

THE REFRACTIVE DISPERSIVE POWER OF ORGANIC COMPOUNDS

Part I. The Refractive Dispersion of Dextro, Lævo and Racemic Forms of Borneol, Camphor, Camphoric Acid, Camphoric Anhydride and Camphor Carboxylic Acid

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Received July 14, 1947

IN this series of investigations on the refractive dispersion of organic compounds, we describe, in this part, our experiments on enantiomeric and racemic forms of five terpene derivatives. The earlier formulæ of Gladstone and Dale¹ $\left(\frac{n-1}{d}\right)$ and of Lorenz and Lorentz² $\frac{n^2-1}{(n^2+1)d}$ for refractive power neglect the effect of dispersion. This effect cannot be neglected especially in the case of substances in which the wavelengths of the characteristic absorption bands controlling the dispersion are not far removed from those of the spectral region for which observations are made.

Maxwell³ in 1869 proposed the following dispersion equation in the form of a question set at the Mathematical Tripos examination in the University of Cambridge:

$$n^2 = a^2 + \Sigma \frac{b_0 \lambda^2}{\lambda^2 - \lambda_0^2}.$$

This equation was also put forward by Sellmeier in 1871 and is known as the Maxwell-Sellmeier or shortly the Sellmeier equation for refractive dispersion. It is very similar to the Drude equation⁴ for rotatory dispersion:

$$[a] = \Sigma \frac{k_0}{\lambda^2 - \lambda_0^2}.$$

Each term of the summation in the two equations has two constants. In the Drude equation the two constants are k_0 (rotation constant) and λ_0^2 (dispersion constant). Similarly the Sellmeier equation has two constants, b_0 (refraction constant) and λ_0^2 (dispersion constant). In addition there is the constant term a^2 , which when added to the summation term represents the square of the refractive index of the medium for a stationary electric field.

Both the rotatory dispersion equation of Drude and the refractive dispersion equation of Sellmeier suffer from the same defect: they do not take

into account the degradation of light energy due to absorption and thus break down when measurements are made in the region of absorption, as the influence of the neglected friction term begins to make itself felt.

The Dispersion Constant λ_0^2 :

As far as theoretical and experimental evidence goes, λ_0^2 the dispersion constant which represents the square of the wavelength of the dominant absorption band, controlling the refractive dispersion and optical rotation of the medium appears to be identical in both cases. Lowry's⁵ work on the rotatory dispersion of quartz in the visible region of the spectrum gives the following equation for rotatory power:

$$\alpha = \frac{11.6064}{\lambda^2 - 0.010527} + \frac{13.42}{\lambda^2 - 78.22} - \frac{4.3685}{\lambda^2}$$

in which α represents the rotation in degrees per millimetre for a given value of λ .

Gifford's values⁶ for the refractive index of quartz for the ordinary ray fit in a Sellmeier equation:

$$n^2 = 1.35375 + \frac{1.00317 \lambda^2}{\lambda^2 - 0.010627} - \frac{0.8275 \lambda^2}{\lambda^2 - 78.22}$$

in which the values of λ_0 's (the wavelengths of the dominant absorption bands) are those derived from Lowry's equation of rotatory dispersion of quartz above mentioned.

Pickard and Hunter⁷ measured the natural rotatory dispersion, refractive dispersion and absorption spectrum of *d*- γ nonyl nitrite and found the following almost identical values of λ_0 in the three cases:

$\lambda_0 = 3680 \text{ \AA U.}$ (rotatory dispersion measurements),

$\lambda_0 = 3730 \text{ \AA.U.}$ (from measurements of refractive index),

$\lambda_0 = 3670 - 3720 \text{ \AA.U.}$ (from direct photographic measurements of absorption).

It, thus, appears that the characteristic absorption bands which rotatory dispersion and refractive dispersion equations predict have a real existence and are identical.

It is with a view to place this relation on a sure experimental foundation that we have undertaken in this and subsequent papers the determination of the wavelengths of the dominant absorption band (λ_0) from measurements of refractive dispersion.

