

STUDIES ON THE DEPENDENCE OF OPTICAL ACTIVITY ON CHEMICAL CONSTITUTION

Part XXIX. The camphor- β -sulphonates (*d*-, *l*-, & *dl*-) of *o*-, *m*-, *p*-aminobenzoic acids, *p*-aminoazobenzene and *o*-toluoazo-*o*-toluidine

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THE present investigation is in continuation of earlier work¹ and consists in the study of rotatory dispersion of camphor- β -sulphonates of *o*-, *m*- and *p*-aminobenzoic acids, *p*-aminoazobenzene and *o*-toluoazo-*o*-toluidine. One of the objects of the work is to study the effect of substituting the carboxyl group for hydrogen in *o*-, *m*- and *p*- positions in the benzene ring of the anilino camphor- β -sulphonates on the rotatory powers of the resulting compounds. Similarly the azo group has been included in this study. As these are all primary amine salts, the occurrence of mutarotation, where it occurs, has been ascribed to the change of the structure of the salt with the production of a ketimine or anil.

INFLUENCE OF WAVE LENGTH ON ROTATORY DISPERSION

The rotatory dispersion has been determined in the visible region of the spectrum for 12 wavelengths from λ 6708 Å.U. to λ 4358 Å.U. (Tables IV to VIII). It is found to be "simple" as it obeys the one-term Drude's equation, $[\alpha] = \frac{K_0}{\lambda^2 - \lambda_0^2}$. In this equation K_0 , the "rotation constant," may be taken as the measure of 'absolute' rotation for the wavelength λ for which $\lambda^2 - \lambda_0^2 = 1$ square micron. This value of λ is always in the infra-red and is slightly greater than 10,000 Å.U. The 'absolute' rotations (K_0) are thus numerically, but not dimensionally, identical with the magnitude of $[\alpha]$. Comparison of rotatory powers and rotation constants at this wavelength, where $\lambda = \sqrt{1 + \lambda_0^2}$, may be regarded as those for corresponding conditions of wavelength, in which the effects of dispersion are eliminated.

THE PHYSICAL IDENTITY OF ENANTIOMERS

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

law of Molecular Dissymmetry, according to which the optical and their opposite isomers possess rotatory powers identical in magnitude but opposite in sign. Out of 302 observations, in as many as 293 cases the differences in the numerical value of the rotatory power of the dextro and lævo isomers correspond to a difference of 0.02° in the observed angle of rotation and in the remaining 9 cases this difference is 0.03° which is the limit of experimental error allowed in such measurements.

NATURE OF THE RACEMIC MODIFICATION

The melting points of racemic modifications of camphor- β -sulphonates of *o*-aminobenzoic acid and of *o*-toluazo-*o*-toluidine are higher than those of their optical isomers. They are, therefore, true *dl*-compounds. The melting point of the racemic form of camphor- β -sulphonate of *p*-amino benzoic acid is identical with those of its optical isomers whereas the melting points of the racemic forms of salts of camphor- β -sulphonic acid with *p*-amino azo benzene and *m*-aminobenzoic acid are lower than those of their optical isomers. That the racemic forms of these salts are also *dl*-compounds was determined in the following way: a small amount of the *d*-form was added to the corresponding racemic modification in each case and the melting point of the mixture was found to be lowered. This clearly shows that these racemic camphor- β -sulphonates are also true *dl*-compounds.


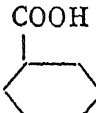
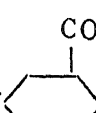
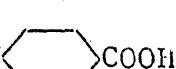
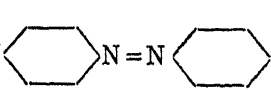
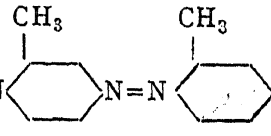
THE EFFECT OF SOLVENT ON ROTATORY POWER

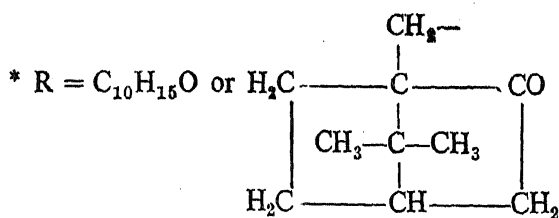
It is observed that the order of rotatory power of the position isomerides of salts of *o*-, *m*-, and *p*-aminobenzoic acids with camphor- β -sulphonic acids for Hg_{5461} in different solvents is pyridine $>$ ethyl alcohol $>$ methyl alcohol $>$ water (Table I), whereas the sequence of increasing dielectric constant of the solvent is pyridine (12.4) $<$ ethyl alcohol $<$ (25.8) $<$ methyl alcohol (31.2) $<$ water (80). Hence it is obvious that the sequence of dielectric constants of the solvents follows the same order as that of rotatory power but in the opposite sense.

