

XXXIII.—*The Effect of Constitution on the Rotatory Power of Optically Active Nitrogen Compounds. Part I.*

By MARY BEATRICE THOMAS and HUMPHREY OWEN JONES.

THE investigation of the effect of the constitution of carbon compounds on their rotatory power has occupied a large number of workers for some years past. The work received a great stimulus in 1890, when the hypotheses of Crum Brown and Guye were suggested, and seemed to offer a possibility of establishing some relation between the molecular structure of a compound and its optical rotatory power.

The hypothesis of Guye, which assumes that the masses of the groups attached to the carbon atom are the chief factors which determine the optical rotatory power of a molecule, is capable of being tested by experiment, and during the past fifteen years an enormous mass of data has been accumulated with that object in view. At first, the results obtained seemed to be in fairly good agreement with the predictions of the hypothesis; but latterly this has not been so, and it has been found that the optical rotatory power of the compounds examined, which are almost invariably liquid or solid non-electrolytes, is affected to such a large extent by molecular association, the nature of the solvent, and by temperature, that it is difficult to apply a real test to the hypothesis.

Electrolytes seem to be free from some of these disturbing causes. In dilute aqueous solution, the Oudemans-Landolt law holds within

very narrow limits for strong electrolytes and especially for salts, so that complications due to the effect of solvents and of molecular association are avoided, and there remains only the effect of temperature, which, in cases where it neither alters the electrolytic dissociation to any extent nor causes hydrolytic dissociation, might be expected to be fairly regular if not small. The rotatory power of an ion may be regarded as a constant independent of external conditions except temperature.

It is therefore probable that any regularities in the rotatory power of compounds would be more evident in the case of ions than of undissociated molecules. The examination of the rotatory power of a series of ions, the constitution of which could be varied, would therefore be of interest as affording a test of the applicability of Guye's hypothesis, and might possibly indicate in what direction a further connection between constitution and rotatory power is to be sought.

Suitable carbon compounds into which a number of similar groups of different masses can be introduced are difficult to obtain. Patterson (Trans., 1904, 85, 1116) examined potassium methyl, ethyl, and *n*-propyl tartrates, and found that the rotatory power of these compounds was dependent to a great extent on concentration and temperature, and that each of the compounds exhibited a maximum rotatory power at a different temperature. These substances, therefore, seem to be affected largely by external conditions, and some part of the effect may be due to hydrolysis.

The simplest compounds available for this purpose are the active sulphur and selenium salts, but in these compounds there is little scope for substitution; the salts might in some cases be very difficult to resolve into their optical antimers and, judging from the compounds hitherto examined, they exert only a feeble rotatory power.

The substituted ammonium compounds containing an asymmetric nitrogen atom seem to offer a better field for investigation. These compounds can be resolved into their optical antimers with moderate ease, their salts are extensively ionised in solution and are not hydrolysed, and the groups present, being all alkyl groups, might therefore be expected to produce similar effects on the rotatory power. Further, in the salts of the two bases hitherto examined, namely, phenylbenzyl-methylallylammonium salts and phenylbenzylmethylethylammonium salts, there is such a great difference in their rotatory powers ($[M]_D = 166^\circ$ and $[M]_D = 19^\circ$ respectively for the ions) that the effect of constitution is sufficiently well marked to be readily examined.

The investigation of compounds with similar substituting radicles is important, since here the effect of mass would not be so likely to be masked by the very considerable effect of constitution noticed in many cases, such, for instance, as $-\text{CO}\cdot\text{C}_6\text{H}_5$ and $-\text{CO}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_5$.

Here again the choice of compounds is limited to some extent, since in practice it is only convenient that the last group introduced shall be either methyl, allyl, or benzyl: the iodides of these radicles are the only ones which, as a rule, react extensively with tertiary amines when these contain aromatic and other heavy alkyl groups. Two series of compounds were chosen and examined; these all contain the phenyl and methyl groups, each series consisting of five compounds, one set containing the benzyl group together with ethyl, *n*- or isopropyl, isobutyl, and isoamyl, the other containing the allyl group together with the same five aliphatic groups.

The methyl compounds of both series have already been shown by one of us to be inactive. The ethyl compound of the benzyl series had been previously examined and a preliminary examination of the ethyl compound of the allyl series had also been made (Trans., 1903, 83, 1418; 1904, 85, 223). The examination of the *n*-propyl and isobutyl compounds of the benzyl series has been undertaken by Wedekind, and his results have recently appeared (Wedekind and Fröhlich, *Ber.*, 1905, 38, 3438 and 3933).^{*} Thus, including the phenylbenzylmethylallylammonium compounds first resolved by Pope and Peachey, there are now eleven optically active quinquivalent nitrogen compounds known, which fall naturally into two series of six, both including the last-named compound.

During the course of the work, a number of interesting observations have been made on the methods of resolving these compounds and on their properties, which will be mentioned in due course.

Method of Resolving the Compounds.

The method used for the resolution of the substituted ammonium compounds was that of Pope and Peachey, and consisted in fractional crystallisation of the *d*-camphorsulphonate or *d*-bromocamphorsulphonate of the base from a suitable solvent. In the preparation of the camphorsulphonate and bromocamphorsulphonate, some trouble was frequently occasioned by the formation of a crystalline double compound of silver iodide and the substituted ammonium iodide, which was partially soluble in organic solvents. This is often avoided by the addition of a little methyl alcohol or water, or by the use of excess of silver camphorsulphonate or bromocamphorsulphonate, but best by adding the ammonium iodide in successive small quantities to the mixture of silver salt and solvent. The choice of solvent is in some cases of the utmost importance, whilst in others almost every

^{*} We have delayed the publication of our results until now, in order that Wedekind and Fröhlich might publish their work on these compounds. Their experiments will be discussed later.

possible solvent effects resolution. To avoid the possibility of racemisation, which appears to take place at higher temperatures in some cases, it is well, as a rule, to use a solvent of low boiling point, and acetone is the one which has been found most generally useful. The other solvents which have been found useful are ethyl acetate, ethylal, methylal, chloroform, and water. Pope and Peachey (Trans., 1899, 75, 1127) laid some stress on the necessity for using a dry non-hydroxylic solvent to avoid hydrolytic dissociation; this we have not found to be necessary; we have frequently used moist acetone and ethyl acetate, and have in two cases found that the bromocamphorsulphonate was readily resolved by crystallising from boiling water.

Some cases were found where resolution of the camphorsulphonate could not be effected, whilst the bromocamphorsulphonate was easily resolved, and *vice versa*; in other cases, it was possible to resolve both, though the resolution of one of them was usually difficult. Since the object of this investigation was merely to determine the value of the molecular rotatory power of the ion, we have been content to isolate the salt of one of the *d*- or *l*-isomerides only, the less soluble of the salts derived from *d*-camphorsulphonic or *d*-bromocamphorsulphonic acid, to determine its rotatory power in aqueous solution, and thus to obtain the rotatory power of the substituted ammonium ion by difference.

Effect of Concentration on the Rotatory Power of Camphorsulphonates.

In order to determine the extent to which the rotatory power of the salts of these bases in aqueous solution was affected by dilution, *d*-phenylbenzylmethylallylammonium *d*-camphorsulphonate, already described by Pope and Harvey (Trans., 1901, 79, 828), was isolated by repeated crystallisation from acetone, and its rotatory power in aqueous solutions of different concentration determined. The salt melted at 172—173°; 1.0044 grams were dissolved in water and the solution weighed 16.932 grams. This solution was examined in a 2-dcm. tube,* its density taken, then it was diluted and the operation repeated at a temperature of 16°.

Strength of solution in grams per 100 grams of solution.	α_D in 2-dcm. tube.	Specific gravity.	$[\alpha]_D$.	$[M]_D$.
5.93	5.47°	1.016	45.4°	214.0°
3.02	2.78	1.004	45.8	216.0
1.54	1.42	1.002	46.0	216.7
1.064	1.00	1.001	46.9	221.0
0.783	0.73	1.000	46.6	219.5
0.553	0.52	1.000	47.0	221.0

* Unless otherwise stated, all the determinations of rotatory power given in this paper have been carried out in 2-decimetre tubes in a Landolt-Lippich triple field polarimeter supplied by Schmidt and Haensch.

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The above numbers show that dilution affects the rotation to a slight extent, but that in this particular case the variation is almost within the limits of experimental error when the concentration of the solution is not more than 1 per cent.

The values obtained by Pope and Harvey for a 0.8 per cent. solution were about 218.6° .

A similar experiment was made with *l*-phenylbenzylmethylisooamylammonium *d*-camphorsulphonate ($[M_D]_{235^\circ}$, see p. 296), and this also showed that the effect of dilution was quite small and negligible for solutions more dilute than 1.5 per cent.

The bromocamphorsulphonates were examined in very dilute solution, so that the effect of concentration was in this way eliminated.

The Rotatory Power of Ions at Different Temperatures.

In order to determine the effect of change of temperature on the rotatory power of the ions under examination, some solutions of the active salts were examined at intervals of about 10° between 10° and 50° : the results are given for each compound. The effect of temperature change on the ammonium salts of *d*-camphorsulphonic acid and *d*-bromocamphorsulphonic acid, and also on phenylbenzylmethylallylammonium *d*-camphorsulphonate, was examined with the following results. The densities of the solutions used were between 1.001 and 1.000 at 15° , and for the other temperatures have been taken equal to those of water at the same temperature, since the effect of density is in these cases negligible.

