# 28. *The Influence of Solvents and of Other Factors on the Rotation of Optically Active Compounds. Part XXXII. The Rotation Dispersion of Esters of Dibenzoyl-*d*-tartaric Acid in Various Solvents.*

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In Part XXXI (J., **1933**, 760) it was shown that *o*-nitrobenzyl dibenzoyl-*d*-tartrate, in dilute solution in quinoline, gave a type of anomalous rotatory dispersion not hitherto observed in any other tartrate, and opposite to that found in a considerable number of tartrates. This type of anomalous dispersion being of some special interest, we have examined the rotation of the dibenzoyl derivatives of methyl, ethyl, n-*propyl*, and n-*butyl* *d*-tartrates, in the hope of finding further examples of this phenomenon; but, although our observations confirmed, in general, those already published, in no case did we find an equally definite region of anomalous dispersion, and, therefore, our results may be quite briefly summarised.

The relative experimental data are given on p. 102, and are represented in Fig. 1, where, except for the *n*-butyl ester in quinoline, only the graphs for green light are shown.

For the methyl ester a distinct minimum occurs in the *T–R* curve for green light in ethylene bromide at a temperature of about 50°, whereas in quinoline, the graph appears to be approaching a minimum at a considerably lower temperature, in agreement with which, the actual rotation is lower; much the same thing applies to solutions in pyridine and nitromethane. For the ethyl ester a minimum appears in all its three solvents, but at a higher temperature in quinoline than in the other two, and, corresponding to this, it has a higher (absolute) rotation value. The *n*-propyl ester shows a very similar behaviour, but with a tendency for the minimum to move towards a higher temperature, and this tendency is more pronounced in the *n*-butyl ester. The rotation of the last ester in quinoline rises as the temperature falls, in such a way as to cross the zero axis and become positive, in the sequence red, yellow, green, blue; and the temperature rotation curves just begin to intersect one another at a temperature of zero, below which the region of visibly anomalous dispersion would doubtless develop. The phenomenon, however, is by no means so marked here as in the case of *o*-nitrobenzyl dibenzoyl-*d*-tartrate, but the curves are all obviously of the same character and show a similar behaviour, as regards rotation value and the position of the minimum, to those previously described; the sets of curves appear to be of a similar type, and to correspond to the region *uvwxyz* of Fig. 4*a* of Part XXXI * (*loc. cit.*, p. 763).

It ought, however, to be pointed out that if these sets of curves are really analogous, their data ought to lie on one and the same characteristic diagram, and it will be seen from Fig. 2 that this is not satisfactorily the case. The data on the left-hand side for *n*-butyl dibenzoyl-*d*-tartrate (marked by crosses) are sufficiently regular. The data on the right (marked by circles) form the characteristic diagram for *o*-nitrobenzyl dibenzoyl-*d*-tartrate and should lie upon the lines of the other diagram, continued. The lines for $r_2$ and *y* are almost congruent, but that for *b* is somewhat off, whilst that for *v* is markedly so. This last line is also distinctly curved. At the present stage and with rather scanty data it is idle to speculate on this discrepancy, and we content ourselves by mentioning its existence and by recalling the fact that similar cases have been observed. Pickard and Kenyon (J., 1915, **107**, 35) found that the specific rotatory powers of *l*-menthol and of many of its derivatives can be co-ordinated on one characteristic diagram, but that the results for the nitrobenzoic esters and especially the *o*-compound did not fit in well. Similarly in Part XXVII of this series of papers (J., 1929, 2042) it was found that the data for violet light in the case of methyl α-*m*-nitrobenzoyloxypropionate did not fit well on the characteristic diagram for other derivatives of methyl lactate.

