86. *Studies in Solvent Action. Part VIII. Rotatory Powers of the* l-*Menthyl Esters of* o-*Nitro-,* 2 : 4-*Dinitro-, and* p-*Nitro-benzoic Acids in Relation to the Solvent, Concentration, Temperature, and Wave-length of Light.*

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BINARY liquid mixtures, in which the components do not react chemically, have proved of great value in the study of molecular association and related phenomena. The properties of such mixtures are dependent on the forces between the molecules of the same substance, on the one hand, and between those of different substances, on the other. Debye and Keesom have shown that these forces are of an electrical nature and tend to cause association of the single molecules. Errera (*Z. physikal. Chem.*, 1928, **138**, 332; 1929, **140**, 273) has produced evidence that the forces concerned may be of two kinds, giving rise to two types of molecular association, *viz.*, dipolar, which must be ascribed to the electrostatic forces of the permanent dipoles, and dipoleless, caused by the van der Waals forces usually assumed to explain the association of homopolar molecules. In the former case the effective forces are fixed by the size and strength of the dipoles and the form of the molecules themselves, and are generally much more powerful than the forces concerned in the latter case, which has its greatest significance when non-polar mixtures are considered. Experimental data concerning electrical polarisation have been successfully explained on this hypothesis (cf. Debye, " Polar Molecules," 1929), and Errera (" Dipole Moment and Chemical Structure," 1931, 101) has shown that there is, in binary liquid mixtures, a sympathetic variation between the polarisation and other physical properties such as vapour pressure and viscosity.

That molecular association is effective in the phenomena of optical rotatory power was suggested by Frankland (J., 1899, **75**, 347) and supported by Pope and Peachey (*ibid.*, p. 1111). This assumption was, however, severely criticised by Patterson (J., 1901, **79**, 167), who sought to establish a relationship between the rotation of an optically active solution and the internal pressure of the solvent. Modern theory would seem to indicate that there is little fundamental difference between the two points of view, internal pressure as well as molecular association being largely determined by the polar nature of the liquid. For instance, Hildebrand (" Solubility," 1924, 85) states that " polar molecules have an abnormally great attraction for each other, producing greater cohesions, internal pressures . . . and tending to squeeze out, as it were, non-polar or slightly polar molecules from their midst," and Errera (*op. cit.*) concludes that dipolar association corresponds to a drawing together of the molecules by electrostatic forces which may be compared to the forces between the ions in a crystal lattice. It is therefore surprising that Patterson, Dunn, Louden, and Buchanan (J., 1932, 1715) should describe attempts to connect rotation data with dipole moment or specific inductive capacity as being of little significance.

Of the factors affecting molecular association, dipole association would appear to be the most amenable to investigation in connexion with optical rotation, owing to its very great effect and to the large number of well-established values of dipole moments now available. In earlier papers of this series a relationship has been shown to exist between the rotatory power of an optically active solution and the dipole moment of the solvent. It has been found that, in general, the rotation varies in the opposite sense to the dipole moment of the solvent throughout a series of solvents derived from the same parent hydrocarbon. An explanation of this observation has been advanced in terms of dipolar association, and numerous results have been brought forward in support of this hypothesis. During these investigations apparent deviations from the general rule were encountered, and although, in the main, these are explicable on the above hypothesis by a consideration of space models of the molecules involved, yet it was thought that the explanation was still incomplete.

Previous experience had shown that solvent influences are best observed with optically active compounds of simple molecular structure with a strongly polar group situated near the asymmetric centre. The menthyl esters of the nitrobenzoic acids were therefore considered suitable solutes with which to extend the investigations. The general rule for solvent effects being now recognised, the opportunity was also taken to study other factors which cause variation in rotation, *viz.*, change of concentration, temperature, and wave-length, in order to submit the dipole association hypothesis to a more rigorous test.