The substances employed in the present investigations are the *d*-, *l*- and *dl*- forms of borneol, camphor, camphoric acid, camphoric anhydride and camphor carboxylic acid. The rotatory dispersion of camphor carboxylic acid will be described in a separate communication and that of the other four compounds in their dextro and lævo forms has already been reported by one of us.⁸ The refractive dispersion of these compounds for the *d*-, *l*- and *dl*- forms are given in Tables III to VII. The observed and calculated values of refractive index for the five wavelengths for the three stereoisomeric forms as shown reveal remarkable agreement, the differences between the observed and calculated values being within 1 part in 7000. In these Tables III to VII, the rotatory dispersion equations⁸ for the compounds are also given alongside the refractive dispersion equations for the sake of comparison of their dispersion constants (λ_0^2). In Table I, the values of λ_0 as derived from rotatory dispersion and refractive dispersion measurements are given.

TABLE I

Comparative Tabular Statement of Values of (1) "Absolute" rotation (Drude Equation); (2) "Absolute" refractive index (Sellmeier equation); (3) the wavelength of the dominant absorption band from Drude and Sellmeier equations in Å.U.

Compound	$[\alpha]^*_{abs} = k_0$ (Drude eqn.)	$n^*_{abs} = \sqrt{a^2 + b_0(1 + \lambda_0^2)}$ (Sellmeier eqn.)	λ_0 (from Drude eqn.)	λ_0 (from Sellmeier eqn.)
Borneol ..	11.8	1.3591	1921	1962
Camphor	{ 2950 1924	1912
Camphoric acid ..	14.84	1.3596	2184	2231
Camphoric anhydride ..	0.3041	1.3555	..	2076
Camphor carboxylic acid	16.94	1.3605	2550	2589

* The values of $[\alpha]_{abs}$ and n_{abs} are calculated for the wave-length at which $\lambda^2 - \lambda_0^2 = 1$ square micron.

The differences between the values of λ as deduced from rotatory dispersion equation and refractive dispersion equation range from 12 Å.U. in the case of camphors to 47 Å.U. for camphoric acids. For Borneols this difference is 41 units. The agreement between the two values of λ is therefore very close. Camphor has a complex rotatory dispersion represented by a two-term Drude equation*

$$[\alpha] = \frac{21.91}{\lambda^2 - 0.087} - \frac{11.50}{\lambda^2 - 0.037}$$

* This equation is recalculated from data given in Table III of Singh and Mahanti's paper (Proc. Ind. Acad. Sci., A, 1935, 2, 389).

which gives two absorption bands at $\lambda 1924 \text{ \AA.U.}$ and $\lambda 2950 \text{ \AA.U.}$ The refractive dispersion equation of Sellmeier gives only one band at $\lambda 1912 \text{ \AA.U.}$, which corresponds to one of the characteristic absorption bands at $\lambda 1924 \text{ \AA.U.}$ deduced from rotatory dispersion equation. The other band corresponding to $\lambda 2950 \text{ \AA.U.}$ is not revealed by the three-constant Sellmeier equation as we have taken only one term in the summation. If a second term of the summation is also taken, it will result in a five-constant equation. The evaluation of this equation will be a tedious mathematical operation and it will be futile to attempt it as two out of the five spectral lines for which observations were taken are too close, namely Na_{5893} and H_{5876} . In fact as we have only 4 lines for the refractive index measurements, it is impossible to calculate the five-constant Sellmeier equation having two terms in the summation. It is, therefore, not possible to find out the second dominant absorption band $\lambda 2950 \text{ \AA.U.}$ from the refractive dispersion equation with the present data. The direct determination of the absorption of camphor in alcohol gives a band whose maximum is at $\lambda 2874 \text{ \AA.U.}$ according to Baly⁹ *et al.*, and at $\lambda 2890 \text{ \AA.U.}$ according to Hartley.¹⁰ These are nearly identical in wavelengths with the second band at $\lambda 2950 \text{ \AA.U.}$ deduced from the rotatory dispersion equation. In the graphs of Baly and Hartley, there is a second band whose maximum is not reached at $\lambda 2200 \text{ \AA.U.}$ and may be considerably below this wavelength. As it is in the far ultra violet region, it has not yet been determined. It appears, however, that it may correspond to the band at $\lambda 1912 \text{ \AA.U.}$ and $\lambda 1924 \text{ \AA.U.}$ deduced from refractive dispersion and rotatory dispersion equations respectively.

