

# STUDIES ON THE DEPENDENCE OF OPTICAL ACTIVITY ON CHEMICAL CONSTITUTION

Part XXXIII. The Rotatory Dispersion of the Enantiomorphic Forms of *p*-Aminobenzene sulphonylamido-2-thiazolecamphor- $\beta$ -sulphonate, *p*-Sulphonamidophenyliminocamphor, Camphor- $\beta$ -sulphonylchloride, Camphor- $\beta$ -sulphonyl- $\alpha$ -pyridylamide and Camphor- $\beta$ -sulphonyl- $\alpha$ -thiazoleamide

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In a previous communication,<sup>1</sup> the camphor- $\beta$ -sulphonates (*d*-, *l*- and *dl*-) of some heterocyclic bases were studied. In the present paper we have extended our work to the optically active and racemic forms of *p*-aminobenzenesulphonamido-2-thiazolecamphor- $\beta$ -sulphonate, *p*-sulphonamidophenyliminocamphor, camphor- $\beta$ -sulphonylchloride, camphor- $\beta$ -sulphonyl- $\alpha$ -pyridylamide and camphor- $\beta$ -sulphonyl- $\alpha$ -thiazoleamide.

## INFLUENCE OF WAVELENGTH ON ROTATORY DISPERSION

The rotatory dispersion of all the optically active substances described in this paper has been determined in the visible region of the spectrum for 12 wavelengths from  $\lambda_{6708}$  Å.U. to  $\lambda_{4358}$  Å.U. (Tables III to VII). It is found to be "simple" as it can be expressed by the one-term Drude's equation,

$$[\alpha] = \frac{k_0}{\lambda^2 - \lambda_0^2}$$
 In this equation,  $k_0$  is a constant which is independent of the effects of dispersion. It may be considered as a measure of the absolute rotatory power of the substance. It refers to that wavelength  $\lambda$ , where  $\lambda^2 - \lambda_0^2 = 1$  square micron, a value of  $\lambda$  not very much greater than 10,000 Å.U. Since measurements recorded in the present investigation are upto 6708 Å.U., an extrapolation, when the dispersion is simple, to a value of  $\lambda$  slightly greater than 10,000 Å.U., is both simple and accurate. In such cases,  $k_0$  may be termed the "Absolute" rotation of the compound.

## THE PHYSICAL IDENTITY OF ENANTIOMERS

The rotatory power of *d*- and *l*- enantiomers (Tables III to VII) are identical within the limits of experimental error and thus support Pasteur's

law of Molecular Dissymmetry according to which the optically active and opposite isomers possess rotatory powers identical in magnitude but opposite in sign. In the case of all the compounds described in this paper, the calculated values of rotatory power ( $c$ ) for different wavelengths agree with the observed ones ( $o$ ). The calculated values ( $c$ ) and the differences ( $o - c$ ) are omitted from the Tables (III to VII) for the sake of economy of space. Out of 526 observations recorded, in as many as 468 cases, the differences between the observed and the calculated values of specific rotations correspond to a deviation of  $0.02^\circ$  or less in the observed angle of rotation, and in as many as 37 cases this deviation lies between  $0.02^\circ$  and  $0.03^\circ$ . Only in 23 cases, mostly for  $Hg_{4358}$  and  $Cd_{6439}$  (mercury violet and cadmium red)—lines difficult to read—this difference lies between  $0.03^\circ$  and  $0.05^\circ$ . These deviations between the observed and the calculated values of rotatory power are, however, of the nature of casual experimental errors.

#### NATURE OF THE RACEMIC MODIFICATIONS

The melting points of the racemic modifications of *p*-aminobenzene-sulphonylamido-2-thiazole camphor- $\beta$ -sulphonate, *p*-sulphonylamidophenyl-aminocamphor, camphor- $\beta$ -sulphonylchloride and camphor- $\beta$ -sulphonyl- $\alpha$ -pyridylamide are higher than those of their optical isomers. They are, therefore, true *dl*-compounds in the solid state. The melting point of the racemic form of camphor- $\beta$ -sulphonyl- $\alpha$ -thiazole amide is identical with that of its optical isomer. That the racemic form of this substance is also a true *dl*-compound was determined in the following way: a small amount of the *d*-form was added to the corresponding racemic modification and the melting point of the mixture was lowered showing thereby that the racemic modification is a true *dl*-compound.

#### THE MOLECULAR ROTATORY DISPERSION OF CAMPHOR- $\beta$ -SULPHONATES IN AQUEOUS SOLUTION AND COMPARISON OF THE VALUE OF $[M]_D^{35^\circ}$ OF CAMPHOR- $\beta$ -SULPHONATE ION IN WATER

The values of  $[M]_\lambda^{35^\circ}$  in aqueous solution for *p*-aminobenzene sulphonylamido-2-thiazole-*d*-camphor- $\beta$ -sulphonate are given in Table I. Its value of  $[M]_D^{35^\circ}$  is found to be  $+65.73^\circ$ . As this value of the rotatory power of the salt is higher than the mean value of  $[M]_D^{35^\circ}$  of the camphor- $\beta$ -sulphonate ion ( $53-54^\circ$ )<sup>2</sup> and as the observed molecular rotatory power of the salt in aqueous solution is the sum of the rotatory powers of the active acid ion and the non-ionised molecule, it is clear that the undissociated molecule has higher rotatory power and that the salt is not completely electrolytically dissociated even in 0.5% aqueous solution.

