

The evidence thus obtained leads us to conclude that element 87 occurs in samarskite. Furthermore, this element yields a chloride volatilizable at 1000° , and its alum is the least soluble in the alkali series. A name for the element will not be announced until additional confirmatory data are obtained.

ITHACA, NEW YORK

NOTES

Objections to a Proof of Molecular Asymmetry of Optically Active Phenylaminoacetic Acid.—In a recent paper¹ G. L. Clark and G. R. Yohe have given what purports to be "a proof of molecular asymmetry in optically active phenylaminoacetic acid." It is the purpose of the present note to point out that the molecular asymmetry of this compound, however likely it may be, by no means follows from the arguments or evidence adduced in the above paper.

The procedure employed by Clark and Yohe is the following. Using the density and x-ray data, they first decide that crystalline *l*-phenylaminoacetic acid is orthorhombic and contains four molecules in the unit of structure. They then remark: "These considerations alone would narrow down the possible space groups to the following: C_{2v}^1 , C_{2v}^2 , C_{2v}^3 , C_{2v}^4 , C_{2v}^5 , C_{2v}^6 , C_{2v}^7 , C_{2v}^8 , C_{2v}^9 , C_{2v}^{10} , Q^1 , Q^2 , Q^3 , Q^4 ." x-Ray data are then examined with reference to the abnormal spacing requirements of the space groups in this list, and all of these particular space groups eliminated except C_{2v}^5 . "The conclusion is, therefore, that *l*-phenylaminoacetic acid belongs to space group C_{2v}^5 , which by its purely geometric derivation demands four asymmetric molecules per unit cell" (there are four equivalent positions in the general case in C_{2v}^5 and there are no special cases of equivalent positions); "Thus the classical theories of van't Hoff and Le Bel are confirmed, for here an examination has been made of an optically active substance, and the space group of the crystal requires that the molecule be asymmetric."

The main error in the above argument is the initial restriction of the possible space groups to the fourteen listed. The datum, four molecules in an orthorhombic unit, leaves for consideration not fourteen but fifty-six space groups, *i. e.*, all of the orthorhombic space groups except C_{2v}^{19} , Q_h^{24} and Q_h^{27} ; for all orthorhombic space groups except these three afford one or more ways of arranging four molecules in a unit provided the molecules are not assumed to be asymmetric.² Thus, although their investiga-

¹ G. L. Clark and G. R. Yohe, *THIS JOURNAL*, **51**, 2796 (1929).

² For example in the space group C_{2v}^{11} , 4 equivalent molecules possessing a plane of symmetry can be placed at $(u, 0, v)$, $(\bar{u}, 0, v)$, $(\frac{1}{2} + u, \frac{1}{2}, v)$, $(\frac{1}{2} - u, \frac{1}{2}, v)$ or again at $(0, u, v)$, $(0, \bar{u}, v)$, $(\frac{1}{2}, \frac{1}{2} + u, v)$, $(\frac{1}{2}, \frac{1}{2} - u, v)$; in the same space group equivalent molecules possessing a digonal axis can be placed at $(\frac{1}{2}, \frac{1}{2}, u)$, $(\frac{3}{2}, \frac{3}{2}, u)$, $(\frac{1}{2}, \frac{3}{2}, u)$,

tion was prosecuted for the stated purpose of testing the molecular asymmetry of the substance studied, Clark and Yohe, entirely without argument or justification, eliminated from discussion the forty-two orthorhombic space groups which provide positions in the unit cell for four non-asymmetric equivalent molecules. This removes all significance from their subsequent treatment so far as the question of molecular asymmetry is concerned.

That Clark and Yohe's proof of molecular asymmetry through the attribution of the space-group symmetry C_{2v}^5 to the crystal cannot be accepted is also shown by the following argument. The authors state: "One of the chief purposes of the investigation was to show that a unique structural analysis can be made by means of x-ray diffraction results alone and without adopting the invariable practice of depending upon previous crystallographic information." But the space-group criteria for C_{2v}^5 are identical with those for Q_h^{11} , so that Clark and Yohe's data alone could not possibly be used to indicate C_{2v}^5 uniquely.

The assumption of molecular asymmetry along with the datum, 4 molecules in an orthorhombic unit, does limit the space groups to the fourteen listed by Clark and Yohe. A different question may accordingly now be raised. Suppose that one is willing, as doubtless many are, to grant the molecular asymmetry of *l*-phenylaminoacetic acid from its constitution; can the work of Clark and Yohe not then be taken as a satisfactory space-group determination? For a number of reasons, it cannot.

In the first place there is no adequate demonstration that the crystal is even orthorhombic. Clark and Yohe have shown that the structure possesses three unequal translations which, within the error of measurement, are at 90° with each other. However, it is well known that the mere possession of three unequal axes at substantially 90° to each other is insufficient to classify a crystal as orthorhombic;³ the vital question is whether the crystal possesses the requisite *symmetry*, *i. e.*, at least either two mutually perpendicular two-fold rotation axes or else two mutually perpendicular reflection planes. The authors present no evidence on this point.

But even if it be assumed that the crystal is orthorhombic and that the molecules are asymmetric, the space group C_{2v}^5 is not demonstrated by the $(\frac{3}{2}, \frac{1}{2}, u)$; finally 4 molecules not all equivalent possessing a digonal axis and two planes of symmetry can be disposed in the positions $(0, 0, u)$, $(\frac{1}{2}, \frac{1}{2}, u)$ and $(\frac{1}{2}, 0, u)$, $(0, \frac{1}{2}, u)$.

