THE REFRACTIVE DISPERSIVE POWER OF ORGANIC COMPOUNDS

Part III. The Refractive Dispersion of Dextro and Racemic Forms of Phenyl-, and o-, m- & p-Tolyl-iminocamphors and -aminocamphors

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A STUDY of the refractive dispersion of *d*-, *l*- and *dl*-forms of borneol, camphor, camphoric acid, camphoric anhydride and camphor carboxylic acid was made in Part I of this series of investigations.[1] The values of the refractive indices in alcoholic solution were found to be, within limits of experimental error, identical for all the three forms. Further this equality was noticed to hold for a wide range of wavelengths in the violet, green, yellow and red regions of the spectrum. In the present paper we have made a study of the effect of unsaturation and of position isomerism in the dextro and racemic forms of aryl derivatives of imino-, and amino-camphors on their refractive dispersion.

The variation of the refractive index of a substance with wavelength is given by the well-known Maxwell-Sellmeier equation:

$$n^2 = a^2 + \Sigma \frac{b_0 \lambda^2}{\lambda^2 - \lambda^2_0},$$

where 'n' is the refractive index for a particular wavelength λ, λ_0 is a wavelength characteristic of the substance, 'b_0' the refraction constant and 'a^2' another constant. The characteristic wavelength, λ_0, is supposed to represent an absorption band. In the case of optically active compounds, the variation of rotation with wavelength is also connected with the position of an absorption band or bands in the ultra-violet region given by the Drude equation:

$$[\alpha]_\lambda = \Sigma \frac{k_0}{\lambda^2 - \lambda^2_0}.$$

The values of λ_0, the " Characteristic " wavelength, deduced from rotatory dispersion[2] and refractive dispersion measurements are nearly equal; in

other words, there is a very close agreement between the position of the ultra-violet absorption bands deduced from refractive and rotatory dispersion data.

In the one-term Drude equation for substances exhibiting " simple " dispersion the elimination of the influence of dispersion for the proper correlation of the rotatory power with chemical constitution can be effected by making $\lambda^2 - \lambda_0^2 = 1$. For this value of λ, known as the " absolute wavelength ", the specific rotation, $[a]$, becomes numerically (not dimensionally) equal to the rotation constant, ' k_0 '. The value of k_0 may be regarded as a measure of the absolute optical rotatory power of the substance for the wavelength λ, where $\lambda = \sqrt{1+\lambda_0^2}$, in which the effects of dispersion are eliminated. In the same way (Table I), it is possible to eliminate the effect of dispersion in the study of refractive index by substituting $\lambda^2 - \lambda_0^2 = 1$ sq. micron in the simplified Maxwell-Sellmeier equation so that the value of the " absolute refractive index " is given by

$$n_{abs} = \sqrt{a^2 + b_0 \ (1 + \lambda_0^2)}$$

We have now made a study of the aryl derivatives of imino- and aminocamphors (d- and dl-) with the object of finding out the effect of substituting a methyl group for a hydrogen atom in the *ortho-*, *meta-*, and *para-* positions of the benzene nucleus and of breaking the conjugation between the carbonyl and the azethenoid groups and the benzene ring on their refractive index in the visible region of the spectrum.
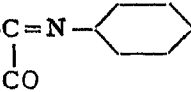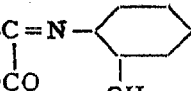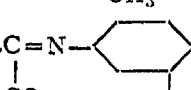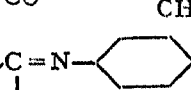
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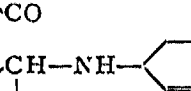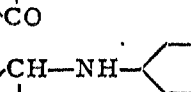
The compounds were prepared and purified by the methods described by Singh and collaborators.[2, 3]

The refractive indices were determined with a Pulfrich Refractometer maintained at a constant temperature of 38° C. The concentration of the solutions in absolute alcohol was one per cent. (namely, one gram per 100 c.c. of solution). The light sources used consisted of a hydrogen discharge tube for wavelengths H_{6563}, H_{5876} and H_{4861}; mercury arc for wavelength Hg_{5461} and sodium flame for Na_{5893}. For the arylaminocamphors, a sixth line, Hg_{4359}, is also taken.

The experimental results are given in Tables II to IX. A summary of the results is given in Table I.

