

STUDIES ON THE RELATION BETWEEN CHEMICAL CONSTITUTION AND ULTRAVIOLET ABSORPTION SPECTRA OF OPTICALLY ACTIVE AND RACEMIC COMPOUNDS

Part VII. Correlation of Absorption Maxima, λ_{\max} , and Characteristic Wavelengths, λ_{0s} , of Camphor- β -Sulphonyl-phenyl, -tolyl (*o*-, *m*- and *p*-) and Naphthyl (α - and β -)-amides

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Received March 19, 1958

ABSTRACT

The ultraviolet absorption spectra of camphor- β -sulphonyl-phenyl, (*o*-, *m*- and *p*-) tolyl, (α - and β -) naphthylamides have been determined in methyl alcohol, ethyl alcohol, and chloroform. The absorption spectra of all the compounds show two absorption bands: one varying from 267 to 284 $m\mu$, the longer absorption maximum (λ_{\max}) due to selective absorption of the keto group, and the other shorter one, ranging from 226 to 230 $m\mu$, due to general absorption of the saturated molecules. The values of the characteristic wavelengths, λ_{0s} , obtained from Drude's one-term equation, have been compared with the absorption maxima, λ_{\max} , obtained by direct measurements. There are marked discrepancies in the values of λ_0 and λ_{\max} . An explanation of the discrepancies is given.

The nature of racemic modifications of the compounds has also been discussed.

In continuation of Part VI¹ of this series, we describe, in this communication, the ultraviolet absorption spectra of (*d* and *dl*) camphor- β -sulphonyl-phenyl, *o*-tolyl, *m*-tolyl, *p*-tolyl and naphthyl (α - and β -)-amides in methyl alcohol, ethyl alcohol and chloroform. The 'characteristic' wavelengths, λ_{0s} , calculated from Drude's rotatory dispersion *one-term* equation² have been compared with the absorption maxima, λ_{\max} , obtained by direct measurements.

The absorption measurements of the dextro and the racemic forms of these compounds have been studied with a view to throw further light on the nature of these racemic modifications investigated by us² earlier by the application of melting point-composition diagram of Roozeboom,

EXPERIMENTAL

The compounds mentioned above were prepared and purified according to methods described previously.² The absorption measurements were carried out in spectroscopically pure solvents with Beckman DU Spectrophotometer. The molecular extinction coefficients, ϵ , were calculated from optical density at different wavelengths, but only their peak values (ϵ_{\max}) corresponding to the absorption maxima, λ_{\max} , are given in Table I. The absorption spectra curves (Figs. 1-6) were prepared by plotting the molecular extinction coefficients (ϵ) against the corresponding wavelengths (λ).

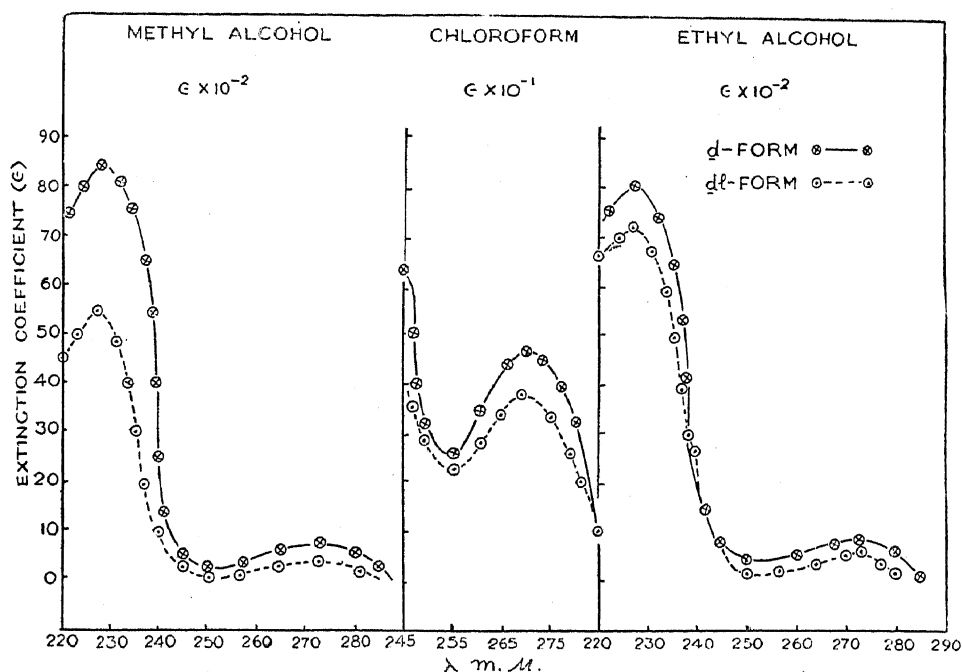


FIG. 1. Camphor- β -sulphonylphenylamides.

The rotatory dispersion of *d*-camphor- β -sulphonyl- α -naphthylamide, which was not given in chloroform in the earlier paper,² has been determined and recorded in Table VI.