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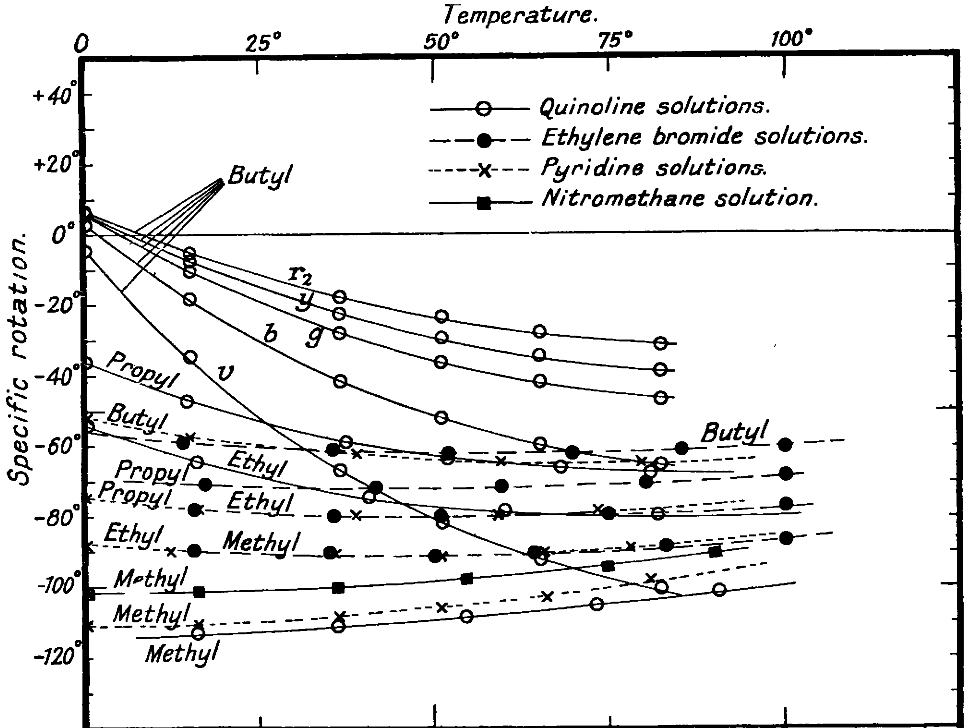
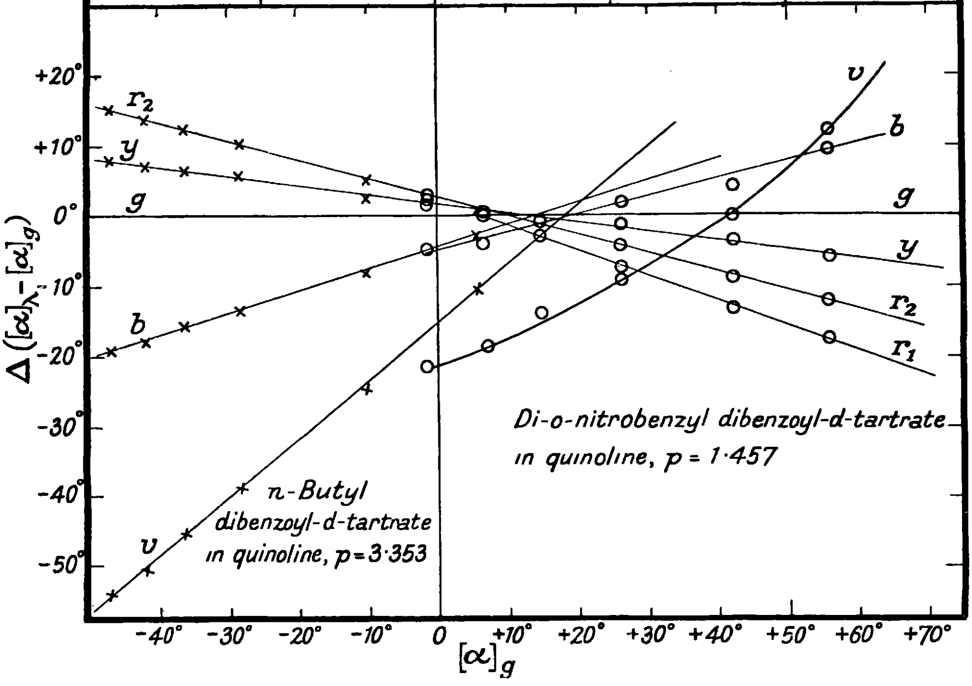
* A further point, relating to solvent influence, is of interest. The graphs for the methyl, ethyl, and *n*-propyl esters in ethylene bromide are almost identical respectively with those for the ethyl, *n*-propyl, and *n*-butyl esters in pyridine. These solvents and esters are thus very closely alike in their mutual influence.

FIG. 1.