TABLE I

Comparative Tabular Statement of Values of (1) "Absolute" Molecular Rotation Constant (K_0) (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 $A°.U.$

| 1	2	3	4	5	6	7	8
Compound	Position Isomeride	$*[M]^{85°}_{abs} = k_0$ (Drude Equation) for $\lambda = \sqrt{1+\lambda_0^2}$	$n^{38°}_{abs} = \sqrt{a^2+b_0(1+\lambda_0^2)}$ (Maxwell-Sellmeier Equation) for $\lambda = \sqrt{1+\lambda_0^2}$	$*\lambda_0$ (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 C_8H_{14} (C=N—phenyl, CO)	un.	309·4	1·3520	3821	3804	3812	+17
2 C_8H_{14} (C=N—phenyl-CH₃, CO) ortho	ortho	221·8	1·3518	3845	3824	3835	+21
3 C_8H_{14} (C=N—phenyl-CH₃, CO) meta	meta	295·2	1·3518	3962	3989	3975	−27
4 C_8H_{14} (C=N—phenyl—CH₃, CO) para	para	375·8	1·3515	3947	3915	3931	+32
5 C_8H_{14} (CH—NH—phenyl, CO)	un.	72·71	1·3522	2748	2737	2743	+11
6 C_8H_{14} (CH—NH—phenyl-CH₃, CO) ortho	ortho	65·27	1·3513	2040	2030	2035	+10
7 C_8H_{14} (CH—NH—phenyl-CH₃, CO) meta	meta	74·25	1·3511	2114	2131	2122	−17
8 C_8H_{14} (CH—NH—phenyl—CH₃, CO) para	para	63·8	1·3515	2417	2378	2398	+39

* These figures in columns 3 and 5 are taken from Singh, B. K. and Singh, K., Unpublished results.

TABLE II

Refractive Dispersion of d- *and* dl-*Phenyliminocamphors*

$$C_8H_{14} \Big\langle {}^{C\,=\,N-\bigcirc}_{CO}$$
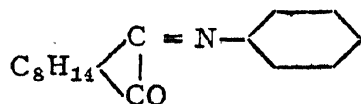
$$n^2 = 1 \cdot 8043 + \frac{0 \cdot 02049\lambda^2}{\lambda^2 - 0 \cdot 1447}; \qquad \lambda_0^2 = 0 \cdot 1447; \qquad \lambda_0 = 0 \cdot 3804$$

$$\dagger \, [a]_\lambda^{35^\circ} = \frac{128 \cdot 4}{\lambda^2 - 0 \cdot 1460}; \qquad \lambda_0^2 = 0 \cdot 1460; \qquad \lambda_0 = 0 \cdot 3821$$

	$\ddagger n_0$	$\ddagger n_d$	$n_d - n_c$	$\ddagger n_r$	$n_r - n_c$
H_{6563} ..	1·3547	1·3546	−0·0001	1·3545	−0·0002
Na_{5893} ..	1·3560	1·3561	−0·0001	1·3560	±0·0000
H_{5876} ..	1·3560	1·3560	±0·0000	1·3561	+0·0001
Hg_{5461} ..	1·3580	1·3580	±0·0000	1·3579	−0·0001
H_{4861} ..	1·3628	1·3626	−0·0002	1·3627	−0·0001

† The rotatory dispersion equations in Tables II to IX are taken from Singh, B. K. and Singh, K., Unpublished results.

‡ n_c denotes refractive index calculated from the refractive dispersion equation ; n_d and n_r stand for the refractive index for the dextro and racemic forms respectively. These abbreviations apply to Tables II to IX.

TABLE III

Refractive Dispersion of d- *and* dl- *Ortho Tolyliminocamphors*

$$C_8H_{14} \Big\langle {}^{C\,=\,N-\bigcirc}_{CO} \; {}_{CH_3}$$
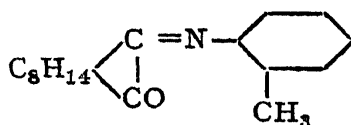
$$n^2 = 1 \cdot 8038 + \frac{0 \cdot 02058\lambda^2}{\lambda^2 - 0 \cdot 1462}; \qquad \lambda_0^2 = 0 \cdot 1462; \qquad \lambda_0 = 0 \cdot 3824$$

$$[a]_\lambda^{35^\circ} = \frac{87 \cdot 0}{\lambda^2 - 0 \cdot 1478}; \qquad \lambda_0^2 = 0 \cdot 1478; \qquad \lambda_0 = 0 \cdot 3845$$

	n_c	n_d	$n_d - n_c$	n_r	$n_r - n_c$
H_{6563} ..	1·3546	1·3546	±0·0000	1·3547	+0·0001
Na_{5893} ..	1·3562	1·3561	−0·0001	1·3561	−0·0001
H_{5876} ..	1·3562	1·3560	−0·0002	1·3559	−0·0003
Hg_{5461} ..	1·3580	1·3580	±0·0000	1·3581	+0·0001
H_{4861} ..	1·3630	1·3631	+0·0001	1·3630	±0·0000

