53. *Studies in Solvent Action. Part IX. Rotatory Powers of the* l-*Menthyl Esters of* m-*Nitro- and* 3 : 5-*Dinitro-benzoic Acids in Relation to the Solvent, Concentration, Temperature, and Wave-length of Light.*

By Andrew McLean.

The molecular rotation of menthyl benzoate is less than that of the three mononitrobenzoates irrespective of the solvent employed (Cohen and Armes, J., 1905, **87**, 1190; Kenyon and Pickard, J., 1915, **107**, 35). In benzene solution, however, although the 2 : 6-dinitro-compound shows a further increase in rotation over that of the *o*-nitro-compound, yet the rotations of the 2 : 4- and the 3 : 5-dinitro-ester are less than those of the *o*- and the *m*-nitro-ester respectively (J., 1906, **89**, 1479). In Part VIII (J., 1934, 351), this somewhat unexpected result was pointed out in connexion with the 2 : 4-dinitrobenzoate, and it was suggested that it might be due to a type of solvent–solute combination. The present paper deals with polarimetric and other investigations on the menthyl esters of *m*-nitro- and 3 : 5-dinitro-benzoic acids, gives further evidence of the validity of the suggestion previously advanced, and attempts to correlate the data with current theories concerning the effect of solvents on optical activity.

The esters were prepared by heating the acid chlorides with 2 mols. of *l*-menthol, steam-distilling the excess of menthol, extracting the ester with ether, and working up the extract in the usual way. The *m*-nitrobenzoate was obtained as a pale yellow, viscous oil of rotation slightly higher than that recorded by Cohen. The 3 : 5-dinitro-ester crystallised from alcohol in long colourless needles, which were rather less soluble in most solvents than the nitrobenzoic esters hitherto employed.

Solvent Effects.—The effect of solvents on the rotatory powers of the two esters is very similar, so they may be considered together (see Table I). The most striking feature revealed by these results is that, with increasing polarity of solvent, the molecular rotation of the solution increases, *i.e.*, the solvent effect usually observed with this type of compound is reversed. A second point is that, although the rotations of the *m*-nitrobenzoate in benzene and toluene are greater than those of the 3 : 5-dinitrobenzoate, the range of variation of $[M]_\lambda$ is wider in the case of the latter compound, with the result that in solvents of medium and high polarity the dinitro-ester has the higher rotations.

In the course of the previous work (Part VIII) with mono- and di-nitrated menthyl benzoates in solution, evidence was obtained from molecular-weight measurements at

TABLE I.

Solvent.	Limiting values. α_{6708}.	α_{4358}.	$[M]_{6708}$.	$[M]_{6563}$.	$[M]_{5893}$.	$[M]_{5463}$.	$[M]_{4861}$.	$[M]_{4358}$.	$\mu \times 10^{18}$ (solvent).
l-Menthyl *m*-nitrobenzoate ($t = 20°$, $c = 4$ approx., $l = 1$).									
C_6H_6	−2·70°	−7·18°	−208·0°	−217·2°	−268·0°	−317·3°	−418·2°	−553·0°	0
$C_6H_5{\cdot}CH_3$	2·79	7·19	210·1	217·6	268·0	317·7	416·5	541·4	0·5
$C_6H_5{\cdot}O{\cdot}CH_3$	2·85	7·22	213·3	222·3	280·0	322·7	420·8	540·5	1·25
C_6H_5Br	3·02	8·09	221·5	231·8	286·8	340·4	449·8	593·4	1·50
$C_6H_5{\cdot}CHO$	3·19	8·62	221·8	232·2	286·4	341·4	451·2	599·4	2·74
$C_6H_5{\cdot}NO_2$	3·16	*6·57	216·8	227·8	284·1	339·7	450·9	—	3·90
$C_6H_5{\cdot}CN$	3·12	8·47	231·5	240·3	295·3	353·1	465·9	628·3	3·85
†C_6H_{12}	2·47	6·84	188·6	196·2	242·8	289·4	384·2	522·4	0
l-Menthyl 3 : 5-dinitrobenzoate ($t = 20°$, $c = 4$ approx., $l = 1$).									
C_6H_6	−2·21°	−5·60°	−191·5°	−200·2°	−247·1°	−293·5°	−382·2°	−486·4°	0
$C_6H_5{\cdot}CH_3$	2·35	5·71	204·9	213·6	264·1	309·4	399·2	496·6	0·5
$C_6H_5{\cdot}O{\cdot}CH_3$	2·52	6·20	217·6	226·3	279·0	329·1	424·1	535·5	1·25
C_6H_5Br	2·61	7·03	227·9	235·7	295·1	351·0	463·6	613·8	1·50
$C_6H_5{\cdot}CHO$	2·65	7·45	232·0	244·3	304·8	365·2	487·9	652·6	2·74
$C_6H_5{\cdot}NO_2$	2·78	*5·94	242·7	255·8	321·2	386·7	518·6	—	3·90
$C_6H_5{\cdot}CN$	2·90	8·24	250·4	261·6	327·2	391·1	528·5	711·3	3·85
†C_6H_{12}	Ester practically insoluble.								

