

THE REFRACTIVE DISPERSIVE POWER OF ORGANIC COMPOUNDS

Part II. The Camphor- β -sulphonates (*d*- and *dl*-) of *o*-, *m*-, *p*-Toluidines, *o*-, *m*-, *p*-Iodanilines, α -Amino-pyridine, α -Aminothiazole, *p*-Aminobenzenesulphonamide and 6-Methoxy-8-aminoquinoline

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IN Part I of this series of investigations,¹ the refractive dispersion of dextro, lævo and racemic forms of several terpene derivatives was described. It was pointed out that the earlier formulæ of Gladstone and Dale² $\left(\frac{n-1}{d}\right)$ and of Lorenz and Lorentz,³ $\frac{n^2-1}{(n^2+1)d}$ for refractive power were defective as they do not take into account the effects of dispersion. This difficulty was removed by the work of Maxwell and Sellmeier⁴ who proposed the dispersion formula as

$$n^2 = a^2 + \Sigma \frac{b_0 \lambda^2}{\lambda^2 - \lambda_0^2} \quad (\text{i})$$

It is found that generally one term of the summation in this equation when added to a constant a^2 is sufficient to represent correctly the refractive dispersive power of different types of organic compounds of varying complexity.

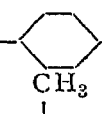
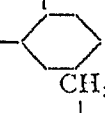
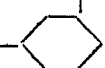
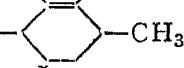
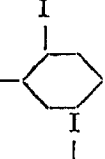
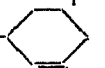

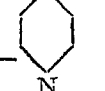
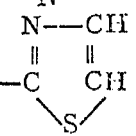
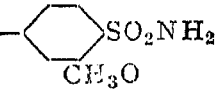
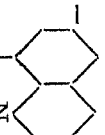
In this paper we record the results of our experiments on the refractive dispersion of the camphor- β -sulphonates (*d*- and *dl*-) of eleven aromatic and heterocyclic primary amines in aqueous solution (Tables II–XII). The refractive dispersion of these salts can be satisfactorily expressed by the Maxwell-Sellmeier simplified expression,

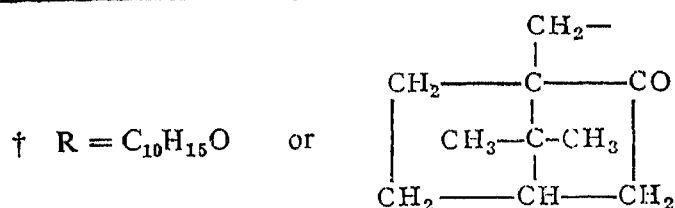
$$n^2 = a^2 + \frac{b_0 \lambda^2}{\lambda^2 - \lambda_0^2}, \quad (\text{ii})$$

in which b_0 is the refraction constant and λ_0^2 the dispersion constant. The constant term a^2 , when added to one term of the summation in equation (i), namely, $\frac{b_0 \lambda^2}{\lambda^2 - \lambda_0^2}$ gives the square of the refractive index of the medium for a stationary electric field. The values of λ_0 s—the wavelengths of the

TABLE I

Comparative Tabular Statement of Values of (1) "Absolute" Rotation (Drude Equation); (2) "Absolute" Refractive Index (Maxwell-Sellmeier Equation); (3) the Wavelength of the "Characteristic" Absorption Band (λ_0) from Drude and Maxwell-Sellmeier Equations in $A^\circ.U.$