Ammonium d-Camphorsulphonate.

Three solutions, 1.6 per cent., 2 per cent., and 1.8 per cent., were used. The values given are obtained from curves plotted with the means of the three experiments, which were very concordant. The value of α_D measured was about 0.8° .

<i>t.</i>	$[\alpha]_D$.	$[M]_D$.
10°	19.9°	49.5°
20	20.7	51.6
30	21.8	53.6
40	22.3	55.6
50	23.1	57.6

Pope and Peachey (Trans., 1899, 75, 1085) give $[\alpha]_D$ 20.7° and $[M]_D$ 51.7° at 16° .

Ammonium d-Bromocamphorsulphonate.

The value of $[M]_D$ for the acidic ion of this salt has long been taken as 270° , but Kipping (Trans., 1905, 87, 628) has shown that

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the true value is more nearly 280° . The specimen examined had been recrystallised several times from water, and $[\alpha]_D 275^\circ$ at 15° . The determination of the rotatory power of three solutions at different temperatures gave as a mean the following results.

The concentration of the solutions was about 1 per cent., and the observed rotation was therefore about 1.7° .

t .	$[\alpha]_D$.	$[M]_D$.
10	83.5°	273°
20	84.7	277
30	86.25	282
40	87.46	286
50	89.0	291

d-Phenylbenzylmethylallylammonium d-Camphorsulphonate.

Two experiments were made with solutions of about 1.4 per cent., and gave as a mean the following results; the observed rotation at 20° was 1.27° .

t .	$[\alpha]_D$.	$[M]_D$.	$[M]_D$ for basic ion.
10°	46.0°	217.0°	167.5°
17	46.3	218.1	167.1
30	46.8	220.5	166.9
40	47.2	222.0	166.4
50	47.3	222.5	164.4

From the observations recorded above, it was expected that the effect of change of temperature on the rotatory power of the series of ions under examination would be small. This, however, was not found to be the case; the rotatory power of some of the compounds was found to be affected to a considerable extent by temperature change, whilst that of others altered but little. When the effect of the acidic ion was taken into account, it was found that the rotatory power of the basic ion in all cases diminished with increase of temperature.

In many of the measurements recorded later, the value of α_D is so small that great accuracy cannot be claimed for the results, which are, however, quite accurate enough to leave no doubt as to the relative magnitudes of the rotatory powers of all the compounds.

Rotatory Power of the Substituted Ammonium Iodides.

In all cases where the solubility of the iodide in water was small enough, it was precipitated from solutions of the camphorsulphonate or bromocamphorsulphonate by the addition of potassium iodide solution; the rotatory power of the iodide so recovered was examined in solution in alcohol and in chloroform. The rotatory power in chloroform was always greater than that of the same iodide in alcohol. The iodides

retained their rotatory power in alcoholic solution in the cold, but racemised in chloroform solution at the ordinary temperature with varying velocity; this is attributed to partial dissociation into benzyl or allyl iodide and tertiary amine and subsequent recombination, resulting eventually in equilibrium with equal quantities of the *d*- and *l*-isomerides. Observations of the velocity of racemisation at different concentrations show that the reaction is one of the first order which was to be expected on the above view of the process. The phenomenon of autoracemisation will probably be found to be exhibited only by compounds containing the allyl and benzyl groups, since they appear to have other properties in common; these groups are usually those the iodides of which react most readily with tertiary amines; they are replaced by the methyl group by the action of methyl iodide, and quaternary compounds containing them undergo a gradual change in molecular weight in chloroform solution. These peculiarities are still under investigation, and other compounds are now being resolved, some of which contain neither the benzyl nor the allyl group, in order, if possible, to confirm the above view that the allyl and benzyl groups alone cause racemisation, and also to extend further the study of the relation between optical rotatory power and constitution in these compounds.

*The Benzyl Series.**

d-Phenylbenzylmethylethylammonium *d*-Camphorsulphonate.

This compound has already been described by one of us (Trans., 1904, 85, 224); the *dB*, *dA*, and *lB*, *lA* salts were found to have $[M]_D \pm 71 \cdot 1^\circ$. And hence the value of $[M]_D$ for the basic ion was given as $\pm 19 \cdot 4^\circ$.

The effect of temperature change on the rotatory power of the *dB*, *dA* salt was now examined with the following results.

0.448 gram in 13.638 grams of solution (density = 1.004 at 20°).

<i>t</i> .	α_D .	$[\alpha]_D$.	$[M]_D$.	$[M]_D$ for basic ion.
10°	1.00°	15.15°	69.2°	19.7°
20	1.01	15.3	69.9	18.3
30	1.05	15.9	72.8	19.2
40	1.06	16.1	73.5	17.9
50	1.08	16.4	75.1	17.5

The values of $[M]_D$ for the ions here obtained are smaller than the actual values, since the solution used was comparatively concentrated (3.27 per cent.). The real value is probably about 2° higher in each case.

* A note on the *isopropyl* and *isocamyl* compounds of this series has already been published (*Proc. Camb. Phil. Soc.*, 1904, 13, 38).

The *n*-propyl and *isobutyl* compounds have been prepared and resolved (the *l*-component was isolated) by Wedekind and Fröhlich (*loc. cit.*). Their experiments on the *n*-propyl compound have been repeated, and the *isobutyl* compound has been resolved by a different method. These experiments are here described, as there are some discrepancies between the results of these chemists and ours as regards the melting point and the hygroscopic nature of some of the salts.

Phenylbenzylmethyl-n-propylammonium iodide was prepared by mixing equivalent quantities of methylpropylaniline and benzyl iodide. The crystalline salt began to separate out almost immediately, and on recrystallisation from alcohol was deposited in colourless prisms which melted with decomposition at 167°. Wedekind and Fröhlich give 147° as the melting point.

0.1872 gave 0.1020 H₂O and 0.3805 CO₂. C = 55.43 ; H = 6.06.

C₁₇H₂₂NI requires C = 55.58 ; H = 5.99 per cent.

Phenylbenzylmethyl-n-propylammonium d-camphorsulphonate was prepared by mixing the calculated quantities of the iodide and silver *d*-camphorsulphonate, boiling with ethyl acetate, and filtering. On concentrating and cooling the filtrate, the salt was deposited in prisms, which after four recrystallisations from ethyl acetate, melted at 188°. The crude substance gave $[\alpha]_D$ 14.59° and $[M]_D$ 68.72°; this high rotation was probably due to the presence of some silver camphorsulphonate as impurity, for on further recrystallisation the value for $[M]_D$ became 50.8°, and the iodide precipitated from it was inactive in alcoholic solution. Acetone was also used as a solvent, but did not effect resolution.

Phenylbenzylmethyl-n-propylammonium d-bromocamphorsulphonate was prepared as described by Wedekind and Fröhlich (*loc. cit.*). It was purified by repeated crystallisation from ethyl acetate and separated in colourless needles which were stable in air and melted with decomposition at 148°. These authors state that the compound is too hygroscopic to permit of a melting point determination. We found, however, that the purified salt was not visibly affected when left on the laboratory bench overnight, and that it gave quite a sharp melting point. After crystallising six times from ethyl acetate, the rotatory power was found to be practically constant, the following result being obtained :

0.295 gram in 15.118 grams of solution gave $\alpha_D - 0.17^\circ$, whence $\alpha_D - 4.36^\circ$ and $[M]_D - 23.96^\circ$. Hence $[M]_D$ for the basic ion is -299° , a value slightly higher than, but agreeing fairly well with, that given by Wedekind and Fröhlich.

Methylisopropylaniline was prepared by heating together methyl-

aniline and *isopropyl* bromide in molecular proportions for eight hours on a water-bath in a reflux apparatus. When left overnight, the contents of the flask solidified to a mass of the crystalline hydrobromide; this was decomposed with aqueous caustic potash, the oil dried over solid caustic potash, and distilled. The fraction boiling at 211—214° was colourless and almost pure. It gave a crystalline platinichloride which separated from hot alcohol in small, yellow needles melting at 193—194° with decomposition.

Phenylbenzylmethylisopropylammonium iodide was deposited in the crystalline form on mixing equivalent quantities of methylisopropylaniline and benzyl iodide. The crystals began to separate within half an hour after mixing, and in twenty-four hours a solid cake was obtained. The substance was recrystallised from methylated spirit, and was deposited in long, colourless prisms belonging to the oblique system and melting at 133°.

0.2545 gave 0.5141 CO₂ and 0.1291 H₂O. C = 55.09; H = 6.07.

C₁₇H₂₂NI requires C = 55.58; H = 5.99 per cent.

Phenylbenzylmethylisopropylammonium d-camphorsulphonate was prepared by boiling equivalent quantities of the silver salt of the acid and the substituted ammonium iodide with moist ethyl acetate. After filtering from silver iodide, the salt was deposited on cooling in large tables melting at 174—175°. Attempts were made to resolve it into its *d*- and *l*-components by fractional crystallisation from ethyl acetate, acetone, or ethylal. After repeated crystallisations from ethyl acetate, however, [M]_D 49.7°, from ethylal [M]_D 50.8°, and from acetone [M]_D 50.0°, showing that no resolution had been effected. The iodide recovered by addition of potassium iodide was quite inactive in alcohol solution.

