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An X-Ray Examination of Crystals of Triphenylmethyl Chloride and Bromide

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Although triphenylmethyl compounds are of great structural interest in connection with the chemistry of Gomberg's free radicals, a survey of literature reveals that Mark and Noethling[1a] made the only attempt so far to examine some such compounds (namely, triphenylmethylcarbinol and bromide) by means of X-rays. In the case of triphenylmethyl bromide they made a direct determination of the hexagonal *a* axis, but their determination of the hexagonal *c* axis cannot be considered satisfactory. Their space group consideration is likewise subject to a similar uncertainty.[2] Their results for triphenylmethylcarbinol are also equally doubtful.

We have recently carried out an X-ray examination of crystals of triphenylmethyl chloride and bromide and have made a satisfactory determination of their unit cells. The crystals have the Laue symmetry C_{3i} and belong to one of the following two space groups: C_3^1-H3, $C_{3i}^1-H\bar{3}$. The halogen atoms could be approximately located, but we have not been able to establish the configuration of the trigonal triphenylmethyl groups in these crystals. We report in this paper the results which we have obtained.

Triphenylmethyl bromide was prepared by treating triphenylcarbinol with a solution of hydrogen bromide in glacial acetic acid.[3] The crude product was dissolved in ligroin and boiled with active charcoal to remove some colored impurities. It was then recrystallized from ligroin, from which crystals were obtained by slow evaporation in a desiccator. Triphenylmethyl chloride, as commercially available, contains an appreciable quantity of carbinol. Such a commercial sample of the chloride was purified by dissolving it in ligroin and treating the solution with a suitable amount of acetyl chloride. The same method of crystallization was used as for the bromide. The crystals were prepared and kept in desiccators, as both the bromide and the chloride are easily hydrolyzed into carbinol on prolonged contact with moisture. The bromide is more reactive than the chloride in this respect.

The chloride crystals obtained are colorless and all have the form of a simple rhombohedron. The faces belong either to the form $\{10\bar{1}1\}$ or to $\{01\bar{1}1\}$.[4] The pale yellow crystals of bromide from ligroin show all of the hexagonal prism forms $\{11\bar{2}0\}$, both rhombohedral forms $\{10\bar{1}1\}$ and $\{01\bar{1}1\}$, and basal pinacoid $\{0001\}$. Only one rhombohedral form appears with the hexagonal prism and basal pinacoid on the bromide crystals obtained from the carbon disulfide solution, in agreement with the observation of Hintze.[5]

By taking rotation photographs of both bromide and chloride around their hexagonal *a* and *c* axes as well as some other prominent directions, it is found that their hexagonal unit cells have the following dimensions:

	a_0, Å.	c_0, Å.
Bromide	13.86 ± 0.02	13.36 ± 0.03
Chloride	13.97 ± 0.02	13.17 ± 0.02

The choice of unit cells of such dimensions was confirmed by a powder photograph of the chloride.

This set of axial lengths accounts quite well for the values of the interfacial angles obtained from our own goniometric measurements as well as those of Hintze.[5]

	Bromide			Chloride	
	Measured (Hintze)	Measured (Authors)	Calculated from c/a = 0.9639	Measured (Authors)	Calculated from c/a = 0.9427
(1011): (0111)	79°52′	80°10′	80°13′	79°12′	79°16′
(1011): (0001)	47°57′	48° 4′	48° 4′		

The densities of the bromide and the chloride as determined by the flotation method are 1.42 and 1.26 g./cc., respectively. Thus for both crystals there are six molecules in the hexagonal unit cell, the calculated densities being 1.44 and 1.24 g./cc., respectively.

The Laue symmetry of these crystals can be readily determined from equi-inclination Weissenberg photographs taken around the crystallographic axes.[6] The photographs taken around the *c* axis show C_6 plane-group symmetry for the $(hki0)$ reflections but only C_3 symmetry for the other layer-line reflections. Thus the Laue group is C_{3i}. The lattice is shown to be hexagonal and not rhombohedral by the presence of reflections for which $h - k + l \neq 3n$. Since there is no systematic absence in the $(000l)$ reflections, the crystals belong to one of the following space groups: $C_{3i}^1-H\bar{3}$, C_3^1-H3. These two space

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[1a] H. Mark and W. Noethling, *Z. Krist.*, **65**, 435 (1927).

[2] P. P. Ewald and C. Hermann have also expressed doubt about the validity of the space group assignment; see "Strukturbericht," 1913–1928, p. 729.

[3] Wieland, *Ber.*, **42**, 3024 (1909).

[4] It is not possible to tell, however, exactly which of these two forms actually appear as crystal faces. It is not unlikely that both forms are possible.

[5] Hintze, *Z. Krist.*, **9**, 545 (1884); Groth, *Chem. Krist.*, Vol. **V**, p. 291.

[6] M. J. Buerger, *Z. Krist.*, **91**, 262 (1935).

groups differ only by a center of symmetry. We tend to believe that the space group $C_{3i}^1 - H\bar{3}$ is the more probable. This is borne out by the morphological assignment of the crystal class as C_{3i}. The correct choice of the space group can, however, only be justified by a final structure determination.