1	2	3	4	5	6	7	8
No.	Compound	$[\alpha]_{\text{abs}}^{35^\circ} = k_0$ (Drude Equation for $\lambda = \sqrt{1 + \lambda_0^2}$)	$n_{\text{abs}}^{35^\circ} = \frac{\sqrt{a^2 + b_0(1 + \lambda_0^2)}}{\lambda = \sqrt{1 + \lambda_0^2}}$ (Maxwell-Sellmeier Equation for $\lambda = \sqrt{1 + \lambda_0^2}$)	λ_0 (From Drude Equation)	λ_0 (from Maxwell-Sellmeier Equation)	λ_0 (Mean value of columns 5 and 6)	Difference of columns 5 and 6
1 ^a	$\dagger R \cdot SO_3H \cdot H_2N$ - 	3.400	1.3301	3606	3620	3613	-14
2 ^a	$R \cdot SO_3H \cdot H_2N$ - 	3.367	1.3284	3562	3540	3551	+22
3 ^a	$R \cdot SO_3H \cdot H_2N$ - 	3.310	1.3285	3536	3533	3534	+3
4 ^a	$R \cdot SO_3H \cdot H_2N$ - 	3.390	1.3289	3597	3571	3584	+26
5 ^b	$R_S \cdot SO_3H \cdot H_2N$ - 	3.110	1.3316	3669	3659	3664	+10
6 ^b	$R \cdot SO_3H \cdot H_2N$ - 	3.268	1.3319	3664	3667	3666	-3
7 ^c	$R \cdot SO_3H \cdot H_2N$ - 	3.207	1.3319	3658	3637	3647	+21
8 ^c	$R \cdot SO_3H \cdot H_2N$ - 	3.367	1.3292	3289	3292	3290	-3
9 ^c	$R \cdot SO_3H \cdot H_2N$ - 	4.155	1.3297	3537	3544	3540	-7
10 ^d	$R \cdot SO_3H \cdot H \cdot H_2N$ - 	2.793	1.3301	3668	3676	3672	-8
11 ^e	$R \cdot SO_3H \cdot H_2N$ - 	3.294	1.3290	3131	3172	3151	-41



The abbreviation for which R stands is the same in all the Tables I to XII.

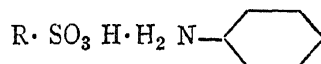
^a The values in columns 3 and 5 are taken from Singh, B. K., Perti, O. N., and Singh, B. N., *Proc. Lahore Phil. Soc.*, 1944, 6, 15; *Allahabad University Studies*, 1944, 37.

^b The values in columns 3 and 5 are taken from Singh, B. K., and Manhas, K. M. S., *Proc. Ind. Acad. Sci.*, 1949, 29, 107.

^c The values in columns 3 and 5 are taken from Singh, B. K., and Manhas, K. M. S., *Ibid.*, 1947, 26, 61.

^d The values in columns 3 and 5 are taken from Singh, B. K., and Perti, O. N., *Ibid.*, 1945, 22, 84.

TABLE II
Refractive Dispersion of Anilincamphor- β -sulphonates

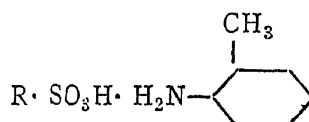


$$\left\{ \begin{aligned} n^2 &= 1.7578 + \frac{0.01121\lambda^2}{\lambda^2 - 0.1311}; & \lambda_0^2 &= 0.1311 \\ [\alpha]^* &= \frac{3.400}{\lambda^2 - 0.1300}; & \lambda_0^2 &= 0.1300 \end{aligned} \right.$$

λ	$n_{\text{Calculated}}$ (c)	n_{Dextro} (d)	n_{d-c}	n_{Racemic} (r)	n_{r-c}	n_{d-r}
Li ₆₇₀₈	1.3314	1.3317	+0.0003	1.3316	+0.0002	+0.0001
Na ₅₈₉₃	1.3322	1.3324	+0.0002	1.3321	-0.0001	+0.0003
Hg ₅₇₈₀	1.3324	1.3324	± 0.0000	1.3324	± 0.0000	± 0.0000
Hg ₅₄₆₁	1.3330	1.3331	+0.0001	1.3330	± 0.0000	+0.0001
Hg ₄₃₅₈	1.3390	1.3389	-0.0001	1.3390	± 0.0000	-0.0001

* The rotatory dispersion equation is taken from Singh, Perti and Singh, *Proc. Lahore Phil. Soc.*, 1944, 6, 15; *Allahabad University Studies*, 1944, 37, 57.

