STUDIES ON THE DEPENDENCE OF OPTICAL ROTATORY POWER ON CHEMICAL CONSTITUTION

Part XXV. The Rotatory Dispersion of Salts of Camphor-β-Sulphonic Acids with Ammonia, o-, m- and p-Nitranilines, Pyridine and p-Aminobenzene Sulphonamide

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In a previous communication[1] the study of rotatory dispersion of salts of camphor-β-sulphonic acids with aniline, o-, m-, p-toluidines, α- and β-naphthylamine and ar-tetrahydro-α-naphthylamine was described. In the present paper we have extended this work to camphor-β-sulphonates of ammonia, o-, m- and p-nitranilines, pyridine and p-aminobenzene sulphonamide. The influence of chemical constitution, the nature of the solvent, and wavelength of light on rotatory power has also been discussed.

Schreiber and Shriner's[2] and our previous work[1] have shown that the primary amine salts of camphor-β-sulphonic acids undergo mutarotation in non-aqueous solvents and that it is the result of a structural change in the salt into ketimine or anil. This change is possible only in the case of camphor-β-sulphonates of primary amines and is not possible in the case of salts with secondary and tertiary amines. This view is further supported by our present studies: the camphor-β-sulphonates of primary amines, namely, o-, m-, and p-nitraniline and p-aminobenzene sulphonamide, undergo mutarotation in non-aqueous solvents, whereas those of pyridine, which is a tertiary amine, do not behave in this way as was to be expected (*vide* Tables IV to VIII).

THE EFFECT OF CHEMICAL CONSTITUTION ON ROTATORY POWER

All the compounds investigated in this paper exhibit " simple dispersion " and obey Drude's one term equation, $[\alpha] = \dfrac{K}{\lambda^2 - \lambda_0^2}$. In this equation, K the rotation constant, may be taken as a measure of the rotatory power of the compound for that wavelength (λ) for which $\lambda^2 - \lambda_0^2 = 1$ sq. micron. This value of λ_0 is always found to lie in the infra-red region and is slightly greater than 10,000 Å.U. The constant K which is thus independent of the wavelength, may be termed the absolute rotation of the compound. In

Table I the comparative values for $[\alpha]^{35°}_{5461}$ and K (within brackets) are given for different solvents. In Table A the order of rotatory power for position isomerides in different solvents for $[\alpha]^{35°}_{5461}$ is given, the order of K is also given within square brackets.

TABLE A

Solvent	$[\alpha]_{5461}$
Methyl alcohol	$\{$ o- $< p$- $< Un$- $< m$- $\{$ $[o$- $< p$- $\lessgtr m$- $< Un$-$]$
Ethyl alcohol	$\{$ o- $< p$- $< m$- $< Un$- $\{$ $[o$- $< p$- $< n$- $< Un$-$]$
Pyridine	$\{$ p- $< o$- $< m$- $< Un$- $\{$ $[o$- $< p$- $< m$- $< Un$-$]$

On comparing values of K the sequence of position isomerides in all the solvents is o- $< p$- $< m$- $< Un$- but for $[\alpha]_{5461}$ the sequence in methyl alcohol is o- $< p$- $< Un$- $< m$-, in ethyl alcohol, o- $< p$- $< m$- $< Un$-, and in pyridine p- $< o$- $< m$- $< Un$. In the comparison of $[\alpha]$ the choice of wavelength 5461 A.U. is quite arbitrary. By selecting different wavelengths different results follow ; thus the order of position isomerides in pyridine for $[\alpha]_{5893}$ is o- $< p$- $< m$- $< Un$-, which is different from that observed for Hg $_{5461}$. These results are neither in agreement with Frankland's " lever arm " hypothesis[3,3a] nor with the electrostatic modification as suggested by Rule[4] according to both of which the *meta* isomer should be intermediate between *ortho* and *para*.