Relative intensity measurements have been made on the ($hki0$) and the ($0k\bar{k}l$) reflections of both the bromide and the chloride by means of the multi-film method.[7] The crystals used in taking these Weissenberg intensity photographs were all so small that the correction for absorption would be negligible. The Lorentz polarization factor corrections were made by the use of Lu's chart.[8] We obtained thus relative structure values for the ($hki0$) and ($0k\bar{k}l$) reflections.[9] The fact that hardly any reflections appear beyond $(\sin \theta/\lambda) = 0.45$ Å.$^{-1}$ seems to indicate large temperature factors.

An attempt to locate the halogen atoms in these crystals was made by constructing two Patterson functions $P(xy)$ and $P(yz)$ for the bromide, as it is believed that peaks arising from the halogen–halogen interactions would stand out more prominently for the bromide than for the chloride. Peaks were found at $\pm$ (1/3, 2/3) in P (x, y) which are almost as high as the peak at (0, 0). This is to be expected from the fact that all the ($hki0$) reflections with $h - k \neq 3\,n$ are either very weak or altogether absent. There are very large peaks in P (y, z) close to $\pm$ (1/3, 2/3). Therefore the positions of the halogen atoms very probably correspond to a slightly distorted rhombohedral structure.

In the space group $C_3^1 - H3$ there are three sets of one-fold special positions, at ($00z$); (1/3, 2/3, z'); and (2/3, 1/3, z''); and one set of three-fold general positions, at (x, y, z), ($\bar{y}$, $x - y$, z), ($y - x$, $\bar{x}$, z). On imposing a center of symmetry at the origin, we obtain for the space group $C_{3i}^1 - H\bar{3}$ three corresponding sets of two-fold special positions and one corresponding set of general positions.[10] For the purpose of a more general discussion we may therefore consider the six halogen atoms in the unit cell as grouping themselves into two groups of three each, each group fulfilling the spatial symmetry of $C_3^1 - H3$. The two groups are related by a center of symmetry if the over-all spatial symmetry is $C_{3i}^1 - H\bar{3}$.

The only sets of three-fold positions (x, y, z), ($\bar{y}$, $x-y$, z), ($y-x$, $\bar{x}$, z) which will give rise to peaks at (0, 0) and $\pm$ (1/3, 2/3) in P (x, y) are as follows: A, (0, 1/3, z), (1/3, 0, z), (2/3, 2/3, z); B, (0, 2/3, z'), (2/3, 0, z'), (1/3, 1/3, z'). Either the two groups of halogen atoms occupy two similar sets of positions AA$'$ (or BB$'$); or they occupy the two sets of positions AB. In either case there would be in P (y, z) at least as many Br–Br interactions at (1/3, 0) as at (0, 0). But there are no corresponding peaks in P (y, z), so that both possibilities are ruled out. We conclude therefore that the six halogen atoms must occupy the following special positions: ($00z_1$), (1/3, 2/3, z_2), (2/3, 1/3, z_3), ($00z_1'$), (1/3, 2/3, z_2'), (2/3, 1/3, z_3'). The peaks in the Patterson function $P(y,z)$ are not sufficiently well resolved to permit us to make a satisfactory determination of the z parameters of the halogen atoms, although we think it likely that the positions of the halogen atoms correspond approximately to a rhombohedral structure. Around each of these halogen atoms the point symmetry is C_3. Thus the three-fold axes of the molecules coincide with those in the crystal, although the molecules fall into three (or six) crystallographically non-equivalent groups. We are at present not able to propose a reasonably simple arrangement of the trigonal triphenylmethyl groups which accounts for the intensity data of those ($hki0$) reflections for which $h - k \neq 3$ n. Incidentally it is interesting to note from packing considerations that the triphenylmethyl groups are not likely to have a planar configuration.

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Summary

The X-ray examination of crystals of triphenylmethyl chloride and bromide has shown that the hexagonal units of structure have the dimensions $a_0 = 13.86 \pm 0.02$ A. and $c_0 = 13.36 \pm 0.03$ Å. for the bromide and $a_0 = 13.97 \pm 0.02$ Å. and $c_0 = 13.17 \pm 0.02$ Å. for the chloride. There are six molecules in the unit cell, and the space group is either $C_{3i}^1 - H\bar{3}$ or $C_3^1 - H3$. The halogen atoms have been located approximately, but the configuration of the triphenylmethyl group in these crystals has not been determined.

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(7) J. J. De Lange, J. M. Robertson, and I. Woodward, *Proc. Roy. Soc.* (London), **A171**, 398 (1939).

(8) C. S. Lu, *Rev. Sci. Instr.*, **14**, 331 (1943).

(9) These relative structure factor values will be supplied upon request to the authors.

(10) In the space group $C_{3i}^1 - H\bar{3}$ there are also two sets of one-fold special positions with point symmetry C_{3i} and two sets of three-fold special positions with point symmetry C_1. Since the halide molecule is not centro-symmetrical, these special positions need not be considered