189. *The Influence of Solvents and of Other Factors on the Rotation of Optically Active Compounds. Part XXXI. The Rotation Dispersion of the Nitrobenzyl Tartrates.*

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In earlier papers of this series, it has been suggested that if the rotation of tartaric acid or its derivatives could be examined over a sufficient range, the temperature–rotation curves for different colours of light would show a number of maxima and minima in the manner represented in Fig. 1c inset, and that other active compounds appear to behave in a similar fashion.

In continuance of this investigation, we have compared the rotations of the three nitrobenzyl esters of *d*-tartaric acid under different conditions. Their acetyl and benzoyl derivatives are not easily soluble in convenient organic media, and were generally examined in pyridine, quinoline, and nitromethane; the melting points of these derivatives being a little high, we have not examined the substances in the homogeneous condition.

m-*Nitrobenzyl* d-*Tartrate and its Derivatives.*—The data for these three compounds are given on p. 765 and are represented by the graphs in Fig. 1a, where the behaviour for green light only is shown, that for other colours being sufficiently indicated by the inset diagram.

The rotation of *m*-nitrobenzyl *d*-tartrate * is much the same for mercury green light in pyridine ($p = 2{\cdot}76$), and in quinoline ($p = 1{\cdot}56$, graphs 1 and 2), but, as the temperature rises, it diminishes slightly from + 73·5° and 77° respectively at 0°, to + 55° and 53·5° at 90°, the diminution being a little more rapid in pyridine than in quinoline. The family of *T–R* curves is very similar in the two cases, and closely resembles the general curves Fig. 1c in the region *ik*, all the graphs being convex to the point of origin of the diagram, but they are apparently approaching a minimum value. In nitromethane ($p = 1{\cdot}39$, graph 7), a minimum does actually appear; the general curves of Fig. 1c are shifted so far to the left that the region *klm* has come into view. This minimum moves to a lower temperature as the wave-length of the light decreases.

The diacetyl derivative, at the ordinary temperature, has a considerably higher rotation in quinoline ($p = 1{\cdot}48$, graph 4) than has the parent substance, and the rotation diminishes, also much more rapidly, from 174° at 0°, to 82·5° at 90°. The influence of pyridine ($p = 1{\cdot}66$, graph 3) is of like character, but less marked; the rotation diminishes from 77° at zero, to 38° at 90°. The dibenzoyl derivative shows a similar behaviour in an exaggerated fashion, the rotation falling from 322° at zero to 87·4° at 90° in quinoline ($p = 1{\cdot}47$, graph 6), and in pyridine ($p = 1{\cdot}63$, graph 5) from 148° at zero to 26·5° at 90°. The family of *T–R* curves for the diacetyl and the dibenzoyl derivative, in both pyridine and quinoline, appears to belong to the region *ik* of the general curves, but pyridine displaces the graph more towards the left, so that, in it, the minimum is a little more nearly approached.

p-*Nitrobenzyl* d-*Tartrate and its Derivatives.*—The general behaviour of these compounds is of a very similar character, but with slight variations. The rotations of the parent ester in quinoline ($p = 4{\cdot}213$, Fig. 1b, graph 2) and in pyridine ($p = 2{\cdot}205$, graph 1) lie

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* This ester was first prepared by Miss Isabella S. Caldwell, who also made some measurements of its rotation dispersion.

fairly close, but not quite so close, together; the corresponding graphs (4 and 3) for the diacetyl derivative are depressed and do not intersect, whilst those for the dibenzoyl derivative (graphs 6 and 5) are raised and rather more separated from each other. The various families of graphs appear to correspond to much the same region, *ik*, of the general curves of Fig. 1c, but, also as before, pyridine appears to displace the *T–R* curves as a whole more towards the left. The parent ester was too little soluble in nitromethane to permit of examination. Its behaviour, therefore, cannot be compared with that of *m*-nitrobenzyl *d*-tartrate in this solvent.

In all these cases the families of graphs suggest a minimum similar to that shown in Fig. 1c, at *l*. Further, the graphs of any one family show no tendency to cut each other, and therefore give no definite indication of anomalous dispersion in this region.

o-*Nitrobenzyl* d-*Tartrate and its Derivatives.*—These esters proved to be of special interest, since, although they exhibited features similar to some already recorded, they also presented a behaviour not hitherto observed in the tartrates. The relevant graphs are shown in Figs. 2, 3, and 4, where the *T–R* curves for all the colours of light used are reproduced, since the evidential value of a family of curves is much greater than that of a single curve.

FIG. 1B. FIG. 1A.