Phenylbenzylmethylisopropylammonium d-bromocamphorsulphonate was prepared in a similar manner, the solvent used being ethyl acetate. The salt was deposited on cooling the filtrate from the silver iodide in colourless, lustrous prisms, which, on recrystallising, melted with decomposition at 184°.

0.2255 gave 0.4840 CO₂ and 0.1291 H₂O. C = 58.54; H = 6.36.

C₂₇H₃₀O₄NBrS requires C = 58.9; H = 6.54 per cent.

The mother liquors deposited more crystals, and afterwards on evaporation left a gummy residue.

The salt was resolved into its *d*- and *l*-constituents by fractional crystallisation from chloroform, acetone, ethyl acetate, or water, the salt of the levorotatory base being in each case the less soluble.

After three recrystallisations from ethyl acetate the rotatory power was examined at 15°: 0.116 gram in 16.798 grams of aqueous solution

(density = 1.002) gave $\alpha_D - 0.31^\circ$, whence $[\alpha]_D - 22.4^\circ$ and $[M]_D - 123^\circ$.

After two additional crystallisations, 0.227 gram in 15.401 grams solution gave $\alpha_D - 0.65^\circ$, whence $[\alpha]_D - 22.0^\circ$ and $[M]_D - 121^\circ$.

0.183 gram in 12.49 grams of solution gave $\alpha_D - 0.66^\circ$, whence $[\alpha]_D - 22.5^\circ$ and $[M]_D - 124^\circ$.

The value of $[M]_D$ may therefore be taken as -123° at 15° , and the value of $[M]_D$ for the basic ion as 398° .

A nearly saturated solution of concentration 1.431 per cent. (density = 1.002 at 17°) gave the following results at temperatures between 7° and 50° :

$t.$	$\alpha_D.$	$[\alpha]_D.$	$[M]_D.$	$[M]_D$ for basic ion.
7°	-0.65°	-22.6°	-124.0°	396°
17	0.62	21.6	119.0	395
30	0.53	18.5	102.0	384
50	0.44	15.5	85.2	376

l-Phenylbenzylmethylisopropylammonium iodide was precipitated from the solution of the *d*-bromocamphorsulphonate by the addition of potassium iodide solution and purified by recrystallisation from alcohol.

The crystals were prisms belonging to the tetragonal system, and differ therefore from those of the inactive iodide, which belong to the oblique system (see below). The inactive salt is therefore a racemic compound. The melting point, 132° , was slightly lower than that of the inactive compound, 133° . Both compounds, however, decompose at the melting point, and the melting point of mixtures of active and inactive iodide is only slightly ($0.5-1^\circ$) lower than that of the former.

The following determinations of rotatory power were made:

0.102 gram in 10.464 grams of ethyl alcohol solution gave $\alpha_D - 1.83^\circ$ (density = 0.811), hence $[\alpha]_D - 116^\circ$ and $[M]_D - 425^\circ$.

0.103 gram in 12.933 grams of solution (density = 0.794) gave $\alpha_D - 1.47^\circ$, whence $[\alpha]_D - 116.2^\circ$ and $[M]_D - 427^\circ$.

The rotatory power of the solutions of the iodide in alcohol did not change when left for three days in the tube.

The rotatory power of the substance in chloroform was also determined. 0.109 gram in 25.069 grams of solution (density = 1.50) gave $\alpha_D - 1.80^\circ$, whence $[\alpha]_D - 138.0^\circ$ and $[M]_D - 506^\circ$.

0.110 gram in 21.192 grams of solution (density = 1.496) gave $\alpha_D - 2.15^\circ$, whence $[\alpha]_D - 138.2^\circ$ and $[M]_D - 507^\circ$.

This solution slowly racemised on standing.

Time in hours after first observation.	α_D
0	-2.15°
2	1.86
4	1.61
6	1.31
24	0.4

After two days, the solution was practically inactive.

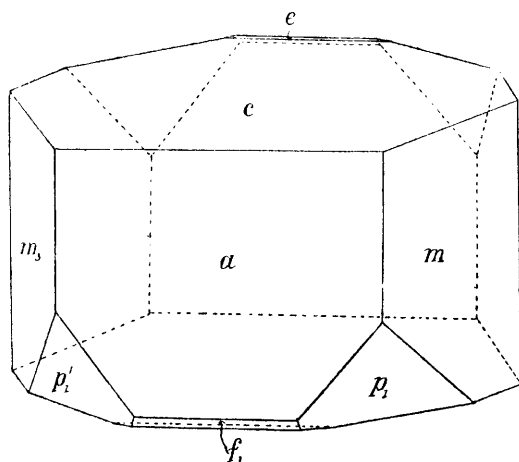
Crystalline Form of d- and l-Phenylbenzylmethylisopropylammonium Iodides.

The examination of the crystals of the active and inactive iodides was considered important, since the crystals seemed to differ, and the inactive iodide was probably a racemic compound. Mr. G. R. Dain, of Clare College, kindly undertook their examination, and we are indebted to him for the following account of them.

l-Phenylbenzylmethylisopropylammonium Iodide.

The crystals were invariably long prisms which were found to belong to the oblique system. The pinacoids $a\{100\}$ and $c\{001\}$ were

FIG. 1.



dominant. The prisms $m\{110\}$ were well developed and gave good reflections. The other forms which were nearly always present gave bad images on the goniometer, and the domes $e\{101\}$ and $f\{201\}$ were mere lines. No general forms were observed, and there was no

evidence of hemihedrism ; in fact, certain vicinal faces indicated the existence of a plane of symmetry.

Crystalline system. Oblique : $a : b : c = 1.613 : 1 : 1.476$, $\beta = 76^\circ 4'$.

Forms observed : $a\{100\}$, $c\{001\}$, $m\{110\}$, $e\{\bar{1}01\}$, $f\{\bar{2}01\}$, and $p\{\bar{2}11\}$.

The angles $ac = (100) : (001) 76^\circ 4'$, $mm_1 = (110) : (\bar{1}10) 65^\circ 8'$, and $p_1p' = (21\bar{1}) : (\bar{2}11) 103^\circ 54'$ were taken as parametral angles, and from fifty to seventy measurements of each were taken.

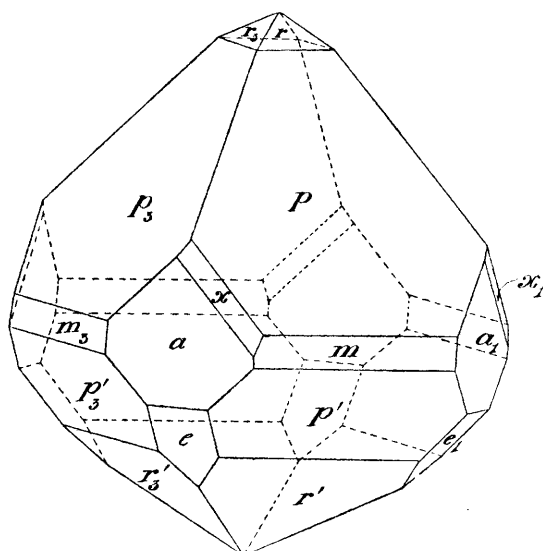
Calculation and measurement gave the following table of angles :

ce	$= 001 : \bar{1}01$	$45^\circ 13'$	am	$= 100 : 110$	$57^\circ 26'$
ef	$= \bar{1}01 : \bar{2}01$	$27 18$	em	$= \bar{1}01 : 110$	$106 11$
fa'	$= \bar{2}01 : \bar{1}00$	$31 25$	mp_1	$= 110 : 21\bar{1}$	$28 14$
ap_1	$= 100 : 21\bar{1}$	$47 47$	p_1e_1	$= 21\bar{1} : 10\bar{1}$	$45 35$
ap	$= 100 : \bar{2}11$	$132 13$	p_1f_1	$= 21\bar{1} : 20\bar{1}$	$38 3$

d-Phenylbenzylmethylisopropylammonium Iodide.

The crystals (Fig. 2), which belong to the tetragonal system, were found to have two distinct habits ; the commoner were short, squat crystals

FIG. 2.



with the pyramid faces of the form $p\{111\}$ well developed ; the other type were long, distorted prisms closely resembling the crystals of the inactive iodide ; the prismatic form was due to the development of the faces (111) , (100) , $(\bar{1}\bar{1}1)$, and $(\bar{1}00)$. The similarity in appearance

between these crystals of the inactive and active iodides is extended to the magnitudes of some of the principal angles.

There is little doubt that the only element of symmetry is a single tetrad axis, and that the crystals belong to the acleistous tetragonal class (Class III, Lewis), members of which are very rare. Proof of this could not be obtained by demonstrating that the axis was pyroelectric, nor could definite evidence be obtained from etched figures; but the two ends of the crystals were invariably developed differently, at one end $\{111\}$ is dominant, while at the other $\{11\bar{2}\}$ is the dominant form. Again, although no definite faces of any general form $\{hkl\}$ were observed, indications of the existence of vicinal faces were obtained which were so disposed as to exclude the existence of diad axes perpendicular to the tetrad axis.

Crystalline system. Tetragonal. Acleistous tetragonal class.
 $c = 1.0676$.

Forms observed: $a\{100\}$, $m\{110\}$, $p = \tau\{111\}$, $p' = \tau\{11\bar{1}\}$, $r = \tau\{112\}$, $r = \tau\{11\bar{2}\}$, $e = \tau\{10\bar{1}\}$, and $x = \tau\{322\}$.