* α_{4861}. † C_6H_{12} = *cyclo*Hexane.

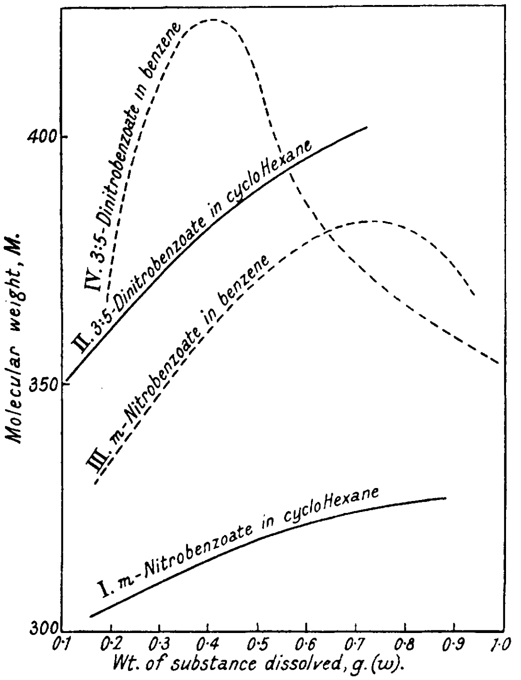
increasing concentrations which pointed to the abnormal molecular state of the 2 : 4-dinitrobenzoate dissolved in benzene. This difference, which showed itself, when molecular weight was plotted against concentration, as a maximum followed by a minimum in a region which included the concentration of the polarimetric solutions, was interpreted (cf. Turner, "Molecular Association," pp. **33**, **37**) as indicating combination between solvent and solute accompanying increasing molecular (dipolar) association of the solute. Accordingly, the molecular weights of the two esters now under discussion were determined ebullioscopically in non-polar solvents of benzenoid and of non-benzenoid character, *viz.*, benzene and *cyclo*hexane respectively; the method employed was that of Menzies and Wright (*J. Amer. Chem. Soc.*, 1921, **43**, 2314). The results are detailed in Table II and plotted in Fig. 1.

TABLE II.

w.	*e.*	*M.*	*w.*	*e.*	*M.*	*w.*	*e.*	*M.*	*w.*	*e.*	*M.*
m-Nitrobenzoate. *M*, calc., 305.						3 : 5-Dinitrobenzoate. *M*, calc., 350.					
Solvent, *cyclo*hexane; ebullioscopic weight constant (*k*) = 28·6.											
W = 20·19; b.p. = 81·0°.						*W* = 18·75; b.p. = 81·2°.					
0·1940	0·090°	306	0·6021	0·269°	317	0·1315	0·057°	352	0·5360	0·207°	395
0·3980	0·180	313	0·7766	0·336	328	0·2462	0·102	368	0·6469	0·249	396
						0·3860	0·155	380			
Solvent, benzene; ebullioscopic weight constant (*k*) = 26·1.											
W = 22·82; b. p. = 80·0°.						*W* = 22·65; b. p. = 80·2°.					
0·1966	0·068	331	0·7298	0·217	385	0·2117	0·065	375	0·8291	0·262	365
0·3483	0·111	359	0·9286	0·287	370	0·4046	0·108	432	1·0427	0·342	351
0·5202	0·161	369				0·6068	0·183	382			

