

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.

CONTRIBUTION NO. 297 FROM
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PASADENA, CALIFORNIA
RECEIVED OCTOBER 8, 1929
PUBLISHED OCTOBER 5, 1931

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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_3^2 . 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_3^2 , 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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RECEIVED APRIL 13, 1931
PUBLISHED OCTOBER 5, 1931

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.

ent interpretations of the x-ray films are invited. Hence in spite of objection the contention of molecular asymmetry follows. We would amend the paper to "a possible proof" (which was implied always rather than *the* proof).

(3) The first criticism of Huggins, also implied by Pauling and Dickinson, is pertinent in stating that there is a second possibility to that of the assumption of asymmetric molecules. This has been fully considered although not specifically mentioned in the paper. The selection of one of two alternatives, a process which can scarcely be justly called a mistake, was based upon every possible deduction from our chemical knowledge. For tolidine and diphenic acid particularly is this decision clear-cut. Among x-ray workers there is a very real question as to whether molecules actually do arrange in the manner of the alternative which was not selected. Astbury and Yardley, while mentioning that an assumption is involved, certainly ignore the results of such a possibility in illustrating possible deductions from data on pages 228 and 232. The same kind of reasoning from x-ray data concerning molecular symmetry which we have used or the reverse process of direct assumption of molecular asymmetry in order to deduce the space group have also been emphasized in several papers by other workers.⁴

(4) Regardless of the statement by Huggins that "the assignment of 3,3'-diaminodimesityl to C_{2h}^5 cannot be correct, for space groups containing symmetry planes are impossible for optically active crystals," this crystal *does* show a plane of symmetry. In Fig. 1 is reproduced an oscillation photograph which shows the 002, 004, 006, 102, 104, 106 plane reflections while the corresponding $h0l$ where l is odd are missing. *Inasmuch as the type of isomerism here studied has no analog among the crystals which have been investigated, inasmuch as there is NO ASYMMETRIC CARBON ATOM in the usual sense in these diphenyl derivatives and inasmuch as the real cause of stereoisomerism in such compounds is still under investigation, the word impossible is extreme to say the least.* The experimental negatives are available to anyone; from these we have definitely eliminated, so far as we can tell, any other possibility. Read, Campbell and Barker⁵ found that *d*- and *l*-isohydrobenzoin sometimes crystallize in forms which have a plane symmetry. This would seem to explode the old assumption that optically active compounds always crystallize in enantiomorphous forms.

(5) The next point in the Huggins' communication represents a misunderstanding on the part of the critic. If the reflection is not present,

⁴ Hengstenberg and Mark, *Z. Krist.*, **70**, 285 (1929), (diphenyl, etc.); *ibid.*, **72**, 301 (1929), (glucose and other carbohydrates); Caspari, *J. Chem. Soc.*, 573, 2944 (1926); 1093 (1927); *Phil. Mag.*, **1**, 1276 (1927); Sponsler and Dore, *THIS JOURNAL*, **53**, 1639 (1931).

⁵ Read, Campbell and Barker, *J. Chem. Soc.*, 2306-2309, 2315 (1929).

one space group is possible; if present that is ruled out. In the two cases cited there were faint blurs on some but not all of the films where the $0l0$ planes were in a position to reflect. No other $0k0$ planes give reflections. These films were submitted to several disinterested people for opinion as to whether these faint markings were reflections or not, the general consensus being that by comparison with all other interferences they were not. In order to be fully scrupulous concerning the data, these spots were mentioned and in the case of tolidine the resulting possibility as to space group

