3-Aminofluorenone.—Five grams of sodium sulfide was added over a period of two hours to 100 cc. of boiling alcohol containing 1 g. of 3-nitrofluorenone and 2 g. of ammonium chloride. After refluxing for an additional hour it was poured into cold water and extracted with ether. The ether was extracted with dilute hydrochloric acid and on neutralization a deep yellow precipitate was obtained. It was not possible to get a better melting point than 142–146°. Following the procedure of Eckert and Langecker,[7] who encountered similar difficulties, the amine was acetylated. Recrystallization from alcohol gave 3-acetylaminofluorenone.

3-Acetylaminofluorenone was hydrolyzed by boiling with 20% hydrochloric acid. It yielded 3-aminofluorenone, Table I.

Summary

A new synthesis of 3-nitrofluorenone has been described and Bardout's characterization of this compound has been substantially confirmed.

The following melting points, uncorrected unless otherwise stated, have been found for 3-nitrofluorenone and related compounds:

	M. p., °C.
3-Nitrofluorenone	235–236(239–240, cor.)
3-Nitrofluorenone oxime	224–225
3-Aminofluorenone	157–158
3-Acetylaminofluorenone	215–216

The values of the latter two compounds given by Eckert and Langecker have been confirmed but their values for 3-nitrofluorenone and 3-nitrofluorenone oxime as well as those of Schmidt and Soll are shown to be in error.

CINCINNATI 21, OHIO RECEIVED DECEMBER 3, 1947

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Synthesis and Spectrum of 2-Cyclopropylpyridine*

BY RAYMOND P. MARIELLA, LOWELL F. A. PETERSON[1] AND ROBERT C. FERRIS[2]

Some recent work by Klotz[3] has shown that the cyclopropane ring, when adjacent to an olefinic or carbonyl group, produced spectra which could be interpreted in terms of resonance due to hyperconjugation. This effect had also been observed by Carr and Burt,[4] who examined the spectra of compounds in which the cyclopropane ring was in "conjugation" with both a carbonyl group and the benzene ring. From these spectra it was not possible to secure information regarding the extent of conjugation of the cyclopropane grouping alone with the aromatic nucleus.

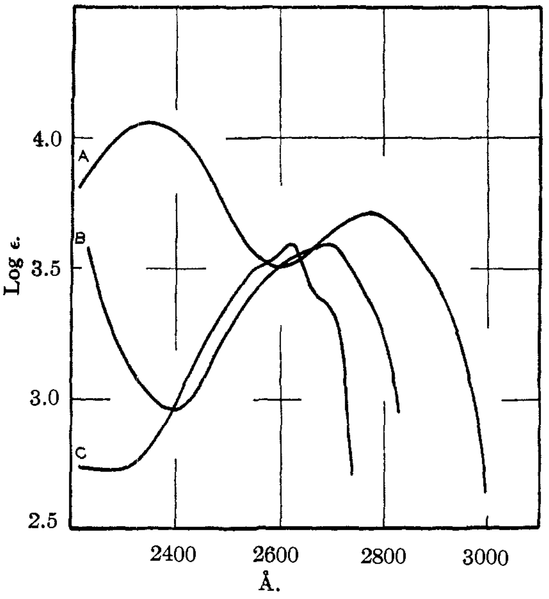

Fig. 1.—Absorption spectra of 2-vinylpyridine, A; 2-cyclopropylpyridine, B; and 2-*n*-propylpyridine, C.

In the present work, 2-cyclopropylpyridine (IX) was synthesized. This compound has the cyclopropane ring alone in conjugation with a highly aromatic nucleus.[5] A comparison of its absorption spectrum with those of 2-*n*-propylpyridine (VIII) and 2-vinylpyridine (X) (Fig. 1), showed the cyclopropane compound to have a maximum (2690 Å.) between that of the similarly conjugated (2775 Å.) and non-conjugated (2620 Å.) system.

Since the maximum for pyridine itself is at 2530 Å.,[6] the presence of an alkyl or alicylic group in the α position causes a shift of the maximum to longer wave lengths. This effect appears greater with the cyclopropyl group than with the *n*-propyl group, and confirms chemical evidence long known[7] that the cyclopropane ring possesses a certain degree of unsaturation. The phenomenon no doubt occurs because the electrons of cyclopropane are rendered especially polarizable by the unusual angle between the bonds.