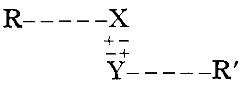
Within the limits of concentration of the determinations (which cover that of the polarimetric solutions) the solutions fall into two classes: (*a*) those in *cyclo*hexane, in which the shape of the curve is normal for increasing molecular association of solute with increase of concentration, and (*b*) those in benzene, the curves of which may be interpreted, in the same way as before, as showing both molecular association of solute and solvent–solute combination. It is also to be observed that for each ester the curve for *cyclo*hexane lies below the corresponding one for benzene, in one case over the whole range of concentrations and in the other over about half the range. Observation (*b*) suggests that solvent–solute combination tends to show itself as an increase in the measured molecular weight. In his experiments on the molecular weights of metals in mercury, Ramsay (J., 1889, **55**, 521) took this view, arguing that the total effect was the measurement of the molecular weight of the addition compound. Turner (*op. cit.*, p. 37), on the other hand, points out that the action of combination is to be regarded as merely reducing the amount of free solvent, thereby virtually concentrating the solution and leading to a lower calculated molecular weight since the elevation of the b. p. and depression of the f. p. will be increased. Whilst Turner's objection is probably valid with respect to Ramsay's solutions, in which the proportions of the components were one atom of solute to 25—100 atoms of solvent, it is hardly likely to hold in the present cases, where the ratio is 1 mol. of solute to 2000—4000 mols. of solvent.

FIG. 1.

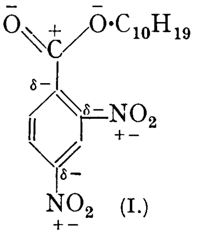


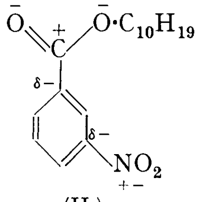
The simple theory of dipolar association, solvent–solute combination being ignored, indicates that association of the ester should be greater in *cyclo*hexane than in benzene under the same conditions, for the latter has the higher dielectric constant. It is therefore to be expected that, in cases where dipolar association is the predominant factor over the whole range of concentrations, the curve for *cyclo*hexane solutions will lie above that for benzene solutions. The polarimetric data for the esters already examined (J., 1934, 351) were in agreement with the predictions of the dipolar association hypothesis, so presumably this was the predominant influence; the molecular-weight data accordingly agreed with the above conclusions. However, the two esters now under discussion seem to show no agreement with the predictions of the simple theory of dipolar association in respect to their polarimetric behaviour. It is therefore not surprising that the diagrams for molecular weight against concentration are also displaced in comparison with those already obtained. It seems reasonable to assume that molecular combination between solvent and solute is the predominant factor in the present binary systems.

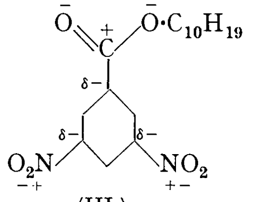
Hitherto, in discussing the effect of solvents on optically active molecules, orientation of the permanent dipoles as depicted in the inset has been sufficient to explain the majority of the effects observed. However, it was at no time assumed that this mechanism represented completely the influence of solvents, and evidence of other operative factors was sought. Now that the formation of addition compounds in optically active solutions, which exhibit rotations different from those expected on the above mechanism, has been established with some degree of certainty, an indication is forthcoming of the direction in which further influences may be found.

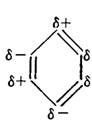


The following structural formulæ emphasise the polar nature of the substances which have been found to form addition compounds with benzene and at similar concentrations show abnormal rotatory powers in benzenoid solvents :


(I.)


(II.)


(III.)


(IV.)

The benzene nucleus in (III) is nearly electrically symmetrical; in (II), the two polar groups both tend to induce a negative charge on the carbon atom in position 5, so that the aromatic ring is again approaching electrical symmetry; in (I), the total effect of the substituent groups is to induce a negative charge on the carbon atom in position 6, but the electrical symmetry of the benzene ring in this molecule probably will be much less than that of (II) or (III). Taken in conjunction with the fact that the curves for the molecular weight plotted against concentration demonstrate that the formation of addition compounds is less with (I) than with (II) and (III), this reasoning leads to the conclusion that electrical symmetry of the optically active molecule is a significant factor in addition-compound formation.