In the case of salts of camphor- β -sulphonates with *p*-aminoazobenzene it is, however, found that the order of decreasing rotatory power for Li_{6708} is methyl alcohol $>$ pyridine which is also the sequence of their dielectric constants.

As already pointed out in our previous work 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.

TABLE I

No.	Structural formula	Solvent				
		Water (80)†	Methyl Alcohol (31.2)	Ethyl Alcohol (25.8)	Pyridine (12.4)	Chloro- form (5.2)
1	*R·SO ₃ H·NH ₂ 	‡20.50 (3.400)	32.40 (6.284)	36.40 (6.997)	36.10 (7.57)	45.30 (9.276)
2	R·SO ₃ H·H ₂ N 	20.50 (3.56)	30.50 (5.95)	32.50 (6.271)	36.0 (7.123)	..
3	R·SO ₃ H·H ₂ N 	19.50 (3.335)	29.00 (5.697)	30.00 (5.618)	34.50 (6.935)	..
4	R·SO ₃ H·H ₂ N 	20.00 (3.475)	27.00 (5.113)	31.00 (5.777)	35.50 (7.139)	..
5	R·SO ₃ H·H ₂ N 	..	24.00§	..	15.00§ (4.01)	..
6	R·SO ₃ H·H ₂ N 	21.00§ (7.535)	..



† The figures in brackets stand for the dielectric constant of the solvent.

‡ Rotations are for Hg₅₄₆₁.

§ Rotations are for Li₆₇₀₈.

|| The values for rotation constant, K₀ (absolute rotation) are given in brackets.

¶ These values are taken from Singh, B. K., *et al.*, *Proc. Lahore Phil. Soc.*, 1944, 6, 15.

THE MOLECULAR ROTATORY DISPERSION OF CAMPHOR-β-SULPHONATES IN AQUEOUS SOLUTION AND COMPARISON OF THE VALUE OF (M)_D^{35°} OF CAMPHOR-β-SULPHONATE ION IN WATER

Table II gives the values of [M]_λ^{35°} in aqueous solution for salts of *o*-, *m*- and *p*-aminobenzoic acids with camphor-β-sulphonic acids. The mean value of [M]_D^{35°} for the camphor-β-sulphonic ion is 53.54°. The value of [M]_D^{35°} for the salts of *o*-, *m*- and *p*-aminobenzoic acids with camphor-β-sulphonic acid is 56.63°, 55.98° and 57.52° respectively. As these values of the rotatory power of the salts are slightly higher than the mean value

TABLE—II

No	Camphor- β -sulphonates of	Concentrates in gm./100 ccs.	$[M]_{\lambda}^{35}$ in aqueous solution											
			Li 6708	Cd 6438	Li 6104	Na 5893	Hg 5780	Hg 5461	Ag 5209	Cd 5086	Cd 4800	Cd 4678	Li 4603	Hg 4358
1	1-carboxy-2-aminobenzene	1.0000	40.36	45.28	52.91	56.63	62.69	75.65	89.54	97.95	124.2	139.4	150.7	200.8
2	1-carboxy-3-aminobenzene	1.0000	38.19	42.91	50.21	55.98	59.51	71.91	85.23	93.35	118.7	133.6	144.4	193.6
3	1-carboxy-4-aminobenzene	1.0000	39.41	44.20	51.69	57.52	61.17	73.79	87.34	95.52	121.2	135.9	146.9	184.7