TABLE IV

Refractive Dispersion of d- *and* dl- *Meta Tolyliminocamphors*

$$C_8H_{14} \diagdown \begin{array}{c} C = N - \bigcirc \\ | \\ CO \end{array} \quad CH_3$$
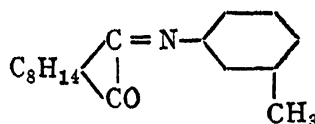
$$n^2 = 1\cdot8087 + \frac{0\cdot01603\lambda^2}{\lambda^2 - 0\cdot1591}; \qquad \lambda_0^2 = 0\cdot1591; \qquad \lambda_0 = 0\cdot3989$$

$$[\alpha]_\lambda^{35^\circ} = \frac{115\cdot8}{\lambda^2 - 0\cdot1570}; \qquad \lambda_0^2 = 0\cdot1570; \qquad \lambda_0 = 0\cdot3962$$

	n_c	n_d	$n_d - n_c$	n_r	$n_r - n_c$
H_{6563} ..	.1·3543	1·3545	+0·0002	1·3545	+0·0002
Na_{5893} ..	1·3558	1·3559	+0·0001	1·3559	+0·0001
H_{5876} ..	1·3559	1·3560	+0·0001	1·3561	+0·0002
Hg_{5461} ..	1·3576	1·3580	+0·0004	1·3580	+0·0004
H_{4861} ..	1·3631	1·3633	+0·0002	1·3630	−0·0001

TABLE V

Refractive Dispersion of d- *and* dl- *Para Tolyliminocamphors*

$$C_8H_{14} \diagdown \begin{array}{c} C = N - \bigcirc CH_3 \\ | \\ CO \end{array}$$

$$n^2 = 1\cdot8042 + \frac{0\cdot01932\lambda^2}{\lambda^2 - 0\cdot1533}; \qquad \lambda_0^2 = 0\cdot1533; \qquad \lambda_0 = 0\cdot3915$$

$$[\alpha]_\lambda^{35^\circ} = \frac{147\cdot4}{\lambda^2 - 0\cdot1558}; \qquad \lambda_0^2 = 0\cdot1558; \qquad \lambda_0 = 0\cdot3947$$

	n_c	n_d	$n_d - n_c$	n_r	$n_r - n_c$
H_{6563} ..	1·3543	1·3543	±0·0000	1·3545	+0·0002
Na_{5893} ..	1·3560	1·3561	+0·0001	1·3561	+0·0001
H_{5876} ..	1·3560	1·3558	−0·0002	1·3560	±0·0000
Hg_{5461} ..	1·3579	1·3580	+0·0001	1·3581	+0·0002
H_{4861} ..	1·3635	1·3633	−0·0002	1·3635	±0·0000

TABLE VI

Refractive Dispersion of d- *and* dl- *Phenylaminocamphors*

$$C_8H_{14} \Big\langle {}^{CH-NH-\bigcirc}_{CO}$$

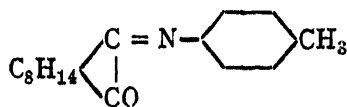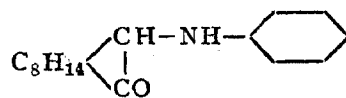$$n^2 = 1.7702 + \frac{0.05434\lambda^2}{\lambda^2 - 0.07493}; \qquad \lambda_0^2 = 0.07493; \qquad \lambda_0 = 0.2737$$

$$[\alpha]_\lambda^{35°} = \frac{29.78}{\lambda^2 - 0.07551}; \qquad \lambda_0^2 = 0.07551; \qquad \lambda_0 = 0.2748$$

	n_c	n_d	$n_d - n_c$	n_r	$n_r - n_c$
H_{6563} ..	1.3550	1.3549	−0.0001	1.3550	±0.0000
Na_{5893} ..	1.3563	1.3563	±0.0000	1.3562	−0.0001
H_{5876} ..	1.3563	1.3565	+0.0002	1.3565	+0.0002
Hg_{5461} ..	1.3575	1.3575	±0.0000	1.3575	±0.0000
H_{4861} ..	1.3600	1.3602	+0.0002	1.3603	+0.0003
Hg_{4359} ..	1.3638	1.3638	±0.0000	1.3639	+0.0001