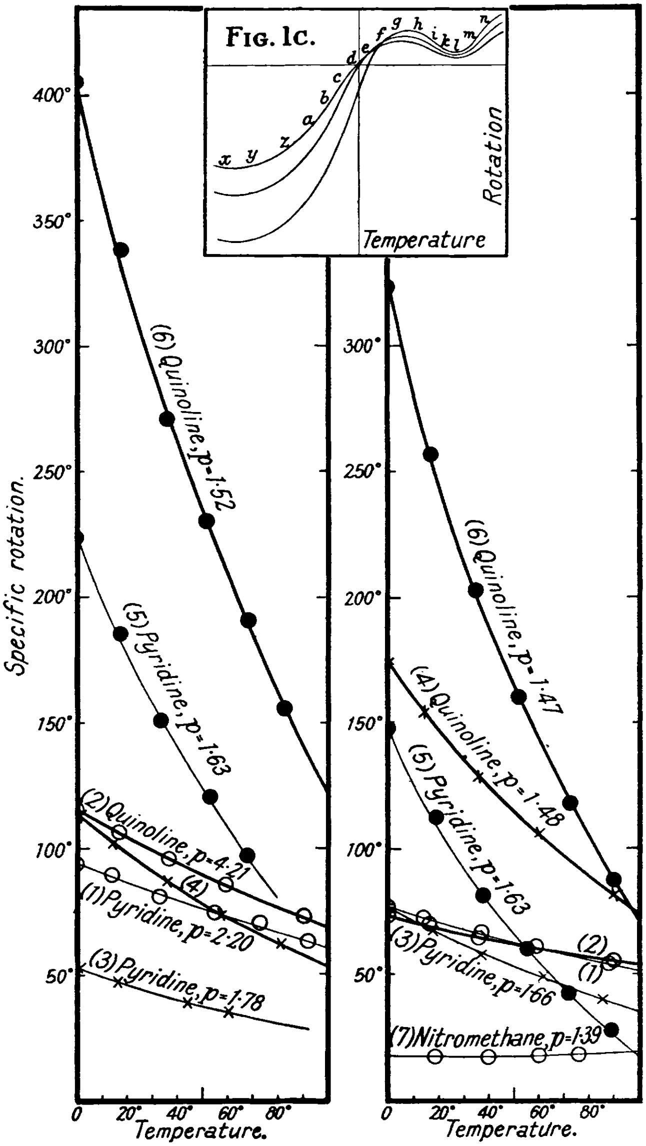


FIG. 1B.—*Temperature–rotation curves for* p-*nitrobenzyl* d-*tartrate and derivatives in various solvents.* (*Graph* 4, *in quinoline*, $p = 1·55$.)

FIG. 1A.—*Temperature–rotation curves for* m-*nitrobenzyl* d-*tartrate and derivatives in various solvents.* (*Graph* 1, *in pyridine*, $p = 2·76$. *Graph* 2, *in quinoline*, $p = 1·56$.)

The rotational behaviour of the simple ester *o*-nitrobenzyl *d*-tartrate, Fig. 2, in pyridine ($p = 1·62$) is shown in the uppermost group of curves (thin lines). It is to be noticed that, (1) the sequence of the rotations is in the normal order, violet greatest and red least; (2) the *v* curve exhibits a maximum in the neighbourhood of a temperature of 25°, there being, perhaps, a slight shift of this maximum towards a lower temperature as the wave-length of the light increases.

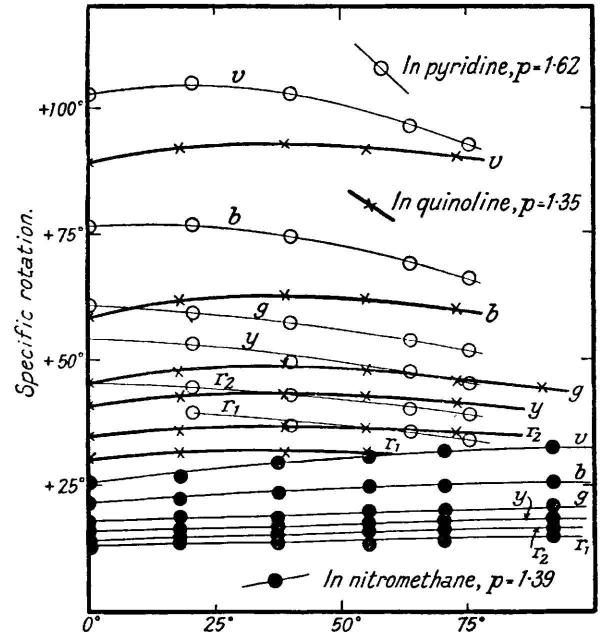
In quinoline (thick lines) the behaviour is similar, but the maximum occurs at a somewhat higher temperature, *viz.*, in the neighbourhood of 35°. The temperature at which the maximum rotation occurs does not alter much with change of wave-length.

In nitromethane the rotation is less, and the trend of the graphs suggests a maximum at some high temperature, probably *ca.* 150°. At the same time there is much less separation (dispersion) of the curves. The curvature, as in the two previous cases, is concave to the point of origin of the diagram.

In general, the maximum in the *T–R* curves for different solvents occurs at lower temperatures as its value increases, much as in ethyl tartrate itself (J., 1908, **93**, 1844; 1913, **103**, 148).

FIG. 2.

Temperature–rotation curves for o-*nitrobenzyl* d-*tartrate in various solvents.*



The uppermost set of curves for the diacetyl derivative (Fig. 3) represents the influence of quinoline, and the general behaviour is apparently similar to that of the *m*- and *p*-esters in this solvent. The graphs, which are widely separated at low temperatures, approach one another gradually in such a way as to suggest a minimum rotation at a moderately high temperature.