The angles $(111) : (\bar{1}\bar{1}\bar{1})$ and $(11\bar{1}) : (\bar{1}\bar{1}\bar{1})$ were taken as parametral. Measurement and calculation gave the following table of angles:

$mp = 110 : 111$	$33^{\circ}31'$	$ax = 100 : 322$	$11^{\circ}28'$
$pr = 111 : 112$	$19\ 26$	$xp = 322 : 111$	$42\ 25$
$rr_2 = 112 : \bar{1}\bar{1}\bar{2}$	$74\ 6$	$ep' = 10\bar{1} : 11\bar{1}$	$36\ 7$
$pp_2 = 111 : \bar{1}\bar{1}\bar{1}$	$112\ 58$	$pp_1 = 111 : \bar{1}\bar{1}\bar{1}$	$72\ 14$

All the other angles are readily obtained from the above table. The angles in the zone am are naturally all 45° .

d-Phenylbenzylmethylisopropylammonium iodide was precipitated by addition of potassium iodide solution to a solution of the gummy residue containing the bromocamphorsulphonate of the *d*-base, which was left by evaporation of the mother liquors when no further separation of crystals took place. The rotatory power of this was examined in alcoholic solution and gave $[M]_D 314^{\circ}$. The *d*-iodide is therefore still contaminated with some of the *l*-iodide.

Methylisobutylaniline was prepared in the manner previously described by one of us (Trans., 1903, 83, 1408). The fraction collected boiled at $225-228^{\circ}$. The base gave a crystalline platinichloride which melted at $180-184^{\circ}$.

Phenylbenzylmethylisobutylammonium iodide was prepared by mixing equivalent quantities of the base and benzyl iodide. The deposition of crystals began almost immediately, and after twenty-four hours a solid mass was obtained. The salt was recrystallised from alcohol, from which solvent it was deposited in stellate aggregates of prisms

which melted at 148°. Wedekind and Fröhlich (*loc. cit.*) give the melting point as 130--131°.

0.2095 gave 0.4345 CO₂ and 0.122 H₂O. C = 56.56; H = 6.47.

C₁₈H₂₄NI requires C = 56.69; H = 6.30 per cent.

Phenylbenzylmethylisobutylammonium d-camphorsulphonate was prepared in the usual manner, and, after recrystallising from acetone, was obtained in colourless crystals which melted at 181°. No resolution was effected by crystallising from acetone, ethyl acetate, or a mixture of methylal or chloroform and light petroleum. After three recrystallisations from ethyl acetate, $[M_D]$ 50.3°, and the iodide recovered by the addition of potassium iodide to the aqueous solution was found to be inactive in alcoholic solution.

The *d-bromocamphorsulphonate* was therefore prepared by extracting the calculated quantities of silver salt and substituted ammonium iodide with boiling acetone, evaporating off the excess of solvent, and allowing to stand. The salt is very soluble in acetone and does not crystallise easily from this solvent. It was found that better crystals were obtained when the salt was dissolved in hot water and the solution allowed to cool slowly. The mixture of the two isomerides is first converted into an oil on treatment with hot water and subsequently dissolves; the crystals of the salt of the levorotatory base, which is only slightly soluble in water, separate first, and on concentrating the mother liquor the salt of the dextrorotatory base is precipitated as a gummy residue. The salt of the levorotatory base was deposited in groups of lustrous prisms, which were unchanged on standing in air and melted at 180°. Wedekind and Fröhlich (*loc. cit.*) state that the salt is strongly hygroscopic and melts at 165°. We found that when purified it could be left exposed on the laboratory bench for weeks without change.

0.2015 gave 0.4390 CO₂ and 0.1171 H₂O. C = 59.42; H = 6.46.

C₂₈H₃₅O₄NBrS requires C = 59.56; H = 6.74 per cent.

The rotatory power became constant after crystallising seven times from water or acetone.

0.134 gram in 18.526 grams of aqueous solution gave α_D -0.13°, whence $[\alpha]_D$ -8.99° and $[M]_D$ -50.68°.

0.1125 gram in 15.354 grams of solution gave α_D -0.12°, whence α_D -8.19° and $[M]_D$ -46.18°.

0.082 gram in 15.128 grams of solution gave α_D -0.09°, whence $[\alpha]_D$ -8.3° and $[M]_D$ -46.82°. The density of these solutions is practically that of water.

Hence the mean value for $[M]_D$ for the basic ion at 15° is -323°.

l-Phenylbenzylmethylisobutylammonium iodide was precipitated from the solution of the bromocamphorsulphonate by addition of potassium iodide solution. Determination of its rotatory power in alcohol gave the following results :

0.063 gram in 11.404 grams of solution (density = 0.80) gave $\alpha_D - 0.82^\circ$, whence $[\alpha]_D - 97.3^\circ$ and $[M]_D - 370.7^\circ$.

0.062 gram in 12.00 grams of solution (density = 0.80) gave $\alpha_D - 0.82^\circ$, whence $[\alpha]_D - 99.2^\circ$ and $[M]_D - 377.9^\circ$.

The active iodide dissolved easily in chloroform, and a determination of its rotatory power showed that it racemised rapidly in chloroform solution in the dark.

Thus, 0.1165 gram in 22.078 grams of solution (density = 1.5) gave $\alpha_D - 1.52^\circ$, whence $[\alpha]_D - 96.0^\circ$ and $[M]_D - 366^\circ$; after one and a half hours, $\alpha_D - 1.09^\circ$; after three and a half hours, $\alpha_D - 0.71^\circ$; after six hours, $\alpha_D - 0.20^\circ$, and after seven hours the solution was inactive.

Another determination taken within ten minutes of making up the solution gave $\alpha_D - 1.09^\circ$ for 0.083 gram in 22.5 grams of solution, whence $[\alpha]_D - 98.5^\circ$ and $[M]_D - 375^\circ$. This solution also became inactive after seven hours. It is therefore probable that $[M]_D$ in chloroform is really about 390° and greater than in alcohol.

Methylisoamylaniline was obtained by mixing equivalent quantities of methylaniline and *isoamyl* bromide and heating on a water-bath for sixteen hours or until the mixture had solidified to a crystalline mass. The hydrobromide was treated with aqueous caustic potash, the oil separated, dried over solid caustic potash, and fractionated. The oil distilling from 246° to 248° , which was almost colourless, was collected and used for the experiments. The platinichloride was precipitated as a pale yellow powder from solutions of the hydrochloride, but on dissolving it in alcohol it underwent some decomposition and could not be purified.

Phenylbenzylmethylisoamylammonium iodide was prepared by mixing *methylisoamylaniline* and benzyl iodide in molecular proportions. Crystals began to be formed almost immediately, and after an hour a solid cake was obtained. The solid was crystallised several times from alcohol; colourless, fine needles were deposited, which melted sharply at 156° when heated rapidly.

0.2043 gave 0.4325 CO_2 and 0.1266 H_2O . C = 57.7; H = 6.8.

$\text{C}_{19}\text{H}_{26}\text{NI}$ requires C = 57.72; H = 6.58 per cent.

Phenylbenzylmethylisoamylammonium d-camphorsulphonate was prepared by boiling equivalent quantities of phenylbenzylmethylisoamylammonium iodide and silver *d*-camphorsulphonate with acetone. In order to avoid the formation of the double compound of the ammonium

iodide and silver iodide, it was found advisable to get the silver salt finely powdered, to cover it with acetone, and to add the iodide in successive small quantities, shaking and boiling after each addition. The silver iodide was filtered off and the filtrate heated on the water-bath until all the acetone was driven off; on allowing the residue to cool in a desiccator, it crystallised readily. The salt is fairly soluble in ethyl acetate and in acetone. It was found that after repeated crystallisation from acetone the melting point of the salt rose gradually and the rotatory power fell, became zero, and then the levorotation increased.

It is clear that the salt of the *l*-base is being separated. In several experiments with quantities varying from 30 to 100 grams of the camphorsulphonate, the material was exhausted after some twenty or twenty-five crystallisations, when the value of $[M]_D$ was about -220° * and not constant. Finally, about 270 grams of the salt were prepared and repeatedly crystallised from hot acetone; after sixteen crystallisations, 10 grams of the salt were left, melting at $170-171^\circ$ and having $[M]_D - 219^\circ$.

This was crystallised twice, when the melting point rose to $176-177^\circ$ and $[M]_D$ to -230° . The salt was again crystallised twice; the melting point became $179-180^\circ$ and $[M]_D - 235^\circ$. Further recrystallisation did not change either the melting point or the rotatory power, so that the pure salt of the *l*-base has been isolated.

0.1163 gave 0.2975 CO_2 and 0.0875 H_2O . C = 69.76; H = 8.36.

$\text{C}_{29}\text{H}_{41}\text{O}_4\text{NS}$ requires C = 69.74; H = 8.22 per cent.

The following determinations of rotatory power were made in aqueous solution at 15° .

0.120 gram in 12.585 grams of solution gave $\alpha_D - 0.9^\circ$ (density = 1.000), hence $[\alpha]_D - 47.2^\circ$ and $[M]_D - 235.4^\circ$.

0.131 gram in 12.387 grams gave $\alpha_D - 1.00^\circ$ (density = 1.000), hence $[\alpha] - 47.5^\circ$ and $[M]_D - 235.8^\circ$.