*Temperature–rotation curves of esters of dibenzoyl-*d*-tartaric acid.*





*Characteristic diagrams of* n*-butyl dibenzoyl-*d*-tartrate and* o*-nitrobenzyl dibenzoyl-*d*-tartrate.*

FIG. 2.

## EXPERIMENTAL.

The colours of light used were as follows :

| | $r_2$. | $y$. | $g$. | $b$. | $v$. |
|---|---|---|---|---|---|
| λ, Å.U. ........................... | 6243 | 5790 | 5461 | 4916 | 4358 |

*Methyl Dibenzoyl-*d*-tartrate.*—This compound was prepared by the method of Frankland and Wharton (J., 1896, **69**, 1585), and purified by recrystallisation from absolute alcohol until of constant rotation in pyridine solution : $[\alpha]_{5461}^{20^\circ}$ = − 109 3° ($c$ = 2·466) ; m. p. 135°.

*Rotations of methyl dibenzoyl-*d*-tartrate.*

| $t$. | $d$. | $[\alpha]_{r_2}$. | $[\alpha]_y$. | $[\alpha]_g$. | $[\alpha]_b$. | $[\alpha]_v$. |
|---|---|---|---|---|---|---|
| In nitromethane ($p$ = 1·601). | | | | | | |
| 0° | 1·1655 * | −70·39° | −86·02° | −102·5° | −138·2° | −208·3° |
| 16 | 1·145 | 70·13 | 86·00 | 101·4 | 138·6 | 205·8 |
| 36 | 1·119 | 69·00 | 83·41 | 100·4 | 137·5 | 203·1 |
| 54·25 | 1·093 | 67·85 | 82·10 | 97·74 | 133·0 | 196·9 |
| 74·5 | 1·065 | 65·58 | 80·54 | 94·64 | 128·6 | 190·6 |
| 90 | 1·042 | 63·45 | 76·98 | 90·51 | 123·9 | 182·5 |
| In quinoline ($p$ = 1·419). | | | | | | |
| 16 | 1·099 | −79·50 | −96·47 | −113·3 | −154·9 | −227·8 |
| 36 | 1·083 | 76·98 | 94·17 | 111·3 | 150·5 | 221·3 |
| 54 | 1·069 | 77·52 | 92·39 | 108·8 | 148·5 | 218·2 |
| 73 | 1·054 | 73·53 | 88·90 | 105·3 | 143·0 | 208·9 |
| 90·5 | 1·040 | — | 86·58 | 101·8 | — | — |
| In pyridine ($p$ = 2·118). | | | | | | |
| 0 | 1·0065 * | −76·37 | −93·46 | −110·4 | −150·8 | −224·6 |
| 16·5 | 0·9906 | 77·32 | 93·17 | 110·3 | 151·5 | 223·9 |
| 36·5 | 0·9705 | 75·25 | 92·04 | 108·6 | 147·8 | 218·6 |
| 51 | 0·9561 | 73·57 | 89·19 | 106·0 | 144·3 | 214·6 |
| 66 | 0·9410 | 72·18 | 86·76 | 103·4 | 140·5 | 206·6 |
| 81 | 0·9253 | 69·10 | 82·75 | 98·22 | 133·9 | 198·6 |
| In ethylene bromide ($p$ = 0·9616). | | | | | | |
| 15·5 | 2·174 | −61·98 | −75·44 | −89·54 | −124·0 | −187·8 |
| 35·0 | 2·133 | 63·59 | 77·13 | 90·93 | 125·8 | 188·7 |
| 50 | 2·104 | 63·96 | 77·71 | 91·60 | 126·0 | 187·4 |
| 64 | 2·074 | 63·48 | 76·54 | 90·33 | 124·7 | 185·7 |
| 83 | 2·033 | 62·18 | 75·67 | 88·86 | 122·7 | 180·3 |
| 100 | 1·999 | 61·37 | 73·55 | 87·04 | 118·7 | 175·4 |

* Density values marked by an asterisk, here and throughout, were obtained by extrapolation from the other data.

*Ethyl Dibenzoyl-*d*-tartrate.*—Prepared by the method of Frankland and Wharton (*loc. cit.*), the fraction of b. p. 218—220°/0·3 mm. solidified and was repeatedly recrystallised from aqueous alcohol ; m. p. 63·5° (Frankland and Wharton give m. p. 62·5° ; Wood and Nicholas, J., 1928, 1689, give m. p. 63·5°) ; $[\alpha]_{5461}^{20^\circ}$ = − 90·84° ($c$ = 2·15 in pyridine).