In pyridine, which, as a rule, has a very similar influence to quinoline, quite a different behaviour is observed, the form of the curves being reversed. The rotation rises with increase of temperature, in such a way as to display a perfectly distinct region of anomalous dispersion. The sets of curves for this ester in ethylene bromide and in nitromethane are very similar to each other and to those in pyridine; pyridine having the least, nitromethane the greatest, depressing influence. In the diagram, which would otherwise be very confused, only the lines for green and violet in nitromethane and ethylene bromide are shown; they suffice to give an idea of the depression. These curves are certainly similar to those for ethyl tartrate (J., 1916, **109**, 1145) and, taken in pairs, would appear to intersect one another as nearly at the same rotation values as can reasonably be expected. For instance, the graphs for *b* and *r* in homogeneous ethyl tartrate intersect at a specific rotation of 8·1° whilst those for the same colours for *o*-nitrobenzyl diacetyl-*d*-tartrate intersect at 12°; those for *g* and *b* in the former intersect at 11°, and in the latter at 14·5°.

Owing to the physical properties of the ester (see p. 767), it is difficult to correlate its behaviour in pyridine with that in quinoline. We therefore attempted to trace the relationship between the two sets of graphs by examining the rotation of the ester in mixtures of pyridine and quinoline, with the object of following the manner of change-over from the one shape into the other. In a solvent containing approximately two parts of pyridine to one of quinoline (Mixture I), the graphs—also shown in Fig. 3—were obtained: the rate of increase of rotation for violet with rise in temperature is distinctly slower than in pyridine itself, whilst, on the other hand, for yellow and green light, the rotation diminishes. In a solution containing approximately equal quantities of quinoline and pyridine (Mixture II), the graph for violet lies wholly above that for green and yellow, and its shape suggests a maximum towards the left of the diagram. We consider this to indicate that if the graphs representing the behaviour of this ester in quinoline were extended towards the left of the diagram, they would reach maximum values and then diminish to show a region of anomalous dispersion, analogous, at least, to that produced by pyridine, nitromethane, and ethylene bromide. And conversely, if the pyridine graphs could be extended towards the right of the diagram, they would reach maximum values—for r_2 this was actually observed—and then diminish similarly to those for quinoline, but of course in a much less pronounced

FIG. 3.

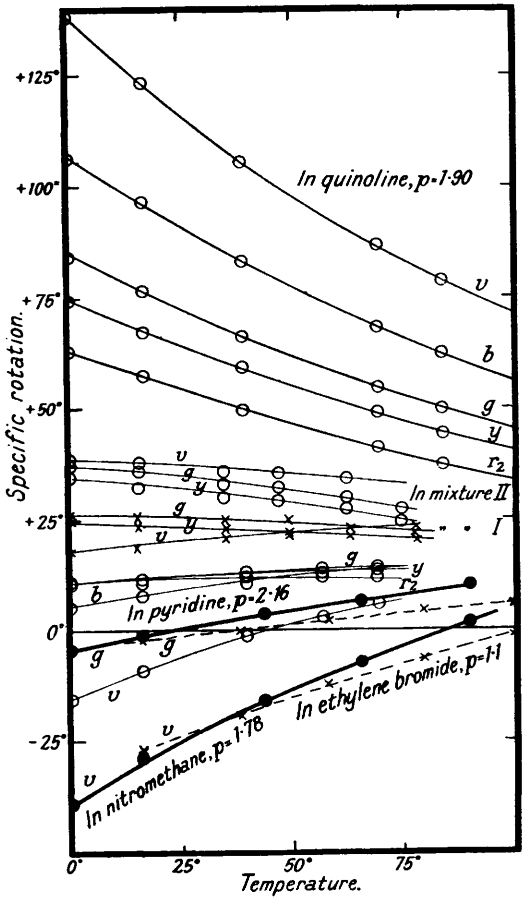


FIG. 4.

