

When the reaction was carried out at 0 to 5° and kept at this temperature for about two weeks 30% of 3-acetyl-1-methylphenanthrene together with a small amount of impure material melting at 152–153° (uncor.) was obtained (D. T.).

Picrate of 3-Acetyl-1-methylphenanthrene (T. H.).—Yellow needles, recrystallized from methanol; m. p. 137–137.5° (cor.).

Anal. Calcd. for $C_{23}H_{17}O_3N_3$: N, 9.07. Found: N, 9.35.⁷

The Oxidation of 3-Acetyl-1-methylphenanthrene (D. T.).—Seventy-five hundredths gram of the acetyl compound together with 2 cc. of fuming nitric acid and 3 cc. of water was heated in a Carius bomb tube for one-half hour on the steam-bath. The tube was then sealed and heated for three hours at 190°. One cc. of nitric acid was added and the tube was reheated at 190° for three hours. The solution was evaporated to dryness and the white residue was washed on a filter with 10 cc. of fuming nitric acid. Esterification of the solid with diazomethane and crystallization from methanol gave white needles melting at 109.5–110°. After recrystallization the melting point was 111–112° (uncor.). The ester did not lower the melting point of an authentic sample of the tetramethyl ester of benzene-1,2,3,5-tetracarboxylic acid (m. p. 110.5–111° (uncor.)), m. p. of the mixture being 111–112° (uncor.).

Oxime of 3-Acetyl-1-methylphenanthrene (T. H.).—Recrystallized from ethanol; white needles; m. p. 180.5–181° (cor.).

Anal. Calcd. for $C_{17}H_{15}ON$: N, 5.62. Found: N, 5.44.⁷

3-Acetamino-1-methylphenanthrene (T. H.).—One gram of the oxime of 3-acetyl-1-methylphenanthrene dissolved in 10 cc. of anhydrous ether and 1 g. of phosphorus pentachloride was added slowly to the cooled solution. The temperature was kept at 15–20° during the reaction. The reaction mixture was then washed with water until washings were no more acid to litmus. The ether solution was dried with anhydrous sodium sulfate, the ether evaporated, the solid residue dissolved in ethanol and treated with Norite; yield about 0.14 g. The 3-acetamino-1-methylphenanthrene was recrystallized from ethanol; white needles; m. p. 188.5–189.5° (cor.).

Anal. Calcd. for $C_{17}H_{16}ON$: C, 81.90; H, 6.07. Found: C, 81.98; H, 6.06.⁷

3-Diacetamino-1-methylphenanthrene (T. H.).—0.2 gram of the monoacetyl derivative was refluxed with 5 cc. of acetic anhydride for thirty minutes and 0.2 g. of sodium acetate. The solution was poured into 50 cc. of water and the precipitate recrystallized from methanol; yield, about quantitative, colorless needles; m. p. 162–162.5° (cor.).

Anal. Calcd. for $C_{19}H_{17}O_2N$: C, 78.33; H, 5.88. Found: C, 78.59; H, 6.11.⁷

3-Amino-1-methylphenanthrene (D. T.).—A solution of 0.8 g. of the oxime of 3-acetyl-1-methylphenanthrene in 10 cc. of acetic acid and 5 cc. of acetic anhydride was treated with dry hydrogen chloride for ten minutes. The mixture was diluted with 10 cc. of acetic acid, 10 cc. of concentrated hydrochloric acid, and 1 cc. of water and refluxed for twelve hours. The precipitate which formed on dilution with water was taken up in ether, dried and the amine hydro-

chloride was precipitated with dry hydrogen chloride. This product was heated for several hours with 500 cc. of water, filtered hot, and cooled. The white flocculent precipitate which separated was crystallized from ethanol containing alkali. There was obtained 0.07 g. of glistening plates; m. p. 126–127° (uncor.). Two more crystallizations from ethanol did not change the melting point.

