

L.—*Studies on the Chemistry of Nitrogen. Enantiomorphous forms of Ethylpropylpiperidonium Iodide.*

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CONSIDERABLE interest attaches to mixed ammonium compounds on account of the uncertainty of their constitution, the valency of nitrogen in these substances being still more or less a matter of conjecture; and although the balance of evidence goes to show that such compounds are 'atomic,' yet the existence of at least two isomers which the presence of pentad nitrogen postulates (at any rate, in the case of radicles of considerable mass) has never been placed beyond doubt, in spite of the evidence brought forward from time to time by Le Bel, Ladenburg and others (see Armstrong: Hofmann Memorial Lecture, Trans., 1896, 69, 666).

Bearing in mind the suggestion made by Lossen (*Annalen*, 1876, 181, 364) in his criticism of the work of V. Meyer and Lecco (*ibid.*, 1876, 180, 173) that any characteristic crystallographic differences possessed by isomeric ammonium compounds are likely to be masked by the addition of heavy molecules, such as those of picric acid or platinum chloride, it was determined to investigate the haloid derivatives of piperidine of the form $C_5H_{10} \cdot R_aR NX$ as these substances may easily be obtained in a state suitable for crystallographic examination.

The iodide of ethylpropylpiperidonium was therefore prepared, on the one hand from ethylpiperidine and propylic iodide and on the other from propylpiperidine and ethylic iodide. After carefully crystallising the products from absolute alcohol, it was found possible to mechanically separate each into a right-handed and a left-handed variety, melting at the same temperature (276°) and differing only in being enantiomorphous.

Now, although the presence of pentad nitrogen would account for

two isomeric piperidonium derivatives, it was not to be expected, nor would it be explicable on any of the usual hypotheses, that these should possess enantiomorphous crystalline structure; it therefore appeared probable that the enantiomorphism might belong to that rare class of which examples are afforded by sodium chlorate, bromate and periodate, guanidine carbonate, ethylenediamine sulphate and possibly benzil—cases in which the spiral arrangement of the molecules in the crystal gives rise to the same phenomena owing to purely crystallogenic causes (see Pope, *Trans.*, 1896, **69**, 971; Barlow, *Phil. Mag.*, 1897, **43**, p. 110), and which may be distinguished from enantiomorphism due to the arrangement of the atoms in space, by the optical inactivity of the substances in solution, as well as by the possibility of changing either form into the other by crystallisation.

Further investigation showed this to be the true explanation. It was found that although ethylpiperidine and propylic iodide fortuitously gave rise to a product in which the left-handed variety predominated, whilst the corresponding product derived from propylpiperidine and ethylic iodide consisted mainly of right-handed crystals, yet each of these was mixed with its mirror-image form; moreover, both forms were found to afford optically inactive solutions, and each on recrystallisation afforded both forms. It was noticed also, as in the case of sodium chlorate, that when only a few large crystals separated from a solution these were invariably nearly all of one kind, whereas a large crop of small crystals consisted, as a rule, of the two forms in about equal quantities.

As far as they go, therefore, the results of these experiments confirm those of Meyer and Lecco (*Annalen*, 1876, **180**, 173), and also the more recent observations of Menshutkin (*Zeit. physik. Chem.*, 1895, **17**, 226), who obtained but a single ethylallylpiperidonium bromide by a similar series of operations. On the other hand, the work has led to the discovery of a substance which is interesting from a crystallographic point of view on account of the rarity of the phenomenon which it exhibits.

The alkylpiperidines used in the preparation of the ethylpropylpiperidonium iodide by the two series of interactions were made by adding the alkyl haloid to the calculated quantity of piperidine (from Kahlbaum) contained in a vessel surrounded by a freezing mixture, the product being subsequently distilled from solid potash (Cahours, *Ann. Chem. Phys.*, 1853, [3], **38**, 76), but it was found to be much simpler, as well as much more economical, to purify them by means of the picrate than to use the method of fractional distillation adopted by Cahours.

Ethylpiperidine picrate, $C_5H_{10}EtN \cdot C_6H_2(NO_2)_3 \cdot OH$, was obtained by

neutralising with a solution of picric acid the crude ethylpiperidine obtained by distilling the hydrobromide, $C_5H_{10}NEt.HBr$, from solid potash. Being almost insoluble in cold water, the picrate began to separate at once, and was easily purified by a single crystallisation from alcohol, in which it is very soluble. Made in this way, it forms bright yellow needles, melting at 167.5° . It is soluble in all the ordinary neutral solvents, such as acetone, ethylic acetate, benzene, &c.

Ethylpiperidine, $C_5H_{10}NEt$, was made from the picrate by mixing the latter with excess of a concentrated solution of caustic potash ($KOH:H_2O = 1:5$), and then distilling in a current of steam, a large distilling flask being used on account of the frothing. The ethylpiperidine was extracted from the distillate by means of ether, and the ethereal solution allowed to stand over solid potash; on subsequent distillation, the whole of the base came over at 128° .