DISCUSSION

The most frequent representation of rotatory dispersion is given by Drude's equation,

$$[\alpha] = \sum \frac{K}{\lambda^2 - \lambda_0^2}$$

TABLE I

| Compound | Solvent | <i>d</i> -isomer | | <i>dl</i> -isomer | | λ_0 in $m\mu$ * $\lambda_0 - \lambda_{max}$ | |
|--|----------------|--------------------------|------------------|--------------------------|------------------|---|-------|
| | | λ_{max} , $m\mu$ | ϵ_{max} | λ_{max} , $m\mu$ | ϵ_{max} | | |
| Camphor- β -sulphonyl- <i>p</i> -phenylamide | Methyl alcohol | 273 | 724.5 | 273 | 260.95 | 296.6 | +23.6 |
| | | 228 | 8442.5 | 227 | 5372.5 | | |
| Camphor- β -sulphonyl- <i>p</i> -phenylamide | Ethyl alcohol | 273 | 808.9 | 273 | 540.5 | 295.0 | +22.0 |
| | | 227 | 8025.0 | 227 | 7042.0 | | |
| Camphor- β -sulphonyl- <i>p</i> -phenylamide | Chloroform | 270 | 460.5 | 271 | 375.0 | 255.0 | -16.0 |
| | | .. | .. | .. | .. | | |
| Camphor- β -sulphonyl- <i>o</i> -tolylamide | Methyl alcohol | 267 | 680.5 | 267 | 638.8 | 279.3 | +12.3 |
| | | 226 | 6442.0 | 226 | 7608.0 | | |
| Camphor- β -sulphonyl- <i>o</i> -tolylamide | Ethyl alcohol | 267 | 609.9 | 267 | 555.3 | 249.0 | -18.0 |
| | | 226 | 7254.6 | 226 | 7062.0 | | |
| Camphor- β -sulphonyl- <i>o</i> -tolylamide | Chloroform | 267 | 890.0 | 267 | 492.0 | 204.9 | -62.1 |
| | | .. | .. | .. | .. | | |
| Camphor- β -sulphonyl- <i>m</i> -tolylamide | Methyl alcohol | 275 | 658.0 | 275 | 1034.0 | 279.3 | +4.3 |
| | | 230 | 12040.0 | 230 | 9469.0 | | |
| Camphor- β -sulphonyl- <i>m</i> -tolylamide | Ethyl alcohol | 275 | 914.15 | 275 | 590.6 | 286.4 | +11.4 |
| | | 230 | 14686.0 | 230 | 7543.5 | | |
| Camphor- β -sulphonyl- <i>m</i> -tolylamide | Chloroform | 273 | 882.8 | 273 | 327.4 | 235.9 | -37.1 |
| | | .. | .. | .. | .. | | |

TABLE I—Contd.

| Compound | Solvent | <i>d</i> -isomer | | <i>dl</i> -isomer | | λ_0 in $m\mu$ * $\lambda_0 - \lambda_{max}$ | |
|--|-------------------|--------------------------|------------------|--------------------------|------------------|---|-------|
| | | λ_{max} , $m\mu$ | ϵ_{max} | λ_{max} , $m\mu$ | ϵ_{max} | | |
| Camphor- β -sulphonyl- <i>p</i> -tolylamide | .. Methyl alcohol | 278 | 706.2 | 278 | 738.3 | 289.8 | +11.8 |
| | | 230 | 8667.0 | 230 | 9148.5 | | |
| Camphor- β -sulphonyl- <i>p</i> -tolylamide | .. Ethyl alcohol | 278 | 741.5 | 278 | 619.5 | 277.5 | — .5 |
| | | 230 | 7961.0 | 230 | 8506.5 | | |
| Camphor- β -sulphonyl- <i>p</i> -tolylamide | .. Chloroform | 276 | 497.5 | 276 | 677.3 | 242.9 | —33.1 |
| | | .. | .. | .. | .. | | |
| Camphor- β -sulphonyl- α -naphthylamide | .. Methyl alcohol | 284 | 6569.0 | 284 | 5348 | 321.0 | +37.0 |
| | | 230 | 9925.0 | 228 | 9353 | | |
| Camphor- β -sulphonyl- α -naphthylamide | .. Ethyl alcohol | 285 | 6590.0 | 285 | 5536 | 288.0 | + 3.0 |
| | | 230 | 9710.4 | 230 | 9462.0 | | |
| Camphor- β -sulphonyl- α -naphthylamide | .. Chloroform | 287 | 4213 | 287 | 6051 | 233.4 | —53.6 |
| | | .. | .. | .. | .. | | |
| Camphor- β -sulphonyl- β -naphthylamide | .. Methyl alcohol | 278 | 4891.0 | 278 | 4177 | 300.2 | +22.2 |
| | | 235 | 10353.0 | 235 | 9460 | | |
| Camphor- β -sulphonyl- β -naphthylamide | .. Ethyl alcohol | 278 | 4641.0 | 278 | 4712.4 | 282.3 | + 4.3 |
| | | 235 | 9817.5 | 235 | 9817.5 | | |
| Camphor- β -sulphonyl- β -naphthylamide | .. Chloroform | 280 | 3463 | 280 | 5783 | 252.8 | —27.2 |
| | | .. | .. | .. | .. | | |

* λ_{0s} obtained from Drude's one-term equation.²† *d*-Camphor- β -sulphonyl-*m*-tolylamide was taken in 0.004 per cent. concentration, whereas 0.01 per cent. solutions of all the other compounds were used.

