

# THE PHYSICAL IDENTITY OF ENANTIOMERS

## Part VIII. The Magnetic Susceptibilities of *Dextro*, *Laevo* and *Racemic* Forms of Camphor- $\beta$ -Sulphonates of Nitrogen Bases

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ACCORDING to the Pasteur's principle of Molecular Dissymmetry the *dextro* and *laevo* forms of a compound possess identical scalar properties.\* Previous investigations<sup>1</sup> on magnetic susceptibilities of *dextro* and *laevo* isomers showed that their values were equal within the limits of experimental error and thus support Pasteur's principle. The present investigation was undertaken to further establish the validity of this principle as well as to study the effect on the magnetic susceptibility of the change of the valency of nitrogen from 3-covalent to 4-covalent state in the formation of substituted ammonium-camphor- $\beta$ -sulphonates. The magnetic susceptibilities of the racemic modifications were also studied since a comparison of the values of susceptibilities of the racemic forms with those of their *dextro* and *laevo* isomers might throw light on the nature of the racemic combination. If the racemic modification were an equimolecular mixture of *d*- and *l*-components, there should be no difference in the values of magnetic susceptibilities, whereas if the racemic form were a compound its magnetic susceptibility might be different from that of *d*- and *l*-form.

\* Campbell (*Trans. Faraday Soc.*, 1930, 26, 560; *J. Amer. Chem. Soc.*, 1931, 53, 1661) reported slight, but distinct differences in the rotatory power and other physical properties of the *dextro* and *laevo*-forms of mandelic and camphoric acids and disputed the validity of Pasteur's principle of molecular dissymmetry. Körtum (*Ber.*, 1931, 64 B, 1506) in the case of mandelic acids (*d*- and *l*-) showed that if the preparations are sufficiently purified, there are no measurable differences in the rotatory power of the optically active and opposite forms. One of us (Singh, B. K., Mahanti, I., *Proc. Ind. Acad. Sci.*, 1935, 2, 378; *Curr. Sci.*, 1935, 3, 420) showed in 1935 that the rotatory dispersions of the *d*- and *l*-camphoric acids are identical throughout the visible spectrum ( $\lambda = 4358$  to  $6709 \text{ \AA}$ ). In spite of these and other rigid proofs, Bowden wrote in 1938 "The supposed identity of *d*- and *l*-forms is really an unproved assumption" (*The Phase Rule and Phase Reactions*; foot-note, p. 191), and quoted the above mentioned alleged differences for mandelic acids noted by Campbell. In this paper we have adduced more evidence from magnetic measurements in support of Pasteur's great generalisation.

## EXPERIMENTAL

The *l*- and *dl*-forms of camphor- $\beta$ -sulphonic acids were prepared in the same way as Reychler's acid<sup>2</sup> (*d*-camphor- $\beta$ -sulphonic acid). The camphor- $\beta$ -sulphonates of *o*-, *m*- and *p*-nitranilines, pyridine, ammonia, *p*-aminobenzenesulphonamide and aniline were prepared according to methods described in previous communications.<sup>3</sup>

The magnetic susceptibility measurements were carried out by a modified form of Guoy's Balance. The working of the apparatus was checked by making determinations of magnetic susceptibilities of compounds with known values. In Table I are recorded some of the results. Water with the value of  $\chi - 0.720 \times 10^{-6}$  was taken as a standard for these measurements.

TABLE I

Substance	$\chi \times 10^6$ per gm.		Percentage deviation
	Experimental mean of three observations	International Critical Tables	
Potassium chloride ..	0.515	0.516	0.2
Naphthalene ..	0.718	0.717	0.2
Camphoric anhydride ..	0.622	0.620	0.3
1 : 3 : 5-trinitro-benzene ..	0.351	0.352	0.3
Ethyl alcohol ..	0.744	0.744	0.0

For the sake of comparison the values of diamagnetic susceptibilities of bases were also determined. In Table II are recorded the values of gram ( $\chi$ ) and gram molecular ( $\chi_M$ ) susceptibilities of compounds investigated. Table III gives the observed values (O) of  $\chi_M$  and those calculated (C) from the sum of their components; the differences (O - C) are also recorded.