TABLE I

Line	$[M]_{\lambda}^{35^{\circ}}$ in aqueous solution for camphor- $\beta$ -sulphonates of <i>p</i> -aminobenzene-sulphonamido-2-thiazole (0.5000 gm./100 c.c.)
Hg <sub>4353</sub>	265.1°
Li <sub>4603</sub>	180.2
Cd <sub>4678</sub>	168.0
Cd <sub>4800</sub>	155.8
Cd <sub>5086</sub>	119.6
Ag <sub>5209</sub>	107.1
Hg <sub>5461</sub>	87.76
Hg <sub>5780</sub>	68.17
Na <sub>5893</sub>	65.73
Li <sub>6104</sub>	60.87
Cd <sub>6438</sub>	58.43
Li <sub>6708</sub>	38.95

THE EFFECT OF SOLVENT ON THE ROTATORY POWER

The molecular rotatory power,  $[M]_D^{35^{\circ}}$ , of the compounds in different solvents is given in Table II. The sequence of their decreasing rotatory power is given below:

(a) *p*-Aminobenzenesulphonylamido-2-thiazolecamphor- $\beta$ -sulphonates.—

Pyridine > Ethyl alcohol > Methyl alcohol > Water.

The sequence agrees with that of their dielectric constants but in the reverse order.

(b) *p*-Sulphonamidophenyliminocamphors.—

Chloroform > Pyridine > Acetone > Ethyl alcohol > Methyl alcohol.

The above order of decreasing rotatory power is exactly in the reverse order of their dielectric constants.

(c) Camphor- $\beta$ -sulphonylchlorides.—

Pyridine > Methyl alcohol > Ethyl alcohol > Acetone > Chloroform > Benzene.


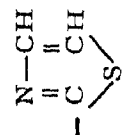
This order of decreasing rotatory power runs exactly parallel to the dielectric constants of the solvents except for pyridine which sometimes behaves abnormally.

(d) Camphor- $\beta$ -sulphonyl- $\alpha$ -pyridylamides.—

Acetone > Chloroform > Pyridine > Ethyl alcohol > Methyl alcohol.

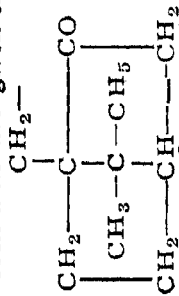
TABLE II

No.	Structural formula	[M] <sup>36°</sup>							
		Water (80)*	Methyl Alcohol (31.2)	Ethyl Alcohol (25.8)	Acetone (21.5)	Pyridine (12.4)	Chloroform (5.2)	Ether 4.3	Benzene (2.28)
1 <sup>c</sup>	† R·SO <sub>3</sub> H·H <sub>2</sub> N [325] <sup>a</sup> 	66.64 (11.05) <sup>b</sup>	105.3 (20.43)	118.3 (22.74)	..	117.3 (24.60)	147.2 (30.15)	..	..
2 <sup>c</sup>	R·SO <sub>3</sub> H·H <sub>2</sub> N [404] 	68.57 (11.28)	113.2 (18.47)	..	..	135.2 (22.68)	..	..	..
3 <sup>d</sup>	R·SO <sub>3</sub> H·H <sub>2</sub> N [481] 	..	96.18 (23.73)	108.2 (24.16)	120.2 (27.00)	..	..	..	..
4	R·SO <sub>3</sub> H·H <sub>2</sub> N·C [487] 	65.73 (14.61)	111.8 (24.12)	116.9 (25.33)	..	126.6 (27.29)	..	..	..
5 <sup>e</sup>	C <sub>8</sub> H <sub>14</sub> [166] 	..	113.6 (13.24)	164.7 (20.04)	180.7 (22.86)	..	175.1 (21.57)	168.2 (20.17)	180.4 (22.91)
6 <sup>e</sup>	C <sub>8</sub> H <sub>14</sub> [241] 	..	1436 (265.4)	1489	1462 (282.2)	..	1597 (302.6)	1424 (265.60)	1622 (303.9)
7	C <sub>8</sub> H <sub>14</sub> [320] 	..	1074 (201.8)	1168 (218.5)	1202 (224.3)	1206 (225.3)	1250 (230.9)	..	..