The menthyl esters of the nitrobenzoic acids have already been examined polarimetrically by Cohen and Armes (J., 1905, **87**, 1190; 1906, **89**, 1479) and by Kenyon and Pickard (J., 1915, **107**, 35). The former authors measured the rotations of the substances in the homogeneous state or in benzene solution for the sodium D line at a few different temperatures; the latter workers carried out a more extensive investigation at four different wave-lengths, but the solvents they employed were too few in number and of too widely different type to show any regularity.

Solvent Effects.—With the short, representative series of benzene derivatives employed as solvents, the changes in rotatory power of *l*-menthyl *o*-nitrobenzoate are in excellent agreement with the above-noted regularity, as shown in Table I. In order to economise space, only the limiting values of α_λ are given here and in the following tables. The rotation values in *cyclo*hexane, which is not strictly a benzenoid solvent, are included in the tables and will be referred to later.

Table I.

l-*Menthyl* o-*nitrobenzoate* ($t = 20°$, $c = 4$, $l = 1$).

(All rotations negative.)

Solvent.	Limiting values. α_{6708}.	α_{4358}.	$[M]_{6708}$.	$[M]_{6563}$.	$[M]_{5893}$.	$[M]_{5463}$.	$[M]_{4861}$.	$[M]_{4358}$.	$\mu \times 10^{18}$ (solvent).
C_6H_6 ………………	5·31°	22·45°	403·6°	427·1°	566·1°	713·8°	1069°	1708°	0
$C_6H_5{\cdot}CH_3$ …………	5·11	21·02	389·6	410·2	536·7	671·0	993·5	1603	0·5
$C_6H_5{\cdot}OCH_3$ ………	4·58	18·96	349·2	368·2	480·3	602·3	891·4	1446	1·25
C_6H_5Br ……………	4·43	18·15	338·3	355·2	462·9	580·4	860·3	1386	1·50
$C_6H_5{\cdot}CHO$ …………	3·84	15·54	292·7	308·0	400·3	500·1	737·1	1184	2·74
$C_6H_5{\cdot}CN$ …………	3·67	14·43	276·7	289·4	373·9	465·1	684·4	1088	3·85
$C_6H_5{\cdot}NO_2$ …………	3·27	* 8·11	248·6	263·1	339·9	422·7	616·7	—	3·90
*cyclo*Hexane ………	4·56	18·52	345·5	362·9	473·5	594·0	877·4	1404	0

* α_{4861} in this case.

The rotatory dispersion in all the solvents is complex, but for each wave-length the rotatory power decreases as the dipole moment of the solvent increases. Hitherto, no attempt has been made to seek quantitative relations in this regularity; but an examination of the values of $[M]_\lambda$ in the above table clearly indicates that in the less polar aromatic solvents, there is, within the limits of experimental error, a quantitative agreement, the lowering of $[M]_{5463}$ being approximately 9° for an increase of 0·1 in the value of the dipole moment, so that, as shown in Table II, $[M]_{5463}$ is given with accuracy by the expression $[M]^{20°}_{5463}$ (solution) $= [M]^{20°}_{5463}$ (benzene) $+ 90°\,\mu$ (solvent). Among the strongly polar solvents the agreement becomes less exact as the polarity increases.

Table II.

Solvent ………………	C_6H_6.	PhMe.	PhOMe.	PhBr.	Ph·CHO.	PhCN.	$PhNO_2$.
$[M]_{5463}$, obs. …………	−714°	−671°	−602°	−580°	−500°	−465°	−423°
$[M]_{5463}$, calc. …………	(714)	669	602	579	467	367	363