*Rotations of ethyl dibenzoyl-*d*-tartrate.*

| $t$. | $d$. | $[\alpha]_{r_2}$. | $[\alpha]_y$. | $[\alpha]_g$. | $[\alpha]_b$. | $[\alpha]_v$. |
|---|---|---|---|---|---|---|
| In quinoline ($p$ = 2·874). | | | | | | |
| 0° | 1·112 * | −36·15° | −44·36° | −53·91° | −75·93° | −117·7° |
| 16 | 1·099 | 44·08 | 54·13 | 64·43 | 90·07 | 137·2 |
| 40·5 | 1·081 | 51·24 | 63·08 | 74·49 | 102·8 | 155·8 |
| 60 | 1·065 | 54·11 | 66·33 | 78·54 | 108·0 | 161·4 |
| 82 | 1·047 | 55·30 | 67·61 | 79·34 | 109·1 | 163·0 |
| In pyridine ($p$ = 4·13). | | | | | | |
| 0 | 1·009 * | −60·50 | −74·18 | −88·06 | −122·6 | −186·6 |
| 12·25 | 0·9970 | 62·20 | 75·97 | 90·01 | 125·2 | 188·8 |
| 35·5 | 0·9743 | 63·22 | 77·34 | 91·49 | 126·2 | 189·8 |
| 51·25 | 0·9585 | 63·54 | 76·74 | 91·05 | 124·9 | 187·8 |
| 65·75 | 0·9441 | 62·75 | 76·17 | 89·80 | 123·8 | 185·1 |
| 78·75 | 0·9307 | 61·49 | 74·92 | 88·33 | 121·3 | 181·0 |
| In ethylene bromide ($p$ = 1·984). | | | | | | |
| 15·5 | 2·16 * | −52·93 | −65·30 | −77·94 | −109·1 | −166·3 |
| 35·5 | 2·122 | 55·12 | 66·94 | 79·79 | 111·0 | 168·7 |
| 50·75 | 2·091 | 55·58 | 67·84 | 80·41 | 111·4 | 167·7 |
| 74·75 | 2·042 | 55·21 | 67·25 | 79·54 | 110·3 | 165·1 |
| 100 | 1·986 | 53·70 | 64·89 | 76·98 | 106·4 | 157·3 |

n-*Propyl Dibenzoyl*-d-*tartrate.*—This *ester* was prepared by the same method as the methyl and the ethyl compound. Propyl tartrate (23 g.) was heated with excess benzoyl chloride (50 g.) for 4 hours at 140—150°, the excess being distilled off under reduced pressure and the residue fractionated. The portion of b. p. 234°/7 mm., dissolved in methylated spirit, crystallised after several days. After several recrystallisations from aqueous alcohol, the product was obtained as fine, white, needle crystals, m. p. 45·5° (Found: C, 64·63; H, 6·30. $C_{24}H_{26}O_8$ requires C, 64·86; H, 6·31%); yield, 15%; $[\alpha]_{5461}^{17\cdot5^\circ} = -78\cdot16^\circ$ ($c = 2\cdot162$ in pyridine).