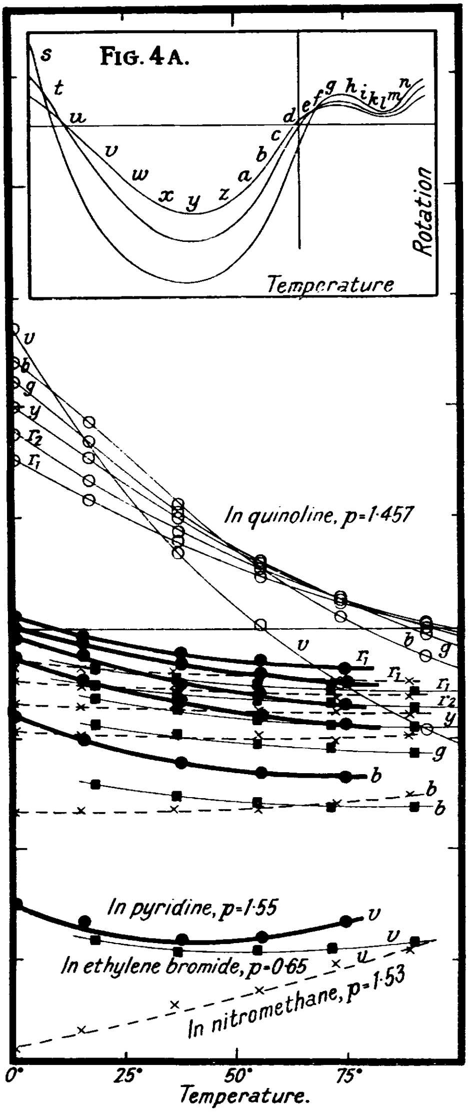


FIG. 3.—*Temperature–rotation curves for* o-*nitrobenzyl diacetyl*-d-*tartrate in various solvents.*
FIG. 4.—*Temperature–rotation curves for* o-*nitrobenzyl dibenzoyl*-d-*tartrate in various solvents.*

degree; or, in other words, the curves for quinoline correspond to the region *hik* of Fig. 1c, and those for the other three solvents to the region *efg*.

The behaviour of the dibenzoyl ester (Fig. 4) is similar in pyridine (p = 1·55, heavy lines), ethylene bromide (p = 0·66, the lowest set of light lines), and in nitromethane (p = 1·53, broken lines). The rotations are almost entirely negative, and, of the three solvents, nitromethane has the greatest depressing effect. In all three cases minima are evident in the *T–R* curves, their positions occurring at different temperatures for different colours of light, moving towards a lower temperature as the wave-length diminishes. The whole family of graphs appears to be displaced to about an equal extent towards the left in pyridine and in ethylene bromide, but less than in nitromethane. The graphs thus appear to correspond to the region *xyz* of Fig. 1c, and to be analogous to those for ethyl dibenzoyltartrate (Frankland and Wharton, J., 1896, **69**, 1583), and for *iso*butyl dibenzoyltartrate (*Proc. Roy. Soc. Edin.*, 1918—19, **39**, 26). In the present case, however, especially in pyridine and in ethylene bromide, there is a marked increase of rotation towards the left of the diagram, so much so that, in pyridine, for the least refrangible colours, the rotation just becomes positive.

The data obtained for this ester in quinoline (Fig. 4, upper set of light lines) are of special interest, and strengthen the inference just drawn. At higher temperatures the sequence of the rotations is the same as that shown in the other solvents examined, but even at as high a temperature as 90° the rotation for the least refrangible colours has become positive. With falling temperature the rotation increases in such a way that the different graphs cut, successively, the axes of zero rotation, and then intersect one another so as to produce a well-marked region of visibly anomalous rotation dispersion, and at a temperature of zero the sequence of the rotations is the opposite to that which holds at 100°. This set of curves, therefore, has the appearance that might be expected on extrapolating those in ethylene bromide and in pyridine towards the left. It seems clear that towards the right of the diagram the graphs for quinoline are tending towards a minimum value, and there is a slight indication of inflexion in the curves towards the left of the diagram, which suggests that they are rising there towards another maximum.

It is noticeable that this region of visibly anomalous dispersion is of a different character from that observed in ethyl tartrate and other similar simple esters. In the latter, with increase of temperature, the rotation increases in passing through the anomalous region, and in the former it decreases. We therefore feel justified in suggesting the extension of the general temperature–rotation curves for the tartrates, shown in the inset diagram of Fig. 4. If such curves for any single tartrate could be examined over a sufficiently wide range of temperature, it seems probable that there would be at low temperatures a region of visibly anomalous dispersion *stuv*, succeeded by a low-value minimum *xyz*, proceeding at higher temperatures to another region of visibly anomalous dispersion, *defg*, which is actually exhibited by ethyl tartrate, etc., and then to a maximum rotation, *ghi*, followed by a minimum, *klm*, without intersection * of the graphs, rising again to another maximum value. Hitherto, no compound has been found exhibiting two such regions of visibly anomalous dispersion, within the range of ordinarily attainable temperatures; the nearest approach to it hitherto recorded being that observed for certain solutions of malic acid in the presence of sodium molybdate (Patterson and Buchanan, J., 1928, 3011).

In recent parts of this series of investigations, stress has been laid on the usefulness of the characteristic diagram of Armstrong and Walker, in correlating optical rotation data. It has been pointed out, however (J., 1916, **109**, 1197; *Proc. Roy. Soc. Edin.*, *loc. cit.*). that, in the region of a maximum or a minimum, the characteristic diagram can be of little use since, in general, the *T–R* curves for different colours of light reach their maximum or minimum values at different temperatures; and further, that a characteristic diagram for the region *abcdefg* of the general curves of Fig. 4A would probably or possibly not be the same as one for the region *hikl*. The data presented in this paper belong largely to regions of maxima and minima and also, we consider, to widely separated regions of the general curves, so that characteristic diagrams could not be expected to correlate them. It seems therefore unnecessary at present to enter into a discussion of the matter.

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* It seems possible that if the rotation in the neighbourhood of this minimum could be sufficiently depressed by some solvent, the different graphs might intersect in such a way as to produce two regions of visibly anomalous dispersion, one on each side of the minimum.