8 <sup>f</sup>	$C_{10}H_{15}O \cdot SO_2 \cdot OH$ [232]	55.94	..	..	..	..	..	..	..
9	$C_{10}H_{15}O \cdot SO_2Cl$ [250.5]	..	119.0 (30.71)	98.95 (24.92)	87.68 (22.23)	124.0 (32.06)	..	80.16 (19.28)	71.39 (17.44)
10 <sup>g</sup>	$C_{10}H_{15}O \cdot SO_2Br$ [295]	..	..	..	..	..	..	76.6	..
11 <sup>g</sup>	$C_{10}H_{15}O \cdot SO_2NH_2$ [231]	..	..	..	..	..	..	3.465	..
12 <sup>g</sup>	$C_{10}H_{15}O \cdot SO_2NH$ [307]	..	..	..	..	..	..	206.5	..
13	$C_{10}H_{15}O \cdot SO_2 \cdot NH$ —  [308]	..	107.2 (24.65)	110.9 (26.63)	141.7 (37.06)	123.2 (30.75)	..	127.8 (30.95)	..
14	$C_{10}H_{15}O \cdot SO_2NH$ —  [314]	..	109.9 (26.07)	117.7 (28.80)	149.1 (39.59)	130.3 (32.03)	..	138.1 (33.20)	..

\* The values of dielectric constants are given in brackets.

† R =  $C_{10}H_{15}O$  or



α The values in square brackets refer to molecular weights.

β The values in brackets refer to molecular rotation constant,  $\frac{M \times k}{100}$ , in Drude's equation.

γ The values of  $\frac{M \times k}{100}$  for (1) & (2) are calculated from Singh, B. K., and Perti, O. N., *Proc. Ind. Acad. Sci.*, 1945, 22, 8.

δ The values of  $\frac{M \times k}{100}$  for (3) is taken from Singh, B. K., and Manhas, K. M. S., *ibid.*, 1947, 26, 61.

ε The values of  $\frac{M \times k}{100}$  for (5) & (6) are calculated from Singh, B. K., Mallik, H. P., and Bahaduri, B., *J. I. C. S.*, 1931, 8, 6.

f The values are taken from Hilditch, T. P., *Jour. Chem. Soc.*, 1912, 101, 192.

g The values for Nos. 10, 11 and 12 are taken from Armstrong, H. E. and Lowry, T. M., *ibid.*, 1902, 81, 1441.

The sequence agrees with that of their dielectric constants in the reverse order except for acetone.

(e) *Camphor- $\beta$ -sulphonyl- $\alpha$ -thiazoleamides.*—

Acetone > Chloroform > Pyridine > Ethyl alcohol > Methyl alcohol.

This sequence is again in the reverse order of their dielectric constants except for acetone.

Similar results follow if we compare the order of molecular rotation constants,  $K_0$ , with the dielectric constants of the solvents in which the dispersion of these compounds is observed. The values of  $k_0$ 's are given in brackets (Table II).

As already pointed out in our previous work<sup>1,3</sup> it would, however, be more rational to compare the rotatory power of the solutions with their dielectric constants and not with the dielectric constants of the solvents.

#### THE EFFECT OF SUBSTITUENT GROUPS ON ROTATORY POWER

Rule<sup>4</sup> has 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 constants of substituted acetic or benzoic acids or on the basis of electronic theory and that the order is

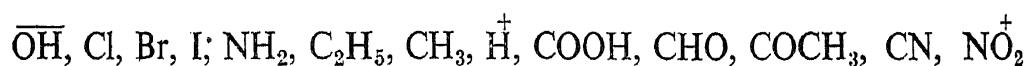


TABLE A

No.	Structural formula	$[\alpha]_D^{20}$ in chloroform
I ..	$\text{C}_{10}\text{H}_{15}\text{O}\cdot\text{SO}_2\cdot\text{OH}$ (a)	39.47°
II ..	$\text{C}_{10}\text{H}_{15}\text{O}\cdot\text{SO}_2\cdot\text{Cl}$ (b)	32.0°
III ..	$\text{C}_{10}\text{H}_{15}\text{O}\cdot\text{SO}_2\cdot\text{Br}$ (c)	26.0°
IV ..	$\text{C}_{10}\text{H}_{15}\text{O}\cdot\text{SO}_2\cdot\text{NH}_2$ (c)	1.5°
V ..	$\text{C}_{10}\text{H}_{15}\text{SO}_2\cdot\text{N}$ (c)	-33.5°

(a) Hilditch, T. P., *Jour. Chem. Soc.*, 1912, **101**, 192.

(b) The present measurements were made at 35° C.

(c) Armstrong, H. E., and Lowry, T. M., *Jour. Chem. Soc.*, 1902, **81**, 1441.

In Table A the values of  $[\alpha]_D^{20}$  in chloroform of camphor- $\beta$ -sulphonic acid and its four derivatives are given. On comparing these values of  $[\alpha]_D^{20}$ , it is found that the order of rotatory power for the different substituents is  $\text{OH} > \text{Cl} > \text{Br} > \text{NH}_2$  which runs exactly parallel to the above mentioned polar series.

THE RELATION BETWEEN CHEMICAL CONSTITUTION AND ROTATORY POWER

In Table II the molecular rotatory powers,  $[M]_D^{35^\circ}$ , of 14 compounds in different solvents are given. The values of Drude's molecular rotation constants,  $\frac{M \times k}{100}$ , have also been included for the sake of comparison and are shown in brackets.