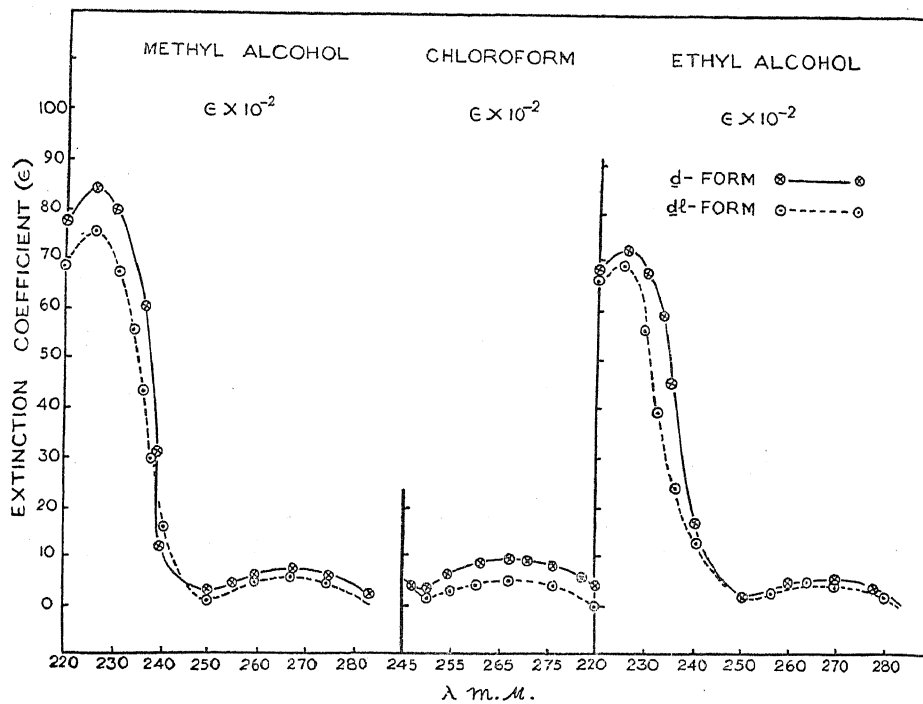


FIG. 2. Camphor- β -sulphonyl-*o*-tolylamides.

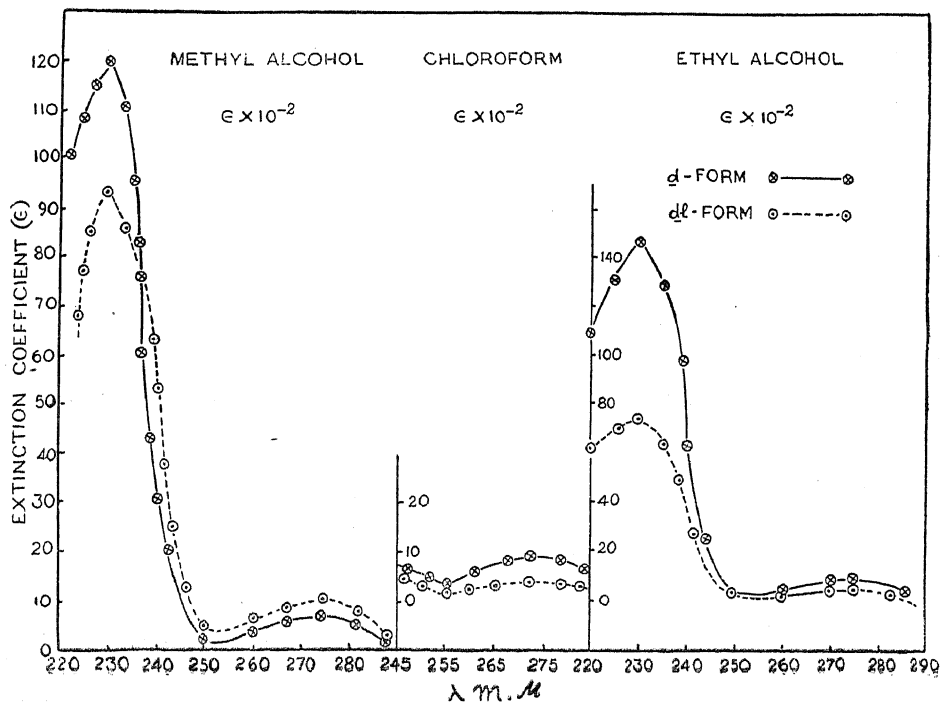


FIG. 3. Camphor- β -sulphonyl-*m*-tolylamides.