If the shift to longer wave lengths is to be interpreted as a "hyperconjugation" effect, then in the case of 2-cyclopropylpyridine we can postulate that certain ionic structures exist, which in addi-

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(2) Present address: University of Utah, Department of Chemistry, Salt Lake City, Utah.

(3) Klotz, THIS JOURNAL, **66**, 88 (1944).

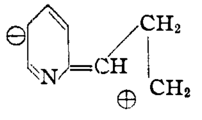
(4) Carr and Burt, *ibid.*, **40**, 1590 (1918).

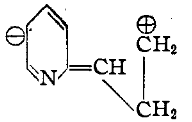
(5) After the initial submission of this manuscript a paper appeared (Rogers, *ibid.*, **69**, 2544 (1947)), in which the absorption spectrum of cyclopropylbenzene was given. This compound also showed a shift in the maximum toward longer wave lengths when compared with propylbenzene, which was interpreted as a hyperconjugation effect.

(6) Fischer and Steiner, *Compt. rend.*, **175**, 882 (1922).

(7) Kohler and Conant, THIS JOURNAL, **39**, 1404, 1699 (1917).

tion to the usually written hyperconjugation forms, contribute to the excited structure. Two of the twelve possible additional forms are listed below (I and II).


I


II

Since the three-membered ring is not necessarily coplanar with the pyridine ring these resonance forms probably do not contribute as much as expected, causing the shift from *n*-propyl to cyclopropyl to be small but still measurable.

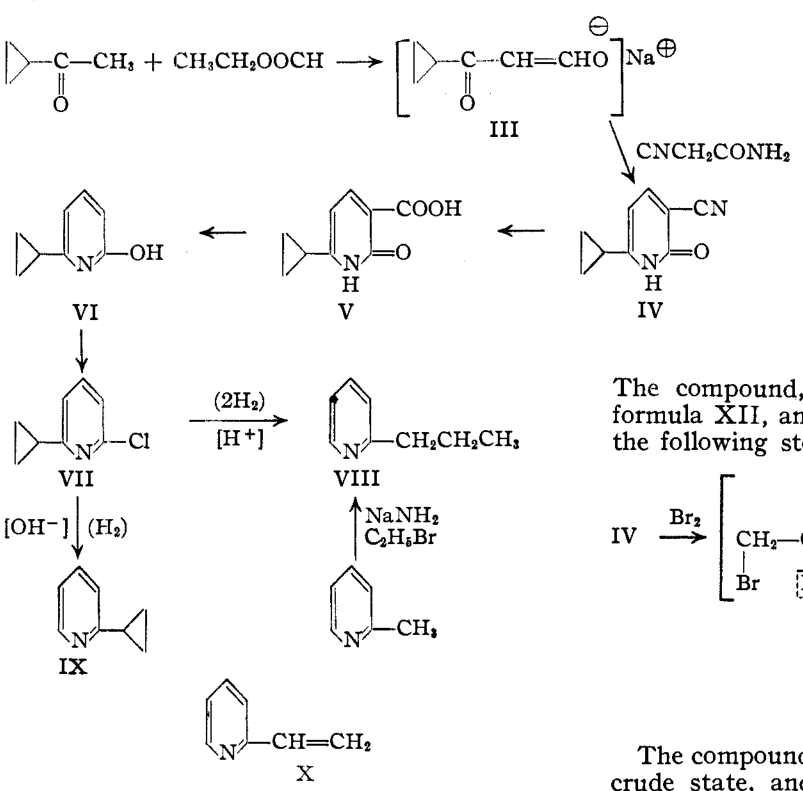
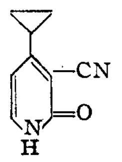


Fig. 2.

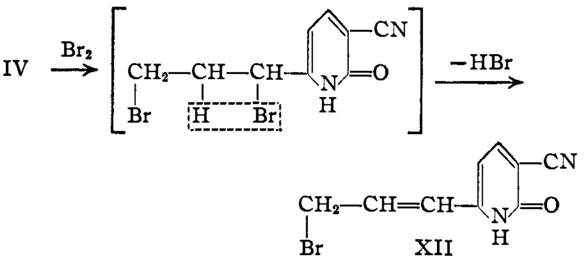
The maximum due to the cyclopropane ring itself, probably about 2100 Å., was beyond the range of the instrument used.