How, then, may this formation take place between benzene and molecules of the types (I), (II), and (III) in order to affect the rotation of the latter? The benzene molecule is non-polar, and so could not take part in an association involving permanent dipoles, but consisting, as it does, of a symmetrical ring of conjugated double bonds, it is easy to imagine such a system becoming polarised by induction as in (IV) on the approach of molecules of the electrical types (I), (II), or (III). The formation of molecular compounds between the two components could then take place by hexapolar association, which would not differ in essence from dipolar association, but would involve a greater degree of orientation of the component molecules with respect to each other. The strength of such a union would probably depend on the symmetry of the electrical field of the aromatic nucleus in the ester molecule and, therefore, the order of stability of the addition compounds, (III),C_6H_6>(II),C_6H_6>(I),C_6H_6, is to be expected. The decrease in rotatory power of the ester molecules due to hexapolar association will, accordingly, be in the order (III)>(II)>(I).*

With the introduction of a substituent into the benzene ring, the whole structure of the solvent molecule becomes electrically unsymmetrical owing to repulsion or attraction of electrons, *i.e.*, the substituent exerts a controlling influence on the electrons in other parts of the ring. This controlling influence will be proportional to the polarity of the entering group. As a result, the polarisation of the electrons by a system of charges outside the molecule will be less facile than in the unsubstituted benzene molecule. By application of this reasoning to binary liquid systems such as solutions of molecules (I), (II), or (III) in pure monosubstituted benzenes containing substituents of increasing polarity, it follows that the induced polarisation of the solvent ring by the solute molecule will decrease as the polarity of the substituent in the solvent molecule increases; consequently, compound formation of the above type between solute and solvent will decrease in the same manner. Thus the lowering of the rotations of molecules (I), (II), and (III) due to compound formation would be greatest in benzene solution, less in solvents of intermediate polarity, and least in strongly polar solvents such as nitrobenzene and benzonitrile.

The conclusion may therefore be drawn, that, with the optically active esters now being discussed, hexapolar association alone would lead to the highest rotations being observed in strongly polar solvents, and the lowest in non-polar solvents. However, association of the permanent dipoles has also to be taken into consideration, and the evidence already recorded in this series of papers makes it practically certain that the effect of this factor with this type of solute will be exactly the reverse of that of hexapolar association. In the absence of other dominant influences, the relative strengths of these two factors will determine the order of the rotations in a series of similar solvents derived from the same hydrocarbon. It would seem that solutions of the *m*-nitro- and 3 : 5-dinitro-benzoates present particularly good examples of systems where hexapolar association is predominant; the increasing influence of dipolar association with increase in strength of the solvent dipole is seen, however, in both cases with nitrobenzene solutions, the rotations of which tend to fall amongst the values for solutions in solvents of inter-

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* It is of interest that Briegleb (*Z. physikal. Chem.*, 1934, *B*, **26**, 63), as a result of his work on the molecular complexes formed between nitro-compounds and hydrocarbons, has deduced a mechanism which is essentially the same as that outlined above.

mediate polarity. Dipolar association, on the other hand, is apparently the predominant influence in solutions of the 2 : 4-dinitrobenzoate; this is not unexpected, for the 2-nitro-group has the largest effect on the rotatory power, and the data for the *o*-nitrobenzoate show that this group is very sensitive to changes of polarity in the solvent. However, hexapolar association would seem to be fairly strong at the non-polar end of the solvent series, with the result that solutions in such solvents have lower rotations than solutions of the *o*-nitrobenzoate in the same solvents.

The 3 : 5-dinitrobenzoate is much less soluble in benzenoid solvents than the other mono- and di-nitrated menthyl benzoates previously investigated, and for this reason the argument might be advanced that it does not form molecular compounds with these solvents. On the other hand, its solubility in benzenoid solvents is very much greater than in solvents of other types, *e.g.*, alcohol, *cyclo*hexane, and decalin. Furthermore, the 3 : 5-dinitrobenzoate differs strikingly in crystalline form from the other esters, and its m. p. is 80—90° higher than those of the latter, both of which facts suggest that its comparatively low solubility is due to greater strength of intracrystalline forces rather than to small affinity for benzenoid molecules. Finally, the *m*-nitrobenzoate, which is analogous to the 3 : 5-dinitrobenzoate in rotatory power and molecular-weight peculiarities, is a liquid and is very soluble in all benzenoid solvents.

