

(5) Assignment of theoretical formula. The above analytical data, *viz.*, NaOCl, 3.00%, NaCl 2.23%, H₂O 46.85%, As₂O₅ 26.16%, Na₂O 29.75% (by difference only), converted to moles, gives 1.03, 1.00, 68.20, 2.98, 9.20, respectively, whose nearest whole number ratios are 1:1:68:3:9. The 68 for water has to be adjusted to yield the formula: (Na₂AsO₄·11H₂O)₆·NaOCl·NaCl.

(6) Cooling curves were determined in the usual manner, the data shown in Table I being obtained. Run III of this table shows temperatures obtained after melting, cooling and remelting the sample repeatedly. Melting points were also determined for a number of samples in conventional melting point tubes, the temperatures of melting being between 79 and 81°.

(7) The solubility of the compound in water at 30° was determined by withdrawing 5-ml. samples of the saturated solution through a cotton filter and evaporating to dryness

and then igniting at the full heat of a Meeker burner as was done for determining weight loss as shown above. From the weight of this residue the calculated solubility at 30° is 44.46 g./100 ml.

(8) Density was determined with a West pycnometer using benzene, the value 1.7914 at 30°/4° being obtained.

(9) X-Ray diffraction photographs of chlorinated trisodium arsenate and chlorinated trisodium phosphate were taken and the "d" values determined from these photographs. These values for the strongest lines are as follows: for the chlorinated trisodium arsenate, prepared by the "melt" method described herein, 10.1, 5.98, 5.49, 4.40, 4.06, 3.71, 3.35, 3.01, 2.73, 2.48; for a sample of chlorinated trisodium phosphate obtained from the Blockson Chemical Company, Joliet, Illinois, 10.3, 5.98, 5.43, 4.38, 4.01, 3.70, 3.34, 3.01, 2.72, 2.46.
ST. PAUL, MINNESOTA

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY AND PHYSICS, POLYTECHNIC INSTITUTE OF BROOKLYN]

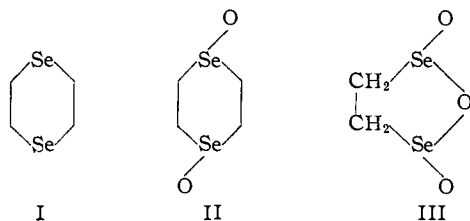
The Crystal Structure of *trans*-Ethanediseleninic Anhydride

BY EDWIN S. GOULD AND BENJAMIN POST

RECEIVED APRIL 30, 1956

The crystal structure of *trans*-ethanediseleninic anhydride (C₂H₄Se₂O₃) has been determined. This compound, the first alkanediseleninic anhydride to be described, crystallizes in the orthorhombic system, space group D^{12h}_{2h}-P_{bcn}; there are four molecules in the unit cell. The molecule is a five-membered heterocyclic ring and has two types of selenium-to-oxygen bonds. The Se-O bonds within the ring (1.82 ± 0.03 Å.) are considerably longer than the "exocyclic" Se-O bonds (1.61 ± 0.03 Å.). The very short intermolecular selenium-to-oxygen distances (2.70 ± 0.10 Å. and 3.11 ± 0.03 Å.) indicate strong intermolecular attraction which is, in turn, reflected in the unusually high density (2.92 g./cc.) of the crystal.

The oxidation of 1,4-diselenane (I) with 40% peroxyacetic acid yields several solid products. Among these was the expected product, the dioxide II, and there was also isolated a small quantity of



a dense white solid whose composition suggested the seleninic anhydride structure III. The latter compound, presumably arising from oxidative degradation of the diselenane ring system, was of interest since it would represent the first alkanediseleninic anhydride to be reported¹ and also the first example of a five-membered ring containing two non-adjacent selenium atoms. Furthermore, it seemed surprising that an anhydride could be recovered unchanged by recrystallization from aqueous methanol. Finally, if the configuration of the three bonds about the selenium atom is pyramidal, this compound should be, to our knowledge, the first example of a monocyclic acid anhydride capable of existence in *cis*- and *trans*- forms. In view of these points, a confirmation of the assigned structure by X-ray diffraction was undertaken.