TABLE III

No.	Camphor- β -sulphonate of	$[\alpha]_{5461}^{35^{\circ}}$				
		Water	Methyl Alcohol	Ethyl Alcohol	Pyridine	
1	Aniline†	..	*20.50 †(3.400)	32.40 (6.284)	36.40 (6.997)	36.10 (7.57)
2	<i>o</i> -toluidine†	..	19.87 (3.367)	29.60 (5.685)	34.74 (6.88)	36.20 (7.93)
3	<i>o</i> -nitraniline‡	29.97 (3.973)	29.50 (3.666)	31.96 (4.051)
4	<i>o</i> -amino benzoic acid	..	20.50 (3.56)	30.50 (5.95)	32.50 (6.271)	36.00 (7.123)
5	<i>o</i> -chloraniline	..	18.97 (3.078)	26.96 (4.251)	28.97 (5.058)	32.50 (5.379)
6	<i>m</i> -toluidine†	..	18.80 (3.31)	28.90 (5.661)	34.10 (6.79)	35.50 (7.74)
7	<i>m</i> -nitraniline‡	34.47 (5.882)	35.38 (5.432)	35.97 (5.185)
8	<i>m</i> -aminobenzoic acid	..	19.50 (3.555)	29.00 (5.697)	30.00 (5.618)	34.50 (6.953)
9	<i>m</i> -chloraniline	..	20.00 (3.644)	32.00 (6.386)	34.00 (6.945)	34.46 (6.541)
10	<i>p</i> -toluidine†	..	20.20 (3.39)	30.47 (5.96)	35.50 (6.95)	37.60 (7.81)
11	<i>p</i> -nitraniline‡	30.47 (4.536)	30.42 (4.195)	31.42 (4.782)
12	<i>p</i> -aminobenzoic acid	..	20.00 (3.475)	27.00 (5.113)	31.00 (5.777)	35.50 (7.139)
13	<i>p</i> -chloraniline	..	18.98 3.510	31.50 (6.276)	33.50 (6.689)	36.00 (6.42)

* The values refer to $[\alpha]_{5461}^{35^{\circ}}$

† The values for rotation constant K_0 (absolute rotation) are given in brackets.

‡ The values are taken from Singh, B. K., *et al.*, *Proc. Lahore Phil. Soc.*, 1944, 6, 15.

§ The values are taken from Singh, B. K., and Perti, O. N., *Proc. Ind. Acad. Sci., A*, 1945, 22, 84.

|| The values are taken from Singh, B. K., and Perti, O. N., *ibid.*, 1945, 22, 265.

of $[M]_D^{35^\circ}$ of the camphor- β -sulphonate ion (53.54°) 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 these salts are not completely electrolytically dissociated in 1 per cent. aqueous solution.

THE EFFECT OF SUBSTITUENT GROUPS ON ROTATORY POWER

Substituent groups arrange themselves in the following polar series deduced from measurements of inductive capacities:



In Table (III) the values of $[\alpha]_{5461}^{35^\circ}$ in different solvents are given. The values of K_0 , the rotation constants, as above defined, are also given in brackets for the sake of comparison.

Ortho substitution.—On comparing the values of $[\alpha]_{5461}^{35^\circ}$ in water, it is found that —CH₃, —COOH AND —Cl groups cause a decrease in the