EXPERIMENTAL.

The colours of light used were as follows :

	r_1.	r_2.	y.	g.	b.	v.
λ, Å.U.	6716	6234	5790	5461	4916	4358

m-*Nitrobenzyl* d-*Tartrate*.—This ester was prepared by heating a mixture of tartaric acid (11 g.) and *m*-nitrobenzyl alcohol (32 g.) in a current of dry air to 140° for 15 hours. The resulting syrup was dissolved in methyl alcohol and set aside for several days; the ester, which gradually separated, was repeatedly recrystallised from methyl alcohol, and obtained as small, white, hard crystals, m. p. 119°; yield 50% (Found : N, 6·72. $C_{18}H_{16}O_{10}N_2$ requires N, 6·67%).

m-Nitrobenzyl *d*-tartrate in pyridine, $p = 2·761$.

t.	d.	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_b$.	$[\alpha]_v$.
0°	1·01 *	+48·54°	+57·06°	+66·68°	+76·95°	+97·97°	+130·7°
14	0·9968	45·97	54·23	63·72	72·73	91·83	121·9
37	0·9745	42·90	49·72	57·62	66·37	84·10	113·0
59	0·9523	39·54	45·42	53·57	60·85	77·14	103·6
88·25	0·9217	35·00	40·40	47·73	53·87	68·74	92·1

m-Nitrobenzyl *d*-tartrate in quinoline, $p = 1·56$.

0	1·1135*	+47·31	+54·81	+64·33	+73·50	+92·04	+122·2
16	1·101	45·39	51·77	60·95	70·17	88·65	118·2
36	1·085	42·30	48·46	57·03	64·71	83·85	109·4
65·5	1·062	38·69	43·49	51·99	58·99	75·09	103·3
90	1·042	34·98	40·44	48·72	54·94	70·46	92·28

m-Nitrobenzyl *d*-tartrate in nitromethane, $p = 1·39$.

t.	d.	$[\alpha]_{r_2}$.	$[\alpha]_g$.	$[\alpha]_b$.	$[\alpha]_v$.
18·5°	1·144	+13·69°	+17·03°	+18·09°	+19·54°
40	1·114	12·72	17·07	18·11	20·50
60·25	1·087	12·86	17·42	19·73	21·30
76	1·065	13·60	17·95	20·73	25·89

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

m-*Nitrobenzyl Diacetyl*-d-*tartrate*.—This was prepared from nitrobenzyl tartrate by the action of acetyl chloride, with the addition of a drop of pyridine; very fine white crystals, m. p. 107°; yield 33·3% (Found : N, 5·64. $C_{23}H_{20}O_{12}N_2$ requires N, 5·55%).

m-Nitrobenzyl diacetyl-*d*-tartrate in pyridine, $p = 1·658$.

t.	d.	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_b$.	$[\alpha]_v$.
0°	1·0055*	+50·07°	+56·33°	+66·83°	+77·09°	+98·83°	+139·2°
17·5	0·9888	42·82	49·00	58·87	67·04	85·33	120·0
37	0·9694	38·78	43·12	51·81	57·65	74·59	104·7
61·5	0·9448	32·65	36·24	41·51	48·89	62·66	87·2
85·5	0·9194	—	30·88	35·02	40·19	—	—

m-Nitrobenzyl diacetyl-*d*-tartrate in quinoline, $p = 1·479$.

0	1·1122*	—	+124	+150·4	+174·3	+230·8	+330·4
13·5	1·102	—	110·4	131·7	153·8	202·4	291·8
35·5	1·084	—	92·74	109·9	128·3	170·0	245·4
60	1·065	—	76·45	89·7	106·0	139·8	200·0
90	1·041	—	63·30	70·7	81·3	107·5	152·8

m-*Nitrobenzyl Dibenzoyl*-d-*tartrate*.—Prepared by the action of benzoyl chloride on a pyridine solution of *m*-nitrobenzyl tartrate, this formed fine, felted, white needles, m. p. 109°; yield 17% (Found : N, 4·41. $C_{32}H_{24}O_{12}N_2$ requires N, 4·46%).

m-Nitrobenzyl dibenzoyl-*d*-tartrate in pyridine, $p = 1·629$.

0	1·0075*	+94·28	+109·1	+124·8	+147·9	+190·5	+259·4
19	0·9888	71·53	83·26	99·08	112·4	142·0	192·1
37·5	0·9701	53·18	61·87	72·13	81·62	103·4	138·1
55·5	0·9521	39·42	45·80	50·75	60·66	76·00	99·93
72	0·9353	28·85	32·75	34·55	42·27	52·32	67·84
89	0·9179	14·42	20·94	—	27·64	32·66	—

m-Nitrobenzyl dibenzoyl-*d*-tartrate in quinoline, $p = 1·468$.