Experimental

Preparation of Sample.—To 1 cc. of glacial acetic acid was added 200 mg. of 1,4-diselenane.² The mixture was

(1) To our knowledge, the only seleninic anhydride described is benzenediseleninic anhydride, reported by H. W. Doughty, *Am. Chem. J.*, **41**, 336 (1909).

(2) J. D. McCullough and N. Tideswell, *THIS JOURNAL*, **76**, 3091 (1954).

cooled to 0°, and 1.0 cc. of a solution of 40% peroxyacetic acid in glacial acetic was added dropwise. The mixture was allowed to stand 10 minutes, and 2 cc. of ice-water was added. The solution was extracted 3 times with 10-cc. portions of ether, the ether extracts being discarded. The aqueous layer was evaporated to dryness *in vacuo* at 25°. The residue was dissolved in a minimum volume of water at 45°, and the solution quickly diluted with eight times its volume of boiling methanol. Slow cooling yielded 30 mg. (14%) of the anhydride. The compound darkens at 95° to yellow and melts in the range 100–102°.

Anal. Calcd. for C₂H₄O₃Se₂: Se, 67.5. Found: Se, 67.5.

(In this preparation, the main product, 1,4-diselenane dioxide (II), remains in the mother liquor. If, however, ethanol be used as a crystallization solvent, the dioxide crystallizes, leaving the anhydride in the mother liquor.)

The crystals of the anhydride were prism-shaped with well developed faces of the type (110) and (011). Two determinations of density by the flotation method (using mixtures of CCl₄ and CH₂I₂) gave the values 2.96 and 2.87 g./cc. Since the anhydride decomposed slightly upon standing in warm humid air for a week, the individual crystals to be studied were enclosed in small, thin-walled glass capillary tubes. The two crystals upon which our data are based were approximately 0.2 × 0.2 × 0.25 mm. and 0.25 × 0.25 × 0.3 mm.

X-Ray Diffraction Data.—Precession photographs of the zones (*hk*0), (*h*0*l*), and (0*kl*), taken with filtered molybdenum radiation, were used to determine the structure. Two exposures (one 3 hours, one 48 hours) of each of these zones were taken. These photographs gave the orthorhombic cell dimensions (Mo K_α taken as 0.708 Å.): *a* = 4.64 Å., *b* = 9.96 Å., *c* = 11.22 Å. (each ±0.5%), *V* = 518.5 Å.³ This volume, together with the density 2.92 g./cc., yields the figure 3.91 molecules per unit cell.

The intensities of the diffraction spots were estimated visually, using a calibrated comparison strip, and were corrected for Lorentz and polarization factors in the usual way.

The rather high value of the absorption coefficient calculated for this compound ($\mu_{Mo} = 151 \text{ cm.}^{-1}$) indicates that absorption effects cannot be ignored. However, the irregular shapes of our crystals prevented direct calculation of absorption corrections as such, the result being that absorption effects became incorporated in our empirical "temperature factors," obtained later in the course of the structure determination.

Determination of the Structure.—The systematic absences are: $hk0$ if $(h + k)$ is odd, $0kl$ if k is odd, and $h0l$ if l is odd. These establish the space group D_{2h}^{14} - P_{ben} . In addition reflections with indices $(h + k)$ odd were all either very weak or absent. Only nine $h0l$ reflections with h odd were detected; all were weak. If the unit cell were "c" face-centered, all reflections with $(h + k)$ odd would be absent. The structure therefore approximates a "c" face-centered one. The intensities of the $(h + k)$ odd reflections are an indication of the deviation from "c" face-centering.

Since the space group has eightfold general positions, the asymmetric unit should contain one selenium atom, one carbon atom, and one and one-half oxygen atoms. (Throughout this report, the oxygen atom bonded to two selenium atoms will be designated as "cyclic," O_c , whereas the oxygen atom bonded to one selenium atom will be designated as "exocyclic," O_e .) The positions of the hydrogen atoms cannot be determined.

Since the selenium atom has by far the greatest diffracting power, a knowledge of its position will permit phase-determination of essentially all of the structure factors for the zones $(0kl)$ and $(hk0)$, and for the reflections in the $(h0l)$ zone having h even. However, the structure-factor expression for the $h0l$ reflections with h odd includes a " $\sin 2\pi hx$ " term. Since the selenium atom is located close to $x = 0$, its contribution to these reflections is small, and knowledge of its position does not necessarily determine the phases of the nine reflections of this type.

