CCCXXVII.—*The Influence of Solvents on the Rotation of Optically Active Compounds. Part XXV. Bornyl Benzene- and Naphthalene-sulphonates in Various Solvents.*

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WE have examined the rotations of the esters described in the foregoing paper for three colours of light, mercury yellow ($\lambda = 5790$), mercury green ($\lambda = 5461$), and mercury violet ($\lambda = 4358$), in several solvents which, for convenience of reference, are indicated by letters

of the alphabet, namely, (*a*) ethyl alcohol, (*b*) benzene, (*c*) pyridine, (*d*) ethylene dibromide, (*e*) quinoline, (*f*) nitrobenzene. Only one solution was examined in each case at a concentration between 2·5 and 3·5. The data are given in Table I.

TABLE I.

Specific Rotations of Bornyl Sulphonates in Various Solvents.

t = approximately 17·5° throughout.

Solvent.	*a*.	*b*.	*c*.	*d*.	*e*.	*f*.
Concentration	2·5	3·0	3·5	3·5	3·5	3·5
	l-Bornyl naphthalene-β-sulphonate.					
Yellow.....	−14·00°	−14·25°	−14·99°	−19·43°	−17·29°	−13·14°
Green	16·00	16·50	17·28	22·43	20·00	15·14
Violet	26·40	27·17	28·56	37·14	33·14	25·14
	l-Bornyl benzenesulphonate.					
Yellow	−19·00	−19·98	−21·84	−25·60	−26·56	−18·85
Green	22·00	23·15	24·84	29·43	30·57	21·74
Violet	36·40	38·30	41·13	49·00	51·13	36·00
	l-Bornyl naphthalene-α-sulphonate.					
Yellow	−22·80	−20·51	−18·14	−26·28	−27·14	−20·00
Green	26·40	23·50	20·71	30·00	31·14	22·83
Violet	43·60	38·80	34·11	49·57	51·43	38·28

The rotations vary considerably in each case with change of solvent. Bornyl naphthalene-β-sulphonate has the lowest rotation values except for the solution in ethylene dibromide, which overlaps some of the values for other esters. The rotations of the other two esters in the different solvents overlap each other completely, the range of variation being greater, however, with the naphthalene-α-sulphonate than with the benzenesulphonic ester. The different solvents do not influence the rotations in the same way, although there are resemblances. Quinoline, which usually has a powerful exalting or depressing influence, produces the highest rotation in bornyl naphthalene-α-sulphonate and in bornyl benzenesulphonate, and the second highest rotation in bornyl naphthalene-β-sulphonate. In ethylene dibromide, which generally has a powerful influence in the opposite direction to quinoline, bornyl naphthalene-β-sulphonate shows the highest rotation and the other two the second highest. Nitrobenzene produces the lowest rotation in bornyl naphthalene-β-sulphonate and in bornyl benzenesulphonate, and the second lowest in bornyl naphthalene-α-sulphonate. The lowest rotation of this ester is produced by pyridine. There is thus some similarity in the action of the same solvent on the three esters.

The values obtained for the rotation of the three esters in the various solvents were plotted on a characteristic diagram, and lay with good agreement along lines intersecting one another very near

the point of origin of the diagram. It therefore follows that the dispersion coefficients for all these compounds, calculated by the ordinary method, ought to be the same throughout. This is seen by Table II to be roughly the case.

TABLE II.

Dispersion Ratios.

Solvent.	Bornyl benzene-sulphonate. Hg_v/Hg_g.	Bornyl benzene-sulphonate. Hg_y/Hg_g.	Bornyl naphthalene-α-sulphonate. Hg_v/Hg_g.	Bornyl naphthalene-α-sulphonate. Hg_y/Hg_g.	Bornyl naphthalene-β-sulphonate. Hg_v/Hg_g.	Bornyl naphthalene-β-sulphonate. Hg_y/Hg_g.
Alcohol	1·655	0·864	1·625	0·875	1·651	0·863
Benzene	1·654	0·863	1·646	0·863	1·650	0·873
Pyridine	1·655	0·879	1·652	0·868	1·647	0·876
Ethylene dibromide ...	1·665	0·868	1·656	0·866	1·652	0·876
Quinoline ...	1·683	0·878	1·658	0·864	1·667	0·871
Nitrobenzene	1·655	0·867	1·661	0·868	1·675	0·875

This property seems to be characteristic of bornyl and menthyl esters. Indeed the characteristic diagrams for the bornyl sulphonic esters and the menthyl sulphonic esters nearly coincide. Kenyon and Pickard have found (J., 1915, **107**, 35) that most menthyl derivatives lie on the same characteristic diagram with dispersion coefficient mercury violet/mercury green 1·634 to 1·675. The menthyl sulphonic esters have approximately the same coefficient, and lie on the same diagram. The bornyl esters that they plotted had as coefficient V/G = 1·707 to 1·871. The sulphonic esters that we have investigated, however, do not lie on this diagram, but on that which contains the majority of the menthyl compounds.

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