0	1·1135*	+197·0	+233·4	+277·5	+322·3	+426·1	+606·6
16·75	1·100	159·8	188·2	224·7	257·2	342·4	486·5
35	1·085	123·9	147·0	174·6	202·8	265·7	376·5
52	1·072	99·13	116·6	138·7	160·6	210·8	297·5
72·5	1·055	74·47	86·6	103·7	118·0	154·6	216·9
90	1·041	56·87	65·1	75·6	87·4	114·4	158·9

p-*Nitrobenzyl* d-*Tartrate*.—By the action of *p*-nitrobenzyl bromide (23 g.) on sodium tartrate (12 g.) in aqueous alcohol (Reid, *J. Amer. Chem. Soc.*, 1917, **39**, 124), followed by recrystallisation from absolute alcohol until of constant rotation in pyridine, this ester was obtained as fine white crystals, m. p. 164·5°; yield 20%.

p-Nitrobenzyl *d*-tartrate in pyridine, $p = 2{\cdot}205$.

t.	d.	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_{y}$.	$[\alpha]_{g}$.	$[\alpha]_{b}$.	$[\alpha]_{v}$.
0°	1·0097*	+61·15°	+68·89°	+83·14°	+93·80°	+121·5°	—
14	0·9956	54·50	64·30	78·54	89·54	114·1	+158·2°
33	0·9770	51·31	60·29	71·17	80·97	107·1	146·9
55	0·9543	47·19	54·87	63·63	74·57	97·74	131·2
73	0·9362*	44·25	50·58	60·87	70·57	88·06	122·6
92	0·9168	41·57	46·62	56·69	62·77	83·75	110·6

p-Nitrobenzyl *d*-tartrate in quinoline, $p = 4{\cdot}213$.

0	1·125*	+70·57	+83·22	+100·2	+116·1	+150·3	+213·5
17	1·108	64·36	76·15	91·22	106·4	137·7	194·6
36·5	1·092	59·0	69·45	83·49	95·79	124·5	177·3
59·25	1·074	52·62	61·42	74·04	85·61	111·3	156·1
90·5	1·049	45·71	53·25	63·43	73·16	93·9	135·2

p-*Nitrobenzyl Diacetyl*-d-*tartrate*.—When prepared as was the corresponding *m*-derivative, and purified by recrystallisation from absolute alcohol, this gave a 60% yield of fine, white crystals, m. p. 141·5 (Found : N, 5·64. $C_{22}H_{20}O_{12}N_2$ requires N, 5·56%).

p-Nitrobenzyl diacetyl-*d*-tartrate in pyridine, $p = 1{\cdot}782$.

0	1·00675*	+34·35	+39·08	+46·5	+52·84	+66·19	+86·28
16·5	0·9913	30·91	35·19	42·03	46·82	58·92	76·90
44	0·9642	26·69	29·52	—	38·43	48·98	63·65
60·5	0·9471	23·10	26·36	—	34·76	43·17	56·58

p-Nitrobenzyl diacetyl-*d*-tartrate in quinoline, $p = 1{\cdot}552$.

0	1·1117*	+71·15	+82·54	+99·02	+113·8	+149·6	+210·6
14	1·101	62·09	74·37	88·39	102·1	132·3	184·6
36	1·084	54·83	63·13	75·16	86·98	113·1	155·6
58	1·067	46·72	54·41	63·08	73·65	97·07	132·0
81	1·048	—	45·74	53·43	62·0	81·41	113·1

p-*Nitrobenzyl Dibenzoyl*-d-*tartrate*.—To *p*-nitrobenzyl *d*-tartrate (3 g.) dissolved in pyridine, excess benzoyl chloride (18 g.) was slowly added, with heating. After standing over-night, the reaction mixture was poured into water and gently warmed to decompose the excess benzoyl chloride. The benzene extract of this was washed with hydrochloric acid, water, then sodium carbonate solution. After drying over potassium carbonate, the benzene was distilled off and the residue recrystallised from aqueous alcohol; white flaky crystals, m. p. 114°; yield 55·7% (Found : N, 4·61. $C_{32}H_{24}O_{12}N_2$ requires N, 4·46%).

p-Nitrobenzyl dibenzoyl-*d*-tartrate in pyridine, $p = 1{\cdot}631$.

0	1·008*	+129·4	+161·0	+190·4	+224·0	+295·2	+425·8
17·5	0·9906	113·4	132·3	160·1	185·6	243·8	353·8
33·5	0·9745	93·71	110·0	132·6	151·0	201·1	292·6
53	0·9550	74·63	87·44	103·0	120·7	157·9	228·3
68	0·9396	61·87	70·96	81·77	97·25	126·6	183·1

p-Nitrobenzyl dibenzoyl-*d*-tartrate in quinoline, $p = 1{\cdot}522$.