Substituent groups may be arranged according to their polarities. Rule[4] has also shown that the arrangement of groups according to their polarities follows a general order, with minor differences, whether the order is deduced from benzene substitution data, influence of various groups on dissociation constant of substituted acetic or benzoic acids or on the basis of electronic theory, and that the order is :

$$\overline{OH},\ Cl,\ Br,\ I,\ Et,\ \overline{Me},\ \overset{+}{H},\ COOH,\ CHO,\ COCH_3,\ CN,\ \overset{+}{NO_2}$$

Since the effect of polar groups is traceable on rotatory power,[5] it is found that in general the replacement of a hydrogen atom in an optically active compound by a positive substituent displaces the rotation in the opposite sense to that due to a negative substituent, and further, in general, a positive group should increase the rotation and a negative group should cause a decrease in rotation. In Table B a comparison is made of the effects of $-CH_3$ and $-NO_2$ groups, the rotations are given as $[\alpha]^{35°}_{4561}$ and the values of K are also given within brackets.

TABLE B

Camphor-β-sulphonates of	$[\alpha]_{5461}^{35°}$ in solvent		
	Methyl alcohol	Ethyl alcohol	Pyridine
1. Aniline[1]	32·40 (6·284)	36·40 (6·997)	36·10 (7·57)
2. o-Toluidine[1]	29·60 (5·685)	34·74 (6·88)	36·20 (7·93)
o-Nitraniline	29·97 (3·793)	29·50 (3·666)	31·94 (4·051)
3. m-Toluidine[1]	28·90 (5·661)	34·10 (6·79)	35·50 (7·74)
m-Nitraniline	34·47 (5·882)	35·38 (5·432)	35·97 (5·185)
4. p-Toluidine[1]	30·47 (5·96)	35·50 (6·95)	37·60 (7·81)
p-Nitranilne	30·47 (4·536)	30·42 (4·195)	31·42 (4·782)

On comparing the values of K for pyridine it is found that in all the three cases, *i.e., ortho, meta* and *para* substituents, the displacement caused by the electronegative $-CH_3$ group is in the opposite sense to that caused by the electropositive $-NO_2$ group. Comparison of $[\alpha]_{5461}$ in pyridine leads to similar conclusions except in the case of *meta* substituent. The values in other solvents are not in general agreement with the rule probably owing to the solvent effect. True comparisons can, however, be made only in the liquid state in the absence of solvents.

The electronegative $-CH_3$ group should cause a decrease in rotation.[6] The results recorded in Table B bear this out. It is found that substitution of $-CH_3$ whether in the *o-, m-* or *p*-position causes a decrease in rotation in all the solvents except in the case of *ortho* and *para* substituents in pyridine. On the other hand, the effect of electropositive $-NO_2$ group should be to cause an increase in the rotation.[7] The results given in Table B do not conform to this. Here again, the choice of the wavelength 5461 A.U. is quite arbitrary. If, however, we select the wavelength 5209 A.U. for comparison we find that in pyridine, *m*-nitranilino camphor-β-sulphonates have higher rotations than aniline salts.
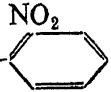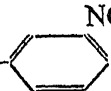
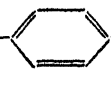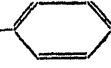EFFECT OF SOLVENT ON ROTATORY POWER

It is observed (Table I) that for nitraniline salts the order of decreasing rotatory power for Hg_{5461} is pyridine > methyl alcohol > ethyl alcohol > acetone, that for pyridine salts pyridine > methyl alcohol > ethyl alcohol > water, and that for *p*-aminobenzene sulphonamide salts pyridine <
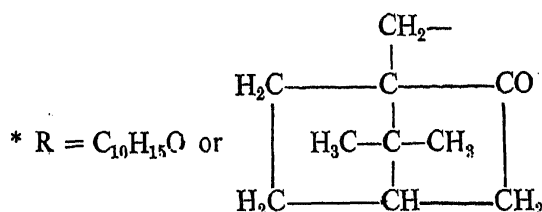
methyl alcohol > water. With the exception of ethyl alcohol and acetone in the case of nitraniline salts the order of decreasing rotatory power in different solvents runs parallel in the reverse sense with the sequence of the dielectric constants of these solvents.