In this equation the summation contains several partial rotation terms, such as,

$$\frac{K'}{\lambda^2 - \lambda_0'^2}, \frac{K''}{\lambda^2 - \lambda_0''^2}, \frac{K'''}{\lambda^2 - \lambda_0'''^2}, \dots$$

where K' , K'' , K''' , , etc., represent the rotation constants and λ_0' , λ_0'' , λ_0''' , etc., the 'characteristic' wavelengths governing the rotation. According to theoretical considerations, the 'characteristic' wavelengths, λ_{0s} , are those at which the molecule absorbs radiation strongly and these should correspond to the frequencies of the equivalent classical electronic oscillators in the molecules. In the case of most optically active organic compounds, it is found that the one-term Drude equation,

$$[\alpha] = \frac{K}{\lambda^2 - \lambda_0^2},$$

is usually sufficient to fit the observed values of rotations. The value of λ_0 in this equation should be equal to the absorption band in the ultraviolet or visible region of the spectrum.

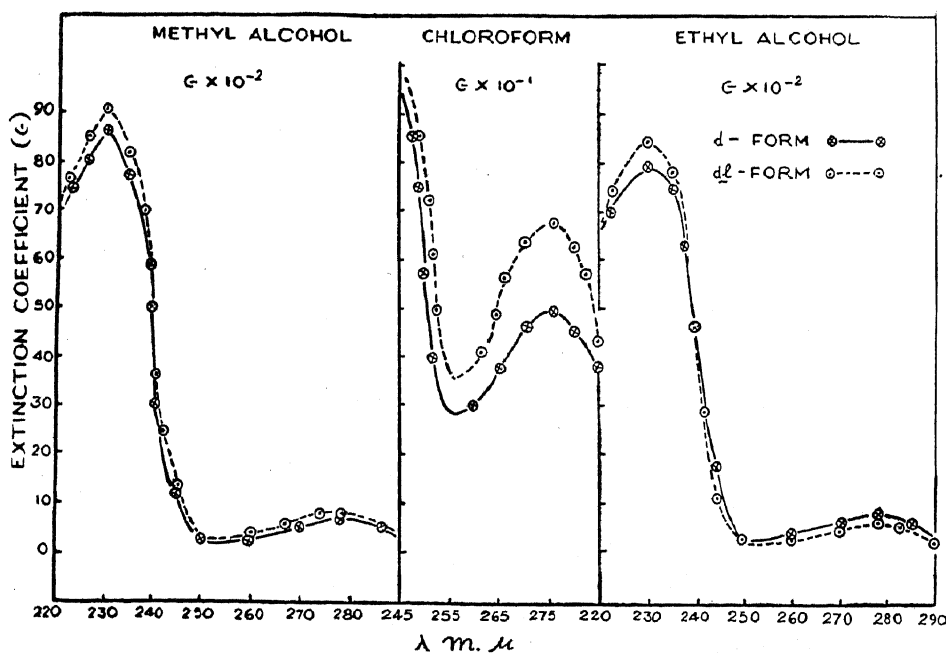


FIG. 4. Camphor- β -sulphonyl-*p*-tolylamides.

As stated in the previous communications,³⁻⁵ generally the rotatory dispersion is expressed by one- or two-term Drude's formula, whereas the sum-

mation includes several terms of which the one or two terms may be more important than the succeeding ones, which either are too small or may nearly cancel each other and are, therefore, neglected. It is, thus, clear that this mode of representation by one- or two-term formula is far from reality. The terms found necessary in one- or two-term equation of Drude, within the limits of experimental error, thus, approximately represent the main contribution to the optical activity. In this paper we have shown that the one-term (*simple*), as well as the two-term (*complex*) equation of Drude, both equally well represent the observed rotatory dispersion of the compounds