These results are in complete agreement with the predictions of the dipole association hypothesis concerning the binary systems involved. Thus, in the menthyl *o*-nitrobenzoate molecule there is a highly polar nitro-group which renders the molecule susceptible to external polar influences, but, owing to the screening effect of the bulky, non-polar menthyl residue, does not confer a strong tendency to dipolar association in the homogeneous substance. This means that the ester will probably exist as single molecules in benzene solution (see Table VII) with a rotation considerably above that exhibited in the homogeneous state. In nitrobenzene solution, however, at low concentration the ester molecules may be regarded as surrounded by the highly polar solvent molecules and, since the nitro-groups in the latter are relatively unscreened, the degree of association between solvent and solute through these polar groups will be of a higher order than that occurring in the homogeneous ester; *i.e.*, the rotatory power of the *o*-nitrobenzoate would be expected to be less in nitrobenzene solution than in the homogeneous state. Kenyon and Pickard (*loc. cit.*) give $[M]^{20^\circ}_{5461}$ — 492·0° for the homogeneous ester, and in agreement with the above reasoning we have $[M]^{20^\circ}_{5463}$ — 714° in benzene and — 423° in nitrobenzene solution.

Each solvent may be regarded as associating with the optically active solute in essentially the same way. Evidently, then, those solvent molecules which are least associated among themselves will be in the most favourable condition for their dipoles to have a maximum effect. This agrees with the fact that solutions in toluene, anisole, and bromobenzene, the molecules of which are of weak or medium polarity and at most only slightly associated, show a lowering quantitatively proportional to the dipole moments of the pure solvents, whilst solutions in benzaldehyde, benzonitrile, and nitrobenzene, the polarity of which increases in that order, progressively diverge from exact proportionality.

The influence of solvents on the rotation of *l*-menthyl 2 : 4-dinitrobenzoate is very similar to that observed with the *o*-nitrobenzoate, as shown in Table III. The same quantitative relationship between lowering of rotation and increase of dipole moment of solvent is again obtained (Table IV), but bromobenzene does not conform to it in this series; this substance is, however, also displaced in the solvent series. The highly polar solvents show the same divergence as before.

TABLE III.

l-*Menthyl* 2 : 4-*dinitrobenzoate* ($t = 20^\circ$, $c = 4$, $l = 1$).

(All rotations negative.)

	Limiting values.							
Solvent.	α_{6708}.	α_{4358}.	$[M]_{6708}$.	$[M]_{6563}$.	$[M]_{5893}$.	$[M]_{5463}$.	$[M]_{4861}$.	$[M]_{4358}$.
C_6H_6	4·02°	17·07°	353·6°	372·5°	490·3°	616·0°	925·1°	1502°
$C_6H_5{\cdot}CH_3$	3·80	15·65	331·6	348·1	455·5	571·5	850·0	1366
$C_6H_5{\cdot}OCH_3$	3·36	13·88	294·1	308·1	403·5	505·2	751·9	1215
C_6H_5Br	3·42	14·01	297·7	316·8	410·0	515·2	763·2	1219
$C_6H_5{\cdot}CHO$	3·17	12·39	275·4	288·3	376·1	466·4	683·6	1076
$C_6H_5{\cdot}CN$	2·95	11·12	258·5	271·7	350·6	433·8	631·0	974·4
$C_6H_5{\cdot}NO_2$	2·72	* 6·62	236·3	250·2	320·6	397·9	575·1	—
*cyclo*Hexane	3·99	15·85	362·7	380·9	494·5	617·3	905·5	1441

* α_{4861}.

TABLE IV.

Solvent	C_6H_6.	PhMe.	PhOMe.	PhBr.	Ph·CHO.	Ph·CN.	$PhNO_2$.
$[M]^{20^\circ}_{5463}$, obs.	−616°	−572°	−505°	−515°	−466°	−434°	−398°
$[M]^{20^\circ}_{5463}$, calc.	(616)	571	504	481	369	270	265

Patterson and Taylor (J., 1905, **87**, 122) advanced the expression $[M]^{20^\circ}_{D}$ (solution) = $[M]^{20^\circ}_{D}$ (homog.) + 0·97° *dv* for menthol in solution; here *dv* is the change in molecular volume of menthol on solution and is presumably due to the change in internal pressure

TABLE V.

l-*Menthyl* p-*nitrobenzoate* ($t = 20^\circ$, $c = 4$, $l = 1$).

(All rotations negative.)