## DISCUSSION

The values of magnetic susceptibilities of dextro and lævo isomers agree within the limits of the experimental error, and thus confirm Pasteur's law. The values of the racemic forms do not, in general, differ appreciably from those of the active forms beyond experimental error. However, in the case of *p*-aminobenzenesulphonamido-camphor- $\beta$ -sulphonates the diamagnetic susceptibility of the racemic form is different from that of the dextro and the lævo isomer (*vide* Table II) and if this difference is genuine, it indicates that the racemic modification is a true *dl*-compound. It has been shown previously<sup>4</sup> that all the racemic modifications investigated in this paper are

TABLE II

Compound	Molecular weight	$\chi \times 10^6$	per gram mol. $\chi \times 10^6$
1 Aniline	93	0.692	64.36
2 Ortho-nitroaniline	138	0.506	69.84
3 Meta-nitroaniline	138	0.503	69.42
4 Para-nitroaniline	138	0.478	65.97
5 Pyridine	79	0.623	49.21
6 <i>p</i> -Aminobenzene sulphonamide	172	0.466	80.15
7 <i>d</i> -Camphor- $\beta$ -sulphonic acid	232	0.584	135.5
8 <i>l</i> -Camphor- $\beta$ -sulphonic acid	232	0.584	135.5
9 <i>dl</i> -Camphor- $\beta$ -sulphonic acid	232	0.586	135.9
10 <i>o</i> -Nitroanilino- <i>d</i> -S*. 2H <sub>2</sub> O	406	0.490	198.9
11 " " <i>l</i> - " "	406	0.493	200.1
12 " " <i>dl</i> - " "	406	0.485	196.9
13 <i>m</i> -Nitranilino- <i>d</i> -S	370	0.553	204.6
14 " " <i>l</i> - " "	370	0.549	203.2
15 " " <i>dl</i> - " "	370	0.551	203.9
16 <i>p</i> -Nitranilino- <i>d</i> -S. 3H <sub>2</sub> O	424	0.505	214.1
17 " " <i>l</i> - " "	424	0.502	212.8
18 " " <i>dl</i> - " "	424	0.496	210.3
19 Pyridino- <i>d</i> -S	311	0.597†	185.7
20 " <i>l</i> - " "	311	0.590†	183.5
21 " <i>dl</i> - " "	311	0.585†	182.0
22 <i>p</i> -Aminobenzenesulphonamido- <i>d</i> -S	404	0.505	204.0
23 " " <i>l</i> - " "	404	0.508	205.2
24 " " <i>dl</i> - " "	404	0.488	197.2
25 Anilino- <i>dl</i> -S	325	0.584	189.8
26 Ammonium- <i>d</i> -S	249	0.566	140.9

\* S denotes camphor- $\beta$ -sulphonic acid.

† Values actually determined in solution (aqueous) and calculated for solid.

TABLE III

Compound	$\chi \times 10^6$	$\chi \times 10^6$	O-C
	per gram mol. (observed)	per gram mol. (calculated)	
	O	C	
1 <i>o</i> -Nitroanilino- <i>d</i> -S*. 2H <sub>2</sub> O	198.9	231.26	-32.36
2 " " <i>l</i> - " "	200.1	231.26	-31.16
3 " " <i>dl</i> - " "	196.9	231.66	-34.76
4 <i>m</i> -Nitranilino- <i>d</i> -S	204.6	204.92	-0.32
5 " " <i>l</i> - " "	203.2	204.92	-1.72
6 " " <i>dl</i> - " "	203.9	205.32	-1.42
7 <i>p</i> -Nitranilino- <i>d</i> -S. 3H <sub>2</sub> O	214.1	240.35	-26.25
8 " " <i>l</i> - " "	212.8	240.35	-27.55
9 " " <i>dl</i> - " "	210.3	240.75	-30.45
10 Pyridino- <i>d</i> -S	185.7	184.71	+0.99
11 " <i>l</i> - " "	183.5	184.71	-1.21
12 " <i>dl</i> - " "	182.0	185.11	-3.11
13 <i>p</i> -Aminobenzenesulphonamido- <i>d</i> -S	204.0	215.67	-11.67
14 " " <i>l</i> - " "	205.2	215.67	-10.47
15 " " <i>dl</i> - " "	197.2	216.05	-18.85
16 Anilino- <i>dl</i> -S	189.8	200.26	-10.46
17 Ammonium- <i>d</i> -S	140.9	149.5	-8.6