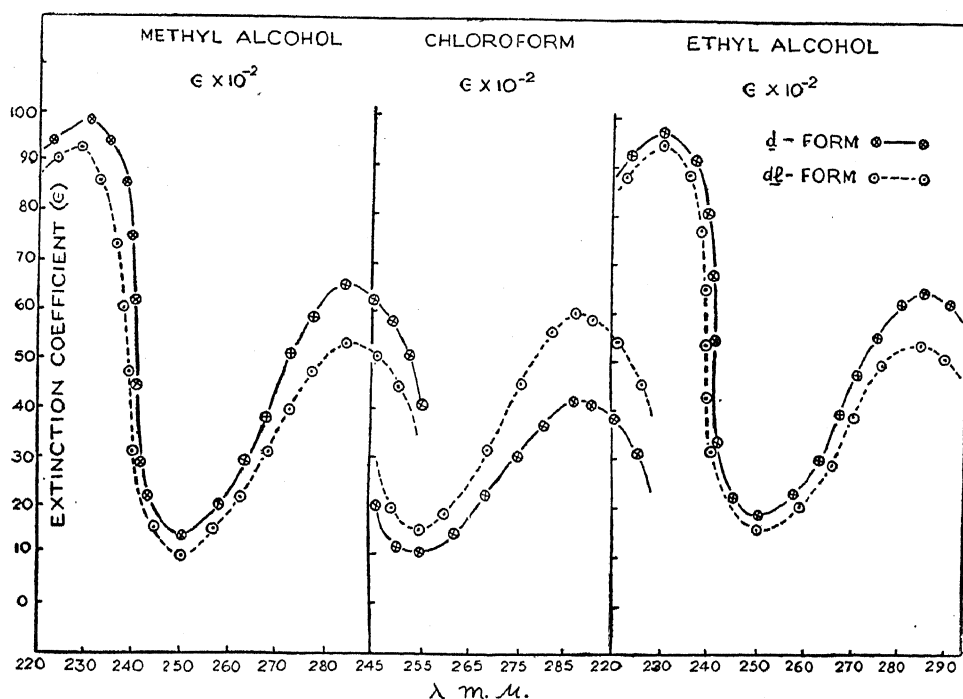


FIG. 5. Camphor- β -sulphonyl- α -naphthylamides.

within the limits of experimental accuracy (Tables II–VI). The rotatory dispersion of the compounds had already been reported ‘*simple*’ as the observed values were in good agreement with those calculated from the *one-term* equation (Tables II–VI) but the characteristic wavelengths derived from the dispersion constants of these equations do not agree with the absorption maxima, λ_{\max} , obtained by our present measurements (Table I). In the column of differences, $\lambda_0 - \lambda_{\max}$, (Table I), these values range from -5 to -62.1 mμ, which are, therefore, considerable in several cases. Working in the reverse way, by substituting both the absorption maxima ($\lambda_{1 \max}$ and

$\lambda_{2 \max.}$) for the characteristic wavelengths (λ_{0s}), governing the rotation, in the two-term (complex) Drude formula for rotatory dispersion, namely,

$$[a] = \frac{K_1}{\lambda^2 - \lambda_{1 \max.}^2} + \frac{K_2}{\lambda^2 - \lambda_{2 \max.}^2},$$

we find that the values of the rotatory powers calculated from these two-term (complex) formulæ like those from one-term (simple) formulæ already reported agree equally well with the observed values of rotatory power (Tables II-VI). The 'characteristic' wavelengths (λ_{0s}) derived from one-term formula, being different from the absorption maxima ($\lambda_{\max.}$) obtained experimentally, are thus hypothetical, which explains the discrepancies between them.

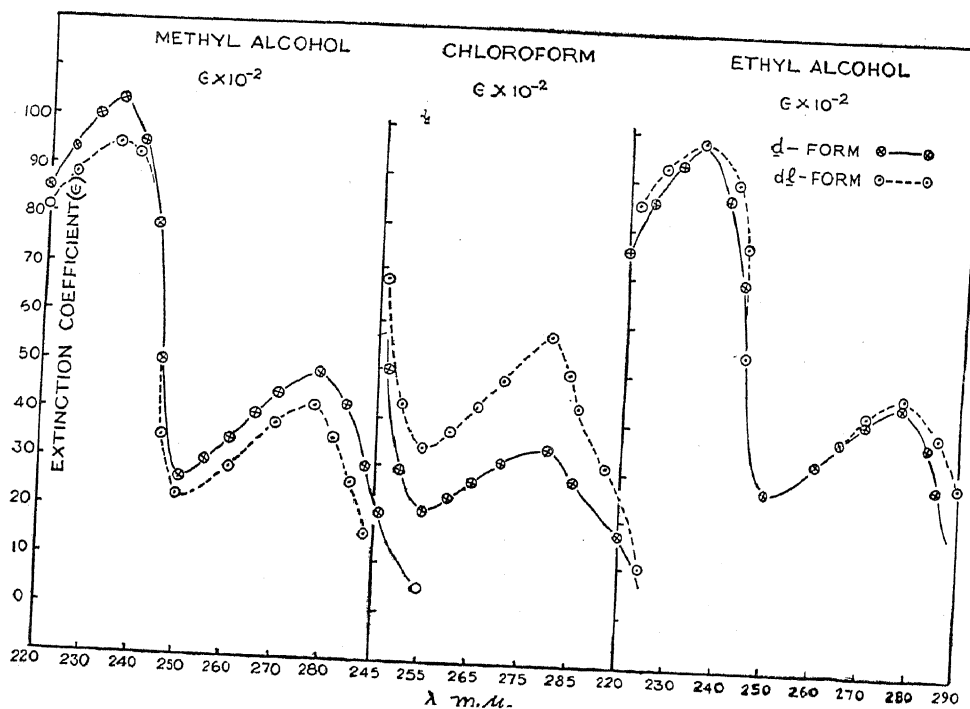


FIG. 6. Camphor- β -sulphonyl- β -naphthylamides.