The application of these ideas to the results obtained with other optically active substances in solution is obvious, for, if the effects of dipolar association and combination with the solvent happened to be nearly equal and opposite, then a solvent series showing little or no regular variation of rotation with polarity of solvent is to be expected. On the other hand, the converse of this statement is not necessarily true, for other factors may be active in masking regularities (*e.g.*, formation of co-ordinate linkages; Rule, Smith, and Harrower, J., **1933**, 376). Further, it is not to be expected that dipolar association and combination with the solvent will always have opposing effects on the rotation of an optically active solute. This has been shown to be probable when the optically active molecule contains a substituent which increases the rotation of the unsubstituted compound, but, if the substituent causes the rotation to be lower than that of the latter, the above effects may be expected to aid one another. It is difficult to obtain a substituent which lowers the rotation of the unsubstituted compound and has a polarity comparable with that of the nitro-group whilst remaining chemically inert towards the solvent, but it is proposed to carry out investigations with the menthyl dimethylamino-benzoates in an attempt to elucidate further the points raised.

TABLE III.

Effect of concentration.

		Limiting values.							
Solvent.	*c.*	α_{6708}.	α_{4358}.	$[M]_{6708}$.	$[M]_{6563}$.	$[M]_{5893}$.	$[M]_{5463}$.	$[M]_{4861}$.	$[M]_{4358}$.
		l-Menthyl *m*-nitrobenzoate ($t = 20°$, $l = 1$).							
C_6H_6	3·960	−2·70°	−7·18°	−208·0°	−217·2°	−268·0°	−317·3°	−418·2°	−553·0°
,,	8·146	5·61	14·90	210·1	218·6	270·3	321·3	423·2	558·0
,,	16·504	11·27	30·12	208·2	217·2	269·5	320·1	420·9	556·8
,,	31·866	21·63	57·53	207·0	215·6	267·5	317·6	417·6	550·5
,,	63·748	43·51	*66·06	206·5	214·4	266·0	316·1	—	—
$C_6H_5{\cdot}NO_2$	4·444	3·16	§6·57	216·8	227·8	284·1	339·7	450·9	—
,,	7·956	5·63	§11·69	215·8	225·0	281·4	337·0	448·2	—
,,	17·896	12·46	§25·76	212·3	221·6	276·8	330·7	438·8	—
,,	32·722	22·12	§46·00	206·2	216·4	270·3	322·5	428·9	—
		l-Menthyl 3 : 5-dinitrobenzoate ($t = 20°$, $l = 1$).							
C_6H_6	4·030	2·21	5·60	191·5	200·2	247·1	293·5	382·2	486·4
,,	8·056	4·49	11·37	195·1	202·5	249·8	295·5	384·9	494·0
,,	9·840	5·50	14·03	195·7	203·5	251·4	297·3	388·1	499·0
$C_6H_5{\cdot}NO_2$	4·009	2·78	§ 5·94	242·7	255·8	321·2	386·7	518·6	—
,,	8·042	5·53	§11·74	240·7	252·0	316·3	379·8	511·0	—

* α_{5463}. § α_{4861}.

TABLE IV.

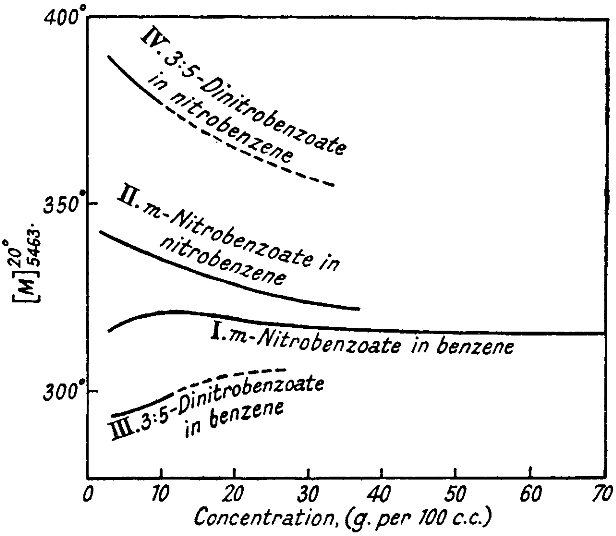
Effect of temperature.