Approximate values of the x , y and z parameters of the selenium atom were determined from the relative intensities of the reflections of the type $h00$, $0k0$ and $00l$, respectively. Using these approximate parameters the structure factors of the reflections in the $(0kl)$ and $(hk0)$ zones were determined. (Since the unit cell is centro-sym-

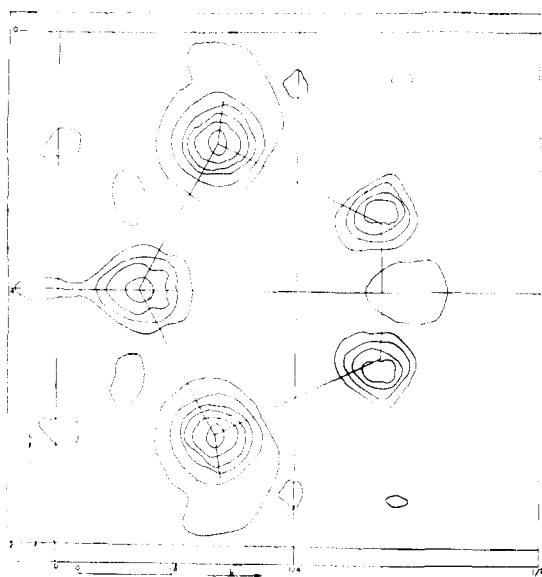


Fig. 1.—Electron-density projection of one molecule of *trans*-ethanediseleninic anhydride on (100). Intersections of "bonds" mark positions of final atomic parameters.

metric, this requires only the determination of the sign of the structure factor.) Electron density projections down the a - and c -axes were calculated; these are shown in Figs. 1 and 2. Note that the projection on (001) determines the y - and z -parameters of Se, and (more approximately) the y - and z -parameters of C and the y -parameter of O_c . The position of O_e is obscured by the Se peak. The projection on (100) confirms the y coordinates of Se, C and O_c and gives an approximate value for the y coordinate of O_e ; however, lack of resolution between C and O_e (from another molecule) permits only a very rough value of the x coordinates of these atoms.

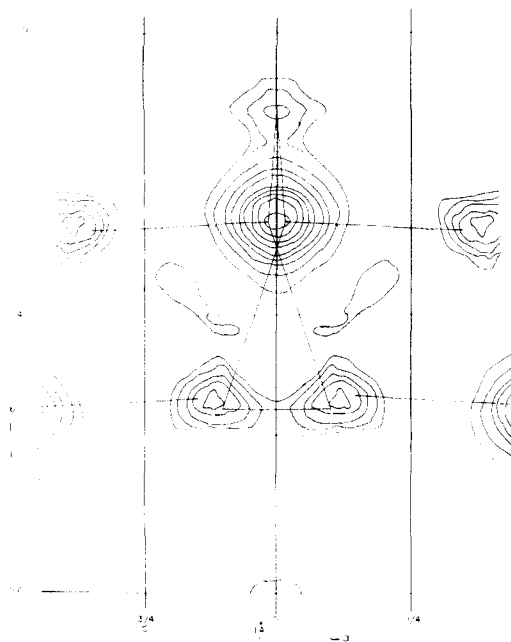


Fig. 2.—Electron-density projection of one molecule of *trans*-ethanediseleninic anhydride on (001). Portions of two selenium atoms from adjacent molecules are included at lower left and lower right. Intersections of "bonds" mark positions of final atomic parameters.

Turning now to the projection on (010), the signs of the reflections having h even are determined by the position of the selenium atom. The signs of the nine weak reflections having h odd must be determined by the positions of C and O_e (since Se is near $x = 0$ and O_c is at $x = 0$). The z -parameter of the carbon atom was taken from the projection on (100) and that for O_e was assumed to be approximately the same as that for Se. The lack of resolution of C and O_e on (001) suggested that these atoms should be about the same distance from $x = 1/4$ (at about 0.33 or 0.17). The asymmetric unit in this projection was chosen as that area lying between $x = 0$ and $x = 1/4$ and between $z = 0$ and $z = 1/2$; this unit is split into two sections by the line $z = 1/4$. Inspection of the intensities of the strongest reflections in this group (102, 104, 302 and 304) indicated that C and O_e must lie in different sections. On these bases, the signs of the nine "odd" reflections were assigned, and the electron density projection on (010) calculated. From the results of the three projections, provisional

parameters for all atoms (except hydrogen) were determined, and the signs of all the zero-layer structure factors were recalculated. The inclusion of carbon and oxygen contributions changed none of the signs in the $(0kl)$ or $(hk0)$ zones nor any of the "even" terms in the $(h0l)$ zone (a total of 96 reflections). Two of the signs of the nine "odd" terms of the $(h0l)$ zone were reversed in the refinement process.