These results furnish strong evidence in support of the Drude equation of rotatory dispersion and the Sellmeier equation of refractive dispersion. It, thus, appears that there is an intimate connection between optical rotatory power and refractive index. Livens¹¹ in 1913 deduced theoretically such a relationship which was subsequently tested experimentally by Peacock.¹² More recently, however, Condon¹³ has put forward a theoretical expression connecting rotatory power with refractive index, namely,

$$a = \frac{16\pi^3 N_1 \beta}{\lambda^2} \cdot \frac{n^2 + 2}{3}$$

but as it contains a parameter β which is not easily capable of evaluation except in some very simple cases, it has not so far found any general application.

In the case of the other substances investigated, the wavelengths of the characteristic absorption bands lie in the remote and not easily accessible spectral region in the ultra violet and a direct verification of the existence of

these bands deduced from the Drude and Sellmeier equations has not yet been realised.

Relation between Rotatory Power (Drude Equation) and Refractive Index (Sellmeier Equation) at corresponding conditions of wavelength

In previous communications,¹⁴ the elimination of dispersion for the proper correlation of rotatory power with chemical constitution has been emphasised. For substances which exhibit simple dispersion and obey Drude's one-term equation, $\alpha = \frac{k_0}{\lambda^2 - \lambda_0^2}$ this may be easily done by making $\lambda = \sqrt{1 + \lambda_0^2}$ and calling this the "absolute wavelength"; k_0 , the rotation constant, then becomes numerically, though not dimensionally, equal to $[\alpha]$ the rotatory power of the medium. This "absolute wavelength" is not much greater than 10,000 Å.U. in the infra-red region of the spectrum. Comparisons of optical rotatory power at this wavelength at which $\lambda^2 - \lambda_0^2 = 1$ square micron, may be regarded as those for corresponding conditions of wavelength, in which the effects of dispersion are eliminated. The values of $[\alpha]$ abs. or k_0 for the wavelength at which $\lambda^2 - \lambda_0^2 = 1$, for the four compounds showing simple dispersion are given in Table I. There is, however, no such easy process available for the complex type of dispersion as exhibited by camphor.

In the same way in studies on refractive index, the effect of dispersion may be eliminated for substances which obey Sellmeier's equation with only one term in the summation, namely, $n^2 = a^2 + \frac{b_0 \lambda^2}{\lambda^2 - \lambda_0^2}$. The expression for the absolute value of refractive index, n_{abs} , for the "absolute wavelength" at which $\lambda^2 - \lambda_0^2 = 1$ square micron, is as below:

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

These "absolute" values of refractive indices are also given in Table I. On comparing $[\alpha]_{abs}$ and n_{abs} . (Table I) for the "absolute wavelength", it is evident that although there is no simple mathematical relationship between them, yet a rough parallelism in their values is discernible. In other words, the compound having higher value of $[\alpha]_{abs}$. shows higher value of n_{abs} . and *vice versa*. This indicates that there is some connection between rotatory power and refractive index.