ABSORPTION SPECTRA CURVES OF CAMPHOR- β -SULPHONYL-PHENYL, *o*-TOLYL, *m*-TOLYL, *p*-TOLYL, α -NAPHTHYL AND β -NAPHTHYLAMIDES

The ultraviolet absorption spectra curves of camphor- β -sulphonyl-phenyl (Fig. 1), *o*-tolyl (Fig. 2), *m*-tolyl (Fig. 3), *p*-tolyl (Fig. 4), α -naphthyl (Fig. 5) and β -naphthyl (Fig. 6) amides (*d* and *dl*) in methyl alcohol, ethyl alcohol and chloroform (chloroform not transparent below 245 $m\mu$) are

TABLE II
Rotatory dispersion of *d*-camphor- β -sulphonyl phenylamide at 35° C.

| Solvent | Methyl alcohol | | | Chloroform | | |
|------------------------|----------------|--|--|------------|---|--|
| | Observed | Calculated | | Observed | Calculated | |
| | $[\alpha]$ | $[\alpha] = \frac{7.292}{\lambda^2 - 0.088}$ | $[\alpha] = \frac{17.22}{\lambda^2 - 0.0745} - \frac{10.412}{\lambda^2 - 0.052}$ | $[\alpha]$ | $[\alpha] = \frac{20.4}{\lambda^2 - 0.065}$ | $[\alpha] = \frac{9.866}{\lambda^2 - 0.0745} + \frac{10.637}{\lambda^2 - 0.052}$ |
| Lines (\AA) | o | c | $o-c$ | o | c | $o-c$ |
| 6708 | 19.5 | 20.14 | 19.69 | 53.0 | 53.98 | + .01 |
| 6438 | 22.0 | 22.52 | 21.94 | 58.0 | 58.37 | -.35 |
| 6104 | 25.5 | 25.63 | 25.5 | 67.5 | 66.34 | +1.22 |
| 5893 | 28.0 | 28.13 | 27.87 | 73.0 | 72.30 | + .8 |
| 5780 | 29.5 | 29.64 | 29.4 | 76.5 | 75.82 | + .8 |
| 5468 | 34.5 | 34.65 | 34.55 | 87.0 | 87.18 | -.0 |
| 5461 | 34.5 | 34.69 | 34.68 | 87.0 | 87.48 | -.3 |
| 5209 | 40.5 | 39.77 | 40.02 | 100.0 | 98.88 | +1.37 |
| 5086 | 43.0 | 42.75 | 43.10 | 105.0 | 105.4 | -.07 |
| 4800 | 51.0 | 51.21 | 52.09 | 120.0 | 123.3 | -3.3 |
| 4678 | 57.5 | 55.76 | 57.01 | 131.5 | 132.5 | -1.0 |
| 4603 | 60.0 | 58.89 | 60.26 | 138.0 | 139.0 | -.42 |
| 4358 | 73.0 | 71.48 | 73.64 | 162.5 | 163.2 | -.02 |

TABLE III
Rotatory dispersion of *d*-camphor- β -sulphonyl-*o*-tolylamide at 35° C.

| Solvent | Methyl alcohol | | | | Chloroform | | | |
|-----------|----------------|--|---|----------------------|------------|---|---|----------------------|
| | Observed | Calculated | | | Observed | Calculated | | |
| | $[\alpha]$ | $[\alpha] = \frac{8.835}{\lambda^2 - 0.078}$ | c | $\theta - c$ | $[\alpha]$ | $[\alpha] = \frac{14.506}{\lambda^2 - 0.506}$ | c | $\theta - c$ |
| Equation | | | $[\alpha] = \frac{15.42}{\lambda^2 - 0.0713}$ | $\lambda^2 - 0.0511$ | | | $[\alpha] = \frac{5.651}{\lambda^2 - 0.0713}$ | $\lambda^2 - 0.0511$ |
| Lines (A) | θ | c | c | $\theta - c$ | θ | c | c | $\theta - c$ |
| 6708 | 23.5 | 23.75 | 23.45 | + .05 | 36.0 | 35.55 | 35.60 | + .4 |
| 6438 | 28.0 | 26.26 | 25.98 | + .26 | 39.0 | 38.94 | 39.00 | + .06 |
| 6104 | 30.0 | 30.00 | 29.77 | + .23 | 40.0 | 43.89 | 43.95 | + 1.05 |
| 5893 | 32.5 | 32.82 | 32.64 | - .14 | 47.5 | 47.52 | 47.98 | - .48 |
| 5780 | 34.5 | 34.51 | 34.35 | + .15 | 50.0 | 49.62 | 49.73 | + .38 |
| 5468 | 40.0 | 39.97 | 40.01 | - .01 | 56.5 | 56.44 | 56.5 | + .06 |
| 5461 | 40.0 | 40.13 | 40.09 | - .09 | 57.0 | 56.62 | 56.5 | + .03 |
| 5209 | 45.5 | 45.69 | 45.83 | - .33 | 63.0 | 63.25 | 63.28 | + .03 |
| 5086 | 49.0 | 48.93 | 49.15 | - .15 | 65.5 | 66.95 | 66.96 | + .01 |
| 4800 | 58.0 | 57.98 | 58.52 | - .52 | 77.0 | 76.89 | 76.89 | + 0.11 |
| 4678 | 62.5 | 62.76 | 63.48 | + .02 | 83.5 | 82.04 | 81.87 | + 1.46 |
| 4603 | 66.5 | 66.03 | 66.90 | - .40 | 86.5 | 85.41 | 85.2 | + 1.09 |
| 4358 | 80.5 | 78.89 | 80.34 | + 1.61 | 97.5 | 98.06 | 97.5 | + 0.56 |