TABLE III
Refractive Dispersion of *o*-Toluidinocamphor- β -sulphonates

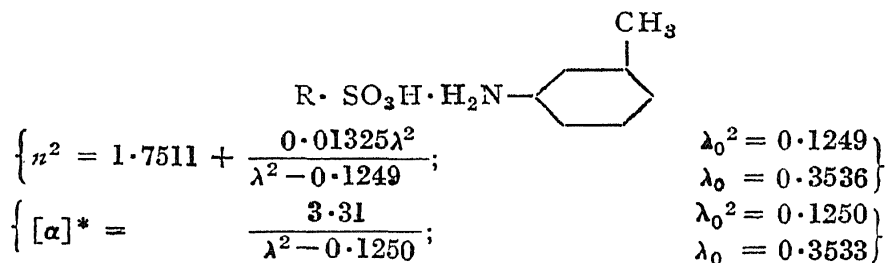


$$\left\{ \begin{aligned} n^2 &= 1.7506 + \frac{0.01326\lambda^2}{\lambda^2 - 0.1253}; & \lambda_0^2 &= 0.1253 \\ [\alpha]^* &= \frac{3.367}{\lambda^2 - 0.1269}; & \lambda_0^2 &= 0.1269 \end{aligned} \right.$$

λ	$n_{\text{Calculated}}$ (c)	n_{Dextro} (d)	n_{d-c}	n_{Racemic} (r)	n_{r-c}	n_{d-r}
Li ₆₇₀₈	1.3300	1.3297	-0.0003	1.3301	+0.0001	-0.0004
Na ₅₈₉₃	1.3306	1.3309	+0.0003	1.3304	+0.0002	+0.0005
Hg ₅₇₈₀	1.3311	1.3311	± 0.0000	1.3310	-0.0001	+0.0001
Hg ₅₄₆₁	1.3317	1.3320	+0.0003	1.3314	-0.0003	+0.0006
Hg ₄₃₅₈	1.3378	1.3377	-0.0001	1.3378	± 0.0000	-0.0001

* The rotatory dispersion equation is taken from Singh, B. K., Perti, O. N., and Singh, B. N., *Proc. Lahore Phil. Soc.*, 1944, 6, 15; *Allahabad University Studies*, 1944, 37.

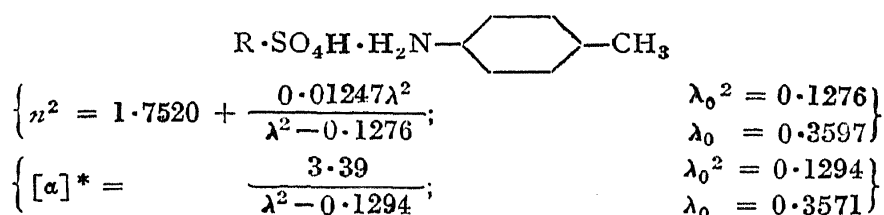
TABLE IV
Refractive Dispersion of *m*-Toluidinocamphor- β -sulphonates



λ	$n_{\text{Calculated}}$ (c)	n_{Dextro} (d)	n_{d-c}	n_{Racemic} (r)	n_{r-c}	n_{d-r}
Li ₆₇₀₈ ..	1.3302	1.3304	+0.0002	1.3304	+0.0002	± 0.0000
Na ₅₈₉₃ ..	1.3317	1.3310	-0.0001	1.3312	+0.0001	-0.0002
Hg ₅₇₈₀ ..	1.3313	1.3313	± 0.0000	1.3314	+0.0001	-0.0001
Hg ₅₄₆₁ ..	1.3319	1.3320	+0.0001	1.3320	+0.0001	± 0.0000
Hg ₄₃₅₈ ..	1.3378	1.3378	± 0.0000	1.3374	-0.0004	+0.0004

* The rotatory dispersion equation is taken from Singh, B. K., Perti, O. N., and Singh, B. N., *Proc. Lahore Phil. Soc.*, 1944, 6, 15; *Allahabad University Studies*, 1944, 37.