TABLE IV. 1-Carboxy-2-aminobenzene-camphor- β -sulphonates

Solvent	Water		Methyl alcohol		Ethyl alcohol		Pyridine	
Concentration { <i>d</i> - in gms./100 c.c. { <i>l</i> -	1.0000 1.0000		1.0000 1.0000		1.0000 1.0000		1.0000 1.0000	
Calculated { $[\alpha]$ { λ_0	$\pm \frac{3.56}{\lambda^2 - .1246}$ 0.3529		$\pm \frac{5.95}{\lambda^2 - 0.1064}$ 0.3262		$\pm \frac{6.271}{\lambda^2 - 0.1053}$ 0.3245		$\pm \frac{7.123}{\lambda^2 - .1005}$ 0.3170	
Line	Obs. $[\alpha]$		Obs. $[\alpha]$		Obs. $[\alpha]$		Obs. $[\alpha]$	
	<i>d</i> -	<i>l</i> -	<i>d</i> -	<i>l</i> -	<i>d</i> -	<i>l</i> -	<i>d</i> -	<i>l</i> -
Hg ₄₃₅₈	+54.00	-55.00	+70.50	-69.00	+74.00	-75.50	+79.50	-80.50
Li ₄₆₀₃	41.50	40.50	56.50	55.00	58.00	58.00	64.00	65.00
Cd ₄₆₇₈	39.00	38.50	53.00	52.00	54.00	55.00	59.50	60.00
Cd ₄₈₀₀	34.00	33.00	47.00	48.00	50.50	50.00	53.50	54.00
Cd ₅₀₈₆	26.50	26.50	38.00	38.50	41.00	41.00	45.50	45.00
Ag ₅₂₀₉	24.00	24.50	35.50	35.50	37.50	38.00	40.50	40.50
Hg ₅₄₆₁	20.50	20.50	30.50	30.50	32.50	32.50	36.00	36.00
Hg ₅₇₈₀	16.50	17.00	25.50	26.00	27.50	27.50	30.00	30.50
Na ₅₈₀₃	15.50	15.50	24.00	24.50	26.00	25.50	28.00	28.50
Li ₆₁₀₄	14.00	14.00	21.50	22.00	23.50	23.50	25.00	26.00
Cd ₆₄₃₈	12.50	13.50	18.50	19.00	20.50	20.00	23.50	23.00
Li ₆₇₀₈	11.00	11.50	17.00	16.50	18.00	18.00	20.50	20.00
	No mutarotation		No mutarotation		Value for Hg ₅₄₆₁ after 24 hours $[\alpha]_{5461}^{35^\circ} = + 28.50^\circ$ for <i>d</i> -salt		No mutarotation	
					$[\alpha]_{5461}^{35^\circ} = + 29.00^\circ$ for <i>l</i> -salt			

TABLE V. 1-Carboxy-3-aminobenzene-camphor- β -sulphonates

Solvent	Water		Methyl alcohol		Ethyl alcohol		Pyridine	
Concentration $\left\{ \begin{array}{l} d \\ \text{in gms./100 c.c.} \\ l \end{array} \right.$	1.0000 1.0000		1.0000 1.0000		1.0000 1.0000		1.0000 1.0000	
Calculated $\left\{ \begin{array}{l} [\alpha] \\ \lambda_0 \end{array} \right.$	$\pm \frac{3.355}{\lambda^2 - .1261}$ 0.3551		$\pm \frac{5.697}{\lambda^2 - .1017}$ 0.3189		$\pm \frac{5.618}{\lambda^2 - .1109}$ 0.3330		$\pm \frac{6.953}{\lambda^2 - .0967}$ 0.3110	
Line	Obs. $[\alpha]$		Obs. $[\alpha]$		Obs. $[\alpha]$		Obs. $[\alpha]$	
	<i>d</i>	<i>l</i>	<i>d</i>	<i>l</i>	<i>d</i>	<i>l</i>	<i>d</i>	<i>l</i>
Hg ₄₃₅₈	.. +52.50°	-53.50°	+64.50°	-63.00°	+71.00°	-71.00°	+74.50°	-73.50°
Li ₄₆₀₂	52.00	51.50	55.00	55.50	61.50	60.00
Cd ₄₆₇₈	.. 36.50	36.00	49.00	48.50	53.50	52.00	57.00	56.00
Cd ₄₈₀₀	.. 31.50	33.00	44.50	44.00	47.50	48.00	52.50	53.00
Cd ₅₀₈₆	.. 26.00	25.00	36.00	36.50	38.00	38.00	44.00	42.50
Ag ₅₂₀₉	.. 23.00	23.00	33.50	34.00	35.50	35.00	39.50	40.00
Hg ₅₄₆₁	.. 19.50	19.50	29.00	29.00	30.00	30.50	34.50	34.50
Hg ₅₇₈₀	.. 15.50	16.00	24.00	24.00	25.50	25.00	29.00	29.50
Na ₅₈₉₃	.. 14.50	14.50	23.50	23.00	23.50	24.00	27.50	27.50
Li ₆₁₀₄	.. 13.50	13.50	21.00	21.50	21.50	21.50	24.50	25.50
Cd ₆₄₃₈	.. 11.50	12.00	18.00	19.00	18.00	19.00	21.50	21.00
Li ₆₇₀₈	.. 10.50	10.00	16.50	16.00	17.00	16.50	19.50	20.00
	No mutarotation		No mutarotation		Value for Hg ₅₄₆₁ after 24 hours [α] ₅₄₆₁ ^{35°} = + 22.50°, for <i>d</i> -salt [α] ₅₄₆₁ ^{35°} = + 22.00°, for <i>l</i> -salt		No mutarotation	

rotatory power in the order $H = \text{COOH} > \text{CH}_3 > \text{Cl}$, whereas the order of decreasing values of K_0 is $\text{COOH} > H > \text{CH}_3 > \text{Cl}$. Thus the groups CH_3 and Cl behave in the opposite sense from COOH , in conformity with the above mentioned polar series. This however, does not hold good in other solvents.