	Limiting values.							
Solvent.	α_{6708}.	α_{4358}.	$[M]_{6708}$.	$[M]_{6563}$.	$[M]_{5893}$.	$[M]_{5463}$.	$[M]_{4861}$.	$[M]_{4358}$.
C_6H_6	2·75°	6·94°	210·0°	218·4°	268·8°	316·9°	413·9°	530·0°
$C_6H_5{\cdot}CH_3$	2·84	7·42	216·4	226·3	278·2	330·0	432·8	565·5
$C_6H_5{\cdot}OCH_3$	2·76	7·24	209·8	218·2	269·1	320·1	421·2	551·1
C_6H_5Br	2·87	7·46	218·3	228·2	280·7	334·1	439·0	567·5
$C_6H_5{\cdot}CHO$	2·86	7·45	218·4	226·8	281·0	333·8	436·8	569·0
$C_6H_5{\cdot}CN$	2·86	7·14	217·2	226·3	277·2	328·1	426·2	542·4
$C_6H_5{\cdot}NO_2$	2·63	* 5·27	200·1	209·7	261·0	308·1	400·8	—
*cyclo*Hexane	2·08	4·73	157·6	164·4	200·0	234·1	296·3	358·4

* α_{4861}.

of the solvent, so it is not surprising that this expression should be similar in form to that involving the dipole moment (μ) of the solvent.

That the rotation values of this ester in all the solvents employed should fall between those for the *o*- and the *p*-nitro-ester (see Table V) is, at first sight, somewhat unexpected, because a nitro-group in both the *o*- and the *p*-position has the effect of raising the rotatory power. This point is discussed in connexion with molecular-weight data (p. 358).

With this ester the range of rotatory powers is very small and there is little agreement between these values and the dipole moments of the solvents; however, the order of the rotations bears a strong resemblance to that obtained by Rule and Dunbar (unpublished) with the unsubstituted *l*-menthyl benzoate in the same series of solvents :

Solvent	C_6H_6.	PhMe.	PhOMe.	PhBr.	Ph·CHO.	PhCN.	$PhNO_2$.
$[M]^{20°}_{5461}$	−280°	−284°	−282°	−293°	−294°	−302°	−279°

Concentration and Temperature Effects.—For the investigation of the influence of concentration and temperature, it was thought advisable to use representatives of both polar and non-polar solvents in each case. Of the former group, nitrobenzene was suitable in both instances, whilst in the latter class, benzene was used in concentration experiments and decalin in work on change of temperature. Both series of results are given in Table VI; concentration, *c*, is given as g. per 100 c.c.

If, for any wave-length, the results obtained by changing the concentration of the optically active substance be considered, a general regularity is at once apparent with solutions in both polar and non-polar solvents, *viz.*, that with increasing concentration the value of the rotation approaches that for the homogeneous substance. For example, with the *o*-nitrobenzoate, $[M]^{20°}_{5461}$ (homog.) − 492·0° (Kenyon and Pickard, J., 1915, **107**, 35), the values in benzene and in nitrobenzene solution are all respectively above and below the homogeneous value, but converge towards it with increasing concentration; for the *p*-nitrobenzoate, $[M]^{20°}_{5461}$ (homog.) − 254·2° (*idem, ibid.*) is lower than the rotations in either benzene or nitrobenzene, and accordingly increasing concentration in each case causes a fall in rotatory power. Although no rotation values are available for the 2 : 4-dinitrobenzoate in the homogeneous state—the substance darkens on melting—it is reasonable to assume from its general resemblance to the *o*-nitrobenzoate that its behaviour with respect to concentration will not differ essentially from that of the other compounds considered.

For the benzene solutions, the results of the experiments with the *o*-nitro- and the 2 : 4-dinitro-benzoate are in agreement with Rule, Barnett, and Cunningham's observation on ethyl tartrate (J., 1933, 1217), that "the change in rotation which occurs when the concentration is raised in a non-polar solvent is in the same direction as that observed when a low concentration is employed and the polarity of the medium is increased." For the *p*-nitrobenzoate no regular solvent influence is observable, and comparison with this generalisation cannot be made. The nitrobenzene solutions, being binary systems where both components are strongly polar, present a much more difficult problem and it is not justifiable to draw definite conclusions from the limited data available.

