*H11*),

\* The numbers in parentheses refer to the title program at the end of the report.

Pt[P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]CH<sub>3</sub>I·SO<sub>2</sub>. Also a correlation of color of a complex with the nature of the coordination about a given cation was again stressed and studied.  $\pi$ -Sandwich complexes of uranium(IV) and cerium (III) with cyclooctatetraene and its derivatives (*I4*, *I5*) were described and so was the first structure of a heptavalent neptunium complex (*I6*).

In the session on **intermetallic compounds**, it was stressed that similar formulae, space group and lattice parameters *do not* necessarily lead to isomorphism, the cases of the non-isomorphous Mg<sub>6</sub>Al and Mg<sub>6</sub>Rh being an example (*K1*). Also it was pointed out that high thermal parameters may cover disorder.

The structural basis of the metallic conductivity found in the newly prepared (at 15 to 60 kb) compounds CrP<sub>4</sub> and MoP<sub>4</sub> (*N7*) was suggested to be the rather close approach of the metal ions; the Cr–Cr distance, for example, is only 20% larger than it is in chromium metal. Similarly, for Ni<sub>1/4</sub>Pt<sub>3</sub>O<sub>4</sub> (*K2*), the Pt–Pt distances are almost as short as those in platinum metal, while the nickel can move through channels in the structure to give ionic conductivity. In Eu<sub>3</sub>As<sub>4</sub> (*K4*) the structure is based on a unique space-filling arrangement of trigonal prisms of europium atoms with arsenic atoms at the centers of the prisms. The As–As distances of 2.29 Å are the shortest known and may indicate some double bond formation.

Some interesting studies of **phase changes** were presented. The structure of  $\gamma$ -uranyl dihydroxide (*K10*) is composed of layers of shared octahedra composed of two uranyl oxygen atoms and four hydroxyl oxygen atoms. A hydroxyl group of one layer is hydrogen bonded to a uranyl oxygen atom in an adjacent layer. This structure is very similar to that of the  $\beta$  modification, the major difference being in the nature of the hydrogen bonding. There is a shear relation by which the forms can interconvert, but there is no stable region where the  $\beta$  form is *in equilibrium* with the  $\gamma$  form. Comparison of structural details determined with neutron diffraction for wholly, partially and undeuterated YH<sub>5</sub>O<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O (*N1*) led to the conclusion that the order–disorder phase transformation took place by an inversion of the orientation of the H<sub>5</sub>O<sub>2</sub><sup>+</sup> ion (like the inversion of ammonia). The inverted fraction was, for example, 8% at 25°C and 0% at –155°C. The structures of the high-pressure phases of the tetrahedral halides of C, Si, Ge, Sn and Ti (*G5*) were reviewed and the data

suggested that the stabilities of these phases are governed primarily by geometric packing considerations.

Papers were presented on several **ferroelastic and ferroelectric** compounds. Crystals whose structures are slight distortions of the higher symmetry 'parent structure' (which is usually the higher-temperature structure of the same compound) are called ferroelastic if mechanical stress causes reversible switching between different orientations which are symmetrically equivalent with respect to the parent structure. The atomic shifts involved may only be a few tenths of an Ångstrom unit. Boracite, Mg<sub>3</sub>B<sub>7</sub>O<sub>13</sub>Cl (*F6*, *G9*), normally transforms from a high-temperature cubic phase to a low-temperature highly twinned orthorhombic form, but, on cooling a cubic single crystal in a suitably directed stress field, a single untwinned crystal can be obtained. Subsequent application of stress in other directions causes ferroelastic switching. It was shown that the movements of boron and oxygen atoms must be considered as contributing to the 'ferro' (ferroelectric and ferroelastic) effects as much as are those of the metal and halogen atoms. The structure of Pb<sub>5</sub>Ge<sub>3</sub>O<sub>11</sub> (*G7*), which is both optically active and ferroelectric was reported. Domain reversal by an electric field causes a reversal of both the polarization and the optical rotation, that is, the structure is transformed to its own mirror image. Slight rotations and shifts in the GeO<sub>4</sub> and Ge<sub>2</sub>O<sub>7</sub> groups are involved.

X-ray radial distribution curves for showing ordering detail out to 20 Å were shown for silica glass (*N10*). To obtain such long-range detail, analysis techniques similar to those previously developed to extract long-range radial distribution information from electron scattering from gases were applied to the X-ray scattering data. This previously unreported **long-range order in silica glass** was then related to a tridymite-like ordering.