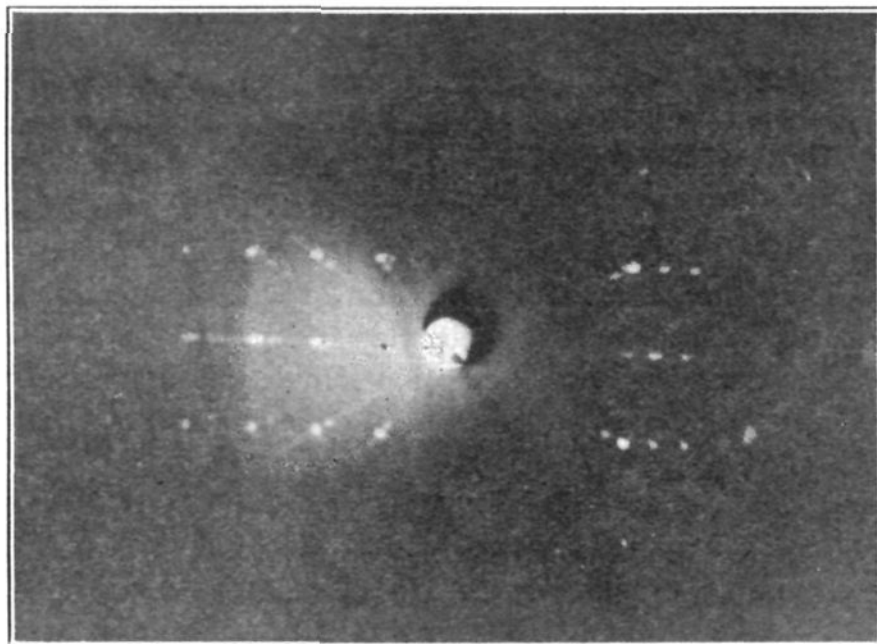


Fig. 1.—Oscillation photograph for diaminodimesityl showing the absence of $h0l$ planes where l is odd. The diffraction interferences appearing upon the 0 layer line or equator on the left side of the primary beam are, respectively: 002, 004, 006, 008. On the first layer line the interferences reading from the center to the left are, respectively: 102, 104, 106, 108.

was cited. Figure 2 is an oscillation photograph for tolidine where $0l0$ and 030 planes are in a position to reflect. There is no trace of interferences for either.

(6) The following additional data answer the question raised concerning dimesityl

- 030, in position to reflect, missing
- 040, in position to reflect, weak
- 050, in position to reflect, missing (Fig. 3)

Figure 3 illustrates very well that with 010 and 030 in position to reflect as well as 020 , only 020 appears.

(7) Relative to diphenic acid, the naming of the axes was arbitrary and there is no proof that this was not entirely admissible. All the space groups

mentioned were carefully considered. C_s^2 and C_{2h}^4 are monoclinic groups while the x-ray and optical data agreed on the orthorhombic. C_{2v}^7 was discarded at the time because it admits of 4 asymmetric molecules in the cell while 8 molecules are actually present. In light of the discussion in