0	1·1125*	+243·8	+289·4	+346·9	+405·8	+541·9	+792·7
17·5	1·099	200·6	240·5	289·9	338·3	450·9	658·0
35·75	1·085	168·1	192·4	235·5	275·9	367·7	537·1
51·5	1·073	—	164·9	199·1	230·5	307·7	447·8
68·25	1·059	—	136·7	162·9	190·7	253·9	368·4
82·5	1·047	—	113·2	134·7	155·8	209·1	303·7

o-*Nitrobenzyl* d-*Tartrate*.—A mixture of tartaric acid (10 g.) with excess of *o*-nitrobenzyl alcohol (30 g.) was heated in a current of dry hydrogen chloride to 110° for 8 hours. The product was repeatedly recrystallised from alcohol (charcoal at first); white, nacreous crystals, m. p. 131°; yield 50% (Found : N, 6·67. $C_{18}H_{16}O_{10}N_2$ requires N, 6·67%).

o-Nitrobenzyl *d*-tartrate in pyridine, $p = 1{\cdot}624$.

t.	*d.*	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_b$.	$[\alpha]_v$.
0°	1·0085*	—	+45·40°	+54·25°	+60·81°	+76·54°	+103·0°
20·5	0·9881	+39·68°	44·51	53·20	59·39	76·74	105·0
40	0·9685	37·08	42·99	49·63	57·35	74·50	102·8
63·75	0·9443	35·67	40·27	47·68	53·93	69·05	96·6
76	0·9315	33·91	39·16	45·25	51·89	66·15	92·9

o-Nitrobenzyl *d*-tartrate in quinoline, $p = 1{\cdot}35$.

0	1·1145*	+30·12	+34·69	+40·93	+45·55	+58·29	+88·76
18	1·100	31·50	35·83	42·65	47·42	61·66	92·19
39	1·083	31·63	36·98	43·38	48·99	62·84	92·76
55	1·070	31·66	36·34	42·83	47·71	62·24	91·70
73	1·056	—	35·46	41·43	46·04	59·80	90·28
90	1·042	—	—	—	44·54	—	—

o-Nitrobenzyl *d*-tartrate in nitromethane, $p = 1{\cdot}387$.

0	1·171*	+13·05	+14·05	+15·97	+17·78	+21·67	+25·60
18	1·145	13·51	15·01	16·39	18·71	22·33	26·81
37·5	1·118	13·58	14·91	16·93	18·66	23·46	29·43
55·5	1·094	13·30	15·70	17·51	19·77	24·84	30·70
70·5	1·073	14·16	16·14	17·99	19·96	24·88	31·73
92	1·042	15·01	16·35	18·39	20·76	25·61	32·58

o-*Nitrobenzyl Diacetyl*-d-*tartrate*.—The action of acetyl chloride on *o*-nitrobenzyl tartrate in pyridine afforded crystals of the *monoacetyl* derivative, m. p. 118—120° (Found : N, 6·16. $C_{20}H_{18}O_{11}N_2$ requires N, 6·05%). By the action of acetic anhydride with addition of a drop of concentrated sulphuric acid, the *diacetyltartrate* was obtained, m. p. 75°; it was purified by recrystallisation from methyl alcohol (Found : N, 5·6. $C_{22}H_{20}O_{12}N_2$ requires N, 5·56%).

o-Nitrobenzyl diacetyl-*d*-tartrate in pyridine, $p = 2{\cdot}162$.

t.	*d.*	$[\alpha]_{r_2}$.	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_b$.	$[\alpha]_v$.
0°	1·0085*	+10·61°	+10·96°	+10·64°	+ 5·393°	−15·46°
16	0·9926	+10·98	+11·39	+11·7	+ 7·894	− 9·06
39·5	0·9690	+12·27	+13·34	+13·49	+10·71	− 1·25
56·75	0·9517	+12·27	+13·58	+14·04	+13·03	+ 3·10
69	0·9396	+12·03	+13·91	+14·31	+13·94	+ 6·06

o-Nitrobenzyl diacetyl-*d*-tartrate in quinoline, $p = 1{\cdot}899$.

0	1·114*	+62·88	+74·59	+84·26	+106·5	+138·2
16·75	1·101	57·51	67·33	76·78	96·70	123·6
39	1·083	49·63	59·40	66·53	83·39	105·7
54	1·071	45·06	53·13	60·46	75·46	95·7
69·5	1·059	41·19	49·12	54·80	68·50	86·8
84	1·047	37·42	44·39	50·05	62·50	78·9

o-Nitrobenzyl diacetyl-*d*-tartrate in pyridine–quinoline mixtures.

Mixture I ($C_5H_5N : C_9H_7N = 22{\cdot}1730 : 10{\cdot}5907$, by wt.), $p = 1{\cdot}986$.

t.	*d.*	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_v$.
0°	1·04*	+24·47°	+26·08°	+17·76°
15·25	1·026	23·59	25·77	18·78
35	1·007	23·02	24·99	20·95
49·25	0·9940	21·81	24·05	21·20
63	0·9809	21·56	22·94	22·94
78	0·9665	20·25	22·07	23·21

Mixture II ($C_5H_8N : C_9H_7N = 22{\cdot}4708 : 22{\cdot}2395$, by wt.), $p = 1{\cdot}969$.

t.	*d.*	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_v$.
0°	1·059*	+34·68°	+37·17°	+38·56°
15·5	1·045	32·23	35·91	38·19
34·5	1·0275*	29·94	33·13	35·88
47	1·016	29·26	32·32	35·48
62·25	1·003	27·57	29·82	34·35
74·75	0·9915	24·52	27·31	—

o-Nitrobenzyl diacetyl-*d*-tartrate in nitromethane, $p = 1{\cdot}778$.

t.	*d.*	$[\alpha]_{r_2}$.	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_b$.	$[\alpha]_v$.
0°	1·1675*	−0·722°	−2·378°	− 4·395°	−13·06°	−39·50°
16	1·147	+1·379	+1·042	− 1·165	− 8·063	−28·85
43·5	1·11	+4·81	+4·590	+ 3·988	− 0·886	−15·86
65·5	1·08	+6·866	+8·037	+ 6·704	+ 3·286	− 7·22
90	1·0465*	+8·90	+9·439	+10·21	+ 8·364	+ 1·78

o-Nitrobenzyl diacetyl-*d*-tartrate in ethylene bromide, $p = 1{\cdot}1$.