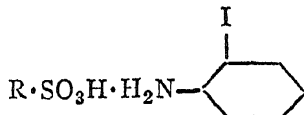
TABLE V
Refractive Dispersion of *p*-Toluidinocamphor- β -sulphonates



λ	$n_{\text{Calculated}}$ (c)	n_{Dextro} (d)	n_{d-c}	n_{Racemic} (r)	n_{r-c}	n_{d-r}
Li ₆₇₀₈ ..	1.3302	1.3303	+0.0001	1.3302	± 0.0000	+0.0001
Na ₅₈₉₃ ..	1.3310	1.3309	-0.0001	1.3311	+0.0001	-0.0002
Hg ₅₇₈₀ ..	1.3311	1.3311	± 0.0000	1.3312	+0.0001	-0.0001
Hg ₅₄₆₁ ..	1.3318	1.3318	± 0.0000	1.3316	-0.0002	+0.0002
Hg ₄₃₅₈ ..	1.3379	1.3379	± 0.0000	1.3380	+0.0001	-0.0001

* The rotatory dispersion equation is taken from Singh, B. K., Perti, O. N., and Singh, B. N., *Proc. Lahore Phil. Soc.*, 1944, 6, 15; *Allahabad University Studies*, 1944, 37.

TABLE VI
Refractive Dispersion of *o*-Iodanilincamphor- β -sulphonates

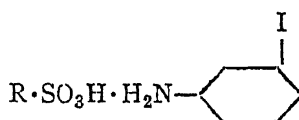


$$\left\{ \begin{aligned} n^2 &= 1.7632 + \frac{0.00865\lambda^2}{\lambda^2 - 0.1339}; & \lambda_0^2 &= 0.1339 \\ & & \lambda_0 &= 0.3669 \\ [\alpha]^* &= \frac{3.11}{\lambda^2 - 0.1346}; & \lambda_0^2 &= 0.1346 \\ & & \lambda_0 &= 0.3659 \end{aligned} \right.$$

λ	$n^{\text{Calculated}}$ (c)	n^{Dextro} (d)	n_{d-c}	n^{Racemic} (r)	n_{r-c}	n_{d-r}
Li ₆₇₀₈	1.3325	1.3328	+0.0003	1.3324	-0.0001	+0.0004
Na ₅₈₉₃	1.3331	1.3330	-0.0001	1.3330	-0.0001	± 0.0000
Hg ₅₇₈₀	1.3332	1.3331	-0.0001	1.3333	+0.0001	-0.0002
Hg ₅₄₆₁	1.3337	1.3335	-0.0002	1.3340	+0.0003	-0.0005
Hg ₄₃₅₈	1.3388	1.3390	+0.0002	1.3389	+0.0001	+0.0001

* The rotatory dispersion equation is taken from Singh, B. K., and Manhas, K. M. S., *Proc. Ind. Acad. Sci.*, 1949, 29, 107.