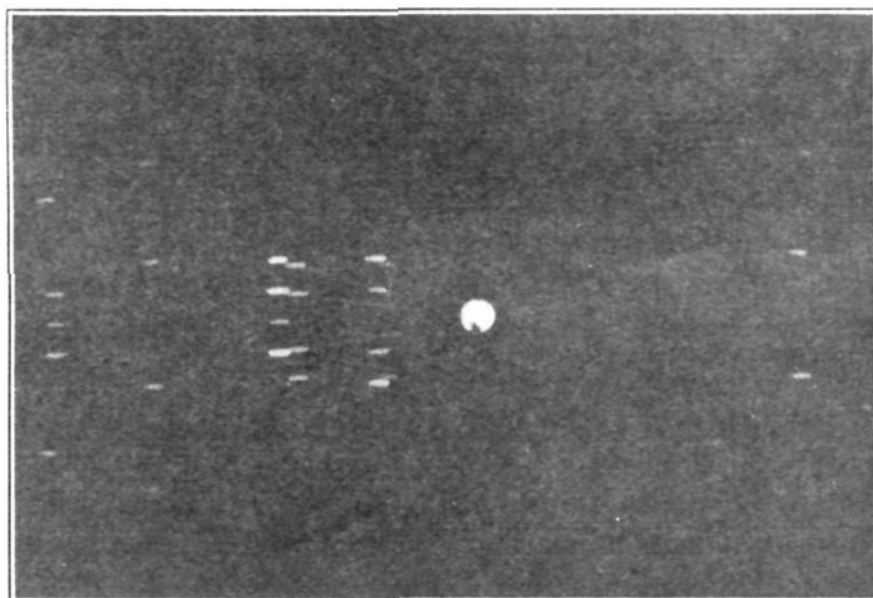


Fig. 2.—Oscillation photograph for tolidine showing absence of 010 and 030. 020 appears alone on the O layer line at the left of the primary beam. 010 if present should appear as the central interference in the first vertical line.

(3), this possibility is not entirely eliminated but it seems very unlikely. This again was a choice between alternatives and involves no mistake. On the other hand, we are perfectly willing to admit that the data on this

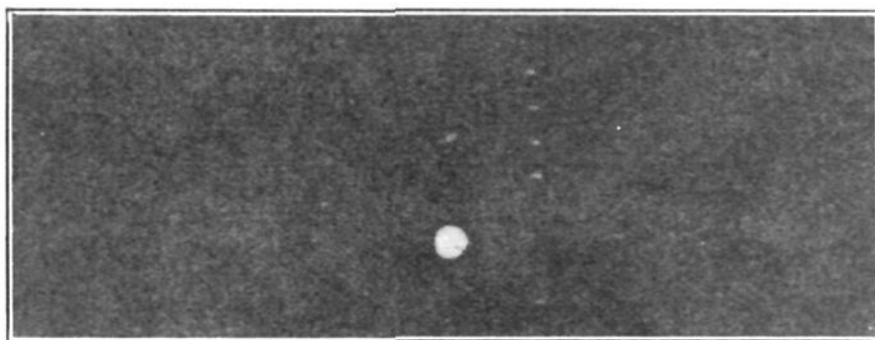


Fig. 3.—Oscillation photograph for dimesityl showing absence of 010 and 030. 020 alone appears on the O layer line.

crystal are not as conclusive as we should like, inasmuch as another interpretation can be given as the result of further careful measurements on the negatives by Dr. Pickett. Inasmuch as the matter is still inconclusive and must be decided by experiments with a Weissenberg goniometer, we

have not considered it advisable to change the data as originally presented. Under the circumstances, however, these new possibilities will be outlined here. Bodwig and Howe⁶ gave results for diphenic acid as monoclinic prismatic $a:b:c = 1.1392 : 1 : 1.1888$, $\beta = 91^\circ 48'$. While the x-ray data and Dr. Wherry's optical examination were in unusually excellent agreement, we have found that the series of interferences which were taken as 106, 107, 108 might be 206, 207, 208, as both were in position to reflect in the same photograph. Calculations seem to agree somewhat better with the latter set. Inspection shows that while the $hk0$ where $h + k$ is odd do not give reflections, a more fundamental abnormality is probably $h0l$ where h is odd and $0k0$ where k is odd, in which case the space group could be monoclinic prismatic, C_{2h}^5 , although the monoclinic angle β is evidently much nearer 90° than that found in the above-mentioned paper.

(8) The criticism in both communications concerning the whole matter of ignorance of the correct use of the rotation method would be extremely important but fortunately this can be dealt with adequately. The critics have placed an extraordinarily narrow and literal interpretation upon the brief sentences appearing in our papers concerning goniometric use of the rotation method. We fully recognize that rational layer line diagrams can be obtained about axes other than those selected as principal axes, and many of these photographs have actually been made, for example in the case of tolidine, in order to identify certain spots not otherwise easy to find. It goes without saying that no dependence would have been placed on the x-ray data concerning axes without full test and confirmation. It seemed self-evident and unnecessary to mention in the light of the microscopic data actually given that before the crystals were mounted on the goniometer head their external form and optical properties were examined under a polarizing microscope in *all* cases, and the crystallographic axes thus indicated were used as axes of rotation. It seems entirely convincing that the detailed optical examination made independently by Dr. Wherry on diphenyl and derivatives in each case *following* the determinations of structure by x-rays, fully confirmed our results.