TABLE IV
Rotatory dispersion of d-camphor-β-sulphonyl m-tolylamide at 35° C.

| Solvent | Methyl alcohol | | | | Chloroform | | | |
|-----------|----------------|---|------------------------------------|-------------------------------------|------------|---|------------------------------------|-------------------------------------|
| | Observed | Calculated | | | Observed | Calculated | | |
| | [α] | [α] = $\frac{8.028}{\lambda^2 - 0.078}$ | $\frac{8.654}{\lambda^2 - 0.0756}$ | $\frac{0.0637}{\lambda^2 - 0.0529}$ | [α] | [α] = $\frac{19.909}{\lambda^2 - 0.0557}$ | $\frac{1.275}{\lambda^2 - 0.0756}$ | $\frac{18.856}{\lambda^2 - 0.0529}$ |
| Lines (Å) | c | c | o-c | o | c | c | o-c | |
| 6708 | 21.5 | 21.58 | 21.5 | ± .0 | 51.0 | 50.51 | .49 | + .11 |
| 6438 | 23.5 | 23.86 | 23.77 | -.27 | 55.5 | 55.49 | .01 | - .41 |
| 6104 | 27.0 | 27.27 | 27.15 | -.15 | 63.5 | 62.85 | .65 | + .22 |
| 5893 | 29.5 | 29.82 | 29.70 | .12 | 68.0 | 68.31 | -.31 | + .76 |
| 5780 | 31.5 | 31.36 | 31.23 | +.14 | 72.0 | 71.55 | +.45 | ± .0 |
| 5468 | 36.5 | 36.33 | 36.14 | +.36 | 82.0 | 81.85 | +.15 | -.33 |
| 5461 | 36.5 | 36.46 | 36.30 | +.16 | 82.0 | 82.12 | -.12 | -.59 |
| 5209 | 41.5 | 41.53 | 41.31 | +.22 | 92.0 | 92.37 | -.37 | -.85 |
| 5086 | 44.0 | 44.45 | 44.19 | +.26 | 98.5 | 98.13 | +.37 | -.12 |
| 4800 | 51.5 | 52.09 | 52.32 | -.23 | 114.5 | 114.0 | +.5 | + .04 |
| 4678 | 55.5 | 57.03 | 56.59 | +.44 | 122.5 | 122.1 | +.4 | + .06 |
| 4603 | 60.0 | 59.99 | 59.53 | +.46 | 130.0 | 127.6 | +2.4 | +1.98 |
| 4358 | 71.0 | 71.68 | 71.0 | ± .68 | 149.0 | 148.3 | + .7 | + .32 |

TABLE V
Rotatory dispersion of d-camphor-β-sulphonyl-p-tolylamide at 35° C.

| Solvent | Methyl alcohol | | | | Chloroform | | | | | |
|-----------|----------------|--|---|--|------------|---|---|--|--------|--------|
| | Observed | Calculated | | | Observed | Calculated | | | | |
| | $[\alpha]$ | $[\alpha] = \frac{7.9296}{\lambda^2 - 0.0841}$ | $[\alpha] = \frac{9.225}{\lambda^2 - 0.0773}$ | $[\alpha] = \frac{1.1956}{\lambda^2 - 0.0529}$ | $[\alpha]$ | $[\alpha] = \frac{20.137}{\lambda^2 - 0.059}$ | $[\alpha] = \frac{4.327}{\lambda^2 - 0.0773}$ | $[\alpha] = \frac{15.846}{\lambda^2 - 0.0529}$ | | |
| Lines (Å) | σ | c | $0-c$ | c | $0-c$ | c | $0-c$ | | | |
| 6708 | 22.0 | 21.67 | .33 | + | 21.74 | .26 | + | 51.48 | 51.5 | ± .0 |
| 6438 | 24.0 | 24.0 | ± .0 | ± | 24.04 | .04 | ± | 56.63 | 56.65 | ± .15 |
| 6104 | 27.5 | 27.49 | ± .01 | ± | 27.50 | .01 | ± | 64.22 | 64.24 | ± .26 |
| 5893 | 30.0 | 30.13 | -.13 | - | 30.11 | .11 | - | 69.85 | 69.85 | ± .15 |
| 5780 | 32.0 | 31.76 | +.24 | + | 31.67 | .33 | + | 73.21 | 73.23 | ± .77 |
| 5468 | 37.0 | 36.90 | +.10 | + | 36.76 | .24 | + | 83.89 | 83.89 | ± .11 |
| 5209 | 42.0 | 42.35 | -.03 | - | 42.07 | .35 | - | 84.26 | 84.17 | ± .17 |
| 5086 | 45.0 | 45.44 | -.44 | - | 45.06 | .44 | - | 94.84 | 94.80 | ± 1.2 |
| 4800 | 54.0 | 54.19 | -.19 | - | 53.51 | .19 | - | 100.0 | 100.89 | ± .11 |
| 4678 | 59.0 | 58.86 | +.14 | + | 57.98 | .14 | + | 117.4 | 117.55 | ± .05 |
| 4603 | 61.5 | 62.90 | -1.4 | - | 61.06 | .44 | - | 126.0 | 126.08 | ± 2.42 |
| 4358 | 73.0 | 74.87 | -1.87 | - | 73.13 | .13 | - | 131.8 | 131.89 | ± 1.11 |
| | | | | | | | | 153.3 | 154.0 | ± .0 |