The flow sheet for the synthesis of 2-cyclopropylpyridine and related compounds is shown in Fig. 2.

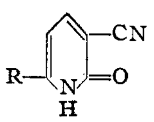
The sodium salt (III) was reported recently,[8] but no yield was given. The condensation of III with cyanoacetamide could have yielded XI instead of IV, but this possibility was eliminated by the isolation of the known compound (VIII), in the acidic reduction of VII. In all steps, the yields were lower than in similar reactions of compounds[9,10] in which the cyclopropyl ring was replaced by a simple alkyl group. In many of the reactions, there was evidence of considerable decomposition and tar formation. This was particularly noticeable in the decarboxylation of V to VI, which succeeded only in small runs of one and a half grams each.


XI

The cyclopropane ring remained fairly stable to reagents such as concentrated hydrochloric acid and phosphorus pentachloride, as evidenced by the isolation of V and VII, which still possessed the alicyclic ring intact. Treatment with bromine, however, immediately destroyed the cyclopropane ring in IV to give a compound containing only *one atom* of bromine, instead of two. The compound, $C_9H_7BrN_2O$, probably has the formula XII, and its formation is postulated by the following steps.



The compound (XII) was quite unstable in the crude state, and purification by crystallization was very difficult. Bromination was assumed to attack the cyclopropane ring because compounds having the general formula XIII, where R is a simple aliphatic group, do not react with bromine in glacial acetic acid.[11]


XIII

The 2-*n*-propylpyridine (VIII) (conyrine) was made by a method similar to that of Chichibabin,[12] and the 2-vinylpyridine was a product obtained from the Reilly Tar and Chemical Corporation.

The authors acknowledge a grant from the

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[8] Chelintsev, *J. Gen. Chem. U. S. S. R.*, **14**, 1070 (1944); *cf. C. A.*, **41**, 101 (1947).

[9] Perez-Medina, Mariella and McElvain, THIS JOURNAL, **69**, 2574 (1947).

[10] Mariella, *ibid.*, **69**, 2670 (1947).

[11] Mariella, unpublished work.

[12] Chichibabin, *Bull. soc. chim.*, [5] **3**, 1607 (1936).

Graduate School, which made some of the work possible.

Experimental[13]

Sodium Salt of Hydroxymethylene Methyl Cyclopropyl Ketone (III).—To 58 g. of sodium metal ribbon in one liter of absolute ether was added a mixture of 185 g. of ethyl formate[14] and 210 g. of methyl cyclopropyl ketone,[15] dropwise over a period of two hours. The reaction mixture was protected from moisture, cooled in an ice-bath, and stirred during the addition. When about one-fourth of the addition mixture had been added, the tan-colored precipitate first appeared, and increased in amount as the addition continued. Stirring was continued for one-half hour after the addition was completed. The cooling bath was then removed, and stirring continued, at room temperature, for an hour and a half. The brown solid was then filtered and dried in a vacuum desiccator. Additional product was obtained by filtering the solid which developed in the filtrate. The combined solids weighed 219 g. (65% yield).

3-Cyano-6-cyclopropylpyridone-2 (IV).—A solution of 115 g. of the sodium salt (III), 84 g. of cyanoacetamide, and piperidine acetate catalyst in 250 ml. of water was refluxed for two hours. (The catalyst was prepared by adding piperidine to a solution of 9 ml. of glacial acetic acid in 25 ml. of water until basic to litmus.) The solution was then diluted with 250 ml. of water, acidified with glacial acetic acid, and cooled in an ice-bath for an hour. The yellow solid, which had formed, was filtered and dried, 73 g. (53% yield). Purification by a carbon treatment and several recrystallizations from alcohol gave a white powder, m. p. 239–240° (dec.).

Anal. Calcd. for $C_9H_8N_2O$: C, 67.48; H, 5.04; N, 17.5. Found: C, 67.39; H, 5.06; N, 17.2.