Case of Camphoric Anhydride

The rotatory dispersion of *d*- and *l*- camphoric anhydrides was determined by Singh and Mahanti⁸ and it was found that the compounds had zero

rotation for the wavelength range λ 6709 to 4358 Å.U. This apparent inactivity is not due to racemisation as the anhydrides on hydrolysis furnish the corresponding camphoric acids of the correct rotation. The anhydride ring is responsible for this phenomenal depression in rotation. Lowry,¹⁵ however, gives $[\alpha]_D = -1^\circ$ for *d*-camphoric anhydride* in chloroform. Making use of this value of $[\alpha]_D$ and that of $\lambda_0^2 = 0.0431$, deduced from the refractive dispersion equation of Sellmeier (Table VI), the Drude equation for camphoric anhydride for the D-line may be written thus:

$$[\alpha]_D = -1^\circ = -\frac{k_0}{(\cdot5893)^2 - 0.0431}$$

whence $k_0 = 0.3041$

$$\text{and } [\alpha]_\lambda = -\frac{0.3041}{\lambda^2 - 0.0431}$$

The Rotatory dispersion Table No. XIII given in the earlier paper of Singh and Mahanti⁸ may, therefore, be modified and substituted by Table II given below.

TABLE II

Rotatory Dispersion of d-Camphoric Anhydride in Chloroform

$$[\alpha]_\lambda^{35^\circ} = -\frac{0.3041}{\lambda^2 - 0.0431} \quad \lambda_0 = 2076 \text{ \AA. U.}$$

Wave-length	Specific rotation
Li ₆₇₀₈	.. -0.75°
Cd ₆₄₃₈	.. 0.82
Li ₆₁₀₄	.. 0.93
Na ₅₈₉₃	.. 1.00
Hg ₅₇₈₀	.. 1.04
Hg ₅₄₆₁	.. 1.19
Ag ₅₂₀₉	.. 1.33
Cd ₅₀₈₆	.. 1.41
Hg ₄₃₅₈	.. 2.07

Physical Identity of Enantiomers

Pasteur's Law of Molecular Dissymmetry¹⁶ holds good rigidly both as regards the vectorial and scalar properties of optically active and their opposite isomers. Numerous recent measurements on rotatory dispersion¹⁷ have confirmed the truth of this law. A series of measurements of their scalar properties such as viscosities¹⁸ has demonstrated that this law applies equally rigidly in their case also. The law was also shown to hold good as regards refractive index.¹⁸ These earlier measurements were made with an Abbe refractometer. Our present measurements (Tables III to VII) are made

with a Pulfrich Refractometer for five wavelengths in the visible region of the spectrum from $\lambda 6563 \text{ \AA.U.}$ to $\lambda 4359 \text{ \AA.U.}$ The refractive indices are identical for the *d*- and *l*- forms within an accuracy of about 1 part in 7,000. The refractive indices of the racemic forms (1 per cent. solution in ethyl alcohol) are identical with those of their optical isomers within about 1 part in 7000. It thus appears probable that the racemates in dilute solution are completely dissociated into their components.

EXPERIMENTAL

The dextro, lævo and racemic forms of borneol, camphor, camphoric acid and camphoric anhydride were prepared and purified according to the methods described by one of us.⁸ Camphor carboxylic acids were prepared according to the method of Bredt.^{19, 20}

The refractive indices were determined with a Pulfrich Refractometer, jacketed with water from a thermostat maintained at 35°C. and may be regarded accurate to 0.0002 unit. The concentration of the solution in absolute alcohol was one per cent., namely, one gram in 100 c.c. of solution, in all cases except camphoric anhydrides for which 0.625 per cent. solutions were made due to their low solubility. The experimental results are given in Tables III to VII.

TABLE III

Refractive Dispersion of *l*-, *d*- and *dl*-Borneols : $\text{C}_8\text{H}_{14} \begin{matrix} \text{CH}_2 \\ | \\ \text{CHOH} \end{matrix}$

$$n^2 = 1.6890 + \frac{0.1524\lambda^2}{\lambda^2 - 0.0385}; \quad \lambda_0^2 = 0.0385$$

$$\left\{ [\alpha]_{\lambda}^* = \frac{11.80}{\lambda^2 - 0.03692}; \quad \lambda_0^2 = 0.03692 \right\}$$