0.131 gram in 12.330 grams gave $\alpha_D - 1.01^\circ$ (density = 1.001), hence $[\alpha]_D - 47.5^\circ$ and $[M]_D - 237.0^\circ$.

0.133 gram in 12.588 grams gave $\alpha_D - 0.99^\circ$ (density = 1.000), hence $[\alpha]_D - 46.90^\circ$ and $[M]_D - 233.8^\circ$.

The effect of concentration on the rotatory power of the salt at 18° was examined as the salt is particularly suitable for the purpose on account of its large rotatory power and its solubility in water.

* The values of $[M]_D$ for the camphorsulphonate and the active iodide previously given (*loc. cit.*) were erroneous.

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Weight of salt in 100 grams of solution.	α_D .	Specific gravity.	$[\alpha]_D$.	$[M]_D$.
2.75	-2.54°	1.004	-46.0°	-229.7°
1.50	1.40	1.002	46.6	232.4
1.02	0.96	1.001	47.1	235.2
0.633	0.59	1.000	46.6	232.6

It is evident from the above numbers that, as in the case of the phenylbenzylmethylallylammonium salt, the value of the rotatory power is constant within the limits of experimental error when the concentration is about 1.5 per cent. or lower.

The mean value of $[M]_D$ for *l*-phenylbenzylmethylisoamyl *d*-camphorsulphonate at 15° is therefore -235.5°, and the value of $[M]_D$ for the basic ion is -287.2°

The effect of temperature change on the rotatory power of the 1.5 per cent. solution above was also investigated (density = 1.002 at 18°).

<i>l</i> .	α_D .	$[\alpha]_D$.	$[M]_D$.	$[M]_D$ for basic ion.
7°	-1.41°	-46.8°	-233.5°	-282.4°
13	1.40	46.6	232.5	282.7
18	1.40	46.6	232.4	283.6
30	1.36	45.3	226.0	279.6
40	1.31	43.8	218.6	274.2
50	1.29	43.1	215.0	272.4

Phenylbenzylmethylisoamylammonium d-bromocamphorsulphonate crystallises readily, is very soluble in acetone, and was therefore crystallised from a mixture of acetone and ethylal. After recrystallising several times, the colourless plates melted at 179—180° and gave $[M]_D$ 195°; the value of $[M]_D$ fell slowly on further crystallisation, but, as it was clear that resolution was not being effected rapidly, the further examination was abandoned.

l-Phenylbenzylmethylisoamylammonium iodide was immediately precipitated as fine needle-shaped crystals when aqueous solutions of the camphorsulphonate and potassium iodide were mixed. The precipitated iodide melts at 151—152° and after recrystallisation from cold alcohol melts at 155—156° when heated rapidly; a mixture of this with the inactive iodide melts practically at the same temperature.

Determinations of the rotatory power of the iodide were made in solution in alcohol and in chloroform.

In alcohol, 0.1440 gram in 10.394 grams gave α_D -1.90° (density = 0.811), hence $[\alpha]_D$ -84.5° and $[M]_D$ -333.8°.

After recrystallising from cold alcohol, 0.1470 gram in 11.067 grams gave α_D -1.87° (density = 0.811), hence $[\alpha]_D$ -87.0° and $[M]_D$ -344°.

0.1140 gram in 10.358 grams gave α_D -1.55° (density = 0.810), hence $[\alpha]_D$ -86.9° and $[M]_D$ -343°.

In chloroform, 0.1340 gram in 18.519 grams gave $\alpha_D - 2.16^\circ$ (density = 1.492), hence $[\alpha]_D - 100^\circ$ and $[M]_D - 395^\circ$.

The solution racemised slowly in the dark at the ordinary temperature; after twenty-eight hours, $\alpha_D - 1.02^\circ$; after forty-eight hours, $\alpha_D - 0.50^\circ$; after seventy-two hours, $\alpha_D - 0.2^\circ$; and after ninety-six hours the solution was completely inactive.

0.1030 gram in 17.259 grams gave $\alpha_D - 1.75^\circ$ (density = 1.49), hence $[\alpha]_D - 98.6^\circ$ and $[M]_D - 390^\circ$.

After one hour, $\alpha_D - 1.67^\circ$; after eighteen hours, $\alpha_D - 0.87^\circ$; after twenty-four hours, $\alpha_D - 0.56^\circ$; after forty-eight hours, $\alpha_D - 0.16^\circ$; and after seventy-two hours the solution was inactive.

*The Allyl Series.**

d-Phenylmethylethylallylammonium *d*-bromocamphorsulphonate was prepared in the usual way from silver *d*-bromocamphorsulphonate and the iodide, $N(C_6H_5)(CH_3)(C_2H_5)(C_8H_5)I + CHCl_3$, prepared by Wedekind, in acetone solution. After filtering off the silver iodide and evaporating most of the acetone on the water-bath, the residue crystallised easily. The salt could be crystallised from acetone, ethyl acetate, or ethylal; it was crystallised several times from a mixture of acetone and light petroleum and then from acetone alone, when it was obtained in short, colourless prisms melting at 138—139°.

0.1582 gave 0.3090 CO_2 and 0.0895 H_2O . C = 53.2; H = 6.28.

$C_{22}H_{32}O_4NBrS$ requires C = 53.1; H = 6.59 per cent.

The salt was recrystallised from acetone until the rotatory power became constant when examined during three successive crystallisations.

0.4576 gram in 25 c.c. solution gave $\alpha_D 2.20^\circ$, $[\alpha]_D 60.1^\circ$, and $[M]_D 292^\circ$.

0.168 gram in 12.457 grams solution gave $\alpha_D 1.80^\circ$, $[\alpha]_D 59.9^\circ$, and $[M]_D 291.2^\circ$.

0.157 gram in 12.317 grams solution gave $\alpha_D 1.52^\circ$, $[\alpha]_D 59.6^\circ$, and $[M]_D 289.6^\circ$.

The value of $[M]_D$ for the salt is therefore 291° , which agrees closely with the number given in a preliminary notice (*Trans.*, 1903, 83, 1420); the value of $[M]_D$ for the basic ion is therefore about 16° at the ordinary temperature (15°).

* A note on the results obtained with this series has already been published (*Proc. Camb. Phil. Soc.*, 1905, 13, 190).

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Two determinations of the effect of temperature change were made with another sample of salt resolved separately. The following result served to show that the change in rotatory power is extremely small.

0.171 gram in 13.25 grams of solution (density = 1.001) at 20°.

t .	α_D .	$[\alpha]_D$.	$[M]_D$.	$[M]_D$ for basic ion.
10°	1.54°	59.6°	290.0°	17.0°
19	1.55	60.0	291.6	14.6
31	1.55	60.0	291.6	9.6
44	1.55	60.0	291.6	3.6
50	1.56	60.3	293.4	2.4

It is curious that the rotatory power of the basic ion should vanish at some temperature above 50° and then become laevorotatory, as it probably would.

Phenylmethyl-n-propylallylammonium Iodide.

A mixture of methyl-*n*-propylaniline and allyl iodide in molecular proportions rapidly sets to a solid, crystalline mass of the quaternary salt; this is very soluble in alcohol, acetone, and ethyl acetate, and was purified by dissolving in alcohol, adding ether until a turbidity was produced, and allowing to stand, when colourless, rectangular tables were deposited. After repeating the process several times, the crystals melted sharply at 109—110° and gave the following results on analysis:

0.2116 gave 0.3815 CO₂ and 0.1217 H₂O. C = 49.1; H = 6.4.

C₁₃H₂₀NI requires C = 49.2; H = 6.3 per cent.

Phenylmethyl-n-propylallylammonium d-camphorsulphonate, prepared in the usual way, crystallised readily from a mixture of acetone and benzene in rhombic plates which melted at 167—168°.

After three crystallisations from acetone, 0.354 gram of the salt dissolved in 12.663 grams of solution gave α_D 0.66° (density = 1.001), hence $[\alpha]_D$ 11.9° and $[M]_D$ 49.8°.

The *d*-camphorsulphonate is therefore not easily resolved.

Phenylmethyl-n-propylallylammonium d-bromocamphorsulphonate crystallised easily from a mixture of acetone and benzene and was then crystallised repeatedly from acetone, in which it becomes less soluble as this process goes on. The salt is thus obtained in lustrous prisms melting at 169—170°.

0.2298 gave 0.466 CO₂ and 0.1475 H₂O. C = 55.3; H = 7.12.

C₂₃H₃₄O₄NBrS requires C = 55.2; H = 6.8 per cent.

The rotatory power of the salt in aqueous solution was found to

increase rapidly at first and then more slowly after recrystallising several times.

0.150 gram in 12.37 grams of solution gave α_D 1.85° in a 2-dcm. tube, hence $[\alpha]_D$ 76.3° , and $[M]_D$ 381.5° .

The salt was then recrystallised twice more from acetone and the first and second crops examined at 15° .

0.106 gram in 12.39 grams of solution gave α_D 1.30° , $[\alpha]_D$ 76.1° ; $[M]_D$ 380.5° .

0.106 gram in 12.45 grams of solution gave α_D 1.30° , $[\alpha]_D$ 76.5° ; $[M]_D$ 382.5° (density = 1.001 in all cases).

Hence $[M]_D$ for *d*-phenylmethyl-*n*-propylallylammonium *d*-bromocamphorsulphonate is 381.5° and the value of $[M]_D$ for the basic ion is 106.5° at 15° .