On the projections shown, the contour lines are drawn at arbitrary intervals. The contour lines about the Se atom are drawn at five times the interval as those about the lighter atoms. $F(000)$ is not included in the summations. The selenium parameters and provisional parameters of the lighter atoms were calculated from the summation values, using the method of Ladell and Katz.³ The parameters were used to calculate structure factors for the zero-layer reflections observed. To correlate the observed intensities with those calculated, an empirical correction of the form

$$F_{\text{calcd}} = F(e^{-B \sin^2 \theta / \lambda^2})$$

was applied. Here F is the sum of the contributions from the selenium atom, the carbon atom, and the 1.5 oxygen atoms in the asymmetric unit and B a combined temperature and absorption factor, typical of the zone. For projections on (100) and (001), B was 1.68 \AA^2 , whereas for the projection on (010) it was only 0.46 \AA^2 .⁴ More exact parameters of the lighter atoms were then obtained by subtracting Fourier projections, based on Se alone, from each of the three Fourier projections. The "back-shifts" in the parameters of the lighter atoms have the following magnitudes

	$\Delta x, \text{ \AA}$	$\Delta y, \text{ \AA}$	$\Delta z, \text{ \AA}$
C	0.01	0.02	0.13
O _c	0	.08	0
O _e	0.06		0.07

No further sign changes resulted from the final adjustment of parameters of the light atoms.

The parameters of each atom in the asymmetric unit are given in Table I, together with the "estimated standard deviations" as calculated by the method of Jeffrey and Cruickshank.⁵ Positions corresponding to these parameters are indicated by the intersections of the "bonds" in the three projections. Note in the projection on (010) that

TABLE I
PARAMETER VALUES FOR *trans*-ETHANEDISELENINIC ANHYDRIDE

	x	y	z
Se	0.013 ± 0.001	0.165 ± 0.0005	0.108 ± 0.0005
C	$0.917 \pm .015$	$.337 \pm .002$	$.188 \pm .002$
O _c	0	$.077 \pm .004$.250
O _e	$0.349 \pm .002$	$.172 \pm .0015$	$.072 \pm .08$

the selenium atoms are not bonded to those O_e atoms closest to them on the projection; (this

(3) J. Ladell and J. L. Katz, *Acta Cryst.*, **7**, 460 (1954).

(4) The smaller empirical "temperature factor" for the $(h0l)$ zone is doubtless a reflection of the larger size of crystal used for data on this zone. This would increase absorption effects which become most important at small values of θ , thus tending to counteract the effect of thermal vibration.

(5) G. A. Jeffrey and D. W. J. Cruickshank, *Quart. Rev.*, **VII**, 369 (1953).

would lead to an impossibly short Se-O bond length of 0.71 \AA). Rather, each selenium atom is bonded to an oxygen atom on the opposite sides of the effective mirrors at $x = 1/4$ and $x = 3/4$. The O_e atoms appearing to be closest to the Se atoms in this projection thus actually belong to molecules in front and in back of the single molecule shown.

The z coordinates assigned to the carbon atoms lie considerably closer to $z = 1/4$ than do the apparent carbon peaks of the projection on (100). This is because a "diffraction ripple" (with a maximum near $z = 0.175$ and a minimum near $z = 0.225$), due to the selenium atom, tends to "pull" the peaks away from $z = 1/4$. On the difference synthesis, the carbon peaks are not so clearly resolved although their positions are doubtless closer to the true values. A similar but less marked effect brings the carbon peaks of the projection on (010) artificially far from $z = 1/4$.

Comparison of F_{calcd} with F_{obs} for the 105 zero-layer reflections⁶ used in this determination gives the value 0.111 for the correlation factor, R , where

$$R = \frac{\sum^N ||F_{\text{obsd}}| - |F_{\text{cald}}||}{\sum^N |F_{\text{obsd}}|}$$

Values for R for the three projections are 0.111, 0.109 and 0.114 for (100), (010) and (001), respectively.