The Nature of Rotatory Dispersion

All the optically active substances described in this paper give " simple[2] dispersion " and can be expressed by one term of Drude's equation, $[\alpha] = \dfrac{K}{\lambda^2 - \lambda_0^2}$. On plotting $1/a$ against λ^2, a straight line was obtained in each case. We have, however, applied the more stringent numerical test by working out these dispersion equations and the results are recorded in Tables III to VIII. It was found that the differences between observed specific rotatory power (o) and that calculated from the equation (c) agreed within

Table I

Structural formula	Solvent					
	Water	Acetone	Ethyl alcohol	Methyl alcohol	Pyridine	Chloroform
*R·SO₃H·NH₃	26·50† (3·99)	..	..	..	..	..
R·SO₃H·H₂N—⟨ ⟩	20·50 (3·40)	..	36·40 (6·997)	32·40 (6·284)	36·10 (7·57)	45·30 (9·276)
R·SO₃H·H₂N—⟨ ⟩ NO₂	..	28·98 (3·502)	29·50 (3·666)	29·97 (3·793)	31·94 (4·051)	..
R·SO₃H·H₂N—⟨ ⟩ NO₂	..	30·47 (4·455)	35·38 (5·432)	34·47 (5·882)	35·97 (5·185)	..
R·SO₃H·H₂N—⟨ ⟩—NO₂	..	28·45 (4·12)	30·42 (4·195)	30·47 (4·536)	31·42 (4·782)	..
R·SO₃H·N⟨ ⟩	26·00 (4·24)	..	38·50 (8·66)	39·96 (8·878)	52·50 (11·24)	..
R·SO₃H·H₂N—⟨ ⟩—SO₂NH₂	16·97 (2·793)	..	..	28·00 (4·571)	33·47 (5·61!)	..

$$* \ R = C_{10}H_{15}O \text{ or}$$

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                  CH₂—
                   |
   H₂C————————C————————CO
                   |
          H₃C—C—CH₃
                   |
   H₂C————————CH————————CH₂
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† Rotations are for Hg_{5461}. The values for rotation constant, k (absolute rotation), are given in brackets.

the limits of experimental error but for the sake of economy of space these differences (o—c) have been omitted from the tables.

THE PHYSICAL IDENTITY OF ENANTIOMERS

The rotatory power of d- and l-forms of these compounds are identical and thus further support Pasteur's principle of Molecular Dissymmetry: out of 472 observations, in as many as 358 cases difference in the numerical value of the specific rotatory power of the opposite isomers corresponds to a difference of less than $0.01°$ in the observed angle of rotation and in 102 cases the corresponding angle lies between $0.01°$ and $0.02°$, which is the limit of experimental error allowed in such measurements ; and only in 10 cases the difference corresponds to between $0.02°$ and $0.03°$, and in two cases the differences are larger ; all these are, however, of the nature of casual experimental errors.

NATURE OF RACEMIC MODIFICATION

The melting points of racemic forms of o- and p-nitraniline and pyridine camphor-β-sulphonates are higher than those of the optically active forms. These racemic forms are, therefore, true dl-coumponds in the solid state. In the case of m-nitraniline and p-aminobenzene sulphonamide camphor-β-sulphonates, a small amount of the d-form was added to the racemic modification and the melting point of the mixture was found to be lowered. Thus these racemic camphor-β-sulphonates are also true dl-compounds.[8]

TABLE II

Camphor-β-sulphonates of	Conc. in gms./100 c.c.	$[M]\lambda^{85°}$ in aqueous solution					
		Hg_{4358}	Li_{4603}	Cd_{4678}	Cd_{4800}	Cd_{5086}	Ag_{5209}
1. Ammonium	1·0000	. . .	154·4	137·0	122·0	89·64	79·68
2. Pyridine	1·0000	224·9	164·8	150·9	133·8	104·2	96·42
3. p-Aminobenzene sulphonamide	1·0016	260·4	145·2	135·1	119·0	92·76	76·65