			Limiting values.							
Solvent.	$d_{t^\circ}^{4^\circ}$.	Temp.	a_{6708}.	a_{4358}.	$[M]_{6708}$.	$[M]_{6563}$.	$[M]_{5893}$.	$[M]_{5163}$.	$[M]_{4861}$.	$[M]_{4358}$.
l-Menthyl *m*-nitrobenzoate ($l = 1$; $p = 3{\cdot}487$ in decalin, $= 4{\cdot}444$ in $C_6H_5{\cdot}NO_2$).										
Decalin	0·8890	20·0°	−2·16°	−5·39°	−212·5°	−222·3°	−274·4°	−323·7°	−414·2°	530·2°
,,	0·8733	40·8	2·12	5·32	212·3	222·3	275·4	324·5	416·7	532·9
,,	0·8604	58·3	2·08	5·22	211·4	221·6	275·5	324·3	417·8	530·6
,,	0·8453	78·6	2·02	5·12	209·0	218·2	272·0	320·7	414·8	529·6
,,	0·8317	97·0	2·00	5·07	210·3	220·8	273·4	324·9	419·6	533·1
$C_6H_5{\cdot}NO_2$	1·1795	39·5	2·99	§6·17	208·5	217·7	272·7	325·7	430·3	—
,,	1·1614	58·5	2·85	§5·90	201·9	210·4	264·2	315·3	418·0	—
,,	1·1241	78·0	2·71	§5·66	195·2	203·8	257·1	307·5	407·6	—
l-Menthyl 3 : 5-dinitrobenzoate ($l = 1$; $p = 3{\cdot}334$).										
$C_6H_5{\cdot}NO_2$	1·2027	20·5	2·78	§5·94	242·7	255·8	321·2	386·7	518·6	—
,,	1·1842	39·5	2·66	§5·59	235·8	247·4	309·4	370·7	495·7	—
,,	1·1659	58·2	2·52	§5·28	226·9	238·5	297·1	355·6	475·3	—
,,	1·1452	79·5	2·40	§4·99	220·1	229·2	288·8	347·5	457·6	—
,,	1·1253	99·8	2·26	§4·78	211·0	220·3	277·3	336·1	446·2	—

§ a_{4861}.

Concentration and Temperature Effects.—As far as possible, the procedure formerly adopted was adhered to, the effects of concentration and of temperature being measured in a non-polar and in a polar solvent in each case. The results are set forth in Tables III and IV. (Owing to the extremely slight solubility of the 3 : 5-dinitrobenzoate in decalin, the temperature effect could not be determined.)

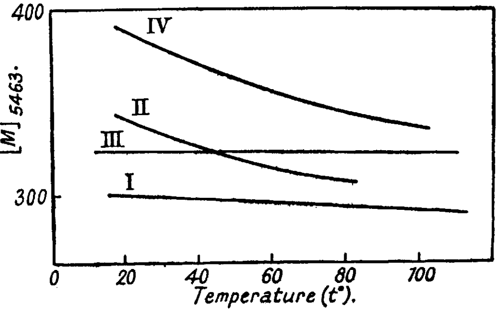
FIG. 2.



In Fig. 2 the values of $[M]_{5463}$ from Table III are plotted against the corresponding concentrations; the resulting curves are shown in full lines. The shapes of the curves are very much those which might be expected if the assumptions already made are valid. The right-hand half of Curve III, Fig. 1, corresponds to 2—4% solutions of the *m*-nitrobenzoate in benzene, and at this concentration combination between solvent and solute is extensive; Curve I, Fig. 2, shows that the rotation of this ester in benzene reaches a low value in this same region. Unfortunately, the ebullioscopic molecular-weight apparatus did not allow the use of greater concentrations of *m*-nitrobenzoate, but from the shape of the corresponding curve for the 2 : 4-dinitrobenzoate (J., 1934, 357), it may be inferred that Curve III, Fig. 1, will, at greater concentrations, reach a minimum and again rise normally, indicating that combination with the solvent becomes relatively less extensive. Correspondingly, Curve I, Fig. 2, rises to a maximum and then falls with increasing concentration towards the value for the homogeneous ester ($[M]^{20°}_{5461} = -300°$). Curve II, for the *m*-nitrobenzoate in nitrobenzene, exhibits a normal trend over the concentration region investigated, *viz.*, an approach towards the rotation value of the homogeneous ester as the concentration increases; no maximum is apparent, indicating that compound formation between the ester and nitrobenzene is inappreciable. The 3 : 5-dinitrobenzoate is a much more difficult compound with which to obtain sufficient data, owing to its slight solubility and to its high m. p., which prevents the determination of its rotation in the homogeneous state. So far as such investigations were possible, however, they indicate that its behaviour is similar to that of the *m*-nitrobenzoate, and the dotted extrapolations of the curves are probably justified.