³ For example, the following monoclinic crystals selected at random satisfy the conditions:

$K_2CH_2(SO_3)_2$, $\beta = 90^\circ 11'$: Groth, "Chemische Krystallographie," III, p. 29;

$C_2H_4I_2$, $\beta = 90^\circ 12'$: Groth, "Chemische Krystallographie," III, p. 35;

NH_4IO_3 , $\beta = 90^\circ 0'$: Groth, "Chemische Krystallographie," II, p. 93;

$MgCa(SiO_3)_2$, diposide $\beta = 90^\circ 9'$: Groth, "Chemische Krystallographie," II, p. 236.

subsequent arguments. The axis of length 9.66 Å. is arbitrarily chosen as the *c*-axis. Reference is then had to the tables of Astbury and Yardley,⁴ which show, for example, that the space group Q^3 demands the halving of the pinacoids (1 0 0) and (0 1 0). Clark and Yohe then eliminate Q^3 because the pinacoid having the spacing 15.2 Å. reflected in the first order. But in the absence of some assurance that the *a*, *b* and *c* axes have been chosen in the crystal and in the tables of Astbury and Yardley in the same relation to the microscopic symmetry elements, all the tables assert is that two (unspecified) pinacoids shall be halved; so that the presence of a first-order reflection from one pinacoid does not itself eliminate Q^3 . What is essentially this same error occurs in the elimination of some other space groups.

There also occurs an error of a different sort. Clark and Yohe state: " C_{2v}^5 calls for halving of $\{h\ 0\ l\}$ if *h* is odd, and halving of $\{0\ k\ l\}$ if *l* is odd. Tables VII and VIII show both of these conditions to be fulfilled" (Table VII is apparently intended to test the first condition, and Table VIII, the second.) These are conditions, as one may readily see in deriving them, that must apply to the planes of two *different* zones if the space group is C_{2v}^5 . But the same data occur in Tables VII and VIII, and all of the reflections given in these two tables are from planes in a *single* zone, *viz.*, the zone whose axis is the 5.05 Å. axis. Accordingly not more than one of the two C_{2v}^5 conditions can be regarded as satisfied.

It may be mentioned that the data presented by Clark and Yohe could not be made the basis of a space-group determination even if treated correctly. Clark and Yohe make use of the presence or absence of reflections from planes on one prism zone only.⁵ But in the absence of a macroscopic crystallographic investigation of the point-group symmetry of the crystal, a knowledge of the systematic presence or absence of reflections from planes of all three prism zones would be necessary for carrying out the complete space-group discussion.

It is scarcely necessary to emphasize that we do not contend that the *l*-phenylaminoacetic acid molecule is symmetrical or that the space-group symmetry of the crystal is necessarily other than C_{2v}^5 ; we do contend that neither the space group C_{2v}^5 nor molecular asymmetry follows from the arguments presented by Clark and Yohe.

Summary

It is shown that the proof presented by Clark and Yohe that the space-group symmetry of crystalline *l*-phenylaminoacetic acid is C_{2v}^5 and that the molecules of the substance are asymmetric is vitiated by the following errors:

⁴ W. T. Astbury and K. Yardley, *Phil. Trans. Roy. Soc.*, **224A**, 221 (1924).

⁵ Interplanar distances for reflections from another prism zone are given in Table IV, but indices are not assigned and the data are not used in the space-group discussion.

1. The crystals are not conclusively shown to be orthorhombic.
2. The 42 orthorhombic space groups permitting the presence of four equivalent symmetrical molecules in the unit are eliminated from discussion without justification and without argument.
3. The 9.66 Å. axis is arbitrarily designated the *c*-axis, and the elimination of space groups is carried out with this unjustified assumption.
4. The 15.2 Å. and 5.05 Å. axes are treated as though they could simultaneously be chosen with two different orientations relative to the microscopic symmetry elements of the crystal.

It is further pointed out that the data published by Clark and Yohe are not sufficiently extensive to be made the basis of a space-group discussion.

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The Use of the Theory of Space Groups in Crystal Structure Determinations.—Those unfamiliar with the theory of space groups find it difficult to judge as to the validity of crystal structure results obtained by its use. For this reason a recent article by Clark and Pickett,¹ in which "unique solutions of the crystal structure for diphenyl and five of its derivatives" are claimed, would seem to require some comment.²

In the first place, in discussing dimesityl the authors state: "Either two molecules with a center of symmetry or four asymmetric molecules may be placed in one unit cell in this space group. Hence the dimesityl molecule must be asymmetric." Reference to tables³ giving the sets of equivalent (*i. e.*, equivalently surrounded) positions for this space group (C_{2h}^5) shows, however, that the molecules might be in two such sets of positions, all centers of symmetry. The same mistake is made in discussing diphenic acid and *o*-tolidine. There is no requirement, chemical or otherwise, that the molecules all be equivalently surrounded. If Clark and Pickett care to base their deductions of structures and molecular symmetry on such an assumption, should we not expect a statement to that effect?⁴

¹ Clark and Pickett, *THIS JOURNAL*, **53**, 167 (1931).

² Similar remarks would also apply to articles by Clark and Yohe, *ibid.*, **51**, 2796 (1929), and Scroggie and Clark, *Proc. Nat. Acad. Sci.*, **15**, 1 (1929).

³ *E. g.*, Wyckoff, "The Analytical Expression of the Results of the Theory of Space Groups," Carnegie Institution Publication No. 318, 1930.

⁴ In the accompanying Note by G. L. Clark, which the Editor has kindly let me see, he reinterprets his data on diphenic acid, concluding that the space group may be C_{2h}^5 . Since he deduces 8 molecules per unit and there can be at most four equivalent positions in the unit, with this space group, the molecules cannot all be equivalent. Yet it is the *neglect* of possibilities of precisely this sort which he attempts to justify at an earlier point in his letter.