practically identical. The absorption curves of the dextro and the racemic forms of these compounds in different solvents (Figs. 1–6) show two maxima, one a weak band, λ_{\max} , varying from 267–84 $m\mu$ which is due to the selective absorption of the free keto group present in the compounds and the other, an intense band, λ_{\max} , ranging from 226–30 $m\mu$ —due to general absorption of the saturated molecules. Camphor- β -sulphonyl phenylamide shows selective absorption at the longer wavelength (λ_{\max} , 273 $m\mu$, ϵ_{\max} , 460.5–808.9 in different solvents, Table I) and the substitution of a methyl group in the *ortho* position of the phenyl nucleus shifts the absorption maximum towards the shorter wavelength side (λ_{\max} , 267 $m\mu$, ϵ_{\max} , 609.9–680), whereas this group in the *meta* position (λ_{\max} , 275 $m\mu$, ϵ_{\max} , 658–914.15) and in the *para* position (λ_{\max} , 278 $m\mu$, ϵ_{\max} , 497.5–741.5) shifts them towards the longer wavelength side (bathochromic effect).

TABLE VI

Rotatory dispersion of d-camphor- β -sulphonyl- α -naphthylamide at 35° C.

| Equation | Solvent | | Chloroform (1 per cent. solution) | | | |
|-----------|------------|----------|---|----------|--|--|
| | Observed | | Calculated | | | |
| | $[\alpha]$ | | $[\alpha] = \frac{14.63}{\lambda^2 - 0.0545}$ | | $[\alpha] = \frac{1.55}{\lambda^2 - 0.0807} + \frac{13.0}{\lambda^2 - 0.0529}$ | |
| Lines (Å) | <i>o</i> | <i>c</i> | <i>o-c</i> | <i>c</i> | <i>o-c</i> | |
| 6708 | 37.0 | 36.99 | + .01 | 36.93 | + .07 | |
| 6438 | 40.0 | 40.63 | – .63 | 40.59 | – .59 | |
| 6104 | 46.0 | 46.0 | ± 0 | 45.99 | + .01 | |
| 5893 | 50.0 | 49.98 | + .02 | 50.01 | – .01 | |
| 5780 | 52.0 | 52.28 | – .28 | 52.36 | – .36 | |
| 5468 | 60.0 | 59.83 | + .17 | 59.92 | + .08 | |
| 5461 | 60.0 | 60.03 | – .03 | 60.11 | – .11 | |
| 5209 | 67.0 | 67.48 | – .48 | 67.65 | – .65 | |
| 5086 | 71.0 | 71.68 | – .68 | 71.90 | – .90 | |
| 4800 | 82.0 | 83.17 | –1.17 | 83.58 | –1.58 | |
| 4678 | 90.0 | 89.04 | + .96 | 89.58 | + .42 | |
| 4603 | 93.0 | 93.0 | ± .0 | 93.63 | – .63 | |
| 4358 | 109.0 | 107.97 | +1.03 | 109.0 | ± 0 | |

The bathochromic shift of the ketonic band is also observed when the phenyl group of camphor- β -sulphonyl phenylamide (273 $m\mu$) is replaced by naphthyl groups (α -, λ_{\max} , 284 $m\mu$, ϵ_{\max} , 4213–6590 and β -, λ_{\max} , 278 $m\mu$, ϵ_{\max} , 3463–4891). The absorption maxima of the naphthyl (λ_{\max} , = 275 $m\mu$) and

the keto ($\lambda_{\max.} = 278 \text{ m}\mu$) groups are nearly equal but the absorptive power ($\epsilon_{\max.}$) of the naphthyl group is much greater than that of the keto. The weaker absorption band of the keto group is thus submerged in the more intense band of the naphthyl group (Figs. 5 & 6 and Table I).

NATURE OF THE RACEMIC FORMS

The racemic forms of the optically active compounds were found to be racemates (*dl*) in the solid state² by the melting point-composition method of Roozeboom. The ultraviolet absorption spectra of the racemic forms have been now found to be nearly identical with those of the corresponding dextro forms (Figs. 1-6): the slight differences being in the values of molecular extinction coefficients, ϵ , in the two cases, whereas the values of absorption maxima ($\lambda_{\max.}$) are identical (Table I). From the nearly identical absorption spectra curves for the dextro and racemic forms, it may be concluded that the racemic forms have almost completely dissociated in very dilute solutions into the optically active and opposite forms.

ACKNOWLEDGEMENT

We thank the Banaras Hindu University for providing research facilities, and the Government of India, Ministry of Education, for the award of a Senior Research Scholarship to one of us (S. M. Verma).

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