TABLE VII
Refractive Dispersion of *m*-Iodanilincamphor- β -sulphonates

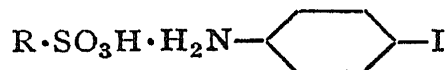


$$\left\{ \begin{aligned} n^2 &= 1.7648 + \frac{0.008138\lambda^2}{\lambda^2 - 0.1345}; & \lambda_0^2 &= 0.1345 \\ & & \lambda_0 &= 0.3664 \\ [\alpha]^* &= \frac{3.268}{\lambda^2 - 0.1342}; & \lambda_0^2 &= 0.1342 \\ & & \lambda_0 &= 0.3667 \end{aligned} \right.$$

λ	$n^{\text{Calculated}}$ (c)	n^{Dextro} (d)	n_{d-c}	n^{Racemic} (r)	n_{r-c}	n_{d-r}
Li ₆₇₀₈	1.3328	1.3328	± 0.0000	1.3327	-0.0001	+0.0001
Na ₅₈₉₃	1.3335	1.3334	-0.0001	1.3332	-0.0003	+0.0002
Hg ₅₇₈₀	1.3336	1.3337	+0.0001	1.3334	-0.0002	+0.0003
Hg ₅₄₆₁	1.3340	1.3338	-0.0002	1.3341	+0.0001	-0.0003
Hg ₄₃₅₈	1.3389	1.3388	-0.0001	1.3390	+0.0001	-0.0002

* The rotatory dispersion equation is taken from Singh, B. K., and Manhas, K. M. S., *Proc. Ind. Acad. Sci.*, 1949, 29, 107.

TABLE VIII
Refractive Dispersion of p-Iodanilinocamphor- β -sulphonates



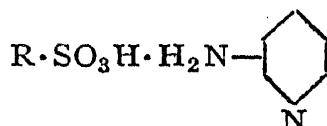
$$\left\{ \begin{aligned} n^2 &= 1.7644 + \frac{0.008404\lambda^2}{\lambda^2 - 0.1333}; & \lambda_0^2 &= 0.1333 \\ & & \lambda_0 &= 0.3658 \end{aligned} \right\}$$

$$\left\{ \begin{aligned} [\alpha]^* &= \frac{3.207}{\lambda^2 - 0.1338}; & \lambda_0^2 &= 0.1338 \\ & & \lambda_0 &= 0.3637 \end{aligned} \right\}$$

λ	$n^{\text{Calculated}}$ (c)	n^{Dextro} (d)	n_{d-c}	n^{Racemic} (r)	n_{r-c}	n_{d-r}
Li ₆₇₀₈	1.3328	1.3327	-0.0001	1.3328	± 0.0000	-0.0001
Na ₅₈₉₃	1.3334	1.3333	-0.0001	1.3335	+0.0001	-0.0002
Hg ₅₇₈₀	1.3336	1.3338	+0.0002	1.3337	+0.0001	+0.0001
Hg ₅₄₆₁	1.3340	1.3341	+0.0001	1.3339	-0.0001	+0.0002
Hg ₄₃₅₈	1.3389	1.3390	+0.0001	1.3387	-0.0002	+0.0003

* The rotatory dispersion equation is taken from Singh, B. K., and Manhas, K. M. S., *Proc. Ind. Acad. Sci.*, 1949, 29, 107.

TABLE IX
Refractive Dispersion of α -Aminopyridinocamphor- β -sulphonates



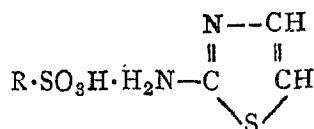
$$\left\{ \begin{aligned} n^2 &= 1.7432 + \frac{0.02134\lambda^2}{\lambda^2 - 0.1084}; & \lambda_0^2 &= 0.1084 \\ & & \lambda_0 &= 0.3289 \end{aligned} \right\}$$

$$\left\{ \begin{aligned} [\alpha]^* &= \frac{4.367}{\lambda^2 - 0.1082}; & \lambda_0^2 &= 0.1082 \\ & & \lambda_0 &= 0.3292 \end{aligned} \right\}$$