Bromination of 3-Cyano-6-cyclopropylpyridone-2.—A solution of 0.50 g. of IV in 10 ml. of glacial acetic acid heated to 60° was treated with a solution of 0.3 ml. of bromine in 5 ml. of glacial acetic acid. A copious evolution of hydrogen bromide gas ensued, as the solution was kept at 60° for ten minutes. The solution was then poured on 50 g. of cracked ice, and the yellow solid, which immediately formed, was filtered and dried, 0.69 g. (93% yield). The crude material soon developed a green color and finally turned black. A pure sample was obtained by treating the yellow solid with Norit in alcohol, followed by five recrystallizations from alcohol and six recrystallizations from benzene. The white solid, so obtained, remained colorless, m. p. 221–222°.

Anal. Calcd. for $C_9H_7BrN_2O$: C, 45.21; H, 2.95; N, 11.7. Found: C, 45.09; H, 3.04; N, 12.0.

6-Cyclopropane-2-oxo-3-pyridine Carboxylic Acid (V).—A solution of 73 g. of IV in 250 ml. of concentrated hydrochloric acid was refluxed for four hours. The solution was then poured into 250 ml. of water, cooled in an ice-bath for an hour, and the gray solid filtered and dried, 44 g. (54% yield). After a carbon treatment and seven recrystallizations from 3:1 water–glacial acetic acid, the pure white solid was obtained, m. p. 248–250° (dec.). The compound was only slightly soluble in cold water and gave a negative ferric chloride test.

Anal. Calcd. for $C_9H_9NO_3$: N, 7.8. Found: N, 7.8.

2-Cyclopropyl-6-pyridol (VI).—A test-tube containing powdered V was heated to 290°. The solid melted and decomposed as carbon dioxide was evolved. A cold finger was then inserted in the test-tube to collect the product which sublimed in the form of white plates. The yields varied, depending upon the amount and purity of the starting material. A maximum of 70% yield was obtained when 1.5 g. of V, purified by two crystallizations from alcohol, was used. The yields fell off sharply if more material was used in the decarboxylation. Additional purification was achieved by a vacuum sublimation at 0.05 mm. and at a temperature of 110–120°, m. p. 165–166°. The white solid gave a deep red ferric chloride test.

Anal. Calcd. for C_8H_9NO: N, 10.4. Found: N, 10.4.

2-Cyclopropyl-6-chloropyridine (VII).—To a solution of 10.5 g. of VI in 16 ml. of phosphorus oxychloride heated to refluxing was added 20 g. of phosphorus pentachloride, in small portions, over a period of one-half hour. The oil-bath temperature was then raised to 165° and kept there for one hour. The phosphorus oxychloride was removed under reduced pressure, 50 g. of ice then added, and the mixture made strongly basic by adding a concentrated potassium hydroxide solution. When this was steam distilled, a colorless heavy oil was obtained, which was separated by two extractions with 100-ml. portions of ether. The ether was dried and removed, and the residue distilled, giving a colorless oil, 4.0 g. (34% yield), b. p. 107–108° (16 mm.), $n^{25}\text{D}$ 1.5512. The liquid darkened very slowly when exposed to light.

Anal. Calcd. for C_8H_8ClN: N, 9.1. Found: N, 9.1.

Reduction of VII in Acidic Solution.—To a solution of 0.193 g. of VII in 15 ml. of absolute alcohol were added a solution of 100 mg. of palladium chloride in one ml. of concentrated hydrochloric acid, one ml. of 15% hydrogen chloride in absolute alcohol, 0.50 g. of Norit and hydrogen. The reduction proceeded at room temperature and atmospheric pressure and stopped in fifty minutes, at which time two moles of hydrogen had been absorbed. There was no distinct break in the hydrogenation curve during the reduction. The mixture was filtered and the liquid filtrate concentrated to a colorless oil. The chloroplatinate of this material did not depress the m. p. 163° of an authentic sample of the chloroplatinate of 2-*n*-propylpyridine.