1. It is seen that the sulphathiazole salt (4) has higher rotatory power than the sulphapyridine salt (3). This supports our previous observation,<sup>1</sup> namely, that the thiazole ring has a higher rotatory effect than the pyridyl nucleus. A comparison of the values of  $\frac{M \times k}{100}$  also bears out similar relationship.

2. (a) The replacement of an hydrogen atom of the phenyl group in the phenyliminocamphor (6) by  $-\text{SO}_2\text{NH}_2$  group in *p*-sulphonamidophenyliminocamphor (7) depresses the rotatory power, whereas a similar replacement in anilincamphor- $\beta$ -sulphonate (1) increases the rotatory power in *p*-aminobenzene sulphonamido camphor- $\beta$ -sulphonate (2).

(b) The values of the molecular rotation constants,  $\frac{M \times k}{100}$  in organic solvents of two compounds (1 and 6, Table II) are depressed by substitution of an hydrogen atom by  $-\text{SO}_2\text{NH}_2$  group (2 and 7, Table II) but are enhanced in water.

3. (a) The replacement of the hydroxy group in camphor- $\beta$ -sulphonic acid (8) by Cl, Br and  $\text{NH}_2$  (compounds numbered 9,10, 11, Table II) decreases the rotatory power in the order  $\text{Cl} < \text{Br} < \text{NH}_2$ . The depression of the rotatory power caused by the  $-\text{NH}_2$  group (II) is phenomenal as the value of  $[M]_D^{17^\circ}$ , in camphor- $\beta$ -sulphonamide (11) in chloroform is as low as  $3.5^\circ$ .

(b) The replacement of an hydrogen atom in the  $\text{SO}_2\text{NH}_2$  group of camphor- $\beta$ -sulphonamide (11) by a phenyl radical (12) enhances the molecular rotatory power considerably from  $3.5^\circ$  to  $206.5^\circ$ . This effect, however, is less marked in pyridyl (13) and thiazole (14) derivatives (Table II).

(c) It will be further observed that the thiazole derivative (14) has higher molecular rotatory power than the pyridyl compound (13) in agreement with the above mentioned observation on salts of camphor- $\beta$ -sulphonic acids (Tables II, 3 and 4).

Similar results follow when a comparison is made of the values of molecular rotation constants,  $\frac{M \times k}{100}$ .





accompanied by a great change (increase) in rotatory power with ring closure.

### EXPERIMENTAL

#### *p*-Aminobenzenesulphonylamido-2-thiazole-camphor- $\beta$ -sulphonates

Molar proportions of *p*-aminobenzene sulphonylamido-2-thiazole and camphor- $\beta$ -sulphonic acid (*d*-, *l*- or *dl*- form) were dissolved separately in absolute ethyl alcohol and ethyl acetate respectively. The two solutions were mixed and allowed to stand. The salt crystallised out on scratching the sides of the container. They were repeatedly recrystallised as white rectangular plates from a mixture of ethyl alcohol and ethyl acetate. These salts are fairly soluble in pyridine and methyl alcohol, less so in ethyl alcohol and water and practically insoluble in acetone, chloroform, benzene and ether. (Found: *d*-salt, m.p. 202° C.–204° C.; eq. wt. = 483.9, S = 20.09%, *l*-salt, m.p. 202° C.–204° C., eq. wt. = 487, S = 19.63%, *dl*-salt, m.p. 208° C.–210° C., eq. wt. = 487, S = 19.81%; C<sub>19</sub>H<sub>25</sub>O<sub>6</sub>S<sub>3</sub> requires eq. wt. = 487, S = 19.7%.)

#### *p*-Sulphonamido phenyl imino camphors

Molar proportions of camphorquinone (*d*-, *l*- or *dl*-form) and *p*-aminobenzenesulphonamide (1.66 gm. and 1.72 gm. respectively) were ground together with anhydrous sodium sulphate (3 gm.). The mixture was suspended in absolute ethyl alcohol (10 c.c.) and refluxed on a water-bath for about six hours. On extraction with water, the compounds precipitated out. They were filtered, washed well with water and after repeated recrystallisations from dilute ethyl alcohol were obtained as yellow glistening rectangular plates. These compounds are fairly soluble in acetone, pyridine, methyl alcohol and chloroform, sparingly so in ethyl alcohol and practically insoluble in water, benzene and ether. The yield was about 2 grams. (Found *d*-salt, m.p. 228° C., S = 10.02%; *l*-salt, m.p. 228° C., S = 9.73%; *dl*-salt, m.p. 240° C., S = 10.12%; C<sub>16</sub>H<sub>20</sub>N<sub>2</sub>SO<sub>3</sub> requires S = 10.00%.)