λ	$n^{\text{Calculated}}$ (c)	n^{Dextro} (d)	n_{d-c}	n^{Racemic} (r)	n_{r-c}	n_{d-r}
Li ₆₇₀₈	1.3309	1.3310	+0.0001	1.3310	+0.0001	± 0.0000
Na ₅₈₉₃	1.3320	1.3321	+0.0001	1.3319	-0.0001	+0.0002
Hg ₅₇₈₀	1.3321	1.3321	± 0.0000	1.3322	+0.0001	-0.0001
Hg ₅₄₆₁	1.3329	1.3328	-0.0001	1.3331	+0.0002	-0.0003
Hg ₄₃₅₈	1.3390	1.3390	± 0.0000	1.3389	-0.0001	+0.0001

* The rotatory dispersion equation is taken from Singh, B. K., and Manhas, K. M. S., *Proc. Ind. Acad. Sci.*, 1947, 26, 61.

TABLE X
Refractive Dispersion of α -Aminothiazolecamphor- β -sulphonates

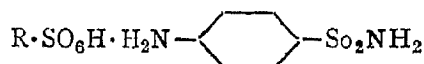


$$\left\{ \begin{array}{l} n^2 = 1.7535 + \frac{0.01311\lambda^2}{\lambda^2 - 0.1256}; \\ [\alpha]^* = \frac{4.155}{\lambda^2 - 0.1251}; \end{array} \right. \quad \left\{ \begin{array}{l} \lambda_0^2 = 0.1256 \\ \lambda_0 = 0.3537 \\ \lambda_0^2 = 0.1251 \\ \lambda_0 = 0.3544 \end{array} \right.$$

λ	$\frac{n_{\text{Calculated}}}{(c)}$	$\frac{n_{\text{Dextro}}}{(d)}$	n_{d-c}	$\frac{n_{\text{Racemic}}}{(r)}$	n_{r-c}	n_{d-r}
Li ₆₇₀₈ ..	1.3310	1.3312	+0.0002	1.3311	+0.0001	+0.0001
Na ₅₈₉₃ ..	1.3319	1.3318	-0.0001	1.3320	+0.0001	-0.0002
Hg ₅₇₈₀ ..	1.3321	1.3321	±0.0000	1.3320	-0.0001	+0.0001
Hg ₅₄₆₁ ..	1.3327	1.3330	+0.0003	1.3329	+0.0002	+0.0001
Hg ₄₃₅₈ ..	1.3387	1.3387	±0.0000	1.3384	-0.0003	+0.0003

* The rotatory dispersion equation is taken from Singh, B. K., and Manhas, K. M. S., *Proc. Ind. Acad. Sci.*, 1947, 26, 61.

TABLE XI
Refractive Dispersion of *p*-Aminobenzene Sulphonamidocamphor- β -sulphonates



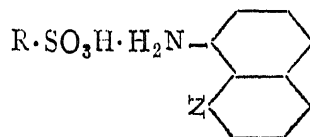
$$\left\{ \begin{array}{l} n^2 = 1.7575 + \frac{0.01017\lambda^2}{\lambda^2 - 0.1351}; \\ [\alpha]^* = \frac{2.793}{\lambda^2 - 0.1346}; \end{array} \right. \quad \left\{ \begin{array}{l} \lambda_0^2 = 0.1351 \\ \lambda_0 = 0.3668 \\ \lambda_0^2 = 0.1346 \\ \lambda_0 = 0.3676 \end{array} \right.$$

λ	$\frac{n_{\text{Calculated}}}{(c)}$	$\frac{n_{\text{Dextro}}}{(d)}$	n_{d-c}	$\frac{n_{\text{Racemic}}}{(r)}$	n_{r-c}	n_{d-r}
Li ₆₇₀₈ ..	1.3312	1.3314	+0.0002	1.3314	+0.0002	±0.0000
Na ₅₈₉₃ ..	1.3320	1.3321	+0.0001	1.3320	±0.0000	+0.0001
Hg ₅₇₈₀ ..	1.3321	1.3321	±0.0000	1.3322	+0.0001	-0.0001
Hg ₅₄₆₁ ..	1.3327	1.3329	+0.0002	1.3328	+0.0001	+0.0001
Hg ₄₃₅₈ ..	1.3389	1.3387	-0.0002	1.3387	-0.0002	±0.0000

* The rotatory dispersion equation is taken from Singh, B. K., and Perti, O. N., *Proc. Ind. Acad. Sci.*, 1945, 22, 84.