Discussion of the Results

Bond distances and angles calculated from the observed parameters are given in Table II.

TABLE II
BOND DISTANCES AND BOND ANGLES IN *trans*-ETHANEDISELENINIC ANHYDRIDE

	Distances, \AA	Angles ⁷
Se-C	1.99 ± 0.04	C-C-Se $107^\circ \pm 2^\circ$
Se-O _e	$1.61 \pm .03$	C-Se-O _e $107 \pm 3^\circ$
Se-O _c	$1.82 \pm .02$	O _e -Se-O _c $106 \pm 2^\circ$
C-C	$1.59 \pm .07$	C-Se-O _e $91 \pm 1^\circ$
Se-Se	$3.19 \pm .01$	Se-O _e -Se $123 \pm 3^\circ$
	(non-bonded)	

Of the bond distances listed, the least precise is that for C-C. Carbon atoms in a given ring are equidistant from $z = 1/4$ (or from $z = 3/4$) and also equidistant from $x = 0$ (or from $x = 1/2$). Hence, any error in the x and z -parameters of carbon will have a twofold effect in the calculation of this bond length, and the apparent departure from the accepted value of 1.54 \AA . is not significant.

Likewise, among the other intramolecular dimensions, there seems no important deviation from the values that might be expected. The length of the C-Se bond confirms that found in 1,4-diselen-

(6) A list of the 105 observed and calculated structure factors has been deposited as Document No. 4875 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C., U. S. A. A copy may be secured by citing the Document number and by remitting \$1.25 for photoprints, or \$1.25 for 35 mm. microfilm in advance by check or money order payable to Chief, Photoduplication Service, Library of Congress.

(7) The method for estimation of the errors in bond angles is that described by D. W. J. Cruickshank and A. P. Robertson, *Acta Cryst.*, **6**, 698 (1953).

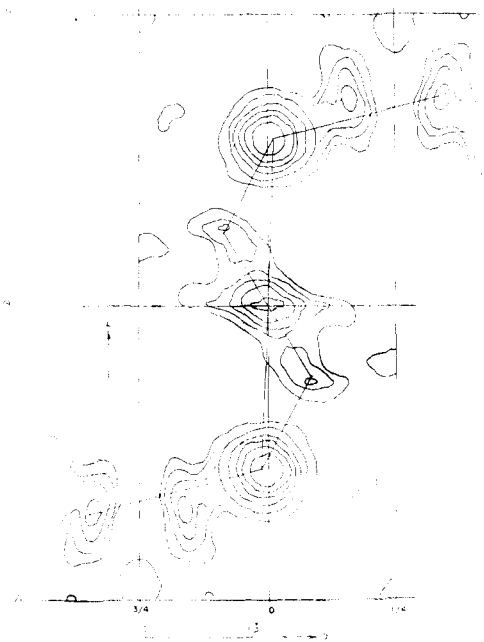


Fig. 3.—Electron density projection of one molecule of *trans*-ethanediseleninic anhydride on (010). Intersections of "bonds" mark the positions of final atomic parameters.

ane⁸ (1.99 ± 0.05 Å.), and in dimethyl selenide,⁹ (1.99 ± 0.01 Å.) There is, however, appreciable contraction on those cases in which the selenium atom is bonded to the carbon atom in a benzene ring¹⁰ and, more particularly, when the selenium atom is bonded also to oxygen.¹¹ The different lengths for the two types of Se—O bond in our compound bring to mind the situation in solid selenium dioxide¹² in which the Se—O bonds comprising the "chain" (1.73 Å.) are shorter than the "side-chain" Se—O bonds (1.78 Å.). The shorter Se—O bond length in our structure is in excellent agreement with that found in gaseous selenium dioxide (1.61 ± 0.03 Å.).¹³ The difference in Se—O bond lengths suggests that the exocyclic Se—O bond might be a "double" bond or at least might have "double bond character." However, the configuration about the selenium atom is wholly different from the configuration about carbon atoms entering into double-bond formation, and such descriptions should be made with reserve.