#### Camphor- $\beta$ -sulphonylchlorides<sup>9</sup>

30 gm. of camphor- $\beta$ -sulphonic acid (*d*-, *l*- and *dl*- form) were suspended in 60 c.c. of dry benzene in a round-bottomed flask and 30 c.c. of well cooled thionyl chloride was gradually added. The flask was fitted with a water condenser guarded with a calcium chloride tube and placed in an ice-bath for overnight. It was then refluxed on a water-bath till the unused camphor- $\beta$ -sulphonic acid had dissolved. The excess of thionyl chloride was distilled off and then the excess of benzene was removed under reduced

pressure. The contents of the flask were then cooled and allowed to crystallise. They were filtered at the pump, washed with petroleum-ether and finally recrystallised as fine prisms out of petroleum-ether (animal charcoal). The mother liquor was also worked out to yield a further crop of crystals. The camphor- $\beta$ -sulphonyl chlorides are soluble in pyridine, acetone, chloroform, benzene, ether, ethyl alcohol and methyl alcohol, very sparingly soluble in petroleum-ether and practically insoluble in water. The yield was about 15 gm. (Found: *d*-compound, m.p. 67° C., S = 12.63%; *l*-compound, m.p. 67° C., S = 12.69%; *dl*-compound, m.p. 72–74° C., S = 12.94%;  $C_{10}H_{15}SO_3Cl$  requires S = 12.77%.)

#### *Camphor- $\beta$ -sulphonyl- $\alpha$ -pyridylamides*

Molar amounts of camphor- $\beta$ -sulphonyl chloride (*d*-, *l*- or *dl*-form),  $\alpha$ -aminopyridine and pyridine were mixed together. The mixture was then refluxed for about 6 hours in an oil-bath at about 150° C. The resulting product in each case was then extracted with water, filtered and finally recrystallised as small rectangular plates from ethyl alcohol. It is fairly soluble in pyridine, chloroform and methyl alcohol, sparingly so in ethyl alcohol and acetone and practically insoluble in benzene, water and ether. (Found: *d*-compound, m.p. 208°–10° C., S = 10.33%; *l*-compound, m.p. 209°–10° C., S = 10.42%; *dl*-salt, m.p. 216°–18° C., S = 10.61%;  $C_{15}H_{20}N_2SO_3$  requires S = 10.4%.)

#### *Camphor- $\beta$ -sulphonyl- $\alpha$ -thiazoleamides*

Molar quantities of camphor- $\beta$ -sulphonyl chloride (*d*-, *l*- or *dl*-form)- $\alpha$ -aminothiazole and pyridine were mixed together and refluxed in an oil-bath at about 150° C. for six hours. The resulting mass in each case was extracted with water, filtered and finally recrystallised as fine needles from ethyl alcohol. It is fairly soluble in pyridine and chloroform, less so in methyl alcohol, ethyl alcohol and acetone and practically insoluble in water, benzene and ether. (Found: *d*-compound, m.p. 238°–40° C., S = 20.57%; *l*-compound, m.p. 238°–40° C., S = 20.12%; *dl*-compound, m.p. 238–40° C., S = 20.49%;  $C_{13}H_{18}N_2S_2O_3$  requires S = 20.4%.)

The rotatory power determinations were made in a 2-dcm. jacketed tube. The rotatory power determinations were carried out at approximately 35° C. The values of  $\lambda_0$  calculated from the dispersion formulæ, are given in Tables III to VII and are expressed as  $\mu$  or  $10^{-4}$  cm.

TABLE III  
p-Aminobenzenesulphonylamido-2-thiazolecamphor-β-sulphonates

Solvent	Water	Methyl alcohol	Ethyl alcohol	Pyridine
Concentration in gm/100 c.c.	0.2500 0.2500	1.0000 1.0000	1.0000 1.0000	1.0000 1.0000
Calculated $\left\{ \begin{array}{l} [\alpha] \\ \lambda_0 \end{array} \right.$	$\pm \frac{3.001}{\lambda^2 - 0.1328}$ 0.3644	$\pm \frac{4.953}{\lambda^2 - 0.1319}$ 0.3631	$\pm \frac{5.203}{\lambda^2 - 0.1304}$ 0.3611	$\pm \frac{5.602}{\lambda^2 - 0.1318}$ 0.3630
Line	Obs. $[\alpha]$	Obs. $[\alpha]$	Obs. $[\alpha]$	Obs. $[\alpha]$
Li <sub>6708</sub>	$d^+$ + 8.00°	$d^+$ + 15.00°	$d^+$ + 16.00°	$d^+$ + 18.00°
Cd <sub>6438</sub>	..	..	..	..
Li <sub>6104</sub>	..	..	..	..
N <sub>26893</sub>	..	..	..	..
Hg <sub>5780</sub>	..	..	..	..
Hg <sub>5461</sub>	..	..	..	..
Ag <sub>5209</sub>	..	..	..	..
Cd <sub>5086</sub>	..	..	..	..
Cd <sub>4800</sub>	..	..	..	..
Cd <sub>4678</sub>	..	..	..	..
Li <sub>4608</sub>	..	..	..	..
Hg <sub>4358</sub>	..	..	..	..
	$d^+$ + 12.00 12.50 13.50 14.00 15.00 18.00 22.00 24.50 32.00 34.50 37.00 54.50	$d^+$ + 18.50 20.00 23.00 24.50 29.50 36.00 40.00 51.50 57.00 62.00 87.50	$d^+$ + 18.00 21.00 24.00 26.00 31.00 37.00 40.50 52.50 57.00 64.00 89.00	$d^+$ + 19.00 24.00 26.00 27.50 33.50 41.00 45.00 56.00 65.00 70.00 100.00
	$l^-$ - 8.50° 9.50 12.00 14.00 15.00 18.00 22.00 24.00 31.50 35.50 38.00 50.50	$l^-$ - 16.00° 18.00 20.00 23.50 24.00 29.00 35.00 40.00 50.00 56.50 62.50 86.00	$l^-$ - 16.50° 19.00 21.00 23.50 25.00 31.50 36.50 40.00 52.50 58.00 63.50 88.50	$l^-$ - 17.50° 20.00 23.00 26.00 28.00 33.50 40.50 44.50 56.00 64.00 70.00 98.00