The rapid progress being made in electron-optical **direct-imaging at atomic-scale resolution** is typified by two papers (*N3*, *N4*) that were given on electron microscopy of crystal structures at approximately 3 Å resolution. It was shown with direct-image micrographs that the nonstoichiometry of TiO<sub>2</sub>·7Nb<sub>2</sub>O<sub>5</sub>, for example, is due to a variety of planar defects as well as to Wadsley intergrowth defects.

**Multiple diffraction**, which takes place when two or more Bragg reflections occur simultaneously, was re-

viewed (*J1*). This effect can cause incorrect intensity measurements in structure work, but can also serve as a useful event for the study of the interaction of wave fields in crystals. Its occurrence can be predicted easily by use of programs which monitor the relation of all reciprocal lattice points to the Ewald sphere at any given moment. It was shown that, for temperature and strain-dependent intensity measurements, the change in lattice constants or orientation can cause additional unsuspected multiple reflections (*J3*).

Methods for **high speed data collection** were discussed including the storage and matching (retrieval) of film-recorded powder patterns (*J7*, *J8*), a computer-controlled single-crystal diffractometer (*J9*), where the emphasis was on checking drifts in standard peak positions rather than intensities (*i.e.* before intensity changes occur), and a high speed, multiple detector, computerized data acquisition system for protein intensity measurements (*J10*). It is estimated that, for the latter, 12000 reflections per hour can be measured with adequate spatial resolution.

In a session on current advances in **computational procedures**, attempts to improve the accuracy of tangent formulae were described (*O1*). A method for specifying the enantiomorph in polar space groups such as *P2*<sub>1</sub> was detailed (*O2*, *O3*). Specific classes of reflections were employed in the structure-invariant relationships to provide distinct enantiomorph discrimination. These classes of reflections were deduced through the calculation of structure invariant cosine averages. This work, with a 78-atom problem as an example, demonstrated the power of current direct methods in the determination of larger molecular structures. It was also demonstrated that direct methods, well proven with X-ray analyses, may be applied to neutron data with equal confidence (*O5*). Descriptions were given of the use of anomalous dispersion data (*O7*), collected at several wavelengths or used together with the tangent formula (*O6*) as a means of solving the phase problem.

Two cases of three independent structure refinements on a given compound were discussed (*O8*, *P12*) and the use of the method of normal probability plots was suggested in **comparing the results**.

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### Title Program

American Crystallographic Association, Albuquerque, 3-7 April 1972.