(9) Regarding Huggins' complaint concerning references to crystallographic data, one of the Groth references is to diphenyl and is given in the paper by Hengstenberg and Mark to which we referred in our own paper. The other is to dimesityl which Jerschoff⁷ gives as monoclinic prismatic, axial ratios $1.2892 : 1 : ?$ $\beta = 95^\circ 48'$. Our results are monoclinic prismatic, axial ratios, $0.957 : 1 : 2.593$, $\beta = 96^\circ 18'$; *i. e.*, our $c:b$ ratio is twice Jerschoff's $a:b$. Although his data are incomplete, we consider them entirely confirmatory rather than otherwise.

⁶ Bodwig and Howe, *Z. Krist.*, **3**, 413 (1879).

⁷ Jerschoff, *Bull. Soc. fr. Min. Par.*, **27**, 198 (1904); Groth, "Chemische Krystallographie," Engelmann, Leipzig, 1919, Vol. V, pp. 7 and 30.

The density of 3,3-diaminodiphenyl is 1.102, which gives a calculated value of 3.993 (or 4) molecules in the unit cell. The reference to Caspari is *J. Chem. Soc.* 573, 2944 (1926); 1093 (1927); *Phil. Mag.*, **1**, 1276 (1927).

We are indebted to Dr. Huggins for calling attention to these omissions which occurred as a result of condensing the paper and a typographical error.

The remaining criticisms of the communications require no comment.

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RECEIVED AUGUST 24, 1931
PUBLISHED OCTOBER 5, 1931

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF LOUISVILLE]

THE REACTIONS OF SOME INORGANIC VANADIUM COMPOUNDS WITH PHENYLMAGNESIUM BROMIDE¹

BY C. C. VERNON

RECEIVED APRIL 10, 1931

PUBLISHED OCTOBER 5, 1931

Introduction

The Grignard reagent reacts with several metallic halides to give organo-metallic compounds of the type R_nM , in which the organic radical (R) is directly attached to the metal (M). In some cases oxides of certain metals react with this reagent² to give compounds of the same type. Vanadium in some of its states of valence may be considered analogous to some metals whose halides and oxides are known to behave in this fashion.

Organic vanadium compounds of the ester, alcoholate and complex types are known, and some have reputed therapeutic value³ but no true organovanadium compound of the type discussed is mentioned in the literature. On the basis of related known compounds it might be expected that organovanadium compounds would be highly unstable.⁴

On the other hand, certain salts of heavy metals have been found to cause a coupling of the organic radicals, when allowed to react with the Grignard reagent.⁵ Probably this difference in behavior is due to the manner in which the equilibria discussed by Gilman and St. John⁶ are

¹ Presented before the Organic Division of the American Chemical Society, Indianapolis, Indiana, April 1, 1931.

² Blicke and Smith, *THIS JOURNAL*, **51**, 1558-1565 (1929).

³ A. Grippa, *Ann. Chem. Appl.*, **20**, 244-248 (1930), [*C. A.*, **24**, 5288 (1930)]; *Vancoram Review*, **2**, 43-46 (1931). This reference summarizes the uses of vanadium in medicine and also gives data on toxicity.

⁴ Bennett and Turner, *J. Chem. Soc.*, **105**, 1057-1062 (1914).

⁵ Gilman and Parker, *THIS JOURNAL*, **46**, 2823-2827 (1924); Gardner and Borgstrom, *ibid.*, **51**, 3375-3377 (1929).

⁶ Gilman and St. John, *ibid.*, **52**, 5017-5023 (1930). This article contains leading references to the work of others along the same line.