TABLE IV  
p-Sulphonamidophenyliminocamphors

Solvent	Methyl alcohol	Ethyl alcohol	Acetone	Pyridine	Chloroform
Concentration in gm./100 c.c.	$\left\{ \begin{array}{l} d- \\ l- \end{array} \right.$	$\left\{ \begin{array}{l} 0.5000 \\ 0.2500 \end{array} \right.$	$\left\{ \begin{array}{l} 0.5000 \\ 0.5000 \end{array} \right.$	$\left\{ \begin{array}{l} 0.5000 \\ 0.5000 \end{array} \right.$	$\left\{ \begin{array}{l} 0.5000 \\ 0.5000 \end{array} \right.$
Calculated $\left\{ \begin{array}{l} [\alpha] \\ \lambda_0 \end{array} \right.$	$\pm \frac{63.06}{\lambda^2 - 0.1588}$ 0.3985	$\pm \frac{68.28}{\lambda^2 - 0.1581}$ 0.3976	$\pm \frac{70.10}{\lambda^2 - 0.1605}$ 0.4006	$\pm \frac{70.26}{\lambda^2 - 0.1617}$ 0.4021	$\pm \frac{72.16}{\lambda^2 - 0.1630}$ 0.4037
Line	Obs. $[\alpha]$	Obs. $[\alpha]$	Obs. $[\alpha]$	Obs. $[\alpha]$	Obs. $[\alpha]$
Li <sub>6708</sub>	$\left\{ \begin{array}{l} d- \\ l- \end{array} \right.$	$\left\{ \begin{array}{l} d- \\ l- \end{array} \right.$	$\left\{ \begin{array}{l} d- \\ l- \end{array} \right.$	$\left\{ \begin{array}{l} d- \\ l- \end{array} \right.$	$\left\{ \begin{array}{l} d- \\ l- \end{array} \right.$
Cd <sub>6436</sub>	+216.5°	+233.6°	+240.5°	+243.8°	+251.7°
Li <sub>6704</sub>	245.0	263.7	279.8	278.6	287.3
Na <sub>5893</sub>	293.4	319.9	331.6	331.8	342.5
Hg <sub>5780</sub>	335.6	365.1	375.8	376.9	390.6
Hg <sub>5461</sub>	352.0	386.3	401.9	405.7	420.6
Ag <sub>5209</sub>	451.8	487.3	509.0	514.6	534.5
Cd <sub>5086</sub>	561.6	634.9	633.9	642.4	667.8
	632.7	679.5	714.4	..	..
	630.1	679.9	715.1	..	..
	630.2	630.1	633.1	642.7	667.3
	560.2	630.1	633.1	642.7	667.3
	451.3	485.7	506.8	515.2	532.0
	353.5	383.5	401.9	408.9	420.3
	335.9	358.6	374.2	376.7	392.2
	293.1	320.2	332.0	334.8	343.5
	248.6	268.8	277.7	276.3	287.7
	-217.8°	-236.4°	-241.3°	-241.8°	-250.6°