Reduction of VII in Basic Solution: 2-Cyclopropylpyridine (IX).—To a solution of 1.26 g. of VII in 25 ml. of 3% alcoholic potassium hydroxide was added 4.0 g. of 5% palladium on charcoal. The hydrogenation proceded at room temperature and atmospheric pressure and was complete in thirty minutes, at which time 0.90 mole of hydrogen had been absorbed. The mixture was filtered, made faintly acid with hydrochloric acid and concentrated. The addition of concentrated potassium hydroxide liberated the free base, which was taken up in ether. The solution was dried, ether removed *in vacuo*, leaving an oil, which on distillation gave 0.65 g. (67% yield), b. p. (750 mm.) 174–175°, $n^{25}\text{D}$ 1.5110, d^{29}_4 0.956. The material possessed the characteristic alkyl pyridine odor. It was observed that the liquid caused a temporary numbing effect when brought in contact with the skin.

The picrate was isolated as pale yellow needles, m. p. 115–117°.

Anal. Calcd. for $C_{14}H_{12}N_4O_7$: C, 48.28; H, 3.47. Found: C, 48.19; H, 3.48.

The chloroaurate was prepared as a yellow powder, m. p. 111–113°.

Anal. Calcd. for $C_8H_{10}Cl_4NAu$: Au, 43.0. Found: Au, 43.0.

The chloroplatinate came down very slowly when a solution of chloroplatinic acid was added to the 2-cyclopropylpyridine hydrochloride in water. The orange solid melted at 159–160°. The mixed m. p. with the chloroplatinate of 2-*n*-propylpyridine was depressed to 140°.

Anal. Calcd. for $C_{16}H_{20}Cl_6N_2Pt$: Pt, 30.1. Found: Pt, 30.1.

2-*n*-Propylpyridine (Conyrine) (VIII).—To 300 ml. of liquid ammonia containing 0.3 g. of ferric nitrate, was added 35 g. of sodium metal. The excess ammonia was allowed to escape and 83 g. of α-picoline (b. p. 128°) was

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[13] Analyses by Miss Patricia Craig and Mrs. Nelda Mold.

[14] Purified according to "Org. Syntheses," Coll. Vol. II, p. 180, b. p. 53.5–54.5°.

[15] A U. S. Industrial Chemicals product. The sample used in this work had a b. p. 110–111°.

added. To this mixture, with stirring, was added 120 g. of ethyl bromide, over a period of four hours. After standing two days, the excess sodamide was decomposed by the addition of 200 ml. of water. The mixture was extracted with ether, the ether solution dried, and the ether removed on a steam-bath. The residue was distilled, giving 8.0 g. (7% yield), b. p. 165-166° (755 mm.),[16] n^{25}_{D} 1.4897, d^{26}_{4} 0.9121.

The picrate was easily isolated as small yellow needles, m. p. 64°.[16]

Anal. Calcd. for $C_{14}H_{14}N_4O_7$: C, 48.00; H, 4.03; N, 16.0. Found: C, 47.89; H, 4.01; N, 15.8.

The chloroplatinate formed very quickly, and resulted in orange plates, m. p. 163-164°.[17]

Anal. Calcd. for $C_{16}H_{24}Cl_6N_2Pt$: Pt, 29.9. Found: Pt, 30.2.

The chloroaurate came down as a yellow powder, m. p. 77°.

Anal. Calcd. for $C_8H_{12}Cl_4NAu$: Au, 42.7. Found: Au, 42.5.

2-Vinylpyridine (X).—A sample from the Reilly Tar and Chemical Corporation was fractionated, and the constant boiling cut, b. p. 60° (17 mm.), used in this work,[18] n^{31}_{D} 1.5442, d^{31}_{4} 0.9661.

The picrate was isolated as a yellow powder, m. p. 152-154°.

Anal. Calcd. for $C_{13}H_{10}N_4O_7$: C, 46.71; H, 3.02. Found: C, 46.73; H, 3.01.

The chloroplatinate melted at 174-175°, and the chloroaurate melted at 143°.[19]

Spectra.—The ultraviolet absorption spectra were obtained with a Beckmann quartz spectrophotometer. All physical constant measurements of the above alkyl pyridines were performed immediately after their isolation. Solutions of known concentrations were made by dissolving weighed quantities of compound in absolute alcohol in a volumetric flask. Dilutions were made volumetrically to give suitable density readings. The solutions were poured into one of two matched silica absorption cells and the second cell was filled with the solvent. Extinction coefficients were calculated from the equation

$$\epsilon = d/cl$$

where c is the concentration of the solute, in moles per liter, l is the thickness of the cell, in centimeters, and $d = \log_{10}(I_0/I)$. I_0 is the intensity of light passing through the solvent, and I is the intensity of light passing through the solution.