A detailed discussion in the light of dipole association of the changes in optical rotation brought about by rise of temperature has already been given (Rule, Barnett, and Cunningham, *loc. cit.*), from which it would seem that temperature effects are likely to be much more complicated than concentration or solvent effects. The first generalisation correlating temperature effects was made by Patterson and his co-workers (J., 1908, **93**, 1836; 1932, 1715); it was a purely empirical observation that, according as the rotation in a given solvent is much below or above that of the homogeneous optically active substance, rise of temperature will respectively raise or diminish the rotation (or cause it to increase very slowly, in the latter case). Rule, Barnett, and Cunningham conclude that in so far as this generalisation implies a convergence of the two types of solvent influence at higher temperatures it is in agreement with the theoretical deductions, which however, in the case of non-polar solvents, allow changes in either direction depending on the ensuing change in the configuration of the active molecule.

TABLE VI.

Effect of concentration.

(All rotations negative.)

Limiting values.

l-Menthyl *o*-nitrobenzoate ($l = 1$, $t = 20°$).

Solvent.	c.	α_{6708}.	α_{4358}.	$[M]_{6708}$.	$[M]_{6563}$.	$[M]_{5893}$.	$[M]_{5463}$.	$[M]_{4861}$.	$[M]_{4358}$.
C_6H_6	7·980	10·39°	43·37°	397·4°	419·1°	550·0°	690·3°	1030°	1658°
,, ...	16·012	20·13	84·04	383·4	405·0	532·6	668·3	997·2	1601
,, ...	31·992	38·39	158·62	366·0	385·4	505·2	633·6	940·2	1512
,, ...	64·036	69·47	285·04	330·8	349·1	455·4	570·5	840·3	1357
$C_6H_5{\cdot}NO_2$	8·058	6·52	* 16·29	246·8	259·6	338·4	421·2	616·5	—
,, ...	16·090	13·24	* 32·81	251·0	263·0	341·8	426·3	622·0	—
,, ...	32·064	26·68	* 66·66	253·9	267·2	348·2	433·3	634·3	—

l-Menthyl 2 : 4-dinitrobenzoate ($l = 1$, $t = 20°$.)

Solvent.	c.	α_{6708}.	α_{4358}.	$[M]_{6708}$.	$[M]_{6563}$.	$[M]_{5893}$.	$[M]_{5463}$.	$[M]_{4861}$.	$[M]_{4358}$.
C_6H_6	8·062	7·99	33·27	346·9	364·9	480·6	604·5	903·1	1445
,, ...	16·072	15·77	65·25	343·7	362·3	476·1	598·9	891·5	1421
,, ...	31·982	30·83	125·12	337·5	353·9	464·3	582·5	860·2	1369
,, ...	48·010	44·90	182·48	327·3	344·1	451·3	563·7	833·7	1330
$C_6H_5{\cdot}NO_2$	4·029	2·72	* 6·62	236·3	250·2	320·6	397·9	575·1	—
,, ...	8·054	5·38	* 13·11	233·8	246·4	317·6	395·5	569·8	—

l-Menthyl *p*-nitrobenzoate ($l = 1$, $t = 20°$).