TABLE VII

Refractive Dispersion of d- *and* dl- *Ortho Tolylaminocamphors*

$$C_8H_{14} \Big\langle {}^{CH-NH-\bigcirc}_{CO} \quad {}_{CH_3}$$
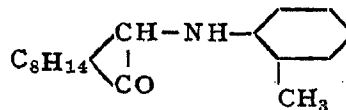
$$n^2 = 1.6705 + \frac{0.1494\lambda^2}{\lambda^2 - 0.0412}; \qquad \lambda_0^2 = 0.0412: \qquad \lambda_0 = 0.2030$$

$$[\alpha]_\lambda^{35°} = \frac{25.4}{\lambda^2 - 0.0416}; \qquad \lambda_0^2 = 0.0416; \qquad \lambda_0 = 0.2040$$

	n_c	n_d	$n_d - n_c$	n_r	$n_r - n_c$
H_{6563} ..	1.3549	1.3547	−0.0002	1.3549	±0.0000
Na_{5893} ..	1.3565	1.3565	±..0000	1.3564	−0.0001
H_{5876} ..	1.3565	1.3566	+0.0001	1.3564	−0.0001
Hg_{5461} ..	1.3579	1.3579	±0.0000	1.3580	+0.0001
H_{4861} ..	1.3607	1.3608	+0.0001	1.3609	+0.0002
Hg_{4359} ..	1.3643	1.3644	+0.0001	1.3642	−0.0001

TABLE VIII

Refractive Dispersion of d- *and* dl- *Meta Tolylaminocamphors*

$$C_8H_{14} \Big\langle \begin{matrix} CH - NH - \\ | \\ CO \end{matrix} \bigcirc \begin{matrix} \\ | \\ CH_3 \end{matrix}$$
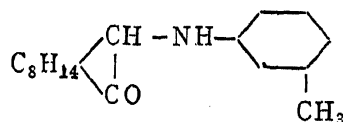
$$n^2 = 1 \cdot 6926 + \frac{0 \cdot 1275 \lambda^2}{\lambda^2 - 0 \cdot 04541}; \qquad \lambda_0^2 = 0 \cdot 04541; \qquad \lambda_0 = 0 \cdot 2131$$

$$[\alpha]_\lambda^{35^\circ} = \frac{28 \cdot 89}{\lambda^2 - 0 \cdot 0447}; \qquad \lambda_0^2 = 0 \cdot 0447; \qquad \lambda_0 = 0 \cdot 2114$$

	n_c	n_d	$n_d - n_c$	n_γ	$n_\gamma - n_c$
H_{6563} ..	1·3546	1·3545	−0·0001	1·3546	±0·0000
Na_{5893} ..	1·3561	1·3562	+0·0001	1·3561	±0·0000
H_{5876} ..	1·3562	1·3562	±0·0000	1·3560	−0·0002
Hg_{5461} ..	1·3575	1·3575	±0·0000	1·3576	+0·0001
H_{4861} ..	1·3602	1·3605	+0·0003	1·3604	+0·0002
Hg_{4359} ..	1·3638	1·3637	−0·0001	1·3638	±0·0000

TABLE IX

Refractive Dispersion of d- *and* dl- *Para Tolylaminocamphors*

$$C_8H_{14} \Big\langle \begin{matrix} CH - NH - \\ | \\ CO \end{matrix} \bigcirc - CH_3$$
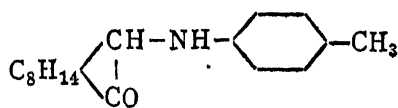
$$n^2 = 1 \cdot 7297 + \frac{0 \cdot 09170 \lambda^2}{\lambda^2 - 0 \cdot 05656}; \qquad \lambda_0^2 = 0 \cdot 05656; \qquad \lambda_0 = 0 \cdot 2378$$

$$[\alpha]_\lambda^{35^\circ} = \frac{24 \cdot 82}{\lambda^2 - 0 \cdot 0584}; \qquad \lambda_0^2 = 0 \cdot 0584; \qquad \lambda_0 = 0 \cdot 2417$$

	n_c	n_d	$n_d - n_c$	n_γ	$n_\gamma - n_c$
H_{6563} ..	1·3547	1·3547	±0·0000	1·3547	±0·0000
Na_{5893} ..	1·3562	1·3561	−0·0001	1·3562	±0·0000
H_{5876} ..	1·3562	1·3560	−0·0002	1·3561	−0·0001
Hg_{5461} ..	1·3575	1·3575	±0·0000	1·3574	−0·0001
H_{4861} ..	1·3603	1·3606	+0·0003	1·3605	+0·0002
Hg_{4359} ..	1·3639	1·3638	−0·0001	1·3639	±0·0000