In methyl alcohol and ethyl alcohol it is found that the substituent groups CH_3 , Cl , COOH and NO_2 cause a decrease in the values of both $[\alpha]_{5461}^{35^\circ}$ and K_0 . The order for $[\alpha]_{5461}^{35^\circ}$ in methyl alcohol being $H > \text{COOH} > \text{NO}_2 > \text{CH}_3 > \text{Cl}$ and for K_0 , $H > \text{COOH} > \text{CH}_3 > \text{Cl} > \text{NO}_2$. The order for $[\alpha]_{5461}^{35^\circ}$ in ethyl alcohol is $H > \text{CH}_3 > \text{COOH} > \text{NO}_2 > \text{Cl}$ and for K_0 , $H > \text{CH}_3 > \text{COOH} > \text{Cl} > \text{NO}_2$. In neither case it agrees with the above mentioned polar series of the substituent groups.

On comparing the values of $[\alpha]_{5461}^{35^\circ}$ in pyridine, however, it is found that the order of decreasing rotatory power is $\text{CH}_3 > H > \text{COOH} > \text{Cl}$

TABLE VI. 1-Carboxy-4-aminobenzene-camphor- β -sulphonates

Solvent	Water		Methyl alcohol		Ethyl alcohol		Pyridine	
Concentration in gm./100 c.c.	d - l -	1.0000 1.0000	1.0000 1.0000	1.0000 1.0000	1.0000 1.0000	1.0000 1.0000	1.0000 1.0000	1.0000 1.0000
Calculated $\left\{ \begin{array}{l} [\alpha] \\ \lambda_0 \end{array} \right.$		$\pm \frac{3.475}{\lambda^2 - 0.1245}$ 0.3528	$\pm \frac{5.113}{\lambda^2 - .1088}$ 0.3298	$\pm \frac{5.777}{\lambda^2 - .1119}$ 0.3348		$\pm \frac{7.139}{\lambda^2 - .1024}$ 0.3200		
Line	Obs. $[\alpha]$		Obs. $[\alpha]$		Obs. $[\alpha]$		Obs. $[\alpha]$	
	d -	l -	d -	l -	d -	l -	d -	l -
Hg ₄₃₅₈	.. +53.00°	-53.00°	+63.00°	-62.00°	+74.00°	+73.00°	+81.50°	-82.50°
Li ₄₆₀₃	.. 40.00	39.00	49.00	49.50	58.00	57.00	65.00	65.50
Cd ₄₆₇₈	.. 37.00	36.50	46.50	46.00	55.00	54.00	61.50	61.00
Cd ₄₈₀₀	.. 32.00	33.00	42.00	42.00	48.00	49.00	55.50	55.00
Cd ₅₀₈₆	.. 26.00	26.00	34.00	34.00	39.00	39.00	45.50	46.00
Ag ₅₂₀₉	.. 23.50	23.50	32.00	31.50	36.00	36.00	42.00	42.50
Hg ₅₄₆₁	.. 20.00	20.00	27.00	27.00	31.00	31.00	35.50	35.50
Hg ₅₇₈₀	.. 16.50	16.00	22.50	23.00	26.00	25.00	31.00	30.50
Na ₅₈₉₈	.. 15.50	15.50	21.50	21.50	24.00	24.00	28.50	29.00
Li ₆₁₀₄	.. 14.00	14.50	19.50	20.00	22.00	22.00	26.00	26.50
Cd ₆₄₃₈	.. 12.00	12.00	17.00	17.50	20.00	19.00	23.00	22.00
Li ₆₇₀₈	.. 11.00	11.50	14.50	15.00	17.00	16.00	20.50	20.50
	No mutarotation		No mutarotation		Value for Hg ₅₄₆₁ after 24 hours $[\alpha]_{5461}^{35^\circ} = + 3.50^\circ$, for d -salt $[\alpha]_{5461}^{35^\circ} = - 3.50^\circ$, for l -salt		No mutarotation	

$> \text{NO}_2$ which is also for K_0 . This follows the order of polarity of the groups except in the case of Cl.