The effect of temperature change on a solution of this salt was examined and found to be negligible.

A 1.08 per cent solution at 15° gave α_D 1.65° between 4° and 48° , so that the value of $[\alpha]_D$ remains practically constant at 76.4° throughout this range of temperature.

The values of $[M]_D$ for the basic ion may therefore be taken as 108.5° at 10° , 104.5° at 20° , 99.5° at 30° , 95.5° at 40° , and 90.5° at 50° .

The active iodide is not precipitated from a strong solution of the bromocamphorsulphonate by the addition of excess of potassium iodide.

The platinichloride is precipitated on the addition of platonic chloride as a pale yellow, crystalline powder extremely sparingly soluble in all solvents, so that its rotatory power could not be determined.

Phenylmethylisopropylallylammonium Iodide.

A mixture of methylisopropylaniline and allyl iodide in molecular proportions rapidly becomes turbid, and in the course of twenty-four hours sets almost completely to a crystalline mass.

This was crystallised several times from hot alcohol and formed colourless prisms melting at 171 – 172° which were analysed with the following result :

0.1620 gave 0.2905 CO_2 and 0.0955 H_2O . C = 48.9 ; H = 6.5.

$\text{C}_{13}\text{H}_{20}\text{NI}$ requires C = 49.2 ; H = 6.3 per cent.

1-Phenylmethylisopropylallylammonium d-Camphorsulphonate.

The above iodide was converted into the *d*-camphorsulphonate in the usual way, and this crystallised partially on standing. The salt is very

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soluble in acetone, and separates from its solutions sometimes in short, thick prisms and tables rather resembling cane sugar crystals in appearance, sometimes as long, needle-shaped crystals, and often as a mixture of the two; as the crystallisation proceeded, the acicular form became the more common. It was found most convenient to dissolve the salt in hot acetone, to add to this solution about one-tenth its own volume of toluene, and then to set this solution in a desiccator over sulphuric acid, when well-formed crystals separated, from which the mother liquor could be much more easily removed than when acetone was used alone.

After several crystallisations, the crystals melted at 167—168° and gave the following result on analysis:

0.2000 gave 0.4802 CO₂ and 0.1477 H₂O. C = 65.4; H = 8.2.

C₂₃H₃₅O₄NS requires C = 65.5; H = 8.3 per cent.

Determinations of the rotatory power showed that this fell slowly on recrystallisation, became zero, and then the levorotation increased.

Thus, after five crystallisations, $[\alpha]_D - 11.3^\circ$, and after eight $[\alpha]_D - 23.2^\circ$.

The salt after recrystallising five or six times always crystallised entirely in needles and long prisms. After the thirteenth crystallisation, it was found that the rotatory power of the salt had become constant, and further repetition of the process three times did not alter the value of $[\alpha]_D$, but it was found that the rotatory power of this salt was affected to a greater extent by temperature than that of any of the other salts examined.

The melting point of the salt was now 168—169°.

The following determinations of the rotatory power were made.

0.258 gram in 12.609 gram solution gave $\alpha_D - 0.48^\circ$ at 20° (density = 1.002), hence $[\alpha]_D - 11.7^\circ$ and $[\alpha]_D - 49.3^\circ$.

0.260 gram in 12.637 grams of solution (density = 1.002 at 20°).

<i>t.</i>	α_D .	$[\alpha]_D$.	$[\alpha]_D$.
13'	-0.52°	-12.62°	-53.1°
20	0.49	11.9	50.0
26	0.48	11.65	49.1
40	0.36	8.74	36.8
45	0.33	8.02	33.8

0.286 gram in 13.367 grams of solution (density = 1.002 at 20°).

<i>t.</i>	α_D .	$[\alpha]_D$.	$[\alpha]_D$.
9°	-0.55°	-12.83°	-54.0°
13	0.53	12.4	52.05
25	0.46	10.84	45.27
32	0.40	9.35	39.38
50	0.28	6.40	27.58

It is extremely difficult to get really concordant results with a salt

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of this kind with its small rotatory power and large temperature effect, but by taking a mean of the above results we get the following values of $[M]_D$ for the basic ion, which are probably not far from the truth.

103.5° at 10°, 100.6° at 20°, 96.6° at 30°, 91.6° at 40°, and 86.6° at 50°.

The value of $[M]_D$ for the salt at 15° is taken to be 52°, and for the basic ion 102.6°; this value may be slightly smaller than the true one, and on account of the great experimental error it is impossible to decide from these data whether the *n*- or the *iso*-propyl compound has the greater rotatory power; it may be assumed that they are very nearly identical.

Phenylmethylisopropylallylammonium d-bromocamphorsulphonate was prepared and found to crystallise readily; it was very soluble in water, sparingly soluble in methylal, but more so in acetone and ethyl acetate. Specimens were recrystallised several times from acetone and others from ethyl acetate and the rotatory powers of the different fractions examined, and were found to vary between 274° and 277° and not to be altered by further crystallisation. This salt is therefore not resolved by recrystallisation from these solvents. The salt melted at 169—171° and gave the following result on analysis:

0.1599 gave 0.3222 CO₂ and 0.0987 H₂O. C = 54.9; H = 6.86.

C₂₃H₃₄O₄NBrS requires C = 55.2; H = 6.8 per cent.

1-Phenylmethylisopropylallylammonium iodide was slowly precipitated in beautiful, lustrous prisms when solutions of the camphorsulphonate and potassium iodide were mixed. The iodide is so soluble that small quantities only could be recovered. The crystals melted at the same temperature, 171—172°, as the inactive iodide, and were rather sparingly soluble in cold alcohol and less soluble in chloroform, so that accurate determinations of the rotatory power were difficult, as they were necessarily affected largely by experimental error.

The following results were obtained:

In alcohol:

0.158 gram in 10.604 grams of solution gave α_D - 0.50° (density = 0.810), hence $[\alpha]_D$ - 20.7° and $[M]_D$ - 65.7°.

0.165 gram in 9.101 grams of solution gave α_D - 0.59° (density = 0.811), hence $[\alpha]_D$ - 20.0° and $[M]_D$ - 63.4°.

In chloroform:

0.125 gram in 21.805 grams of solution practically saturated gave α_D - 0.52° (density = 1.499), hence α_D - 30.3° and $[M]_D$ - 96°.

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The solution racemised at a very slow rate.

After two, nine, and fourteen days, α_D was -0.47° , -0.26° , and -0.15° , respectively, and after standing about a month the solution was inactive.

Phenylmethylallylisobutylammonium iodide was prepared by mixing the calculated quantities of methylisobutylaniline and allyl iodide. An oil was deposited at first, which on standing for twenty-four hours was converted into a solid, crystalline mass. The crystals were very soluble in alcohol, chloroform, or acetone, from any of which solvents they are deposited as an oil which slowly crystallises. They were recrystallised from hot ethyl acetate, in which they are easily soluble, and were deposited on cooling in long prisms which melt at 143° .

0.1986 gave 0.3707 CO_2 and 0.1195 H_2O . C = 50.9; H = 6.70.

$\text{C}_{14}\text{H}_{22}\text{NI}$ requires C = 50.75; H = 6.65 per cent.

Phenylmethylallylisobutylammonium d-camphorsulphonate was prepared by extracting a mixture of the substituted ammonium iodide and silver *d*-camphorsulphonate with boiling acetone to which a few drops of methyl alcohol had been added, and filtering from the precipitated iodide. On allowing the filtrate to stand over sulphuric acid in a desiccator, the salt was deposited in rhombic prisms. These were purified by recrystallisation from benzene or acetone and melted at 173° with decomposition.

0.1604 gave 0.3895 CO_2 and 0.1190 H_2O . C = 66.5; H = 8.24.

$\text{C}_{24}\text{H}_{37}\text{NSO}_4$ requires C = 66.21; H = 8.50 per cent.

The salt was resolved into its *d*- and *l*-constituents by fractional crystallisation from acetone. After four recrystallisations from this solvent, 0.579 gram in 14.56 grams of aqueous solution gave α_D 0.07° , whence $[\alpha]_D$ 0.88° and $[M]_D$ 3.83° . After two more recrystallisations, 0.302 gram in 14.494 grams of solution gave α_D -0.06° , whence $[\alpha]_D$ -1.44° and $[M]_D$ -6.26° .

On further recrystallisation, a solution containing 0.2625 gram of the salt in 15.122 grams of solution (1.785 per cent.) gave the following results (density = 1.002 at 15°):

t .	α_D .	$[\alpha]_D$.	$[M]_D$.	$[M]_D$ for basic ion.
7°	-0.04°	-1.13°	-4.93°	-54.46°
13	-0.01	-0.28	-1.24	-51.8
30	$+0.06$	$+1.71$	$+7.44$	-46.16
50	$+0.1$	$+2.87$	$+12.5$	-45.1

Repetition of the experiments gave similar results.

In the determination of the rotatory power of this compound, a large experimental error is necessarily involved, seeing that the observed rotation is very small; the values obtained for the molecular

rotation of the basic ion at 15° vary between -52° and -57° , so that the value for $[M]_D$ may be taken as -55° . Although great accuracy cannot therefore be claimed for the numbers given, the experimental error is not great enough to affect the place of the ion in the series, which lies between those of the ions containing the *isoamyl* and *isopropyl* groups respectively.

