661. *The Optical Properties of 2-Amino-*n*-octane, 2-Dimethylamino-*n*-octane, and Trimethyl-2-*n*-octylammonium Iodide.*

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The optical properties of *lævo*-2-amino- and *lævo*-2-dimethylamino-*n*-octane are compared. Dissolution in ethanol of the primary amine reduces the activity almost to zero, whereas that of the tertiary amine is converted into a strong dextrorotation. The hydrochloride of the tertiary amine resembles that of the primary amine in that it is associated in several solvents, but unlike the primary amine hydrochloride its rotation in these solvents is not markedly affected by the concentration. The optical properties of the less stable quaternary trimethyl iodide have also been investigated.

The physical properties of 2-amino-*n*-octane and its hydrochloride have been investigated by Mann and Porter (*J.*, 1944, 456) who showed that (*a*) the optical rotation of the free base is markedly affected by certain solvents, *e.g.*, the *dextro*-base in the pure liquid state has $[M]_D$ +8·62°, and in 5·95% benzene solution it has $[M]_D$ +8·5°, but in 8·06% ethanolic solution it has $[M]_D$ +0·88°, the last value being only slightly affected by concentration; (*b*) the hydrochloride of the amine is soluble in a wide variety of polar and non-polar solvents, in many of which it is markedly associated; (*c*) the hydrochloride shows the "acid-effect" of many optically active amines, *e.g.*, the hydrochloride of the *lævo*-amine is dextrorotatory in most solvents. In certain associating solvents, however, the sign of rotation is dependent on the concentration: dilution of a solution initially *dextro* causes the rotation to fall steadily to zero and then to become *lævo*.

These properties indicate strongly that in certain solvents association of the base (or its hydrochloride), with or without the solvent, must almost certainly occur, although the nature of this association in unknown. It was clearly desirable, however, to ascertain whether these properties were determined by the primary amine group as such, and whether they would persist if the nitrogen atom were more effectively shielded from the effect of the solvent by conversion of the primary amine group first into a tertiary amine group and then into a quaternary ammonium radical. For this purpose *lævo*-2-amino-*n*-octane has been converted into 2-dimethylamino-*n*-octane, $CH_3{\cdot}[CH_2]_5{\cdot}CH(NMe_2){\cdot}CH_3$, and its hydrochloride, and into the corresponding trimethyl-2-*n*-octylammonium iodide.

lævo-2-Dimethylamino-*n*-octane was obtained as a colourless liquid, $[M]_D$ −16·0°, which in benzene solution had $[M]_D$ −12° (*c*, 0·509), but in absolute ethanolic solution had $[M]_D$ +26·0° (*c*, 2·123), the latter rotation being virtually unaffected by concentration. This marked change in both the sign and the value of the rotation indicates strongly that in ethanolic solution the base must undergo some interaction with the solvent comparable to that which causes the "acid-effect" on neutralisation by acids. This effect in ethanol is clearly not limited to the tertiary amine: the effect on the primary amine is sufficiently strong to render the *lævo*-amine almost inactive, whilst on the tertiary amine the much stronger effect causes a marked dextrorotation. It is noteworthy that, although both the primary and the tertiary amine are almost insoluble in water, the addition of a trace of water to either base causes a perceptible decrease in rotation, and it is probable that the fundamental cause is the same for both these hydroxylic liquids, although necessarily shown to a much smaller extent by the water.

The crystalline hydrochloride of *lævo*-2-dimethylamino-*n*-octane was soluble in cold water, ethanol, acetone, formamide, dimethylformamide, chloroform, acetonitrile, methylene dichloride, or ethylene dibromide, sparingly soluble in dry benzene, and apparently insoluble in dry ether, light petroleum (b. p. 60—80°), toluene, or carbon tetrachloride. This hydrochloride showed the usual "acid-effect," its solutions in water, dimethylformamide, benzene, methylene dichloride, and ethylene dibromide being dextrorotatory. It is noteworthy that its rotation in all these solvents (unlike that of the primary amine hydrochloride) was only slightly affected by the concentration. On the other hand, whereas the hydrochloride showed no significant association in boiling methylene dichloride, it showed notable association in boiling benzene, and much greater association in freezing ethylene dibromide. It is clear therefore that in the case of this salt, association in solution is not necessarily connected with a marked rotation–concentration gradient.

The white crystalline trimethyl-2-*n*-octylammonium iodide, prepared from the *lævo*-tertiary amine, was soluble in water, dimethylformamide, chloroform, acetonitrile, methylene dichloride, and glycol monomethyl ether: it was insoluble in benzene, toluene, *cyclo*hexane, carbon tetrachloride, or ethyl acetate, but gave pale yellow solutions in dioxan, *cyclo*hexanol, diethyl carbonate, or glycol monomethyl ether acetate. It also showed the "acid-effect," since its solutions in water and dimethylformamide were dextrorotatory; the rotation, however, was not significantly changed on dilution, and in view of this fact and the comparative instability of the iodide, molecular-weight determinations were not made.

These results show, however, that the very marked effect of concentration on the rotatory power of certain solutions of the hydrochloride of the primary amine is not shown by the hydrochloride of the tertiary amine or by the quaternary iodide, although both these hydrochlorides are notably associated in certain solvents. It is clear that considerably more information is required before an attempt can be made to interpret the type of association which these hydrochlorides undergo, and the extent to which the associated micelles are affected or shared by the solvent.