16	2·175	+0·941	−0·157	−1·96	−8·778	−26·96
38	2·13	+2·188	+1·361	+0·0800	−4·455	−18·91
58	2·089	+3·255	+3·038	+2·251	−1·601	−12·28
79·5	2·044	+4·366	+5·284	+4·449	+1·974	− 6·507
100	1·999	+5·685	+5·772	+6·198	+4·691	− 0·995

o-*Nitrobenzyl Dibenzoyl*-d-*tartrate*.—Prepared as for the *m*- and *p*-isomerides, and repeatedly recrystallised from absolute alcohol, this formed fine, very slightly yellow crystals, m. p. 126·5—127°; yield 53·5% (Found : N, 4·62. $C_{32}H_{24}O_{12}N_2$ requires N, 4·46%).

o-Nitrobenzyl dibenzoyl-*d*-tartrate in pyridine, $p = 1·551$.

t.	*d*.	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_{y}$.	$[\alpha]_{g}$.	$[\alpha]_{b}$.	$[\alpha]_{v}$.
0°	1·0085*	+2·079°	+ 0·0800°	− 2·159°	− 6·60°	−19·84°	−62·48°
15·5	0·9922	−1·706	− 3·25	− 6·094	−11·5	−25·19	−66·67
37·5	0·9696	−5·53	− 7·982	−12·6	−16·34	−30·56	−70·44
55·5	0·9519	−7·114	−10·21	−14·95	−20·03	−32·82	−69·95
74	0·9328	−8·989	−12·23	−17·24	−21·74	−33·79	−66·42

o-Nitrobenzyl dibenzoyl-*d*-tartrate in quinoline, $p = 1·457$.

t.	*d*.	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_{y}$.	$[\alpha]_{g}$.	$[\alpha]_{b}$.	$[\alpha]_{v}$.
0	1·114*	+38·23	+43·81	+50·08	+55·84	+65·24	+67·87
17	1·100	+28·97	+33·34	+38·60	+42·19	+46·51	+42·15
37	1·084	+19·82	+21·80	+24·92	+26·22	+28·04	+17·09
55·5	1·069	+11·62	+13·71	+13·55	+14·63	+13·71	+ 0·682
73·5	1·054	+ 6·545	+ 6·829	+ 6·992	+ 6·504	+ 2·521	−12·36
92·75	1·038	+ 0·909	+ 1·322	− 0·0826	− 1·529	− 6·404	−23·18

o-Nitrobenzyl dibenzoyl-*d*-tartrate in nitromethane, $p = 1·529$.

t.	*d*.	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_{y}$.	$[\alpha]_{g}$.	$[\alpha]_{b}$.	$[\alpha]_{v}$.
0	1·1685*	−8·818	−11·82	−16·87	−23·34	−41·82	−95·19
15	1·148	9·086	12·93	17·64	24·05	41·42	91·16
36	1·119	9·683	12·86	17·65	24·30	41·11	85·33
55	1·094	10·73	14·20	18·76	24·36	41·15	81·83
72·5	1·069	11·51	15·94	19·01	25·43	39·61	76·00
89	1·046	11·89	15·33	19·59	24·24	38·04	72·76

o-Nitrobenzyl dibenzoyl-*d*-tartrate in ethylene bromide, $p = 0·6546$.

t.	*d*.	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_{y}$.	$[\alpha]_{g}$.	$[\alpha]_{b}$.	$[\alpha]_{v}$.
18	2·175	−9·044	−12·86	−16·07	−21·73	−35·60	−70·63
36·5	2·137	11·57	15·01	18·63	24·35	38·02	73·23
54·5	2·100*	12·74	16·28	20·91	26·28	39·42	72·93
55	2·099	—	—	—	—	—	—
71·25	2·065	14·06	16·74	21·88	27·06	40·84	72·43
90	2·024	14·47	18·06	22·54	28·54	40·61	71·08

SUMMARY.

An examination of the optical behaviour of the nitrobenzyl esters of tartaric acid, and their acetyl and benzoyl derivatives, has shown that the corresponding *m*- and *p*-derivatives behave in similar fashion in quinoline and pyridine, giving *T*–*R* curves belonging to the region *ik* in Fig. 4A. The *o*-derivatives, on the other hand, appear to belong to several different regions of the general curves, and, in particular, the dibenzoyl ester in quinoline solution exhibits a region and type of rotation dispersion not hitherto observed in the tartrates.

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