In a discussion of the changes in optical rotation predictable by the dipole-association hypothesis, Rule, Barnett, and Cunningham (J., 1933, 1217) concluded that "the temperature–rotation curve for a strongly polar solvent should converge towards that of a non-polar medium as the temperature rises," and also that "in position and direction, the temperature–rotation curve for the homogeneous compound will lie between those observed for solvents of the extreme types." Patterson and co-workers (J., 1908, **93**, 1836, and later) regard the problem of variation of rotation with temperature from a different angle, and conclude that experimentally determined temperature–rotation curves are merely parts of a general temperature–rotation curve the whole of which should theoretically be able to be reproduced by suitable changes of solvent, wave-length, temperature, and substituent in the optically active molecule. From this generalisation, it is deduced that, according as the rotation in a given solvent is much below or above that of the homogeneous optically active compound, rise in temperature will respectively raise or diminish the rotation (or cause it to increase very slowly in the latter case). In Part VIII (*loc. cit.*), it was shown that solutions in which dipole association was predominant, *viz.*, solutions of menthyl *o*-nitro- and 2 : 4-dinitro-benzoates, conformed to the conclusions of Rule, Barnett, and Cunningham, whereas solutions showing no regular variation of rotation with the dipole moment of the solvent obeyed Patterson's rule.

FIG. 3.



I. m-*Nitrobenzoate* (*homogeneous*).
II. ,, *in nitrobenzene.*
III. ,, *in decalin.*
IV. 3 : 5-*Dinitrobenzoate in nitrobenzene.*

The results of the present investigation for one of the wave-lengths employed are set forth graphically in Fig. 3; the values for the homogeneous *m*-nitrobenzoate for λ = 5461 are due to Kenyon and Pickard (J., 1915, **107**, 35). Considering Curves I, II, and III together, one sees that Patterson's deduction is substantiated; the rotations of both decalin and nitrobenzene solutions are above the homogeneous value, and with rise in temperature the decalin value remains practically constant whilst the nitrobenzene value approaches that of the homogeneous ester. The convergence of Curves I and II agrees with Rule's conclusions, but the relative positions of the three curves are not in accord with those conclusions. Curve IV, by itself, adds little to our knowledge of the problem of the effect of concentration, but, in so far as it runs practically parallel to Curve II, it emphasises the general resemblance between the *m*-nitro- and 3 : 5-dinitro-benzoates.

From the data for the five menthyl esters of nitro- and dinitro-benzoic acids detailed in the present and the preceding papers of this series, the following conclusions with respect to the effect of temperature may be drawn. (1) When dipolar association is the predominant factor influencing rotatory power, the generalisations of Rule, Barnett, and Cunningham offer the best indications of the trends of the temperature–rotation curves. (2) When other factors exert forces of the same order as the dipolar association—

probably an irregular solvent series will be obtained—Patterson's deduction allows of a surer prediction of the relative directions of the temperature–rotation curves.

Optical Rotatory Dispersion.—On plotting $1/\alpha$ against λ^2, a smooth curve showing a regular deviation from linearity is obtained in each case. These curves are of the form usually associated with a dispersion equation such as $\alpha = k_1/(\lambda^2 - \lambda^2) \pm k_2/\lambda^2$, but the constants in this equation could not be calculated from the data available. It would seem that the complexity of the dispersion of the esters now being discussed is greater than that of the isomeric esters previously examined; this is not surprising in view of the other evidence of molecular complexity set forth above. Facilities for a more extensive examination over a wider range of wave-lengths were not available, so the possibility of anomalous dispersion and conformity to a four-constant dispersion equation could not be investigated.

SUMMARY.

(1) Solutions of the menthyl esters of *m*-nitro- and 3 : 5-dinitro-benzoic acids in benzenoid solvents show rotatory powers which vary in a similar manner to the dipole moment of the solvent.

(2) An attempt is made to connect these results with the hypothesis of solvent effect advanced in this series of papers.

(3) The effects of concentration and temperature are discussed in the light of current theories.

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