

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.

A similar error also occurs in the treatment of hexachlorodiphenyl. It is stated that C_{2v}^9 "allows for only four asymmetric molecules in the unit cell and hence would necessitate the assumption of polymerization." One need only assume that four of the molecules are in positions not crystallographically equivalent to those occupied by the other four.

The assignment of 3,3'-diaminodimesityl, which "has been resolved into two active forms," to C_{2h}^5 cannot be correct, for space groups containing symmetry planes are impossible for optically active crystals.⁵ This fact lies at the very basis of modern theory of optical activity and is extremely well-grounded experimentally.

The observation of a 010 reflection (listed in Table I) also rules out C_{2h}^5 for this compound, for this space group requires⁶ not only the absence of $h0l$ reflections when l is odd but also the absence of all $0k0$ reflections with k odd. It follows directly from the fundamentals of space-group theory that a structure having the symmetry of this space group can give *absolutely no* reflection of this sort, while structures having the symmetry of some other space group might well give absences such as those observed. (In other words, the "presence" of a reflection is conclusive; a few absences are not.)⁷

In the case of *o*-tolidine, $0k0$ reflections with k odd are said to be "either absent or extremely weak" and in a preliminary paper⁸ they are said to be "so weak that they are only detectable on an over-exposed photograph," the inference being that, although weak, they are definitely

⁵ See Tutton, "Crystallography and Practical Crystal Measurement," The Macmillan Co., London, 1922, Vol. 2, p. 1272, or any other good crystallography or crystallographer.

It is a very common occurrence, familiar to all crystallographers, for crystals belonging to one of the classes of lower symmetry to fail to develop faces indicating that lower symmetry. Such a case is that reported by Read, Campbell and Barker, referred to by George L. Clark in the answer to this note. These authors obtain *d*- and *l*-iso-hydrobenzoin crystals from chloroform which "are morphologically indistinguishable from one another so far as plane faces are concerned." They, "however, have been shown by polarimetric examination to be . . . of two kinds, consisting . . . of the pure *d*- and *l*-forms." They mention that Reis and Schneider [*Z. Krist.*, **69**, 62 (1928)] showed crystals similarly obtained from ether to be pyroelectric: "this behavior, in the case of a monoclinic crystal, proves the class to be enantiomorphous . . . The enantiomorphism of crystal structure in such instances is presumably not in doubt, since it is impossible to arrange wholly dextro- or wholly laevo-particles in such a way as to confer on the assemblage the property of identity with its mirror image. . . . Thus . . . the only question which can be raised is that of the frequency with which enantiomorphism of structure unfolds itself on the surface."

⁶ See, for instance, Astbury and Yardley, *Phil. Trans. Roy. Soc. (London)*, **A224**, 221 (1924).

⁷ See, for instance, Wyckoff, "The Structure of Crystals," Chemical Catalog Co., New York, 1924, pp. 218-221.

⁸ Clark and Pickett, *Proc. Nat. Acad. Sci.*, **16**, 20 (1930).

present.⁹ If so, $Q^4 (= V^4)$, said to be the probable space group and listed alone under the heading "Space group" in the table of summarized "results" on p. 174, is definitely eliminated.⁶

It is assumed that the absence of a 010 reflection is sufficient ground for assigning dimesityl to C_{2h}^5 rather than to C_{2h}^4 or C_2^2 . If several $0k0$ reflections with k odd, all having a chance to reflect, were missing, the space-group assignment would probably be valid.⁷ Whether or not this is the case one is left to guess, although, since practically all the conclusions reached in this article depend on the correctness of the space-group determinations, such crucial information would seem to be especially important. From the data given, one can only say that the space-group assignment *may* be correct.

From diphenic acid $hk0$ reflections were not observed if $(h+k)$ is odd. "The only space group which necessitates this particular spacing is the orthorhombic group $Q_h^{13} (V_h^{13})$," according to Clark and Pickett. However, as the naming of the axes and so of the indices was arbitrary, those space groups (C_2^2 , C_{2h}^4 and C_{2v}^7) having as "abnormal spacings" " $h0l$ halved if $(h+l)$ is odd" should also be considered.¹⁰ If consideration was actually given these possibilities and they were eliminated, the reasons for their elimination should be given. Laue photographs from suitably oriented crystals, for instance, would definitely decide between a monoclinic space group (C_2^2 or C_{2h}^4) and an orthorhombic space group (Q_h^{13} or C_{2v}^7), both in this case and in that of hexachlorodiphenyl.

In the first paper of this series² a "crystal was proven orthorhombic, independently of any optical data" by the observation that "a typical layer line diagram" was produced with either of three mutually perpendicular directions in the crystal parallel to the axis of rotation. A similar line of reasoning seems to have been adopted by Clark and Pickett. This involves the assumption that "layer lines" appear only if the rotation axis is one of the crystallographic reference axes, parallel to the edges of the unit cell, whereas any rotation axis passing through identical points in the structure will give layer lines and, unless one has crystallographic or other information regarding the orientation of the reference axes, the procedure used might easily lead to a unit of incorrect shape and size. In case other means were used to determine the relative directions of the edges of the unit cell, they should at least be mentioned; otherwise the results of the analysis cannot be considered to have much value.

Incidentally, such crystallographic data as are recorded for these crys-

⁹ In the print to be reproduced as Fig. 2 of Clark's Note the 030 reflections are distinctly observable on both sides of the central spot. Whether they will show up when published is, however, very doubtful.

¹⁰ Ref. 6, pp. 227-235.

tals in standard reference works¹¹ should be given for comparative purposes. The density of 3,3'-diaminodimesityl and the reference to Caspari's work are also missing.

It should be mentioned, moreover, that the four sets of coördinates at the top of p. 170 represent only one distinct arrangement of diphenyl molecules, most simply expressed as 000; $\frac{1}{2}$ $\frac{1}{2}$ 0.

In the first equation (p. 168) d should be $1/d$.

Criticism of the speculations under the heading "Discussion of Results" will be omitted as unnecessary in view of the doubtful character of the unique "results."

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The Space Groups and Molecular Symmetry of Optically Active Compounds: A Reply.—The criticisms raised by Pauling and Dickinson against our paper on crystal analysis of optically active phenylaminoacetic acid,¹ and by Huggins against the paper on crystal analysis of diphenyl and some of its active and inactive derivatives,² have certain common grounds, so that those in both communications which are sufficiently specific to deserve comment will be briefly answered.

(1) The chief criticism by Pauling and Dickinson is directed to the logic of presentation and the use of the word "proof" rather than to the experimental results or assignment of space group. Taking our paper as it stands this criticism is largely justified. Increasing experience all over the world demonstrates that instances in which flat positive and incontrovertible statements may be made from x-ray data, particularly on complex organic molecules, as to space group and especially molecular shape and symmetry, are extremely rare. There are almost invariably alternatives, choice between which must be made upon the basis of knowledge from other sources. The long standing difficulty in deciding between staggered or planar structure for the benzene ring is a familiar example.

(2) We insist that the space group C_{2v}^5 assigned for active phenylaminoacetic acid accounts best for the facts after several careful remeasurements of the films, and after use of the Weissenberg goniometer method which removed possible uncertainties in the ordinary rotation results.³ Independ-

¹¹ *E. g.*, Groth, "Chemische Krystallographie," Engelman, Leipzig, 1919, Vol. 5, pp. 7 and 30.

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

² Clark and Pickett, *ibid.*, **53**, 167 (1931).

³ See Schleede and Schneider, "Röntgenspektroskopie und Kristallstrukturanalyse," Berlin, 1929, Vol. I, p. 318.