Perhaps the major structural feature of interest is the tight packing of molecules within the crystal, leading to the very high density, 2.92 g./cc., to our knowledge the highest density reported thus far for an organoselenium compound containing no other heavy atoms. The arrangement of molecules

(8) R. E. Marsh and J. D. McCullough, *THIS JOURNAL*, **73**, 1106 (1951).

(9) E. Goldish, K. Hedberg, R. E. Marsh and V. Schomaker, *ibid.*, **77**, 2948 (1953).

(10) The C—Se bond in selenanthrene is reported by R. G. Wood and G. Williams, *Nature*, **150**, 321 (1942), as 1.96 Å. That in di-*p*-tolylselenium dibromide is reported by J. D. McCullough and R. E. Marsh, *Acta Cryst.*, **3**, 41 (1950) as 1.94 Å.

(11) J. H. Bryden and J. D. McCullough, *ibid.*, **7**, 833 (1954), report a Se—C bond length of 1.903 Å. in benzeneseleninic acid, C₆H₅SeO₂H.

(12) J. D. McCullough, *THIS JOURNAL*, **62**, 1270 (1940).

(13) K. J. Palmer and N. Elliott, *ibid.*, **60**, 1309 (1938).

within the unit cell, as shown in Fig. 4, approaches one centered at the *c*-face. The packing is determined mainly by contact between the selenium atoms and exocyclic oxygen atoms of different rings. The shortest intermolecular selenium—oxygen distance is 2.70 ± 0.10 Å., and there is also a somewhat greater selenium—oxygen distance of 3.11 ± 0.03 Å.; both of these distances are indicated in Fig. 4. The shortest intermolecular

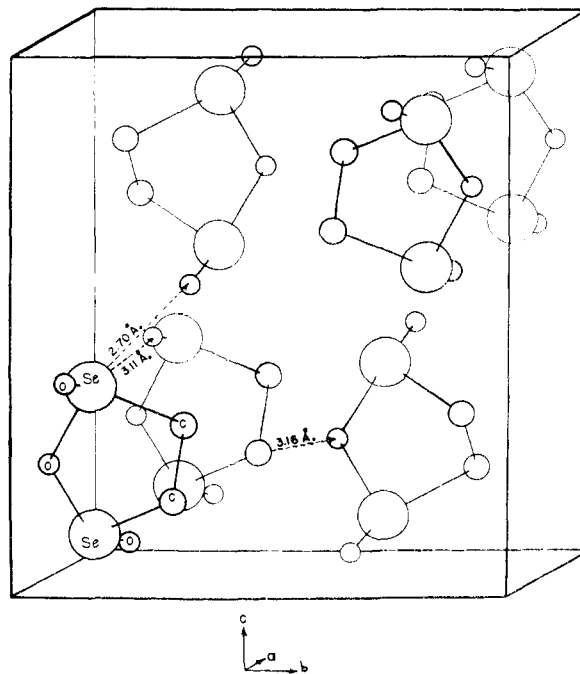


Fig. 4.—The structure of *trans*-ethanediseleninic anhydride.

carbon—oxygen distance is 3.16 ± 0.10 Å. Both of the intermolecular selenium—oxygen distances are significantly less than 3.40 Å., the sum of the van der Waals radii of selenium and oxygen as given by Pauling.¹⁴ However, Pauling's value for the van der Waals radius of selenium (2.00 Å.) is taken from the ionic radius of the selenide ion. Such a value is appropriate for a selenium atom attached to carbon, hydrogen or another selenium. However, the van der Waals radius of a selenium atom bound to two oxygen atoms (and therefore bearing a partial positive charge) should doubtless be smaller, although it would be difficult to say how much smaller. In any event, there is strong dipole—dipole interaction between a given selenium atom and exocyclic oxygen atoms of two different molecules, and the structure may be regarded as consisting of —Se—O_e . . . Se—O_e . . . chains parallel to the *x*-axis and —Se . . . O_e—Se—O_e—Se—O_e . . . chains parallel to the (101) planes (here the dotted lines represent intermolecular contact).

Acknowledgments.—The authors wish to thank Dr. J. Lawrence Katz for a number of helpful discussions and Mr. Boris Paretzkin for assistance during the early experiments.

BROOKLYN 1, NEW YORK

(14) L. Pauling, "The Nature of the Chemical Bond," 2nd edition, Cornell University Press, Ithaca, N. Y., p. 139.