Summary

2-Cyclopropylpyridine was prepared and its ultraviolet absorption spectrum compared with those of 2-*n*-propylpyridine and 2-vinylpyridine. The maximum of 2-cyclopropylpyridine falls in a position between the two comparison compounds. This effect can be interpreted in terms of additional resonance due to hyperconjugation.

EVANSTON, ILLINOIS RECEIVED OCTOBER 6, 1947

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[16] Chichibain, ref. 12, reports a b. p. 173° and a m. p. 76° for the picrate.

[17] Ladenburg, *Ann.*, **247**, 21 (1888), reports a m. p. of 159-160°.

[18] Ladenburg, *Ber.*, **22**, 2585 (1889), reports a b. p. 79-82° (29 mm.).

[19] Ladenburg, *ibid.*, reported the chloroplatinate m. p. 174°, and the chloroaurate, m. p. 144°.

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY
No. 1157]

An Electron Diffraction Investigation of the Structure of Adamantane

BY WERNER NOWACKI AND KENNETH W. HEDBERG

The crystal structure of adamantane ($C_{10}H_{16}$, see Fig. 1) has been investigated by Nowacki,[1] who found a C–C bond distance of 1.54 ± 0.02 Å. on assumption of tetrahedral bond angles, and by Giacomello and Illuminati,[2] who obtained similar results by Fourier methods. A significant difference has been found between C–N distances in the crystal[3] and vapor[4] of hexamethylenetetramine, a molecule whose configuration is closely similar to that of adamantane, and although no such difference would be expected in adamantane, it seemed worth while to study it by electron diffraction in the vapor phase.

The photographs obtained show twelve maxima and shelves extending to q values of about 90 ($q = (40/\lambda)\sin\varphi/2 = (10/\pi)s$).

Experimental

The sample of adamantane, which had been synthesized by Prelog and Seiwerth,[5] was vaporized by use of a high temperature nozzle[6] in the apparatus described by Brockway.[7] The camera distance was about 11 cm. and the electron wave length[8] about 0.06 Å. Corrections were made for film expansion.

Radial Distribution Curve

The radial distribution curve (Fig. 2) was calculated from the equation[9,10] by use of punched

$$rD(r) = \sum_{q=1,2...}^{q\ max} I(q)\ \text{exp.}\ (-aq^2)\sin\left(\frac{\pi}{10}\,q\,r\right)$$

cards[10,11]; the quantities $I(q)$ were taken from the visual curve (Fig. 2) drawn to represent the

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[1] W. Nowacki, *Helv. Chim. Acta*, **28**, 1233 (1945).

[2] G. Giacomello and G. Illuminati, *Ricerca Sci.*, **15**, 559 (1945).

[3] P. A. Shaffer, Jr., THIS JOURNAL, **69**, 1557 (1947).

[4] V. Schomaker and P. A. Shaffer, Jr., *ibid.*, **69**, 1555 (1947).

[5] V. Prelog and R. Seiwerth, *Ber.*, **74**, 1644, 1769 (1941).

[6] L. O. Brockway and K. J. Palmer, THIS JOURNAL, **59**, 2181 (1937).

[7] L. O. Brockway, *Rev. Modern Phys.*, **8**, 231 (1936).

[8] For wave length calibration see C. S. Lu and E. W. Malmberg, *Rev. Sci. Instruments*, **14**, 271 (1943); the lattice constants of zinc oxide given by Lu and Malmberg in kx units were converted to Ångström units.

[9] R. Spurr and V. Schomaker, THIS JOURNAL, **64**, 2693 (1942).

[10] P. A. Shaffer, Jr., V. Schomaker and L. Pauling, *J. Chem. Phys.*, **14**, 659 (1946).

[11] P. A. Shaffer, Jr., V. Schomaker and L. Pauling, *ibid.*, **14**, 648 (1946).