TABLE XII

Refractive Dispersion of 6-Methoxy-8-aminoquinolinocamphor- β -sulphonates



$$\left\{ \begin{aligned} n^2 &= 1.7315 + \frac{0.03158\lambda^2}{\lambda^2 - 0.1006}; & \lambda_0^2 &= 0.1006 \\ [\alpha]^* &= \frac{3.294}{\lambda^2 - 0.3098}; & \lambda_0 &= 0.3131 \\ & & \lambda_0^2 &= 0.098 \\ & & \lambda_0 &= 0.3172 \end{aligned} \right.$$

λ	$\frac{n_{\text{Calculated}}}{(c)}$	$\frac{n_{\text{Laevo}}}{(l)}$	n_{l-c}	$\frac{n_{\text{Dextro}}}{(d)}$	n_{d-c}	$\frac{n_{\text{Racemic}}}{(r)}$	n_{r-c}
Li ₆₇₀₈ ..	1.3312	1.3312	± 0.0000	1.3310	-0.0002	1.3311	-0.0001
Na ₅₈₉₃ ..	1.3327	1.3328	+0.0001	1.3327	± 0.0000	1.3328	+0.0001
Hg ₅₇₈₀ ..	1.3329	1.3329	± 0.0000	1.3329	± 0.0000	1.3330	+0.0001
Hg ₅₄₆₁ ..	1.3338	1.3337	-0.0001	1.3338	± 0.0000	1.3336	-0.0002
Hg ₄₃₅₈

* The rotatory dispersion equation is taken from Singh, B. K., and Manhas, K. M. S., *Proc. Ind. Acad. Sci.*, 1947, 26, 61.

“Characteristic” absorption bands—have been calculated from these equations and are compared with those derived from rotatory dispersion equations of Drude and are found to be in fairly close agreement (Table I). The equations of rotatory dispersion for these eleven salts⁵ are reproduced in Tables II-XII for the sake of comparison.

THE EFFECT OF CONSTITUTION ON THE “CHARACTERISTIC” ABSORPTION BAND IN THE ULTRA-VIOLET REGION

The wavelength of the “Characteristic” absorption band of anilino-camphor- β -sulphonates is 3613 Å.U. The replacement of an hydrogen atom by a methyl group in the corresponding toluidino salts has shifted this band further to the ultraviolet end of the spectrum and the order of this shift in different position isomerides is as follows (Table I, Nos. 1, 2, 3, 4):

$$m > o > p > un.$$

If the substituent group is iodine, the shift of the “Characteristic” absorption band is towards the red end of the spectrum and the order is as follows (Table I, Nos. 1, 5, 6, 7):

$$m > o > p > un.$$

The substitution of the pyridine ring for the benzene nucleus (Table I, Nos. 1 and 8) produces a shift of about 323 Å.U. in the wavelength of the "Characteristic" absorption band towards the ultraviolet side, whereas the thiazole ring (Table I, Nos. 1 and 9) produces a similar but much smaller shift (about 73 Å.U.). The substitution of the sulphonamido group in the para position for an hydrogen atom in the benzene nucleus (Table I, Nos. 1 and 10) produces, however, a small shift of about 59 Å.U. to the red end of the spectrum. The substitution of 6-methoxyquinoline ring for the phenyl group produces a remarkably large shift of about 462 Å.U. of the "Characteristic" absorption band towards the ultraviolet end of the spectrum (Table I, Nos. 1 and 11).