λ	$n^{\text{calculated}}$ (c)	$n^{\text{lævo}}$ (l)	$n^{\text{l-c}}$	n^{dextro} (d)	$n^{\text{d-c}}$	n^{racemic} (r)	$n^{\text{r-c}}$
H ₆₅₆₃	1.3625	1.3626	+0.0001	1.3627	+0.0002	1.3624	-0.0001
Na ₅₈₉₃	1.3640	1.3642	+0.0002	1.3641	+0.0001	1.3639	-0.0001
H ₅₈₇₆	1.3640	1.3641	+0.0001	1.3641	+0.0001	1.3640	±0.0000
Hg ₅₄₆₁	1.3653	1.3652	-0.0001	1.3653	±0.0000	1.3655	+0.0002
Hg ₄₃₅₉	1.3712	1.3710	-0.0002	1.3710	-0.0002	1.3712 ^p	±0.0000

* This equation is calculated from rotatory dispersion data given in Table XV of Singh and Mahanti's paper (*Proc. Ind. Acad. Sci., A*, 1935, 2, 394).

TABLE IV

Refractive Dispersion of l-, d- and dl- Camphors: C_8H_{14} $\begin{matrix} \text{CH}_2 \\ | \\ \text{C}=\text{O} \end{matrix}$

$$n^2 = 1.6657 + \frac{0.1742\lambda^2}{\lambda^2 - 0.0366}; \quad \lambda_0^2 = 0.0366$$

$$\left\{ [\alpha]_{\lambda}^* = \frac{21.91}{\lambda^2 - 0.087} - \frac{11.50}{\lambda^2 - 0.037} \quad \begin{matrix} \lambda_0^2 = 0.037 \\ \lambda_1^2 = 0.087 \end{matrix} \right\}$$

λ	$n_{\text{calculated}}$ (c)	$n_{\text{lævo}}$ (l)	n_{l-c}	n_{dextro} (d)	n_{d-c}	n_{racemic} (r)	n_{r-c}
H ₆₅₆₃ ..	1.3624	1.3622	-0.0002	1.3623	-0.0001	1.3624	±0.0000
Na ₅₈₉₃ ..	1.3640	1.3639	-0.0001	1.3639	-0.0001	1.3640	±0.0000
H ₅₈₇₆ ..	1.3640	1.3641	+0.0001	1.3641	+0.0001	1.3641	+0.0001
Hg ₅₄₆₁ ..	1.3654	1.3653	-0.0001	1.3652	-0.0002	1.3653	-0.0001
Hg ₄₃₅₉ ..	1.3717	1.3716	-0.0001	1.3717	±0.0000	1.3715	-0.0002

* This rotatory dispersion equation has been re-calculated from data given in Table III of Singh and Mahanti's paper (*Proc. Ind. Acad. Sci., A*, 1935, 2, 389).

TABLE V

Refractive Dispersion of l-, d-, and dl- Camphoric Acids: C_8H_{14} $\begin{matrix} \text{COOH} \\ | \\ \text{COOH} \end{matrix}$

$$n^2 = 1.7277 + \frac{0.1153\lambda^2}{\lambda^2 - 0.0489}; \quad \lambda_0^2 = 0.0489$$

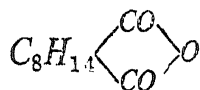
$$\left\{ [\alpha]_{\lambda}^* = \frac{14.84}{\lambda^2 - 0.0477} \quad \lambda_0^2 = 0.0477 \right\}$$

λ	$n_{\text{calculated}}$ (c)	$n_{\text{lævo}}$ (l)	n_{l-c}	n_{dextro} (d)	n_{d-c}	n_{racemic} (r)	n_{r-c}
H ₆₅₆₃ ..	1.3630	1.3629	-0.0001	1.3630	±0.0000	1.3631	+0.0002
Na ₅₈₉₃ ..	1.3645	1.3647	+0.0002	1.3645	±0.0000	1.3647	+0.0002
H ₅₈₇₆ ..	1.3645	1.3646	+0.0001	1.3646	+0.0001	1.3645	±0.0000
Hg ₅₄₆₁ ..	1.3659	1.3658	-0.0001	1.3657	-0.0002	1.3660	+0.0001
Hg ₄₃₅₉ ..	1.3722	1.3722	±0.0000	1.3721	-0.0001	1.3720	0.0002

* This rotatory dispersion equation is taken from Table V of Singh and Mahanti's paper (*Proc. Ind. Acad. Sci., A*, 1935, 2, 390).