Camphor-β-sulphonate of	Conc. in gm./100 c.c.	$[M]\lambda^{35°}$ in aqueous solution					
		Hg_{5461}	Hg_{5780}	Na_{5893}	Li_{6104}	Cd_{6438}	Li_{6708}
1 Ammonium	1·0000	65·98	54·78	51·05	43·57	38·59	32·37
2. Pyridine	1·0000	80 87	65·31	60·64	55·99	46·66	40·42
3. p-Aminobenzene sulphonamide	1·0016	68·57	58·51	52·46	46·37	40·32	34·26

The Molecular Rotatory Dispersion of Camphor-β-Sulphonates in Aqueous Solution and Comparison of the Value of Camphor-β-Sulphonate Ion in Water

Table II gives the values of $[M]_\lambda^{35°}$ in water for salts of ammonia, pyridine and p-aminobenzene sulphonamide with camphor-β-sulphonic acid. The mean value[9] for camphor-β-sulphonate ion in water is $[M]_D = 52°$. The value for $[M]_D^{35°}$ for ammonium, pyridine and p-aminobenzene sulphonamide camphor-β-sulphonates is $51 \cdot 05°$, $60 \cdot 64°$ and $52 \cdot 46°$ respectively. This shows that ammonium and p-aminobenzene sulphonamide salts of camphor-β-sulphonic acids are fairly completely electrolytically dissociated in 1% solution but pyridine salts are not so. A strict comparison would require, however, a knowledge of degree of ionisation of salts with dilution since the observed molecular rotation is due both to the active ion and the non-ionised molecule.

Experimental

Ammonium-camphor-β-sulphonates[10].—A weighed amount of d-, l- or dl-camphor-β-sulphonic acid was taken in a porcelain dish and excess of liquor ammonia added till the acid was completely dissolved. On evaporating to dryness the ammonium salt was obtained. It was then repeatedly recrystallised from a mixture of water and ethyl alcohol. The d-, l- and dl-salts which are crystalline are extremely soluble in water but sparingly so in organic solvents. (Found: d-salt, $NH_4 = 7 \cdot 33\%$; l-salt, $NH_4 = 7 \cdot 42\%$; dl-salt, $NH_4 = 7 \cdot 50\%$; $C_{10}H_{15}OSO_3NH_4$ requires $NH_3 = 7 \cdot 23\%$.)

Nitroanilino-camphor-β-sulphonates[11]. Molar amounts of each of the base and the camphor-β-sulphonic acids were dissolved separately in hot ethyl acetate. The two solutions were then mixed and allowed to stand when the salt crystallised out. They were then repeatedly recrystallised from a mixture of ethyl alcohol and ethyl acetate. They were dried at 80° C. in an air oven and then in vacuum. The camphor-β-sulphonates of o- and p-nitraniline crystallise out as yelllow coloured needles and of m-nitraniline as white flakes. These salts are freely soluble in ethyl alcohol, methyl alcohol, pyridine and acetone; sparingly so in water and insoluble in ethyl acetate, chloroform and benzene. All yield yellow coloured solutions.

o-Nitroanilino-camphor-β-sulphonates: Found: d-salt, M.P. 117–118° C; $S = 7 \cdot 80\%$; l-salt, M.P. 116–118° C., $S = 7 \cdot 93\%$; dl-salt, M.P. 124–125° C., $S = 7 \cdot 78\%$; $C_{10}H_{15}O$. $SO_3H.H_2N.C_6H_4.NO_2.2H_2O$ requires $S = 7 \cdot 88\%$. m-Nitranilino-camphor-β-sulphonates: (Found: d-salt, M.P. 178–180° C., $S = 8 \cdot 72\%$; l-salt, M.P. 179–180° C., $S = 8 \cdot 42\%$; dl-salt, M.P. 171–172° C., $S = 8 \cdot 79\%$; $C_{10}H_{15}OSO_3H.H_2N.C_6H_4.NO_2$ requires $S = 8 \cdot 65\%$. p-Nitranilno-

camphor-β-sulphonates: (Found: d-salt, M.P. 155–156° C., S = 7·39%; l-salt, M.P. 154–156° C., S = 7·66%; dl-salt, M.P. 160–161° C., S = 7·50%; $C_{10}H_{15}OSO_3H.H_2N.C_6H_4.NO_2.3H_2O$ requires S = 7·55%.

