

tals in standard reference works<sup>11</sup> 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,<sup>1</sup> and by Huggins against the paper on crystal analysis of diphenyl and some of its active and inactive derivatives,<sup>2</sup> 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.<sup>3</sup> Independ-

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

<sup>1</sup> Clark and Yohe, *THIS JOURNAL*, **51**, 2796 (1929).

<sup>2</sup> Clark and Pickett, *ibid.*, **53**, 167 (1931).

<sup>3</sup> 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.<sup>4</sup>

(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 Barker<sup>5</sup> 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,

<sup>4</sup> 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).

<sup>5</sup> 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

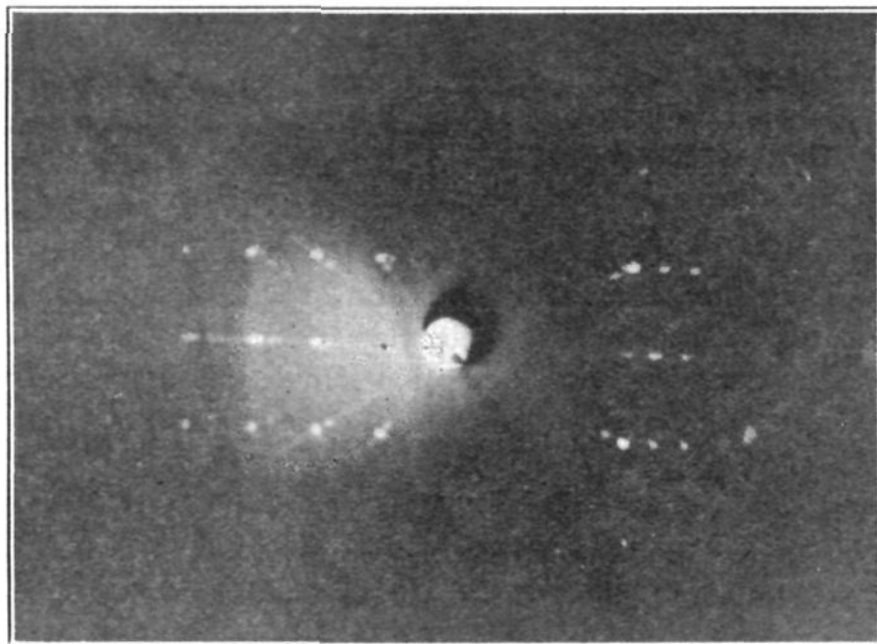


Fig. 1.—Oscillation photograph for diaminodimesityl showing the absence of  $h0l$  planes where  $l$  is odd. The diffraction interferences appearing upon the 0 layer line or equator on the left side of the primary beam are, respectively: 002, 004, 006, 008. On the first layer line the interferences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

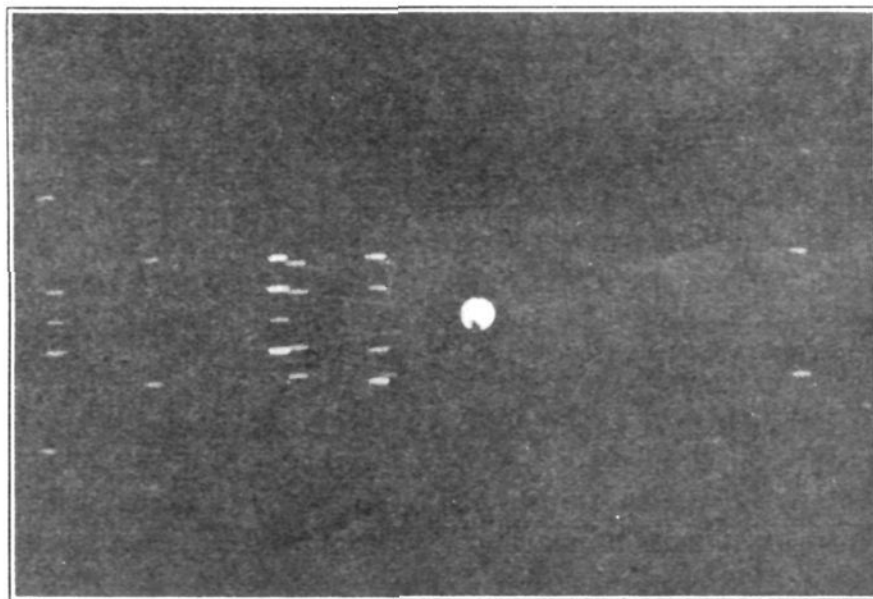


Fig. 2.—Oscillation photograph for tolidine showing absence of 010 and 030. 020 appears alone on the O layer line at the left of the primary beam. 010 if present should appear as the central interference in the first vertical line.

(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

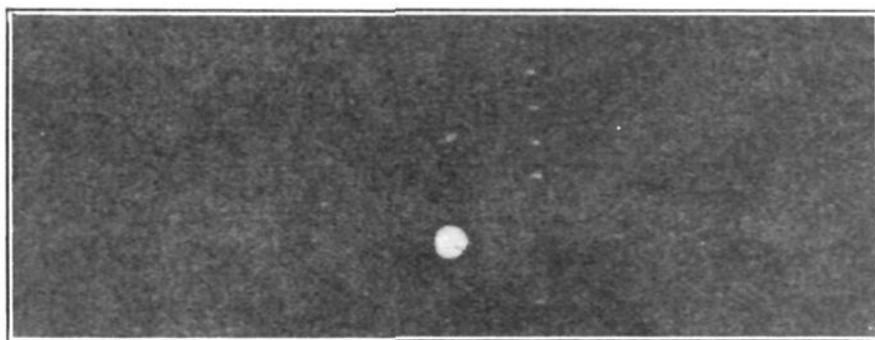


Fig. 3.—Oscillation photograph for dimesityl showing absence of 010 and 030. 020 alone appears on the O layer line.

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 Howe<sup>6</sup> 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  $h k 0$  where  $h + k$  is odd do not give reflections, a more fundamental abnormality is probably  $h 0 l$  where  $h$  is odd and  $0 k 0$  where  $k$  is odd, in which case the space group could be monoclinic prismatic,  $C_{2h}^5$ , although the monoclinic angle  $\beta$  is evidently much nearer  $90^\circ$  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 Jerschoff<sup>7</sup> 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.

<sup>6</sup> Bodwig and Howe, *Z. Krist.*, **3**, 413 (1879).

<sup>7</sup> 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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## THE REACTIONS OF SOME INORGANIC VANADIUM COMPOUNDS WITH PHENYLMAGNESIUM BROMIDE<sup>1</sup>

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### 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 reagent<sup>2</sup> 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 value<sup>3</sup> 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.<sup>4</sup>

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.<sup>5</sup> Probably this difference in behavior is due to the manner in which the equilibria discussed by Gilman and St. John<sup>6</sup> are

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

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

<sup>3</sup> 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.

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

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

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