1-Phenylmethylallylisobutylammonium iodide was precipitated in small, colourless prisms, which melted at 143° , by addition of potassium iodide to aqueous solutions of the camphorsulphonate. Their rotatory power in alcohol and chloroform was determined and gave the following results :

0.114 gram in 15 c.c. of alcohol gave $\alpha_D - 0.29^\circ$ (density = 0.800), whence $[\alpha]_D - 19.08^\circ$ and $[M]_D - 63.15^\circ$.

The iodide was easily soluble in chloroform, and the solution slowly racemised. 0.086 gram in 15 c.c. of chloroform gave $\alpha_D - 0.27^\circ$, whence $[\alpha]_D - 23.55^\circ$ and $[M]_D - 77.95^\circ$; after four hours, $\alpha_D - 0.21^\circ$, after twenty-four hours, $\alpha_D - 0.17^\circ$, after forty-eight hours, $\alpha_D - 0.08^\circ$, and after three days the solution was inactive.

Phenylmethylallylisoamylammonium iodide was prepared by mixing the calculated quantities of methylisoamylaniline and allyl iodide and allowing to stand. After twenty-four hours, the mixture, which at first deposited an oil, had solidified to a crystalline mass. This was recrystallised from a mixture of alcohol and ether or from ethyl acetate and separated as small, colourless prisms which melt at 135° .

0.2052 gave 0.3920 CO_2 and 0.1255 H_2O . C = 52.10 ; H = 6.80.

$\text{C}_{15}\text{H}_{24}\text{NI}$ requires C = 52.17 ; H = 6.96 per cent.

1-Phenylmethylallylisoamylammonium d-camphorsulphonate was prepared by mixing together the calculated quantities of the substituted ammonium iodide and silver *d*-camphorsulphonate and boiling with ethyl acetate, or acetone (in which the salt is very soluble), or benzene, in which it is moderately soluble, and crystallises out on cooling the saturated solution. After twice recrystallising from methylal, the melting point was 155° .

0.2000 gave 0.4385 CO_2 and 0.1567 H_2O . C = 66.61 ; H = 8.71.

$\text{C}_{25}\text{H}_{39}\text{O}_4\text{NS}$ requires C = 66.81 ; H = 8.68 per cent.

The salt was too soluble in acetone, ethyl acetate, and methyl formate to allow of the use of these solvents for the purpose of recrystallising, and when a mixture of any of them with light petroleum was used the salt separated as an oil ; it crystallised easily from benzene in needles, but the aqueous solution of the crystals smelt strongly of benzene even after they had been dried and kept in a

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vacuum desiccator over sulphuric acid for some days ; probably, therefore, they contain benzene of crystallisation. Methylal which had been freed from all traces of methyl alcohol by distillation over caustic potash was found to be the most convenient solvent ; the *l*-salt is sparingly soluble in the cold, and is deposited in long needles on cooling the hot saturated solution. After recrystallising five times from this solvent, the salt appeared to be completely resolved.

0.6225 gram in 15.753 grams of solution gave $\alpha_D + 0.58^\circ$ (density = 1.004), whence $[\alpha]_D 7.31^\circ$ and $[M]_D 32.8^\circ$.

0.4655 gram in 17.157 grams of solution (density = 1.003 at 15°) gave the following results :

<i>t</i> .	α_D .	$[\alpha]_D$.	$[M]_D$.	$[M]_D$ for basic ion.
7°	+0.37°	+6.80°	+30.5°	-18.5°
15	0.39	7.16	32.2	18.4
30	0.42	7.72	34.7	18.9
50	0.48	8.84	39.7	18.9

The mean of these experiments gives $[M]_D - 18^\circ$ for the basic ion at 15° .

The following tables, which contain the melting points and the values of the molecular rotatory powers of the compounds described in this paper and of those previously described, have been prepared for convenience of reference.

Phenyl-methyl-benzyl Series.

	M. p. of iodide.	M. p. of <i>d</i> -camphor- sulphonate.	M. p. of <i>d</i> -bromo- camphor- sulphonate.	$[M]_D$ of ion at 15° .	$[M]_D$ of iodide in alcohol.	$[M]_D$ of iodide in chloroform.
Ethyl	147.8°	181°	—	+19.4°	30°	33.8°
<i>n</i> -Propyl ...	167.0	188	148°	-299.0	-354	-374.0
<i>iso</i> Propyl ...	133.0	175	184	-398.0	-428	-507.0
<i>iso</i> Butyl ...	148.0	181	180	-323.0	-374	-390.0 ?
<i>iso</i> Amyl ...	156.0	178	180	-287.0	-343	-395.0
Allyl	140—142	171	—	+167.0	—	—

Phenyl-methyl-allyl Series.

	M. p. of iodide.	M. p. of <i>d</i> -camphor- sulphonate.	M. p. of <i>d</i> -bromo- camphor- sulphonate.	$[M]_D$ of ion at 15° .	$[M]_D$ of iodide in alcohol.	$[M]_D$ of iodide in chloroform.
Ethyl ...	—	149—150°	138—139°	16.0°	—	—
<i>n</i> -Propyl ...	109—110°	167—168	169—170	106.5	—	—
<i>iso</i> Propyl ...	171—172	168—169	169—171	-102.6	-64.5°	-96°
<i>iso</i> Butyl ...	143	173	—	-55.0	-63.0	-78
<i>iso</i> Amyl ...	135	155	—	-18.0	—	—

No regularities in the melting points are to be observed. It must be remembered, however, that fusion is almost invariably accompanied

by decomposition, and that the melting point depends somewhat on the rate of heating in the case of the iodides. The melting point of the *d*-camphorsulphonate is usually between that of the iodide and the *d*-bromocamphorsulphonate, but there are some exceptions. The melting points of the phenylmethylisopropylallylammonium salts are surprisingly alike.

The following curves show the effect of temperature is of the same kind in all the compounds we have examined.

FIG. 3.—*Phenyl-methyl-benzyl series.*

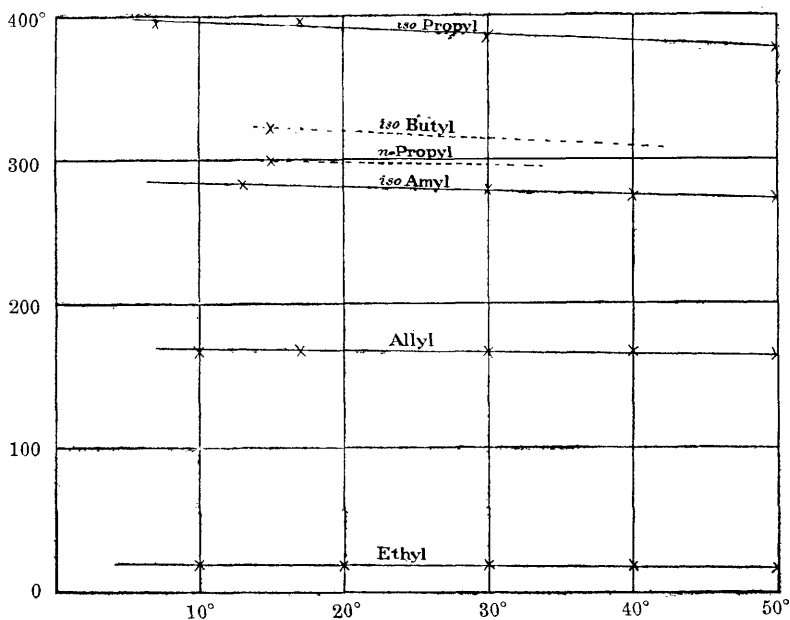
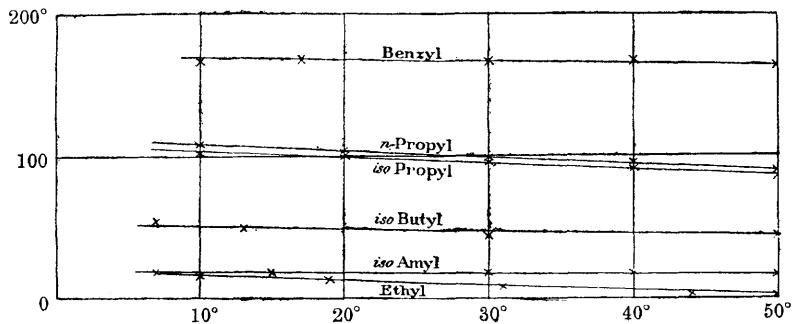


FIG. 4.—*Phenyl-methyl-allyl series.*



Wedekind has expressed his intention of examining the effect of temperature change on the *n*-propyl and *isobutyl* compounds of the benzyl series. There is no doubt that they will behave in a very similar manner to the other salts which we have examined.

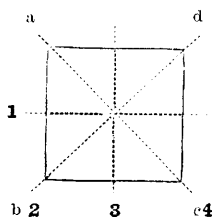
The curves show very clearly that the temperature effect is very regular for all the compounds, and is small compared with that for non-electrolytes or for the compounds examined by Patterson (*loc. cit.*).

The Product of Asymmetry for the Nitrogen Atom.

In the two series of optically active nitrogen compounds described above, the large effect of constitution on the molecular rotation is very striking. The existence of a maximum in each case at the second member and the decline of rotatory power in the higher members is clearly indicated. It was explained in the early part of the paper that any connection which might exist between the rotatory power and the constitution of compounds ought to become evident in this simple case of an ion in which the substituting groups were of similar character. Now, although mass cannot be the only factor which affects the rotatory power, it must be one factor and probably also an important one, and in the present state of our knowledge, while we await a development of the connection between light as an electromagnetic phenomenon and chemical atoms and molecules as electric structures, it is the only one which we can take into account.