Ethylpropylpiperidonium iodide, $C_5H_{10}EtPrNI$.—18.5 grams of propylic iodide (Kahlbaum) were added gradually to 13 grams of ethylpiperidine boiling at 128° ; no immediate action was observed in the cold, but after several days, or after a few hours' warming, the liquid gradually solidified to a mass of white crystals. These were collected and dissolved in cold absolute alcohol; moderately large, triangular, colourless plates melting at 276.5° were deposited after the solution had been exposed over sulphuric acid during several hours. The crystals are soluble in most of the ordinary neutral solvents, such as acetone, ethylic acetate, chloroform, &c., but insoluble in ether, so that the addition of the latter to a solution of the compound in any of the solvents mentioned causes its precipitation in the form of fine needles; these, however, soon change to plates. On analysis 0.2203 gave 0.1820 AgI , or 44.87 per cent. of iodine; the theoretical percentage is 44.83.

The same substance was next prepared by the action of ethylic iodide on propylpiperidine, which was obtained in the purified state from its picrate, (m. p. 108°), in the manner described in the case of the ethyl compound. The product was in every respect identical with that described above.

On examination, it was found, however, that the products of the two interactions were neither of them homogeneous, but that each consisted of a mixture of right-handed and left-handed crystals, the two constituents of each preparation being respectively identical. On heating rapidly in a melting-point tube, either form, whether crushed or whole, fuses at 276° without undergoing decomposition, and a mixture of the two melts at the same temperature. Moreover, on recrystallisation, each variety gives rise to a mixture of both, and no rotation of the plane of polarisation was observed in an 8 per cent. solution of either modification.

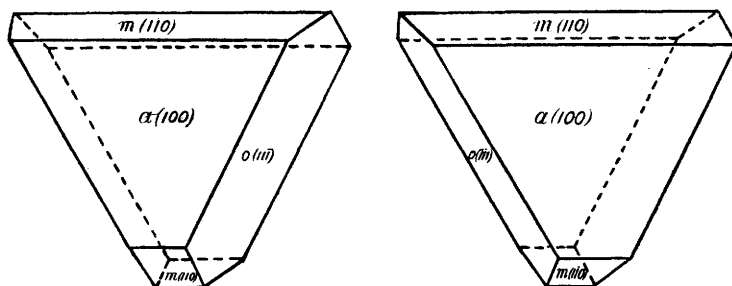
On the other hand, crystallographic examination showed the crystals of ethylpropylpiperidonium iodide to possess all the characteristics of

non-superposeable hemihedrisism. The triangular plates deposited from the cold alcoholic solution by spontaneous evaporation belong to the monosymmetric system, but possess no plane of symmetry. The pinacoid $a\{100\}$ is always dominant, the dome form $m\{110\}$ being relatively small; only half the possible number of faces of the pyramid form $o\{111\}$ are found on any one crystal, the complementary faces being developed on another. All the reflections are poor. Examination under the polarising microscope showed the optic axial plane to be perpendicular to the suppressed plane of symmetry, the acute bisectrix emerging in $a\{100\}$. The double refraction is positive and weak, and the optic axial angle fairly large.

Crystalline System :—Hemimorphic Monosymmetric.

$$a : b : c = 0.639 : 1 : 0.544. \quad \beta = 64^\circ 7'.$$

FIG. 1.



Forms observed.

a	$\{100\}$
c	$\{001\}$
m	$\{110\}$
o	$\{111\}$

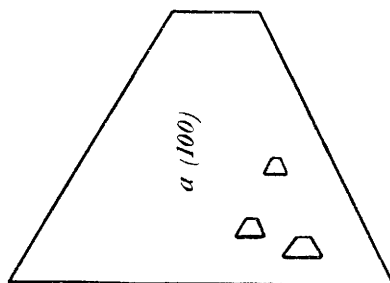
The following angular measurements were obtained.

Angle.	No. of observations.	Limits.	Mean.	Calculated.
$ao = 100 : \bar{1}11$	11	$111^\circ 38' - 112^\circ 42'$	$112^\circ 1\frac{1}{2}'$	$112^\circ 2\frac{1}{2}'$
$ao = 100 : 11\bar{1}$	11	$67 28 - 68 20$	$67 57\frac{1}{2}$	—
$am = 100 : 110$	25	$29 45 - 30 23$	$29 55$	—
$am = 100 : \bar{1}10$	2	$150 7 - 150 2$	$150 4\frac{1}{2}$	$150 5$
$mm = 110 : \bar{1}10$	10	$129 50 - 120 30$	$120 13$	$120 9\frac{1}{2}$
$om = 11\bar{1} : 110$	4	$56 48 - 56 50$	$56 49$	$56 52\frac{1}{2}$
$om = 11\bar{1} : \bar{1}10$	6	$123 6 - 123 20$	$123 13$	$123 7\frac{1}{2}$
$om = 11\bar{1} : \bar{1}10$	9	$83 40 - 84 15$	$84 4$	—
$om = 11\bar{1} : \bar{1}10$	5	$95 49 - 96 10$	$95 58\frac{1}{2}$	$95 86$

Etched figures were formed on $a\{100\}$ by immersing a crystal for a short time in absolute alcohol; these were generally indistinct, owing

to the dulness of the crystal faces. Their appearance is shown diagrammatically in the accompanying figure.

FIG. 2.



The crystals show no signs of being pyroelectric if warmed on a watch-glass and dusted with a mixture of red lead and sulphur, but this is possibly owing to the fact that when thus treated they soon became opaque and split up into a number of small pieces.

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