Meta substitution.—On comparing the values of $[\alpha]_{5461}^{35^\circ}$ in water, the order of decreasing rotatory power is $\text{H} > \text{Cl} > \text{COOH} > \text{CH}_3$; in methyl alcohol $\text{NO}_2 > \text{H} > \text{Cl} > \text{COOH} > \text{CH}_3$, in ethyl alcohol $\text{H} > \text{NO}_2 > \text{CH}_3 > \text{Cl} > \text{COOH}$ and in pyridine $\text{H} > \text{NO}_2 > \text{CH}_3 > \text{COOH} > \text{Cl}$. In none of these cases the order agrees with that of polar series. On comparing the values of K_0 it is, however, found that in water the order is $\text{Cl} > \text{COOH} > \text{H} > \text{CH}_3$ and in pyridine, $\text{CH}_3 > \text{H} > \text{COOH} > \text{Cl} > \text{NO}_2$. This is in conformity with the polar series except for Cl. In methyl alcohol and ethyl alcohol the order is $\text{Cl} > \text{H} > \text{COOH} > \text{NO}_2 > \text{CH}_3$ and $\text{H} > \text{Cl} > \text{CH}_3 > \text{COOH} > \text{NO}_2$ respectively which does not agree with the above mentioned polar series.

Para substitution.—In the case of para substitution the order of $[\alpha]_{5461}^{35^\circ}$ in water is $\text{H} > \text{CH}_3 > \text{COOH} > \text{Cl}$, in methyl alcohol, $\text{H} > \text{Cl} > \text{CH}_3$

TABLE VII. *p*-Amino-azobenzene-camphor- β -sulphonates

Solvent	Methyl alcohol	Pyridine
Concentration in gm./100 c.c. $\left\{ \begin{array}{l} d- \\ l- \end{array} \right.$	1.0000 1.0000	1.0000 1.0000
Calculated $\left\{ \begin{array}{l} [\alpha] \\ \lambda_0 \end{array} \right.$	$\pm \frac{4.01}{\lambda^2 - 0.1827}$ 0.4274
Line	Obs. $[\alpha]$	Obs. $[\alpha]$
Li ₆₇₀₈ Li ₆₁₀₄ Na ₅₈₉₃ Na ₅₇₈₀	$\left\{ \begin{array}{l} d- \\ l- \end{array} \right. \begin{array}{l} +24.00^\circ \\ -25.50^\circ \end{array}$	$\left\{ \begin{array}{l} d- \\ l- \end{array} \right. \begin{array}{l} +15.00^\circ \\ -15.50^\circ \end{array}$ 22.00 21.50 24.50 24.00 26.00 26.50 No mutarotation
	Li ₆₇₀₈ could not be read after 24 hours	

TABLE VIII. *o*-Toluoazo-*o*-toluidino camphor- β -sulphonates

Solvent	Pyridine
Concentration in $\left\{ \begin{array}{l} d- \\ l- \end{array} \right.$ gms./100 c.c.	1.0000 1.0000
Calculated $\left\{ \begin{array}{l} [\alpha] \\ \lambda_0 \end{array} \right.$	$\pm \frac{7.535}{\lambda^2 - 0.0732}$ 0.2706
Line	Obs $[\alpha]$
Li ₆₇₀₈ Li ₆₁₀₄ Na ₅₈₉₃	$\left\{ \begin{array}{l} d- \\ l- \end{array} \right. \begin{array}{l} +21.00^\circ \\ -20.50^\circ \end{array}$ 24.50 24.50 27.00 27.50 Lines could not be read distinctly after 24 hours

=NO₂ > COOH, in ethyl alcohol H > CH₃ > Cl > COOH > NO₂ and in pyridine CH₃ > H > Cl > COOH > NO₂. In the case of water and alcohols the sequence does not correspond to the polar series but in pyridine it is followed except for Cl.

The comparison of the values of K₀ shows that the order in water is Cl > COOH > H > CH₃ and in pyridine CH₃ > H > COOH > Cl > NO₂.