Anal. Calcd. for $C_{15}H_{13}N$: C, 86.91; H, 6.32. Found: C, 86.66, 86.56; H, 6.04, 6.23.

1-Methylphenanthrol-3 (T. H.).—Two grams of 3-amino-1-methylphenanthrene was dissolved in 800 cc. of water containing 8 cc. of concentrated hydrochloric acid and cooled to 2°. A concentrated solution of 1 g. of sodium nitrate was added in portions and the yellow solution allowed to stand in the icebox for one and one-half hours. After addition of 2.5 g. of urea the turbid solution was slowly heated to boiling and the precipitate 1.89 containing a reddish resin filtered off and suspended in a dilute potassium hydroxide solution. On filtering, the solution yielded 0.5 g. of a crimson dye and a colorless filtrate, which was acidified and the precipitated phenanthrol recrystallized from benzene; yield 1.2 g.; m. p. 160–161° (cor.); white needles.

Anal. Calcd. for $C_{15}H_{12}O$: C, 86.51; H, 5.81. Found: C, 86.57; H, 5.42.⁷

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An X-Ray Study of the Calcium–Strontium Alloy Series

BY A. J. KING¹

One would be led to predict from the crystal structure, lattice dimensions and position in the periodic table of calcium and strontium that they would be completely miscible in the solid state and hence form a continuous series of solid solutions. Both crystallize at room temperature with the face-centered cubic type of lattice. The edges of the unit cubes are, respectively: Ca, $a_0 = 5.560 \pm 0.006^2$; Sr, $a_0 = 6.076^3$.

To test this, a series of alloys was prepared and an X-ray diffraction analysis made of each to determine the variation of the unit cell dimensions with the composition. According to Vegard⁴ complete miscibility would be indicated by a linear relation between the atomic composition and the lattice dimensions.

The alloys were prepared from resublimed calcium and strontium whose purity was shown by

- (1) Syracuse University, Syracuse, N. Y.
- (2) Hull, *Phys. Rev.*, **17**, 42 (1921).
- (3) Simon and Vohsen, *Z. physik. Chem.*, **133**, 165 (1928); King, *Proc. Natl. Acad. Sci.*, **15**, 337 (1929); Ebert and Hartmann, *Z. anorg. allgem. Chem.*, **179**, 418 (1929).
- (4) L. Vegard, *Z. Physik*, **5**, 17 (1921); E. R. Jette, *Trans. Am. Inst. Mining Met. Eng.*, **111**, 75 (1934).

analysis to be at least 99.0%. The metals were melted in small iron crucibles 0.75 inch in diameter and 2.25 inches high, which were turned from a low carbon steel rod. Tests have shown that very little iron is dissolved by either of these metals in the liquid state if the duration of contact is kept at a minimum. The crucibles containing the alloys were heated in a Pyrex glass tube in an atmosphere of argon by means of a high frequency furnace. Thorough mixing was assured by use of a pure iron wire stirrer which was oscillated with a solenoid at the top of the tube. After cooling the iron crucible was removed from the alloy by turning it off on a lathe. During this process the alloy was bathed in a stream of dry oil to protect it from the action of the atmosphere. The samples for analysis were prepared by rolling the alloys, under oil, into thin sheets from which were cut narrow strips for the X-ray examination.

All alloys of the series crystallized with a face-centered cubic type of lattice.

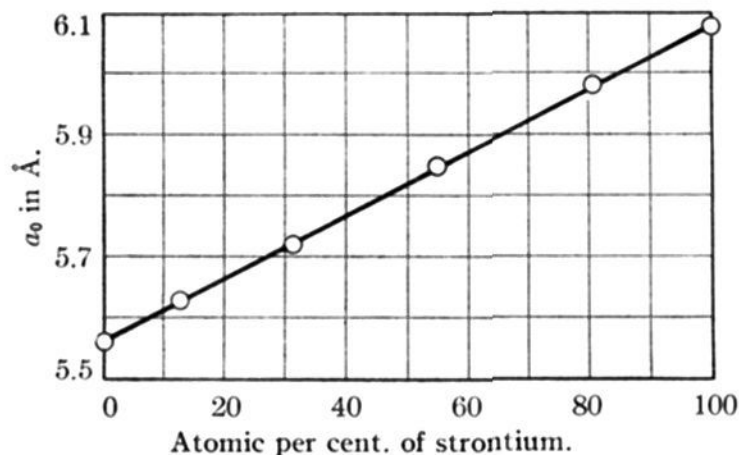


Fig. 1.

