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The polymorphism of triphenylchloromethane. By R. Gerdil and A. Dunand, *Département de Chimie Organique et Laboratoire de Cristallographie aux Rayons-X, Université de Genève, 30 quai Ernest Ansermet, 1211 Genève 4, Switzerland*

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Crystals of $C_{19}H_{15}Cl$ are trigonal (α form) when recrystallized from either pure petroleum spirit or pure benzene whereas triclinic crystals (β form) are formed from petroleum spirit/benzene solutions. The two modifications are apparently equally stable within the range 20–96°C. The triclinic lattice is visualized as a displacive transformation of the hexagonal lattice.

Crystals of triphenylchloromethane grown from ligroin were reported by Wang & Lu (1944) to be hexagonal (Laue group $\bar{3}$). Our current interest in the structure and packing of triphenylmethyl derivatives led us to isolate, under highly specific conditions, a triclinic form (hereafter designated the β form) of triphenylchloromethane, stable at room temperature. Triclinic crystals alone are obtained by recrystallization from a mixture of petroleum spirit and benzene (0.7/0.3 by volume); only the trigonal modification (α form) is obtained from either of the pure solvents. Both crystalline modifications seem to exist at other dilutions. Only the α form is obtained by crystallization from acetone, carbon tetrachloride or toluene, or by sublimation. Although the β form tends to grow more faces than the α form both habits are very much alike and visual identification alone might be deceptive. Therefore the numerous crystals selected from various batches were subsequently identified by X-ray examination. The thermograms (starting at 20°C) of the α and β forms display a broad peak corresponding to fusion at 108–109°C. In both cases a much smaller peak, at 94–96°, almost coalesces with the main one to form a shoulder. The peak-height ratio is roughly 1:10. This transition suggests the occurrence of a third polymorph within a few degrees of the melting point.

Accurate cell dimensions of the α and β forms were measured on a Philips PW1100 diffractometer with small crystals of average cross-section 0.2 mm.

Crystal data

α Form: hexagonal; space group $P3$ or $P\bar{3}$; $a=b=13.998$ (2), $c=13.202$ (4) Å; $V=2240.2$ Å³; $Z=6$; $D_m=1.230$, $D_x=1.240$ g cm⁻³.

β Form: triclinic; space group $P1$ or $P\bar{1}$; $a=14.175$ (3), $b=21.346$ (18), $c=13.079$ (2) Å; $\alpha=99.96$ (1), $\beta=92.71$ (2), $\gamma=106.14$ (2)°; $V=3725.1$ Å³; $Z=10$; $D_m=1.229$, $D_x=1.243$ g cm⁻³.

The structural relationship between the two forms can be visualized as a distortional transformation in which the molecules of the β form are displaced relative to those of the α form without drastic changes in the nearest-neighbour arrangement. This can be deduced from the distribution of the strongest reflexions and from simple geometric considerations of zero layers (see Fig. 1). The volume (V_H) of the hexagonal cell is very nearly $\frac{2}{3}$ of the volume (V_T) of the triclinic cell ($3V_T/5V_H=0.9977$). A new set of axial vectors with the transformation matrix $(1, 0, 0; \frac{1}{3}, \frac{2}{3}, 0; 0, 0, 1)$ can be based upon the vectors of the hexagonal lattice. These vectors define a monoclinic cell (M ; unique axis c) whose a and c axes are equal to and coaxial with the corresponding ones of the primitive hexagonal cell; the volume ratio V_H/V_M is then $\frac{2}{3}$. The points of the monoclinic lattice are either coincident with the points of the hexagonal lattice

or located in special positions $(\frac{1}{3}, \frac{2}{3}, 0)$ or $(\frac{2}{3}, \frac{1}{3}, 0)$ of one hexagonal unit cell. This is pertinent since the 6 Cl atoms contained in the primitive hexagonal cell are expected to occupy special positions x (or y) = 0, $\frac{1}{3}$ or $\frac{2}{3}$, as suggested by the $hk0$ reflexions which are either absent or very weak for $h-k=3n$. Accordingly, the Cl positions will also be characterized by rational lattice indices $\frac{1}{3}, \frac{2}{3}, \dots$ in the monoclinic cell projection. The triclinic cell is now visualized as resulting from a slight distortion of the intermediate monoclinic cell as seen in Fig. 1. The spacings of the (001) planes in the triclinic and hexagonal lattices compare well with values 12.817 and 13.202 Å, respectively. Some groups of very strong reflexions of the triclinic form still closely

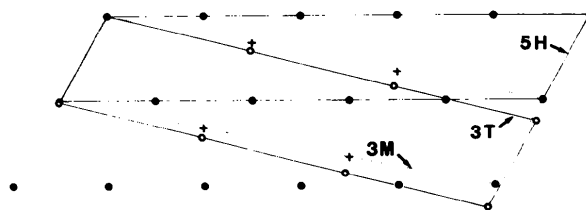


Fig. 1. Structural relationship between the zero layers of the hexagonal (●) and triclinic (○) lattices. Outlined are: quintuply primitive hexagonal cell (5H); triply primitive triclinic cell (3T); intermediate triply primitive monoclinic cell (3M, dotted lines). Some of the lattice points (+) of 3M correspond to special positions with rational indices $\frac{1}{3}, \frac{2}{3}, \dots$ in one hexagonal cell.