- A1 Electronic charge distributions and chemical bonding in simple molecules. P. E. CADE
- A2 Determination of electron distributions by electron diffraction. L. S. BARTELL
- A3 Experimental spin densities. R. M. MOON
- B1 Aspects of the electron density problem. Theoretical and experimental. W. N. LIPSCOMB
- B2 Alternatives in the comparison of experimental and theoretical charge densities. P. COPPENS
- B3 Charge density distribution in tetracyanoethyleneoxide by difference Fourier techniques and population refinement of the diffraction data. D. A. MATTHEWS & G. D. STUCKY
- B4 MASSA (Post-deadline paper)
- C1 The crystal structure of 1,3-*O*-*D*-mannitol borate monohydrate, [1,3-(hydroxyborylene)-*D*-mannitol monohydrate]. J. C. WAL-LACE
- C2 The crystal structures of two Schiff's bases - *N*-benzylidene-*p*-bromoaniline and *N*-(2-naphthylmethylene)-*p*-bromoaniline. B. T. BLAYLOCK & R. F. BRYAN
- C3 The structure of two biologically interesting molecules. W. H. WATSON, J. E. WHINNERY & K. C. GO
- C4 Crystal and molecular structure of maytansine. R. F. BRYAN, C. J. GILMORE & R. C. HALTIWANGER
- C5 A comparison of two anthracene alkylating agents, ICR 489 and ICR 450. A. CHOMYN, J. P. GLUSKER, H. M. BERMAN & H. L. CARRELL
- C6 The structure and absolute configuration of pactamycin. X-ray analysis of desalipactamycate tosylate. D. J. DUCHAMP
- C8 The crystal and molecular structure of alpha promedol alcohol. W. H. DE CAMP & F. R. AHMED
- C9 The crystal structure of heliotrine: A pyrrolizidine alkaloid (mono-ester). S. WODAK
- C10 Crystal and molecular structure of barium 2-sulfuryl-L-ascorbate dihydrate. B. W. McCLELLAND & J. R. EINSTEIN
- C11 Molecular and crystal structures of two compounds of pharmaceutical interest. D. B. COSULICH & F. M. LOVELL
- D1 Refinement of the structure of sucrose. J. C. HANSON, L. C. SIEKER & L. H. JENSEN
- D2 The crystal structure and electron distribution of 1,1'-azobisdicarbamide and acetylene dicarboxylic acid. D. T. CROMER & A. C. LARSON
- D3 The use of liquid-helium data in charge density studies: *p*-nitropyridine *N*-oxide. F. K. ROSS & P. COPPENS
- E1 Crystal and molecular structure of 2,2,3,3,4-pentamethyl-1-phenylphosphetane-1-oxide. A. FITZGERALD, C. N. CAUGHLAN & G. D. SMITH
- E2 The crystal structure of bis-*p*-methoxy-phenyl 2,5-furandicarboxylate. W. C. BRYSON & S. H. SIMONSEN
- E3 The molecular structure of ethyl 2-amino-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carboxylate. S. H. SIMONSEN
- E4 The structures of pyridine and isoquinoline fluvalenes. G. L. WHEELER & H. L. AMMON
- E5 Aminopentafulvenes. 5-ring bond lengths. N.M.R. coupling constants and rotational energies. H. L. AMMON, G. L. WHEELER & L. A. PLASTAS
- E6 The structure of exo-2-methoxy-3-aza-4-keto-7,8-benzobicyclo-[4.2.1]nonene. P. H. WATTS JR, H. L. AMMON, P. H. MAZZOCHI, H. J. TAMBURIN & W. J. KOPECKY
- E7 Crystal structures of two photo-products of *N*-chloroacetyltyramine. D. S. JONES & I. L. KARLE
- E8 The crystal structures of two antimalarials. L. A. PLASTAS & H. L. AMMON
- E9 The crystal and molecular structures of three compounds derived from a benzodiazepine. C. G. CHILDESTER, D. J. DUCHAMP & J. SZMUSZKOVICZ
- E11 The crystal structure of the orange molecular complex lumiflavin bis-(naphthalene-2,3-diol) trihydrate. C. J. FRITCHIE JR & R. M. JOHNSTON
- E12 Crystal structure of bis-10-methyl-*i*-alloxazine sesqui [silver(I)] perchlorate hydrate. G. D. SPROUL & C. J. FRITCHIE JR
- F1 The crystal structure of bikitaite. V. KOCMAN, J. C. RUCKLIDGE & R. I. GAIT
- F2 Tetrahedral sizes of orthopyroxenes and silicon-aluminum ordering. H. TAKEDA
- F3 The crystal structure of scawtite. J. J. PLUTH & J. V. SMITH
- F4 The crystal structure of a titaniferous clinohumite. J. C. RUCKLIDGE & V. KOCMAN
- F5 The crystal structure of gladite, PbCuBi<sub>3</sub>S<sub>9</sub>. I. KOHATSU & B. J. WUENSCH
- F6 Borate framework of boracite and its relationship to the ferroelectric effects. E. DOWTY & J. R. CLARK
- F7 Fully automated computer controlled laboratory. M. SLAUGHTER (Post-deadline)
- G1 Concept of lattice. F. E. WANG & J. R. HOLDEN
- G2 Definition and determination of derivative lattices. A. D. MIGHELL & A. SANTORO
- G3 Application of derivative lattices to the determination of coincidence-site lattices. A. SANTORO & A. D. MIGHELL
- G4 Diamorphism in the three colored, crystallographic, point groups. D. HARKER
- G5 Packing of tetrahedral molecules in molecular crystals. G. J. PIERMARINI & S. BLOCK
- G6 Structural relationships of compounds A<sub>2</sub>BX<sub>4</sub> and A<sub>2</sub>BX<sub>3</sub>. W. EYSEL & T. HAHN
- G7 Domain patterns and crystal structure of Pb<sub>5</sub>Ge<sub>3</sub>O<sub>11</sub>, an optically active ferroelectric. J. P. DOUGHERTY, E. SAWAGUCHI, C. N. W. DARLINGTON & R. E. NEWNHAM
- G8 Neutron diffraction study of vanadium deuterides at various temperatures. M. H. MUELLER, D. G. WESTLAKE & H. W. KNOTT
- G9 Ferroelastic reorientation and detwinning in synthetic boracite. L. P. TORRE, S. C. ABRAHAMS, R. L. BARNES & K. NASSAU
- G10 New ferroelastic crystals - predictions and verification. S. C. ABRAHAMS
- G11 A disordered structure - octafluoronaphthalene. G. S. MANDEL & J. DONOHUE
- H1 The structure of (bicyclo[6.2.0]-deca-2,4,6-triene) hexacarbonyl-diiron, (C<sub>10</sub>H<sub>12</sub>)Fe<sub>2</sub>(CO)<sub>6</sub>. F. A. COTTON & B. A. FRENZ
- H2 The crystal structures of the green and the orange forms of bis(5,5'-diethylbarbiturato) bis(imidazole) nickel(II). B. C. WANG