*Rotations of* n-*propyl dibenzoyl*-d-*tartrate.*

| *t.* | *d.* | $[\alpha]_{r_2}$. | $[\alpha]_y$. | $[\alpha]_g$. | $[\alpha]_b$. | $[\alpha]_v$. |
|---|---|---|---|---|---|---|
| In quinoline ($p$ = 3·27). | | | | | | |
| 0° | 1·1114 * | −23·25° | −29·70° | −36·20° | −52·83° | −85·94° |
| 14·5 | 1·100 | 31·78 | 38·71 | 47·07 | 67·25 | 104·4 |
| 37·5 | 1·082 | 40·05 | 49·26 | 58·99 | 82·77 | 126·4 |
| 51·75 | 1·071 | 43·24 | 52·88 | 63·45 | 88·59 | 135·0 |
| 68 | 1·058 | 45·61 | 56·33 | 66·49 | 92·23 | 139·9 |
| 80·5 | 1·048 | 46·52 | 56·76 | 67·76 | 93·53 | 141·2 |
| In pyridine ($p$ = 3·62). | | | | | | |
| 0 | 1·0073 * | −52·22 | −62·44 | −74·76 | −105·0 | −161·4 |
| 16 | 0·9917 | 52·9 | 65·43 | 77·61 | 108·6 | 165·5 |
| 38·75 | 0·9692 | 54·5 | 66·73 | 79·41 | 110·0 | 167·0 |
| 58·75 | 0·9493 | 54·7 | 67·19 | 79·34 | 109·7 | 164·9 |
| 73·5 | 0·9342 | 53·87 | 66·01 | 77·89 | 108·0 | 162·2 |
| In ethylene bromide ($p$ = 1·647). | | | | | | |
| 17 | 2·154 | −48·18 | −59·26 | −70·84 | −99·51 | −152·4 |
| 41·5 | 2·105 | 49·60 | 60·71 | 72·18 | 100·6 | 152·9 |
| 59·5 | 2·068 | 49·64 | 61·03 | 71·91 | 99·93 | 151·7 |
| 80 | 2·026 | 48·87 | 59·75 | 70·87 | 98·47 | 147·6 |
| 100 | 1·984 * | 47·28 | 57·99 | 68·82 | 94·71 | 142·7 |

n-*Butyl Dibenzoyl*-d-*tartrate.*—A 29% yield of this *compound* was obtained by heating *n*-butyl tartrate (35 g.) and benzoyl chloride (70 g.) to 140—150° for 4 hours. After several refractionations, the main fraction, b. p. 250°/1·3 mm., solidified to a white crystalline solid, m. p. 43° (Found: C, 66·27; H, 6·16. $C_{26}H_{30}O_8$ requires C, 66·39; H, 6·38%); $[\alpha]_{5461}^{15^\circ} = -57\cdot62^\circ$ ($c = 3\cdot64$ in pyridine).

*Rotations of* n-*butyl dibenzoyl*-d-*tartrate.*

| *t.* | *d.* | $[\alpha]_{r_2}$. | $[\alpha]_y$. | $[\alpha]_g$. | $[\alpha]_b$. | $[\alpha]_v$. |
|---|---|---|---|---|---|---|
| In quinoline ($p$ = 3·353). | | | | | | |
| 0° | 1·1105 * | + 6·631° | + 6·497° | + 5·776° | + 2·92° | − 4·65° |
| 15 | 1·099 | − 5·241 | − 7·665 | −10·14 | −18·24 | − 34·61 |
| 36·5 | 1·082 | −17·91 | −22·69 | −28·28 | −41·72 | − 67·08 |
| 51 | 1·071 | −23·85 | −29·68 | −36·36 | −52·11 | − 81·87 |
| 65 | 1·059 | −28·19 | −34·76 | −41·91 | −59·81 | − 92·62 |
| 82·25 | 1·046 | −31·89 | −39·04 | −46·89 | −65·79 | −100·8 |
| In pyridine ($p$ = 3·668). | | | | | | |
| 0 | 1·007 * | −34·64 | −43·49 | −52·22 | −75·09 | −120·0 |
| 15 | 0·9924 | 38·50 | 47·95 | 57·62 | 81·98 | 128·3 |
| 39 | 0·9685 | 42·53 | 52·58 | 62·47 | 87·76 | 134·9 |
| 59·5 | 0·9477 | 44·21 | 54·28 | 64·54 | 89·30 | 137·4 |
| 79·5 | 0·9272 | 44·33 | 54·48 | 64·59 | 89·41 | 136·4 |
| In ethylene bromide ($p$ = 1·705). | | | | | | |
| 14 | 2·158 | −39·92 | −49·38 | −58·83 | −83·73 | −129·5 |
| 35·5 | 2·114 | 41·79 | 51·31 | 61·19 | 86·18 | 131·9 |
| 52 | 2·081 | 42·59 | 52·41 | 62·20 | 86·76 | 132·6 |
| 69·5 | 2·045 | 42·80 | 52·28 | 62·32 | 87·02 | 131·4 |
| 85·25 | 2·0125 * | 42·31 | 52·02 | 61·45 | 85·61 | 128·9 |
| 100 | 1·982 | 41·59 | 51·40 | 60·59 | 83·92 | 127·0 |

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