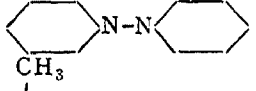


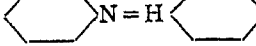
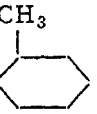
This is in conformity with polar series except for Cl. The order in methyl alcohol and ethyl alcohol is $H > Cl > CH_3 > COOH > NO_2$ and $H > CH_3 > Cl > COOH > NO_2$ respectively and does not agree with the polar series.

It is, therefore, clear that a better agreement is found with the above mentioned polar series of substituent groups for the values of K_0 , the absolute rotation constant, and not for the values of $[\alpha]_{5461}^{35^\circ}$, the specific rotatory power for an arbitrary wavelength. The groups $COOH$ and NO_2 lying on one side of the hydrogen atom in the series behave similarly and opposite to the CH_3 group which falls on the other side.


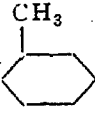
It is also evident that greater accord in rotatory power with the polar effect is found in the case of ortho substituents as might be expected from the closer proximity of the groups to the asymmetric centre in the molecule and is in conformity with our previous observations.²

THE EFFECT OF AZO ARYL GROUP ON ROTATORY POWER

TABLE A

Structural formula	$[\alpha]_{6769}^{35^\circ}$ in Pyridine
$R \cdot SO_3H \cdot H_2N$ 	21.20 (7.57)*
$R \cdot SO_3H \cdot H_2N$  -N-N- 	15.00 (4.01)
$R \cdot SO_3H \cdot H_2N$ 	21.45 (7.93)
$R \cdot SO_3H \cdot H_2N$  -N=H- 	21.00 (7.535)

* The values in brackets stand for K_0 .

The effect of the substitution of H by $-N = N$  in anilino-camphor- β -sulphonates and by $-N = N$  in *o*-toluidino camphor- β -sulphonates is found to depress the rotatory power, though only very slightly in the latter case. A comparison of the values of K_0 also bears out the same result.

THE EFFECT OF POSITION ISOMERISM ON ROTATORY POWER

TABLE B

Solvent	$[\alpha]_{5461}^{35^\circ}$
Water	.. { $m < p < o = Un$ [$m < Un < p < o$]
Methyl Alcohol	.. { $p < m < o < Un$ [$p < m < o < Un$]
Ethyl Alcohol	.. { $m < p < o < Un$ [$m < p < o < Un$]
Pyridine	.. { $m < p < o < Un$ [$m < o < p < Un$]

In Table (B) the order of rotatory power of position isomerides in different solvents for $[\alpha]_{5461}^{35^\circ}$ is given, the order of K_0 is also given in square brackets. On comparing the values of $[\alpha]_{5461}^{35^\circ}$, the sequence of position isomerides in all solvents is $m < p < o < Un$ with the exception that in methyl alcohol the order is $p < m < o < Un$. Similar results with minor differences follow when a comparison is made for the values of K_0 : the order of position isomerides in water is $m < Un < p < o$, in methyl alcohol $p < m < o < Un$, in ethyl alcohol $m < p < o < Un$, and in pyridine $m < o < p < Un$. These results, except in the case of methyl alcohol, do not agree with either Frankland's "lever arm" hypothesis³ or with its electrostatic modification as suggested by Rule,⁴ according to both of which the meta isomer should be intermediate between the ortho and para as regards its rotatory effect.

EXPERIMENTAL

The lævo and racemic forms of camphor- β -sulphonic acid were prepared in the same way as Reychler's acid⁵ (*d*-camphor- β -sulphonic acid):

d-acid: found M.P. 197-8° C.; Eq. wt. = 231.6

l-acid: found M.P. 197-8° C.; Eq. wt. = 233.0

dl-acid: found M.P. 202-3° C.; Eq. wt. = 230.0

$C_{10}H_{15}O \cdot SO_3H$ requires Eq. wt. = 230.0

p-Amino azobenzene camphor- β -sulphonates

Molar proportions of *p*-aminoazobenzene and camphor- β -sulphonic acids were dissolved separately in hot ethyl acetate. The two solutions were then mixed and allowed to stand for sometime, when the salts crystallised out. They were repeatedly crystallised as long deep orange needles from

absolute alcohol and on drying in vacuum turned brick red. They are sparingly soluble in methyl alcohol and pyridine, less so in water and absolute alcohol and practically insoluble in acetone, chloroform and benzene.