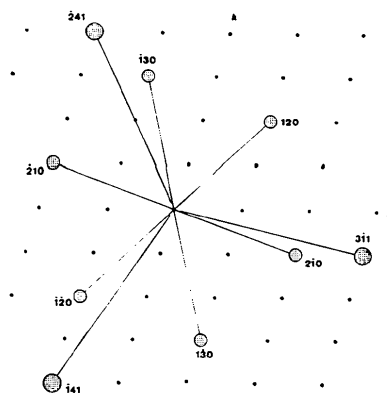


Fig. 2. Groups of very strong reflexions in the reciprocal lattice planes $hk0$ and $hk1$ of the β form. For convenience the two layers are shown superimposed.

display the level symmetry of trigonal systems as shown schematically in Fig. 2. This is to be expected if the heavy atoms occupy special positions in the hexagonal lattice. For instance, reflexions on planes (110), ($\bar{1}20$), and ($2\bar{1}0$), of the trigonal system give rise to strong intensities. The indices of these planes transform to (120), ($\bar{1}30$) and ($\bar{2}10$) respectively in the intermediate monoclinic system and are seen to be among the strongest reflexions in the triclinic system. They form with the equivalent $h\bar{k}0$ reflexions, a group which has

very nearly C_6 symmetry (Fig. 2). Furthermore the three strongest reflexions form an approximately trigonal arrangement in the first reciprocal layer, reminiscent of the upper-layer symmetry of the C_3 point group.

Reference

WANG, S. N. & LU, C. S. (1944). *J. Amer. Chem. Soc.* **66**, 1113–1114.

Book Reviews

Works intended for notice in this column should be sent direct to the Book-Review Editor (M.M. Woolfson, Physics Department, University of York, Heslington, York YO1 5DD, England). As far as practicable books will be reviewed in a country different from that of publication.

Critical evaluation of chemical and physical structural information. Edited by D. R. LIDE JR and M. A. PAUL. Pp. xii + 628, Figs. 108, Tables 85. Washington: National Academy of Sciences, 1974. Price \$26.25.

The rather uninspiring title of this book hides the fact that it is really a record of substantial progress in a variety of methods of structure determination. Or, to anyone who makes a rather superficial use of the methods concerned, it is a record of how to do better.

The book contains the proceedings of the Conference on Critical Evaluation of Chemical and Physical Structural Information held in the U.S.A. in June 1973. It could be called a high-powered conference, and certainly the list of contributors is most distinguished, but the book is a mine of information (even simple advice) on how to get the best from one's measurements.

The word 'structure' is interpreted in its widest molecular sense to include the following types of information: the geometric arrangement of atoms in a free molecule or crystal (symmetry, interatomic distances, bond angles); the description of the forces between these atoms (bond-stretching and bending-force constants, barriers to internal rotation, and other large amplitude motions); molecular parameters related to the electronic charge distribution (electric and magnetic moments, chemical shifts, coupling constants, charge-density maps).

Experimental methods whose data-processing techniques are discussed include gas-phase electron diffraction, rotational, vibrational and optical spectroscopies, liquid-crystal n.m.r., crystallography, and protein crystallography. Emphasis is given to consideration of the accuracy and reliability of the structural information obtained, and stress is made of the pitfalls which can occur when results from separate determinations, by similar as well as different methods, are compared. Other topics considered include the methods of deriving harmonic and anharmonic force fields and data on large-amplitude motions, and there are sections on the determination of electronic charge distributions and the *ab initio* method of calculating structural information.

In his preface to the book, which could be regarded as a reliable review in itself, D. R. Lide Jr makes some general observations about the views expressed by contributors: 'in most of the fields discussed, the statistical treatment of experimental data cannot be regarded as completely satisfactory . . . least-squares fitting techniques now in use

are not necessarily the best way of handling large data sets . . . no fitting technique can be expected to replace completely the judgement of the experimentalist in distinguishing random errors from systematic errors or model deficiencies'.

Some may shudder when confronted with this book and its implications on the need for time-consuming statistical analysis (and for time-consuming *thinking*) but if reliability is required, then the requisite care must be taken: 'fools rush in where angels fear to tread' is a suitable proverbial warning for the unwary! This is not just another book of conference proceedings, but a major milestone in its field.

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Landolt-Börnstein. Numerical data and functional relationships in science and technology. Group III. Crystal and solid state physics. Vol. 7. Crystal structure data of inorganic compounds. Edited by K. -H. HELLWEGE and A. M. HELLWEGE. Part *a*: by W. PIES and A. WEISS. Pp. xxxii + 647. Berlin: Springer, 1973. Price (cloth) DM 436, U. S. \$178.80. Part *g*: by W. PIES and A. WEISS. Pp. 463. Berlin: Springer, 1974. Price (cloth) DM 220, U. S. \$90.20.

The Landolt-Börnstein New Series Group III Volumes *5a* and *5b*, giving crystal data on organic crystals, and volume 6 giving data on elements and intermetallic phases have already been published [for reviews see *Acta Cryst.* (1972). **B28**, 1317–1318; *J. Appl. Cryst.* (1972). **5**, 384]. Volume 7 Parts *a* to *h* are to give data on inorganic crystals (some 18000 compounds). Fig. 1, taken from the inside cover of Volume 7, shows the arrangement of compounds by key elements in Parts *a* to *f*. Thus Part *a*, under review here, gives data on halides. Part *g*, also under review, lists the literature references for Parts *a* to *f* and Part *h* will be a comprehensive index for Volume 7.

The tables of crystal data give the formula of the compound, the space group and lattice parameters, Z (the number of formula units in the unit cell), D_m and D_x (in parentheses), the crystal structure type, whether the atomic positions were determined, how the crystal data were obtained and other incidental information such as colour of