A 4

DISCUSSION

Table I gives the effect of substituting a methyl group for a hydrogen atom in the o-, m- and p-position of the benzene nucleus in phenyliminocamphors and their reduction products. We find that phenyliminocamphor and the o-, m- and p-tolyliminocamphors have practically identical refractive indices for the wavelengths studied. The same is the case for the amino compounds. It thus appears that the position isomerides do not have any appreciable effect on refractive dispersion unlike rotatory dispersion.

Effect of Conjugated Unsaturation on Refractive Index

It is well known that Thiele's conjugated double bonds are associated with enhancement in the value of the refractive index. In the substances investigated in the present work, the conversion of an aryl imino compound to the corresponding amino derivative—involving the breaking of conjugation of double bonds between the carbonyl group, the azethenoid group and the benzene ring—does not produce any noticeable depression in the refractive index. This result is in remarkable contrast with the phenomenal decrease in rotation which accompanies the breaking of the conjugation of double bonds present in the aryl iminocamphor derivatives.

Characteristic Absorption Bands

In the earlier papers[1,4] we have shown that the characteristic absorption bands, $\lambda_0 s$, derived from the Drude equation for rotatory dispersion and from the Maxwell-Sellmeier equation for refractive dispersion are almost identical in magnitude and therefore lend strong support to the view that these wavelengths represent real absorption bands which may be associated with electrons responsible for optical and refractive activity. In some cases where direct absorption measurements have been made, as for example, camphors,[5] these values of $\lambda_0 s$, deduced from dispersion equations, were found to be identical with the wavelengths of actual absorption bands. In the results now presented and summarised in Table I, the values of $\lambda_0 s$, as deduced from Drude[2] and Maxwell-Sellmeier equations, are identical within experimental limits. The differences in the value of λ_0 (Table I, column 8) from the two methods lie between 10 to 39 A°.U.

The refractive indices of the optically active form and the racemic modification are identical.

There is, however, a phenomenal fall in the value of λ_0 on passing from the imino to amino derivatives as deduced from dispersion data (Table I) and may be ascribed to the breaking of the conjugation between the azethenoid and carbonyl groups and the benzene ring which takes place when the

imino compounds are reduced to the corresponding amino derivatives. In the case of the phenyl compounds, the mean fall in the value of λ_0 is 1069 A.°U., while for the *ortho* tolyl compounds it is 1800 A°.U., for the *meta* 1853 A°.U. and for the *para* 1533 A°.U. We thus see that the "characteristic" absorption band has been shifted from the near ultra-violet to the far ultra-violet region of the spectrum.

The abovementioned results seem significant: the study of rotatory[2] and refractive dispersion[1,4] thus enables us by measurements in the visible region of the spectrum to calculate the position of the "characteristic" absorption bands in the far ultra-violet which is ordinarily difficult of experimental investigation by the technique of absorption spectroscopy. The problem is in a way similar to the determination of infra-red bands by Raman Effect, which allows the measurement of the characteristic rotational and vibrational frequencies of the molecules. These frequencies usually have low values and therefore lie in the infra-red region of the spectrum where experimental difficulties were also a hindrance in their determination. The Raman Effect solves this difficult problem for, as is well known, the same frequencies, subject to certain exceptions, can be obtained from Raman displacements of the scattered radiations, the wavelengths of which can very well be in any convenient region of the spectrum, *e.g.*, the visible or the quartz ultra-violet.

SUMMARY

1. The refractive indices of several aryl-imino and -amino compounds have been determined in 1 per cent. alcohol solution for 5 or 6 wavelengths in the visible region of the spectrum.

2. The values of the refractive index for the *d-* and *dl-*forms have been found to be identical.

3. The effect of the substitution of a methyl group for a hydrogen atom and of position isomerism on refractive index is negligible.

4. The values of λ_0 determined from the Drude and Maxwell-Sellmeier equations were found to be nearly identical.

5. The effect of breaking the conjugation of double bonds between the carbonyl azethenoid groups and the benzene ring of the aryliminocamphors—resulting in the production of the corresponding amino derivatives—is to lower their "characteristic" wavelengths ($\lambda_0 s$) very considerably.

6. The application of rotatory and refractive dispersion in the visible region of the spectrum for the study of absorption spectra work, especially in the far ultra-violet, has been discussed.

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