Found: *d*-salt; M.P. 203°d-; S = 7.35%

l-salt; M.P. 203°d-; S = 7.32%

dl-salt; M.P. 200°d-; S = 7.63%

$C_{22}H_{27}N_3O_4S$ requires S = 7.45%

o-Toluoazo-*o*-toluidino camphor- β -sulphonates

Molecular proportion of *o*-toluoazo-*o*-toluidine and camphor- β -sulphonic acids were dissolved separately in hot ethyl alcohol. The two solutions were then mixed and allowed to stand when the salts crystallised out. They were repeatedly crystallised as long orange coloured needles and finally dried under vacuum when a yellowish brown powder was obtained. They dissolve in organic solvents giving deep orange red solutions. They are fairly soluble in pyridine and methyl alcohol, less so in chloroform and ethyl alcohol and practically insoluble in water and benzene.

Found: *d*-salt, M.P. 257-8°d-; S = 7.1%

l-salt, M.P. 257-8°d-; S = 7.25%

dl-salt, M.P. 262-4°d-; S = 7.18%

$C_{24}H_{31}O_4N_3S$ requires S = 7%

l-Carboxy-2-aminobenzene- and *l*-carboxy-3-aminobenzene camphor- β -sulphonates:

Molecular proportions of each of the amines 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 salts crystallised out. They were then repeatedly crystallised as white needles from a mixture of ethyl alcohol and ethyl acetate and finally dried in vacuum. They are fairly soluble in water, ethyl alcohol, methyl alcohol and pyridine and practically insoluble in acetone, chloroform and benzene.

l-Carboxy-4-aminobenzene camphor- β -sulphonates

Molecular proportions of the amine and the acids were separately dissolved in ethyl alcohol and on mixing the two solutions, the salts crystallised out. They were repeatedly recrystallised from absolute ethyl alcohol as fine white needles. They are soluble in water, methyl alcohol and pyridine, sparingly so in ethyl alcohol but practically insoluble in acetone, chloroform and benzene.

Found: *o*-compounds:

d-salt, M.P. 154–6° C.; Eq. wt. 184.5; S = 8.35%

l-salt, M.P. 154–6° C.; Eq. wt. 184.5; S = 8.52%

dl-salt, M.P. 163–6° C.; Eq. wt. 183.3; S = 8.80%

m-compounds:

d-salt, M.P. 205° C.; Eq. wt. 184.5; S = 8.53%

l-salt, M.P. 205° C.; Eq. wt. 184.5; S = 8.90%

dl-salt, M.P. 200° C.; Eq. wt. 184.5; S = 8.90%

p-compounds:

d-salt, M.P. 284° d; Eq. wt. 184.5; S = 8.93%

l-salt M.P. 284° d; Eq. wt. 185.7; S = 8.62%

dl-salt, M.P. 284° d; Eq. wt. 183.3; S = 8.54%

$C_{17}H_{23}NO_6S$ requires Eq. wt. 184.5; S = 8.67%

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

SUMMARY

1. The rotatory dispersion of stereoisomeric salts of *o*-, *m*-, *p*- amino benzoic acids, *p*-aminoazobenzene and *o*-toluazo-*o*-toluidine with camphor β -sulphonic acids is found, in different solvents, to obey Drude's one-term equation, $[\alpha] = \frac{K_0}{\lambda^2 - \lambda_0^2}$; it is, therefore, simple.

2. The *d*- and *l*-forms of these compounds possess identical rotatory power and thus further support Pasteur's law of Molecular Dissymmetry.

3. The sequence of the rotatory power in the case of salts of *o*-, *m*-, *p*-amino benzoic acids with camphor- β -sulphonic acids in different solvents runs exactly in the reverse order of the dielectric constants of the solvents, whereas the sequence of the rotatory power of salts of *p*-aminoazobenzene with camphor- β -sulphonic acids follows exactly the same order as the dielectric constant of the solvent.

4. The influence of carboxyl group on rotatory power has been discussed and its polar effect on the rotatory power of the compounds traced.

5. The effect of the replacement of H by the azo aryl group is to depress the rotatory power of the parent compound.

6. The effect of position isomerism on rotatory power has also been discussed.

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