Pyridine-camphor-β-sulphonates.—Molar amounts of the base and the acid were dissolved in hot ethyl acetate. They were then mixed and allowed to stand in a cool place when the salt crystallised out. They were then repeatedly recrystallised from acetone and dried in vacuum over potash. All the three salts gave white needles.

They are freely soluble in water, ethyl alcohol, methyl alcohol and chloroform; less so in acetone and insoluble in benzene, ether and petroleum ether. (Found: d-salt, M.P. 185–190° C., eq. wt. = 310·4; S = 10·05%; l-salt, M.P. 185–190° C.; eq. wt. = 315·0, S = 10·40%; dl-salt, M.P. 189–190° C., eq. wt. = 305·9, S = 10·32%; $C_{10}H_{15}OSO_3H.NC_5H_5$ requires eq. wt. = 311·0; S = 10·30%.).

p-Aminobenzene-sulphonamido-camphor-β-sulphonates.—Molar amounts of p-aminobenzene–sulphonamide and camphor-β-sulphonic acids were dissolved separately in hot ethyl acetate. The two solutions were then mixed and allowed to stand. The salts crystallised out. They were repeatedly recrystallised as white needles from a mixture of absolute alcohol and ethyl acetate and dried in vacuum. They are freely soluble in water, methyl alcohol and pyridine; less so in ethyl alcohol and benzene, and insoluble in ethyl acetate, acetone, chloroform, ether and petroleum ether. (Found: d-salt, M.P. 176–182° C., eq. wt. = 408·0, S = 15·96%; l-salt, M.P. 176–181° C., eq. wt. = 400·0, S = 16·14%; dl-salt, M.P. 173–174° C., eq. wt. = 406·0, S = 15·99%; $C_{10}H_{15}OSO_3H.H_2N.C_6H_4.SO_2NH_2$ requires eq. wt. = 404·0; S = 15·84%.)

The d-, l- and dl-sulphonamide salts are being investigated for their pharmacological actions, the results of which will be described in a separate communication.

The rotatory power determinations were made in a 2-dcm. tube. All the determinations of rotatory power were carried out at 35° C. The value of λ_0, calculated from the dispersion formula, is given in the Tables (III to VIII) and is expressed as μ or, 10^{-4} cm.

TABLE III. *Ammonium-camphor-β-sulphonates in water*

$$[\alpha] = \pm \frac{3\cdot99}{\lambda^2 - \cdot1478}; \quad \lambda_0 = 0\cdot3844$$

Temperature 35° C.

d-Salt		Line	Calculated [α]	l-Salt	
Concentration in gm. 100 c.c.	Observed [α]			Observed [α]	Concentration in gm. 100 c.c.
1·0000	+93·00°	Hg_{4358}	94·56	—91·85°	1·0016
	62·00	Li_{4603}	62·24	62·90	
	55·00	Cd_{4678}	56·11	55·41	
	49 00	Cd_{4800}	48 31	48 42	
	36 00	Cd_{5086}	35·99	35·94	
	32·00	Ag_{5209}	32·31	32·44	
	26·50	Hg_{5461}	26·54	26·96	
	22·00	Hg_{5780}	21·42	21·46	
	20·50	Na_{5893}	20·01	19·96	
	17·50	Li_{6104}	17·76	17·97	
	15·50	Cd_{6438}	14·96	14·96	
	13·00	Li_{6708}	13·20	13·47	
No mutarotation				No mutarotation	