TABLE V  
Camphor-β-sulphonylchlorides

Solvent	Benzene	Chloroform	Acetone	Ethyl Alcohol	Methyl Alcohol	Pyridine
Concentration in { gm./100 c.c.	0.5000 0.5000	1.0000 1.0000	1.0000 1.0000	1.0000 1.0000	1.0000 1.0000	1.0000 1.0000
Calculated { [α] λ <sub>0</sub>	± 6.959 λ <sup>2</sup> -0.1030 0.3209	± 7.697 λ <sup>2</sup> -0.1010 0.3178	± 8.877 λ <sup>2</sup> -0.0935 0.3058	± 9.95 λ <sup>2</sup> -0.09543 0.3089	± 12.257 λ <sup>2</sup> -0.08913 0.2986	± 12.796 λ <sup>2</sup> -0.0888 0.2980
Line	Obs. [α]	Obs. [α]	Obs. [α]	Obs. [α]	Obs. [α]	Obs. [α]
Li <sub>6708</sub>	d <sup>-</sup> +19.50°	d <sup>+</sup> +23.00°	d <sup>+</sup> +24.00°	d <sup>-</sup> +28.50°	d <sup>+</sup> +32.00°	d <sup>-</sup> +34.00°
Cd <sub>6438</sub>	l <sup>-</sup> -21.00°	l <sup>-</sup> -23.00°	l <sup>-</sup> -24.50°	l <sup>-</sup> -27.50°	l <sup>-</sup> -33.00°	l <sup>-</sup> -34.50°
Li <sub>6104</sub>	20.50	25.00	26.00	30.00	35.00	41.50
Na <sub>5893</sub>	25.00	28.50	31.50	35.50	43.50	45.50
Hg <sub>6780</sub>	27.00	32.00	35.00	39.50	47.50	49.50
Hg <sub>5461</sub>	28.50	33.50	37.50	42.00	50.00	52.00
Ag <sub>5209</sub>	30.50	40.00	43.00	49.00	58.50	61.00
Cd <sub>5086</sub>	35.00	44.00	49.00	57.00	68.50	72.00
Cd <sub>4800</sub>	40.00	48.50	53.00	60.00	73.00	74.00
Cd <sub>4678</sub>	45.50	58.50	65.00	74.50	87.50	92.00
Li <sub>4603</sub>	55.00	64.00	70.00	81.00	92.00	95.00
Hg <sub>4358</sub>	62.00	69.50	75.50	85.50	100.00	104.00
	78.50	85.00	91.00	107.00	120.00	124.50

TABLE VI  
Camphor- $\beta$ -sulphonyl- $\alpha$ -pyridylamides

Solvent	Methyl alcohol	Ethyl alcohol	Pyridine	Chloroform	Acetone
Concentration in gm./100 c.c.	$d^-$ 0.2500 $l^-$ 0.2500	0.2500 0.2500	1.0000 1.0000	0.5000 0.5000	0.2500 0.2500
Calculated $\left\{ \begin{array}{l} [\alpha] \\ \lambda_0 \end{array} \right.$	$\pm \frac{8.001}{\lambda^2 - 0.1118}$ 0.3344	$\pm \frac{8.645}{\lambda^2 - 0.1071}$ 0.3273	$\pm \frac{9.983}{\lambda^2 - 0.09768}$ 0.3125	$\pm \frac{10.049}{\lambda^2 - 0.09721}$ 0.3118	$\pm \frac{12.029}{\lambda^2 - 0.08567}$ 0.2927
Line	Obs. $[\alpha]$	Obs. $[\alpha]$	Obs $[\alpha]$	Obs. $[\alpha]$	Obs. $[\alpha]$
$d^+$	+22.00°	+23.00°	+27.50°	+28.50°	+30.00°
$l^-$	-23.00°	-22.50°	-27.50°	-27.50°	-28.00°
Li <sub>6708</sub>	28.50	30.50	30.00	33.00	38.00
Cd <sub>6488</sub>	31.50	33.00	37.00	35.00	42.50
Li <sub>6104</sub>	34.00	36.00	40.00	41.50	46.00
N <sub>26893</sub>	35.50	38.50	41.50	44.00	50.00
Hg <sub>5780</sub>	42.50	45.00	50.00	50.00	56.50
Hg <sub>5461</sub>	52.50	53.00	58.00	56.00	60.50
Ag <sub>5209</sub>	53.00	55.50	62.50	60.00	65.50
Cd <sub>5086</sub>	69.00	69.00	75.00	76.50	80.00
Cd <sub>4800</sub>	70.00	79.50	83.00	82.50	92.50
Cd <sub>4678</sub>	80.00	82.50	87.50	86.00	95.50
Li <sub>4602</sub>	100.50	108.00	..	..	120.00
Hg <sub>4358</sub>	..	104.50	..	..	118.50