Assuming, therefore, that optical rotatory power is determined by the mass of the groups attached to the nitrogen atom, and, further, that these masses are concentrated at the angular points of a regular pyramid on a square base, we can develop an expression for the product of asymmetry which will represent the same facts for nitrogen as the function deduced by Guye (*Compt. rend.*, 1893, 116, 1378) does for carbon. The pyramidal configuration has been shown to be the most probable one for substituted ammonium compounds (*Trans.*, 1905, 87, 1729).

The pyramid has four planes of symmetry, numbered 1 to 4 in the plane projection of the pyramid on its base in the figure.



Let d_1, d_2, d_3, d_4 be the distances of the centre of gravity of the molecule from each of these planes.

These are given by the expressions :

$$d_1 = \frac{\{(a+d) - (b+c)\}l\sin\alpha}{(a+b+c+d+x)},$$

$$d_2 = \frac{(a-c)l}{(a+b+c+d+x)},$$

$$d_3 = \frac{\{(a+b) - (c+d)\}l\sin\alpha}{(a+b+c+d+x)},$$

$$d_4 = \frac{(b-d)l}{(a+b+c+d+x)},$$

where $a, b, c,$ and d represent the masses of the four alkyl groups at the base of the pyramid, x the mass of the acidic radicle at its apex, l half the length of the diagonal of the base, and α the angle between two of the planes, 45° .

There is also d_5 , the distance of the centre of gravity from the basal plane, which may be expressed as

$$d_5 = \frac{\{(a+b+c+d) - x\}h}{(a+b+c+d+x)},$$

where h is the height of the pyramid.

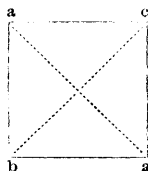
We have therefore the product of asymmetry :

$$P = d_1 \times d_2 \times d_3 \times d_4 \times d_5 \text{ or } P = \frac{\{(a+d) - (b+c)\}\{(a+b) - (c+d)\}(a-c)(b-d)\{(a+b+c+d) - x\}l^4\sin^2\alpha h}{(a+b+c+d+x)^5},$$

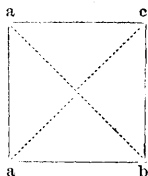
or, since $l, h,$ and α must be assumed to be constant, otherwise the problem becomes too complicated, we get

$$P' = \frac{\{(a+d) - (b+c)\}\{(a+b) - (c+d)\}(a-c)(b-d)\{(a+b+c+d) - x\}}{(a+b+c+d+x)^5},$$

an expression which should measure (to a very rough approximation only) the magnitude of the rotatory power of an optically active nitrogen compound. It satisfies the necessary conditions, namely, that when $a=c$ the compound is inactive, that is, for a compound with the configuration :



but that if $a=b$ or d the compound is not inactive, that is, a compound with the configuration :



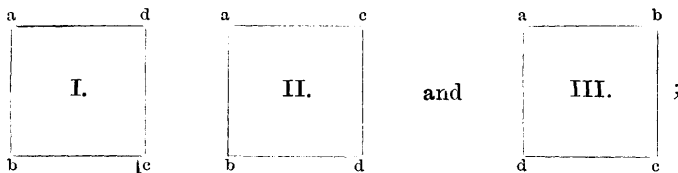
is active, a theoretically possible case which has not been realised experimentally. The above function predicts some curious results, for instance, if $a+b=c+d$ or $a+d=b+c$, the compound should be inactive; this contingency, which would probably not occur, is analogous to the inactivity predicted by Guye's expression for carbon where any two groups are of equal mass, and shows clearly that mass is not the only factor to be considered, a fact which is already sufficiently well recognised.

The above expression, however, refers to the complete molecule, whereas in this paper attention has been confined chiefly to the ions, where the rotatory power is so little affected by external conditions, the solvent is always the same, and the temperature effect is small. In this case, the acidic group x is removed, and its nature does not affect the rotatory power of the basic ion, so that we may put $x=O$, and we have

$$P'' = \frac{\{(a+d) - (b+c)\}\{(a+b) - (c+d)\}(a-c)(b-d)}{(a+b+c+d)^4}$$

This function exhibits the same properties as the foregoing more complicated expression for the product of asymmetry of the whole molecule; three maxima and three minima are possible, and $P=0$, as before, when $a=c$, and also when $a+b=c+d$ or $a+d=b+c$.

There is a practical difficulty in the application of this formula, namely, that there are always three possible configurations for a compound of the type $Na b c d x$ which may be represented for one case thus :



the value of the product of asymmetry is in general different for each of the three arrangements. One of these arrangements is more

stable than the others, and that one is produced during the changes which take place in the formation of the compound from a tertiary amine and alkyl halogen compound.

Until we have some means of determining the configuration of these compounds, it seems legitimate, when possible, to choose those configurations for the compounds in a series, which give values for the products of asymmetry in the same numerical order as the rotatory powers actually found for these compounds.

The values of P'' for the three possible arrangements are given in the table below, together with $[M]_D$ for the basic ion at 15° .

Phenyl-methyl-benzyl Series. $a = C_6H_5(77)$, $b = CH_3(15)$, $c = C_7H_7(91)$,
 d variable.

d .	$[M]_D$ for basic ion.	I. $P'' \times 10^3$.	II. $P'' \times 10^3$.	III. $P'' \times 10^3$.
Methyl	0.0°	0.0	+5.98	+5.98
Ethyl	19.4	0.0	+6.27	0.0
<i>n</i> -Propyl	299.0	-0.08	+4.6	-1.76
<i>iso</i> Propyl	398.0			
<i>iso</i> Butyl.....	323.0	-0.26	+2.46	-1.71
<i>iso</i> Amyl.....	287.0	-0.54	+0.61	-0.99
Allyl	167.0	-0.07	+4.87	-1.66

Phenyl-methyl-allyl Series. $a = C_6H_5$, $b = CH_3$, $c = C_3H_5(41)$,
 d variable.

d .	$[M]_D$ for basic ion.	I. $P'' \times 10^3$.	II. $P'' \times 10^3$.	III. $P'' \times 10^3$.
Methyl	0.0°	0.0	-10.6	-10.6
Ethyl.....	16.0	-0.8	-2.95	-4.0
<i>n</i> -Propyl	106.5	-0.588	-0.44	-0.5
<i>iso</i> Propyl	102.6			
<i>iso</i> Butyl.....	55.0	+0.54	+0.11	+2.73
<i>iso</i> Amyl.....	18.0	+2.14	+0.057	+3.16

The sign of P'' has no significance here as it has in the case of carbon compounds, where changes of constitution are produced in a molecule the configuration of which is always the same, but the sign of its rotation may nevertheless be altered by the change of constitution.

It is at once clear on comparing the above values of the product of asymmetry with the experimental values of $[M]_D$ that there is no simple connection between them. The application of Guye's hypothesis to the nitrogen atom does not therefore give a satisfactory expression connecting the masses of the alkyl groups with the rotatory power of the molecule.

The configuration of the methyl compounds of both series is almost certainly I, since they are inactive. Considering first the benzyl

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series, there is no reason to suspect that the change from a methyl to an ethyl group would necessitate a change of configuration, so that the ethyl compound might be expected to have a very small rotatory power since $P=0$. Now if we assume that the *isopropyl*, *isobutyl*, and *isoamyl* compounds have configuration I, we get a maximum value for P'' at the *isoamyl* compound, but if we assume that they have configuration II and that the *n*-propyl and allyl compounds have configuration III, we get a fair approximation to a relation between P'' and $[M]_D$ for the benzyl series. There is as yet no experimental evidence for these changes of configuration, but that there is a difference of configuration between the *n*-propyl and *isopropyl* compounds of the benzyl series seems extremely probable, as we know of no other case where the change from the normal to the *iso* grouping produces any great change in rotatory power, and in the allyl series the *n*- and *iso*-compounds have practically identical rotatory powers. The allyl group in this case might be expected to behave as a group of smaller weight, since, owing to the double linkage, the centre of gravity of the group is nearer its point of attachment to the nitrogen atom than that of a normal grouping.

In the allyl series, it is still more difficult to see a connection between the values of P'' and $[M]_D$, even with the aid of such arbitrary assumptions about configuration as the above, since the ethyl compound is so clearly out of its place. Now the fact that the rotatory power of the ion in this case vanishes above 50° might lead to some doubt as to its having been resolved at all, but this doubt is removed by the facts that the observed rotation at the ordinary temperature is outside the limits of experimental error, and, that the platinichloride gives an active solution on treatment with sulphuretted hydrogen in water. With the exception of the ethyl compound, the values of P'' given by configuration II are in the same order as the values of $[M]_D$.

Before arriving at any definite conclusion as to the applicability of Guey's hypothesis to the case of nitrogen, it will be necessary to await the results of our further experiments on the four series of compounds corresponding to the above in which the methyl group is replaced by ethyl and then by *isopropyl*.

The expenses of this investigation have been largely defrayed by grants placed at our disposal by the Government Grant Committee of the Royal Society, for which we are glad to make this grateful acknowledgement.

UNIVERSITY CHEMICAL LABORATORY,
CAMBRIDGE.