TABLE IV. *o-Nitranilino-camphor-β-sulphonates*

Solvent	Ethyl alcohol		Pyridine		Methyl alcohol		Acetone	
Concentration in gm./100 c.c. $\begin{cases} d- \\ l- \end{cases}$	1·0000 1·0016		1·0016 1·0000		1·0008 1·0000		1·0008 1·0000	
Calculated $\begin{cases} [\alpha] \\ \lambda_0 \end{cases}$	$\pm\dfrac{3\cdot666}{\lambda^2-0\cdot1744}$ 0·4176		$\pm\dfrac{4\cdot051}{\lambda^2-0\cdot1707}$ 0·4132		$\pm\dfrac{3\cdot793}{\lambda^2-0\cdot1715}$ 0·4141		$\pm\dfrac{3\cdot502}{\lambda^2-0\cdot1791}$ 0·4232	
Line	Obs. $[a]^{35°}$		Obs. $[a]^{35°}$		Obs. $[a]^{35°}$		Obs. $[a]^{35°}$	
	d-	l-	d-	l-	d-	l-	d-	l-
Cd_{5086}	+37·50°	—36·93°	+39·93°	—40·00°	+37·97°	—37·50°	+36·97°	—37·50°
Ag_{5209}	29·50	29·94	31·94	31·50	29·97	30·00	28·98	29·00
Hg_{5461}	23·00	22·46	24·95	25·00	24·98	23·50	23·48	22·00
Hg_{5780}	21·00	21·46	23·46	23·00	21·43	22·00	20·98	21·00
Na_{5893}	18·50	18·46	19·46	20·00	18·98	18·50	17·98	18·50
Li_{6104}	15·50	14·48	16·96	16·50	15·48	16·00	14·98	14·50
Cd_{6438}	13·50	13·98	14·48	15·00	13·98	13·50	12·99	13·50
Li_{6708}	Shows mutarotation. Rotation for Hg_{5461} for d-salt [a]=23·00 after 24 hrs. and for l-salt [a] = 22·46 after 49 hrs.		Solution turned dark after 48 hrs.		Shows mutarotation. Rotation for Hg_{5461} after 24 hrs. for d-salt [a] = 22·98 l-salt [a] = 22·00		Shows mutarotation. Rotation for Hg_{5461} after 23 hrs. for d-salt [a] = 21·48 l-salt [a] = 21·50.	

TABLE V. m-Nitranilino-camphor-β-sulphonates

Solvent	Ethyl alcohol	Pyridine	Methyl alcohol	Acetone
Concentration $\{d\text{-}$ in gm./100 c.c. $\{l\text{-}$	1·0032 1·0016	1·0008 1·0016	1·0008 1·0016	1·0008 1·0016
Calculated $\{[\alpha]$ $\{\lambda_0$	$\pm \dfrac{5·432}{\lambda^2-0·1428}$ 0·3779	$\pm \dfrac{5·185}{\lambda^2-0·1546}$ 0·3932	$\pm \dfrac{5·882}{\lambda^2-0·1294}$ 0·3597	$\pm \dfrac{4·455}{\lambda^2-0·1524}$ 0·3904
Line	Obs. $[a]^{35°}$	Obs. $[a]^{35°}$	Obs. $[a]^{35°}$	Obs. $[a]^{35°}$

Line	Ethyl d-	Ethyl l-	Pyridine d-	Pyridine -	Methyl d-	Methyl l-	Acetone d-	Acetone l-
Cd_{5086}	+46·85°	−46·92°	..	..	+45·46°	−45·92°	+42·46°	−42·43°
Ag_{5209}	41·86	41·43	+44·96°	−44·42°	41·96	41·93	37·47	36·94
Hg_{5461}	35·38	35·43	35·97	35·94	34·47	34·44	30·47	30·95
Hg_{5780}	28·41	28·95	28·48	28·95	28·47	28·95	24·98	24·96
Na_{5893}	26·91	26·45	26·98	26·95	27·47	26·95	22·98	22·46
Li_{6104}	23·93	23·46	23·47	23·46	24·47	23·95	19·98	19·96
Cd_{6438}	19·94	19·46	19·98	19·96	20·48	20·96	17·48	16·97
Li_{6708}	17·44	17·46	17·48	16·97	18·48	17·46	14·48	14·97

Ethyl alcohol: Shows mutarotation. Rotation for Hg_{5461} for d-salt $[a]=29·41$ after 70 hrs. and for l-salt $[a] = 30·45$ after 46 hrs.