TABLE VII  
Camphor-β-sulphonyl-α-thiazoleamides

Solvent	Methyl alcohol	Ethyl alcohol	Pyridine	Chloroform	Acetone
Concentration in $d$ - gm./100 c.c.	0.2500 0.2500	0.2500 0.2500	1.0000 1.0000	0.5000 0.5000	0.2500 0.2500
Calculated $\left\{ \begin{array}{l} [\alpha] \\ \lambda_0 \end{array} \right.$	$8.304$ $\pm \frac{8.304}{\lambda^2 - 0.1098}$ $0.3314$	$9.174$ $\pm \frac{9.174}{\lambda^2 - 0.1026}$ $0.3203$	$10.202$ $\pm \frac{10.202}{\lambda^2 - 0.09819}$ $0.3133$	$11.205$ $\pm \frac{11.205}{\lambda^2 - 0.08279}$ $0.2878$	$12.612$ $\pm \frac{12.612}{\lambda^2 - 0.08162}$ $0.2857$
Line	Obs. $[\alpha]$	Obs. $[\alpha]$	Obs. $[\alpha]$	Obs. $[\alpha]$	Obs. $[\alpha]$
Li <sub>6708</sub>	$d$ - $+22.00^\circ$	$d$ - $+22.50^\circ$	$d$ - $+29.00^\circ$	$d$ - $+30.50^\circ$	$d$ - $+35.50$
Cd <sub>6438</sub>	$l$ - $-23.00^\circ$	$l$ - $-24.00^\circ$	$l$ - $-29.50^\circ$	$l$ - $-29.50^\circ$	$l$ - $-33.00^\circ$
Li <sub>6104</sub>	$d$ - $30.50$	$d$ - $30.00$	$d$ - $31.50$	$d$ - $32.00$	$d$ - $36.00$
Na <sub>5893</sub>	$d$ - $32.00$	$d$ - $32.00$	$d$ - $37.50$	$d$ - $36.50$	$d$ - $42.50$
Hg <sub>5780</sub>	$d$ - $35.00$	$d$ - $37.50$	$d$ - $41.50$	$d$ - $44.00$	$d$ - $47.50$
Hg <sub>5461</sub>	$d$ - $36.50$	$d$ - $44.50$	$d$ - $42.00$	$d$ - $46.50$	$d$ - $50.00$
Ag <sub>5209</sub>	$d$ - $44.00$	$d$ - $47.00$	$d$ - $51.00$	$d$ - $52.00$	$d$ - $55.00$
Cd <sub>5086</sub>	$d$ - $53.50$	$d$ - $51.50$	$d$ - $58.00$	$d$ - $60.00$	$d$ - $64.50$
Cd <sub>4800</sub>	$d$ - $51.50$	$d$ - $55.00$	$d$ - $58.00$	$d$ - $60.00$	$d$ - $62.50$
Cd <sub>4678</sub>	$d$ - $68.00$	$d$ - $74.50$	$d$ - $76.00$	$d$ - $76.00$	$d$ - $73.50$
Li <sub>4603</sub>	$d$ - $80.00$	$d$ - $80.50$	$d$ - $84.00$	$d$ - $84.00$	$d$ - $82.50$
Hg <sub>4358</sub>	$d$ - $81.50$	$d$ - $83.00$	$d$ - $110.00$	$d$ - $110.00$	$d$ - $97.00$
	$l$ - $107.00$	$l$ - $103.50$	$l$ - $103.50$	$l$ - $103.50$	$l$ - $119.50$

## SUMMARY

1. The rotatory dispersion of stereoisomeric compounds described in this paper is found in different solvents to obey the simple dispersion equation of Drude,  $[\alpha] = \frac{K_0}{\lambda^2 - \lambda_0^2}$ .

2. The equality of rotatory dispersions of dextro and lævo forms supports Pasteur's Law of Molecular Dissymmetry.

3. The effect of replacement of OH group in camphor- $\beta$ -sulphonic acid by Cl, Br and NH<sub>2</sub> groups on rotatory power has been discussed and the polar effect of these groups on the rotatory power of the compounds also traced.

4. The effect of different solvents on the rotatory dispersion of the compounds described in this paper has been considered.

5. The thiazole group has a greater effect on rotatory power than the pyridyl nucleus.

6. The remarkably low rotatory power of camphor- $\beta$ -sulphonamide is explained on the assumption of hydrogen bonds of the SO<sub>2</sub>NH<sub>2</sub> group interacting with the oxygen atom of the carbonyl group.

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## REFERENCES

1. Singh, B. K., and Manhas, K. M. S. .. *Proc. Ind. Acad. Sci.*, (A), 1947, **26**, 61.
2. Thomas, M. B., and Jones, H. O. .. *Jour. Chem. Soc.*, 1906, **89**, 284.
3. Singh, B. K., and Bhaduri, B. .. *Proc. Ind. Acad. Sci.*, (A), 1942, **15**, 281.  
 ——— and Tewari, R. K. .. *Ibid.*, 1945, **22**, 20.  
 ——— and Perti, O. N. .. *Ibid.*, 1945, **22**, 265.  
 ——— and Manhas, K. M. S. .. *Ibid.*, 1948, **27**, 1.
4. Rule, H. G. .. 1924, **125**, 1122 ; 1925, **127**, 2188 ;  
 ————— .. 1926, p. 553, 2116 ; 1927, p. 54 ;  
 ————— .. 1928, p. 184.
5. Haller .. *Compt. Rendus*, 1905, **140**, 1205.
6. Werner, A., and Conrad, H. E. .. *Ber.*, 1899, **32**, 3046.
7. Singh, B. K., and Biswas, A. C. .. *Jour. Chem. Soc.*, 1924, **125**, 1895.
8. Lowry, T. M. .. *Ibid.*, 1903, **83**, 968.  
 Singh, B. K., and Mahanti, I. .. *Proc. Ind. Acad. Sci.* (A), 1935, **2**, 378.  
 ——— and Nayar, B. K. K. .. *Ibid.*, 1947, **26**, 261.
9. Smiles, S., and Hilditch, T. P. .. *Jour. Chem. Soc.*, 1907, **91**, 519.