The results of the X-ray analysis are summarized in the table and shown graphically in the figure.

At. % Sr	0	10.26	31.37	54.60	80.60	100
a_0 in Å.	5.560	5.627	5.720	5.847	5.980	6.076
Density	1.539	1.666	1.939	2.180	2.416	2.578

It is obvious that the values of a_0 vary directly with the strontium content. Although no thermal analysis has been reported for this system, it is quite apparent from the above results that calcium and strontium form a continuous series of solid solutions at room temperature.

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Dimorphism of Amylcaine Hydrochloride

BY HENRY R. KREIDER AND AMEL R. MENOTTI

During the investigation¹ of the chemical and physical properties of amylocaine hydrochloride (mono-*n*-amylaminoethyl-*p*-aminobenzoate hydrochloride), a local anesthetic used for dental and medical purposes,² two crystalline forms (rectangular plates, melting at 153.5°, and rods, melting at 176°) were obtained. The absence of alcohol of crystallization and water of hydration was demonstrated by a negative Zeisel ethoxyl determination and by the fact that no loss in weight was observed when the crystals were heated above the melting point, although the lower melting form was transformed into the higher melting form under these conditions. Therefore, a dimorphic habit was indicated.

Experimental

Rectangular Plate Form (Fig. 1).—Two grams of commercially available amylocaine hydrochloride was dissolved in 25 cc. of hot water, the solution cooled to room temperature and the resultant crystals were filtered, washed with cold ethanol and dried in vacuum over sulfuric acid; melting point 153.5° (cor.). When kept at the melting point, the liquid solidified spontaneously or upon scratching the microscope slide, yielding the higher melting form. *Anal.* Calcd. for $C_{14}H_{22}O_2N_2 \cdot HCl$: N, 9.77; Cl, 12.36. Found: N, 9.5; Cl, 12.4.

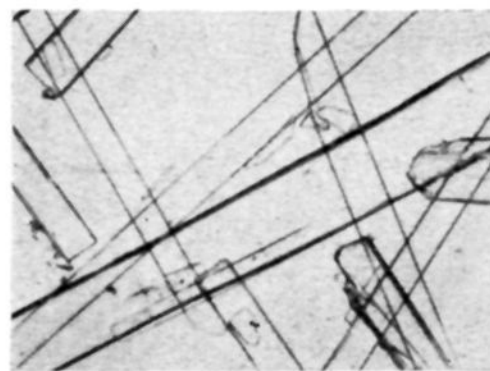


Fig. 1.—Amylocaine hydrochloride, rectangular plate form, m. p. 153.5° ($\times 100$).

Between crossed nicols the crystals appeared as elongated plates with a relatively high birefringence. They exhibited positive elongation and parallel extinction. In convergent polarized light biaxial figures were common, with the acute bisectrix and occasionally an optic axis in the field of view. *Refractive indices* (determined by immersion in organic liquids): $\alpha = 1.510$; $\beta = 1.582$; $\gamma > 1.655$ (all ± 0.002).

Rod Form (Fig. 2).—A saturated solution of amylocaine hydrochloride in boiling *n*-amyl alcohol was cooled slowly in a water-bath to 80°. Long, thick, hexagonal rods were

(1) *J. Am. Med. Assoc.*, **116**, 2020 (1941).

(2) S. D. Goldberg and W. F. Whitmore. *THIS JOURNAL*, **59**, 2280 (1937).