The effects of dispersion can be eliminated from both the Drude as well as the Maxwell-Sellmeier equations by making $\lambda^2 - \lambda_0^2 = 1$; in the case of the Drude equation the value of rotatory power becomes equal in magnitude to that of k_0 , the rotation constant. The value of refractive index, n_{abs} , in the Maxwell-Sellmeier equation for the corresponding wavelength λ , where $\lambda^2 = 1 + \lambda_0^2$, may be taken as the absolute measure of the refractive index of the medium in which the effect of wavelength, *i.e.*, dispersion, is eliminated as in the case of the values of k_0s .

A comparison of k_0s with n_{abs} or $\sqrt{a^2 + b_0(1 + \lambda_0^2)}$, however, reveals no simple relationship: in the case of toluidino camphor- β -sulphonates when k_0 decreases, the corresponding values of n_{abs} also decrease. On the other hand in the case of iodanyl salts the result is opposite.

THE NATURE OF THE RACEMIC FORMS OF THE CAMPHOR- β -SULPHONATES

A glance at Tables II-XII reveals that the refractive indices of the dextro and the racemic forms in the visible spectrum for 5 wavelengths (λ_{6708} to λ_{4358}) are identical in 1% (or less) aqueous solution within the limits of experimental error. In the absence of any differences in the values of refractive indices of the two forms in dilute solutions, it is not possible to draw any unequivocal conclusion regarding the nature of the racemic modification.

THE ROTATORY AND REFRACTIVE DISPERSION STUDIES AS AN AID IN THE DETERMINATION OF THE CHARACTERISTIC ULTRAVIOLET ABSORPTION BANDS; ANALOGY WITH RAMAN SPECTRA IN THE INFRA-RED REGION

We have seen that our studies of refractive and rotatory dispersion, using the Maxwell-Sellmeier and the Drude equations respectively, give us

almost identical values of λ_0s —the wavelengths of the dominant absorption bands of the molecules in the ultraviolet region of the spectrum (Table I). We have not verified these bands by direct measurements in the present work but in Part I of this series¹, the values of the dominant absorption bands for camphor in the ultraviolet region obtained from dispersion data were found to agree with those determined by direct absorption measurements. The utility of rotatory and refractive dispersion studies is thus evident: it has brought the study of the ultraviolet absorption spectra within the region of the visible spectrum technique. The case is, therefore, analogous to the Raman spectra which has enabled the determination of the position of the infra-red absorption bands of molecules by measurements in the visible region.

EXPERIMENTAL

The compounds described in this paper were prepared and purified by methods described elsewhere.⁵

The refractive indices were determined with a Pulfrich Refractometer: water maintained at 33–35° C. was circulated through the jacketed mount of the observation cell containing the solution. The concentration of the aqueous solutions of the salts was 1% (namely, 1.0 gram in 100 c.c. of the solution) except in the case of *o*-, *m*- and *p*-iodanilinocamphor- β -sulphonates for which 0.5% solution were used. The experimental results are given in Tables II–XII.

SUMMARY

1. The refractive dispersion of salts of camphor- β -sulphonic acid (*d*- and *dl*-) with eleven primary aromatic and heterocyclic bases was determined in aqueous solution for five wavelengths (λ_{6708} to λ_{4358}). The results can be accurately represented by the Maxwell-Sellmeier equation, using only one term of the summation.

2. It is found that the values of the wavelengths of the “Characteristic” absorption bands (λ_0s) deduced from the present measurements on refractive dispersion of these salts are almost identical with those deduced from the rotatory dispersion measurements previously described.

3. The effect of replacement of an hydrogen atom of the phenyl group in anilinocamphor- β -sulphonate by different groups has been discussed.

4. The values of the refractive dispersion of the dextro and the racemic salts are identical in dilute solution.

5. The utility of the dispersion studies for the determination of the dominant absorption bands of the molecules in the ultraviolet region has

been stressed and its analogy with Raman spectra for infra-red absorption bands pointed out.

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