Pyridine: Solution turned dark after 48 hrs.

Methyl alcohol: Shows mutarotation. Rotation for Hg_{5461} for d-salt $[a]=28·48$ after 22 hrs. and for l-salt $[a] = 27·45$ after 23 hrs.

Acetone: Shows mutarotation. Rotation for Hg_{5461} for d-salt $[a]=25·48$ after 47 hrs and for l-salt $[a] = 25·95$ after 25 hrs.

TABLE VI. p-Nitranilino-camphor-β-sulphonates

Solvent	Ethyl alcohol	Pyridine	Methyl alcohol	Acetone
Concentration $\{d\text{-}$ in gm.-100 c.c. $\{l\text{-}$	1·0024 1·0008	1·0024 1·0008	1·0008 1·0024	1·0016 1·0024
Calculated $\{[\alpha]$ $\{\lambda_0$	$\pm \dfrac{4·195}{\lambda^2-0·1604}$ 0·4005	$\pm \dfrac{4·782}{\lambda^2-0·1485}$ 0·3854	$\pm \dfrac{4·536}{\lambda^2-0·1500}$ 0·3873	$\pm \dfrac{4·12}{\lambda^2-0·1569}$ 0·3961
Line	Obs. $[a]^{35°}$	Obs $[a]^{35°}$	Obs. $[a]^{35°}$	Obs. $[a]^{35°}$

Line	Ethyl d-	Ethyl l-	Pyridine d-	Pyridine l-	Methyl d-	Methyl l-	Acetone d-	Acetone l-
Cd_{5086}	+41·89°	−41·47°	+43·39°	−43·46°	+41·97°	−41·89°	+40·93°	−40·39°
Ag_{5209}	37·41	37·47	38·91	38·47	36·97	37·41	35·93	35·91
Hg_{5461}	30·42	30·47	31·42	31·97	30·47	30·42	28·45	28·44
Hg_{5780}	25·44	24·98	25·94	26·48	24·98	24·94	23·96	24·44
Na_{5893}	22·44	22·48	23·94	23·98	22·98	22·94	21·96	21·94
Li_{6104}	19·95	19·98	21·44	21·48	20·48	20·45	19·46	18·95
Cd_{6438}	16·95	15·48	17·95	18·48	17·48	16·95	15·97	15·44
Li_{6708}	14·94	14·48	15·94	15·44	15·44	14·94	14·47	14·94

Ethyl alcohol: Shows mutarotation. Rotation for Hg_{5461} for d-salt $[a]=23·42$ after 22 hrs. and for l-salt $[a] = 23·98$ after 48 hrs.

Pyridine: Shows mutarotation. Rotation for Hg_{5461} for d-salt $[a]=28·43$ after 25 hrs. and for l-salt $[a] = 27·48$ after 49 hrs.

Methyl alcohol: Shows mutarotation. Rotation for Hg_{5461} for d-salt $[a]=27·47$ after 22½ hrs. and for l-salt $[a] = 27·43$ after 28 hrs.

Acetone: Shows mutarotation. Rotation for H_{5461} for d-salt $[a]=25·95$ after 25 hrs. and for l-salt $[a] = 25·94$ after 24 hrs.