\* S denotes camphor- $\beta$ -sulphonic acid.

true *dl*-compounds. The present studies indicate that in general the linkages involved in compound formation in the case of racemic modifications are such as do not effect the diamagnetic susceptibility to any appreciable extent.

### *Effect of Position of Isomerism on Magnetic Susceptibility*

The sequence of magnetic susceptibility of position isomerides of nitro-anilines is  $o > m > p$ . On the other hand, the decreasing order of gram susceptibilities ( $\chi$ ) of *o*-, *m*- and *p*-nitranilinocamphor- $\beta$ -sulphonates is  $m > p > o$ . Bhatnagar and collaborators<sup>5</sup> in their study of *o*-, *m*- and *p*-cresyl ethers and *o*- and *p*-phenetidine had come to the conclusion that the ortho should be more diamagnetic than the meta and the para isomerides. Their rule is obviously untenable in the case of *o*-, *m*- and *p*-nitranilinocamphor- $\beta$ -sulphonates where the meta isomer having no water of crystallisation posesesses greater gram susceptibility than either ortho or para isomerides which contain water of crystallisation. These studies, therefore, show that no definite rule is observed in regard to the sequence of magnetic susceptibility of position isomerides.

An examination of the values given in Table III indicates that the observed values (O) of gram molecular susceptibilities ( $\chi_M$ ) of camphor- $\beta$ -sulphonates are generally less than the sum (C) of gram molecular susceptibilities of their components. On Pascal's law the differences, O-C, should be nearly constant since salt formation involves a change of 3-covalent nitrogen to 4-covalent nitrogen in every case. The different camphor- $\beta$ -sulphonates examined in this paper can be divided into three groups, *viz.*, (i) where the difference O-C is negligible as in the case of camphor- $\beta$ -sulphonates of pyridine and *m*-nitraniline, (ii) where O-C is about  $10.5 \times 10^{-6}$  as in the case of salts of ammonia, aniline and *p*-aminobenzenesulphonamide and (iii) where O-C varies from  $26.25 \times 10^{-6}$  to  $34.76 \times 10^{-6}$  as in the cases of *o*- and *p*-nitranilinocamphor- $\beta$ -sulphonates. These results indicate that the formation of salts of camphor- $\beta$ -sulphonic acid with nitrogen bases involves not merely a change of 3-covalent nitrogen to 4-covalent nitrogen but that there are other factors also which influence the value of diamagnetic susceptibility.

### SUMMARY

1. The magnetic susceptibilities of *d*- and *l*-isomers of camphor- $\beta$ -sulphonic acids and some of their salts have been measured and are found to be equal, in conformity with Pasteur's law of Molecular Dissymmetry.
2. The magnetic susceptibilities of the racemic modifications do not, in general, differ appreciably from those of the optically active and oppo-

site forms, hence no definite conclusion on the nature of the racemic form can be drawn from these measurements.

3. The effect of position isomerism on magnetic susceptibility has been studied and it is concluded that no definite rule is obeyed in regard to the sequence of magnetic susceptibility in position isomers.

4. The observed values (O) of gram molecular susceptibilities ( $\chi_M$ ) of camphor- $\beta$ -sulphonates are generally less than the sum (C) of  $\chi_m$  of their components. The camphor- $\beta$ -sulphonates investigated fall into three groups according as O-C is negligible, nearly equal to  $10.5 \times 10^{-6}$  or varies from  $26.25 \times 10^{-6}$  to  $34.76 \times 10^{-6}$ .

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