EXPERIMENTAL.

The source of light for all rotation measurements was the sodium D line, λ 5893.

lævo-2-Amino-*n*-octane, prepared and resolved as Mann and Porter (*loc. cit.*) describe, had b. p. 65·5°/21 mm., and when dried over sodium had $[M]^{19}$ −8·93° (*l*, 0·5 dm.), d^{19} 0·769, n^{22} 1·4232. It was converted into the hydrochloride, which had $[M]^{21\cdot5}$ +6·75° in aqueous 7·77% solution: the free amine, regenerated from this salt, had b. p. 58°/16 mm., $[M]^{19}$ −8·89°, d^{19} 0·771. The addition of traces of water to a sample of the base having α^{19} −2·66° (*l*, 0·5 dm.) reduced the rotation to −2·55°, and that of another to α^{19} −2·65° to −2·52°: the molecular rotation of these samples was not calculated, as the density was not accurately known. Mann and Porter (*loc. cit.*) record [*M*] −8·53° (*l*, 0·4 dm.) for the base, and [*M*] +6·61° for the hydrochloride in 7·77% aqueous solution.

lævo-2-*Dimethylamino*-n-*octane*.—Formic acid (90 c.c.) was slowly added to a cooled solution of the above amine (14 g.) in 40% formalin (54 c.c.), which was then boiled under reflux for 1·5 hours, concentrated under reduced pressure, cooled, basified, and extracted with ether. The ethereal extract was dried (NaOH) and then distilled in a nitrogen atmosphere, the *dimethylamino*-base being obtained as a colourless liquid (11 g., 63%) having b. p. 78°/18 mm., $[M]^{16\cdot5}$ −16·0° (*l*, 0·5 dm.), d^{17} 0·778, n^{20} 1·4271 (Found: N, 8·9. $C_{10}H_{23}N$ requires N, 8·9%). A sample of the amine, having α^{21} −3·82° (*l*, 0·5 dm.), after being moistened with a trace of water, had α^{21} −3·73°. A solution of the amine in benzene (*c*, 0·509) had [*M*] −12° and in absolute ethanol had the rotations: *c*, 0·472, [*M*] +26·6°; *c*, 1·416, [*M*] +25·8°; *c*, 2·123, [*M*] +26·0°.

The ***hydrochloride*** was prepared by neutralising the amine with hydrochloric acid, and evaporation to dryness in a vacuum at room temperature: the residual solid when recrystallised from carefully dried light petroleum (b. p. 60—80°) formed colourless plates, m. p. 144—146° (inserted in bath at 140°) (Found: N, 7·2%; *M*, ebullioscopically in 0·99% methylene dichloride solution, 202; in 1·54%, 197; in 2·08%, 194; ebullioscopically in 0·90% benzene solution, 295; in 1·66%, 337; in 2·59%, 383; cryoscopically in 0·358% ethylene dibromide solution, 598; in 0·510%, 601; in 0·595%, 633. $C_{10}H_{24}NCl$ requires N, 7·2%; *M*, 193·5).

This hydrochloride in solution showed the following rotations, all dextrorotatory. All rotations were determined at 21° ±1° except those in dimethylformamide, which were at 12°.

Water.

c	0·263	0·269	0·395	0·404	0·605	0·790	1·185	1·778	2·665	3·998
α, obs.	0·14°	0·17°	0·19°	0·21°	0·36°	0·48°	0·75°	1·14°	1·68°	2·57°
[*M*]	26·2	29·7	23·3	25·4	29·1	29·4	30·7	31·0	30·6	31·1

Methylene dichloride.

c	0·294	0·387	0·580	0·870	0·882	1·739	2·645	3·967
α, obs.	0·29°	0·42°	0·60°	0·88°	0·87°	1·73°	2·61°	3·86°
[*M*]	48·4	52·4	49·8	48·8	47·9	48·1	47·8	47·1

	Ethylene dibromide.			*Dimethylformamide.*		*Benzene.*		
c	0·229	0·663	0·994	0·891	1·337	0·21	0·31	0·47
α, obs.	0·17°	0·55°	0·85°	0·84°	1·26°	0·14°	0·21°	0·30°
[*M*]	36·8	39·9	41·5	45·5	45·5	31·8	33·3	30·6

lævo-*Trimethyl*-2-n-*octylammonium Iodide*.—Methyl iodide (16 c.c.) was slowly added to an agitated solution of the above *lævo*-tertiary amine (7·2 g.) in ether (100 c.c.). After 5 hours at room temperature, the precipitated white *iodide* was collected (13·55 g., 99%) and after recrystallisation from acetone–benzene obtained as colourless plates, m. p. 223—223·5° (decomp.) (Found: C, 44·2; H, 8·8; N, 4·5. $C_{11}H_{26}NI$ requires C, 44·1; H, 8·8; N, 4·7%). This iodide in solution showed the following dextrorotations.

	Water (16°).		*Dimethylformamide* (17°).						
c	1·113	3·339	0·456	0·684	1·027	1·540	2·310	2·772	3·326
α, obs.	1·04°	3·08°	0·42°	0·60°	0·87°	1·29°	1·90°	2·28°	2·69°
[*M*]	70·0	69·0	68·9	65·5	63·2	62·5	61·8	61·6	60·5

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