TABLE VI

Refractive Dispersion of l-, d- and dl- Camphoric Anhydrides:



$$n^2 = 1.6900 + \frac{0.1412\lambda^2}{\lambda^2 - 0.0431}; \quad \lambda_0^2 = 0.0431$$

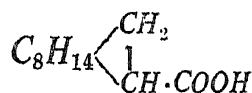
$$\left\{ [\alpha]_{\lambda}^* = \frac{0.3041}{\lambda^2 - 0.0431} \right\}$$

λ	$n^{\text{calculated}}$ (c)	$n^{\text{lævo}}$ (l)	$n^{\text{l-c}}$	n^{dextro} (d)	$n^{\text{d-c}}$	n^{racemic} (r)	$n^{\text{r-c}}$
H ₆₅₆₃ ..	1.3591	1.3590	-0.0001	1.3590	-0.0001	1.3592	+0.0001
Na ₅₈₉₃ ..	1.3607	1.3608	+0.0001	1.3609	+0.0002	1.3608	+0.0001
H ₅₈₇₆ ..	1.3607	1.3607	±0.0000	1.3608	+0.0001	1.3608	+0.0001
Hg ₅₄₆₁ ..	1.3621	1.3621	±0.0000	1.3621	±0.0000	1.3622	+0.0001
Hg ₄₃₅₉ ..	1.3685	1.3685	±0.0000	1.3685	±0.0000	1.3684	-0.0001

* This rotatory dispersion equation is calculated by using λ_0^2 deduced from the refractive dispersion equation given in this Table.

TABLE VII

Refractive Dispersion of l-, d-, and dl- Camphor Carboxylic Acids:



$$n^2 = 1.7765 + \frac{0.0699\lambda^2}{\lambda^2 - 0.0670}; \quad \lambda_0^2 = 0.0670$$

$$\left\{ [\alpha]_{\lambda}^* = \frac{16.94}{\lambda^2 - 0.0650} \quad \lambda_0^2 = 0.0650 \right\}$$

λ	$n^{\text{calculated}}$ (c)	$n^{\text{lævo}}$ (l)	$n^{\text{l-c}}$	n^{dextro} (d)	$n^{\text{d-c}}$	n^{racemic} (r)	$n^{\text{r-c}}$
H ₆₅₆₃ ..	1.3635	1.3635	±0.0000	1.3635	±0.0000	1.3636	+0.0001
Na ₅₈₉₃ ..	1.3650	1.3649	-0.0001	1.3649	-0.0001	1.3649	-0.0001
H ₅₈₇₆ ..	1.3650	1.3650	±0.0000	1.3651	+0.0001	1.3651	+0.0001
Hg ₅₄₆₁ ..	1.3663	1.3661	-0.0002	1.3663	±0.0000	1.3664	+0.0001
Hg ₄₃₅₉ ..	1.3727	1.3727	±0.0000	1.3727	±0.0000	1.3727	±0.0000

* Unpublished results.²⁰

SUMMARY

1. The refractive dispersion of dextro, lævo and racemic forms of borneol, camphor, camphoric acid, camphoric anhydride and camphor

carboxylic acid has been determined in alcohol at 35° C. for five wavelengths. The values of the refractive indices are identical for the three forms and fit in a Sellmeier equation.

2. The equality of the refractive indices of the dextro and lævo forms supports Pasteur's Law of Molecular Dissymmetry.

3. The values of λ_0 , the wavelength of the characteristic absorption band, calculated from the Sellmeier refractive dispersion equations are in remarkable agreement with those deduced from the Drude rotatory dispersion equations.

4. A rotatory dispersion equation for camphoric anhydride, which cannot be determined from its rotatory power data, has been deduced by employing λ_0 calculated from the Sellmeier refractive dispersion equation.

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