TABLE VII. *Pyridino-camphor-β-sulphonates*

Solvent	Water	Ethyl alcohol	Methyl alcohol	Chloroform
Concentration {d- in gm./100 c.c. {l-	1·0000 1·0016	1·0000 1·0016	1·0008 1·0000	1·0000 1·0008
Calculated {$[\alpha]$ {λ_0	$\pm \dfrac{4\cdot24}{\lambda^2-0\cdot1321}$ 0·3634	$\pm \dfrac{8\cdot66}{\lambda^2-0\cdot0707}$ 0·2659	$\pm \dfrac{8\cdot878}{\lambda^2-0\cdot0760}$ 0·2757	$\pm \dfrac{11\cdot24}{\lambda^2-0\cdot0878}$ 0·2963

Line	Obs. $[a]^{35°}$		Obs. $[a]^{35°}$		Obs. $[a]^{35°}$		Obs. $[a]^{35°}$	
	d-	l-	d-	l-	d-	l-	d-	l-
Hg_{4358}	+74·00°	−72·88°	+74·00°	−72·88°	+78·43°	−76·00°	+110·00°	−109·90°
Li_{4603}	53·00	53·41	62·00	62·40	64·95	64·50	91·00	90·42
Cd_{4678}	48·50	48·92	58·50	58·90	60·95	61·50	87·00	86·42
Cd_{4800}	43·00	43·43	56·00	54·96	56·96	57·50	80·00	79·93
Cd_{5086}	33·50	33·94	46·00	45·93	47·96	48·50	67·00	66·44
Ag_{5209}	31·00	30·45	43·50	42·93	45·48	45·00	61·00	61·44
Hg_{5461}	26·00	25·46	38·50	37·94	39·96	40·00	52·50	52·95
Hg_{5780}	21·00	20·96	33·00	33·44	34·97	35·00	45·50	44·96
Na_{5893}	19·50	19·96	31·00	31·45	33·47	33·00	44·00	43·96
Li_{6104}	18·00	17·47	28·50	28·45	30·47	30·00	39·50	38·96
Cd_{6438}	15·00	14·47	25·00	25·45	25·97	26·50	33·50	33·97
Li_{6708}	13·00	13·48	22·50	22·46	22·48	24·00	30·00	30·47
	No mutarotation.		No mutarotation.		No mutarotation.		No mutarotation.	

TABLE VIII. *p-Aminobenzene-sulphonamido-camphor-β-sulphonates*

Solvent	Water	Methyl alcohol	Pyridine
Concentration {d- in gm./100 c.c. {l-	1·0016 1·0008	1·0000 1·0016	1·0008 1·0000
Calculated {$[a]$ {λ_0	$\pm \dfrac{2\cdot793}{\lambda^2-\cdot1346}$ 0·3668	$\pm \dfrac{4\cdot571}{\lambda^2-\cdot1322}$ 0·3636	$\pm \dfrac{5\cdot611}{\lambda^2-\cdot1294}$ 0·3597

Line	Obs. $[a]^{35°}$		Obs. $[a]^{35°}$		Obs. $[a]^{35°}$	
	d-	l-	d-	l-	d-	l-
Hg_{4358}	+64·44°	−63·94°	+81·00°	−77·85°	..	..
Li_{4603}	35·94	36·47	57·00	57·91	+67·44°	−69·00°
Cd_{4678}	33·44	32·97	52·00	52·91	61·95	62·50
Cd_{4800}	29·45	28·97	46·00	46·92	55·95	55·00
Cd_{5086}	22·96	22·48	36·00	36·44	42·96	43·50
Ag_{5209}	18·97	19·48	33·00	32·45	37·47	36·50
Hg_{5461}	16·97	17·48	28·00	27·95	33·47	33·50
Hg_{5780}	14·48	13·98	23·00	22·95	27·97	27·50
Na_{5893}	12·98	12·99	21·00	20·96	24·98	25·50
Li_{6104}	11·48	11·99	18·50	18·97	23·48	22·50
Cd_{6438}	9·98	9·99	16·50	15·97	19·98	19·00
Li_{6708}	8·48	8·49	14·00	13·96	16·98	17·50
	No mutarotation.		Shows mutarotation. Rotation for Hg_{5461} for d-Salt $[a]$=24·50 after 24 hrs. and for l-Salt $[a]$ = 23·96 after 23 hrs.		Shows mutarotation. Rotation for Hg_{5461} for d-Salt $[a]$=28·97 after 24½ hrs. and for l-Salt $[a]$ = 29·00 after 24 hrs.	

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