Solvent.	c.	α_{6708}.	α_{4358}.	$[M]_{6708}$.	$[M]_{6563}$.	$[M]_{5893}$.	$[M]_{5463}$.	$[M]_{4861}$.	$[M]_{4358}$.
C_6H_6	8·010	5·46	13·86	207·9	216·2	267·0	316·4	412·0	527·8
,, ...	16·008	10·82	27·32	206·1	214·5	265·4	313·6	407·6	520·5
,, ...	32·042	21·37	53·71	203·5	212·1	262·1	309·8	403·0	511·5
,, ...	47·996	31·39	† 47·82	199·4	208·2	257·2	303·9	—	—
$C_6H_5{\cdot}NO_2$	8·006	5·17	* 10·28	196·9	206·1	254·5	302·1	391·6	—
,, ...	16·062	10·25	* 20·47	194·7	203·6	252·0	298·7	388·8	—
,, ...	32·028	20·00	* 39·77	190·4	198·7	246·2	291·6	378·8	—

Effect of temperature.

Limiting values.

l-Menthyl *o*-nitrobenzoate ($l = 1$; $p = 3·334$ in decalin, $= 3·342$ in $C_6H_5{\cdot}NO_2$).

Solvent.	$d_{4°}^{t°}$.	Temp.	α_{6708}.	α_{4358}.	$[M]_{6708}$.	$[M]_{6563}$.	$[M]_{5893}$.	$[M]_{5463}$.	$[M]_{4861}$.	$[M]_{4358}$.
Decalin ...	0·8881	21·0°	3·35°	12·40°	345·1°	363·7°	469·9°	580·1°	833·5°	1277°
,, ...	0·8737	40·6	3·22	11·68	337·3	355·1	455·6	563·5	803·3	1223
,, ...	0·8600	59·0	3·09	11·15	328·7	345·8	442·6	546·9	777·7	1186
,, ...	0·8449	79·5	2·98	10·77	322·7	340·0	435·3	536·0	764·5	1166
,, ...	0·8320	96·5	2·91	10·37	320·1	335·5	429·0	527·8	750·0	1140
$C_6H_5{\cdot}NO_2$...	1·1997	20·0	3·27	* 8·11	248·6	263·1	339·9	422·7	616·7	—
,, ...	1·1794	40·8	3·17	* 7·86	245·3	259·2	335·9	418·7	608·3	—
,, ...	1·1625	58·5	3·09	* 7·68	242·7	256·0	333·0	414·6	603·1	—
,, ...	1·1430	79·0	2·97	* 7·44	237·2	249·9	326·6	408·0	594·0	—
,,	1·1242	99·0	2·86	* 7·27	232·2	244·4	319·1	402·0	590·3	—

l-Menthyl 2 : 4-dinitrobenzoate ($l = 1$; $p = 2·311$ in decalin, $= 3·352$ in $C_6H_5{\cdot}NO_2$).

Solvent.	$d_{4°}^{t°}$.	Temp.	α_{6708}.	α_{4358}.	$[M]_{6708}$.	$[M]_{6563}$.	$[M]_{5893}$.	$[M]_{5463}$.	$[M]_{4861}$.	$[M]_{4358}$.
Decalin ...	0·8914	19·0	2·41	* 5·63	409·5	431·5	550·4	676·3	956·4	—
,, ...	0·8756	40·0	2·30	* 5·33	397·8	418·6	534·6	652·1	922·0	—
,, ...	0·8616	58·7	2·21	* 5·09	388·5	409·6	520·4	636·3	894·8	—
,, ...	0·8445	81·7	2·12	* 4·84	380·2	399·9	505·7	622·3	868·0	—
,, ...	0·8312	99·4	2·02	* 4·67	368·2	388·2	493·9	608·5	851·0	—
$C_6H_5{\cdot}NO_2$...	1·2021	21·0	2·72	* 6·62	236·3	250·2	320·6	397·9	575·1	—
,, ...	1·1830	40·6	2·69	* 6·52	237·5	250·7	321·3	399·8	575·4	—
,, ...	1·1660	58·0	2·64	* 6·42	236·4	248·8	321·4	399·3	574·8	—
,, ...	1·1450	79·8	2·57	* 6·31	234·4	247·1	321·0	399·5	575·4	—

l-Menthyl *p*-nitrobenzoate ($l = 1$; $p = 3·412$ in decalin, $= 3·344$ in $C_6H_5{\cdot}NO_2$).

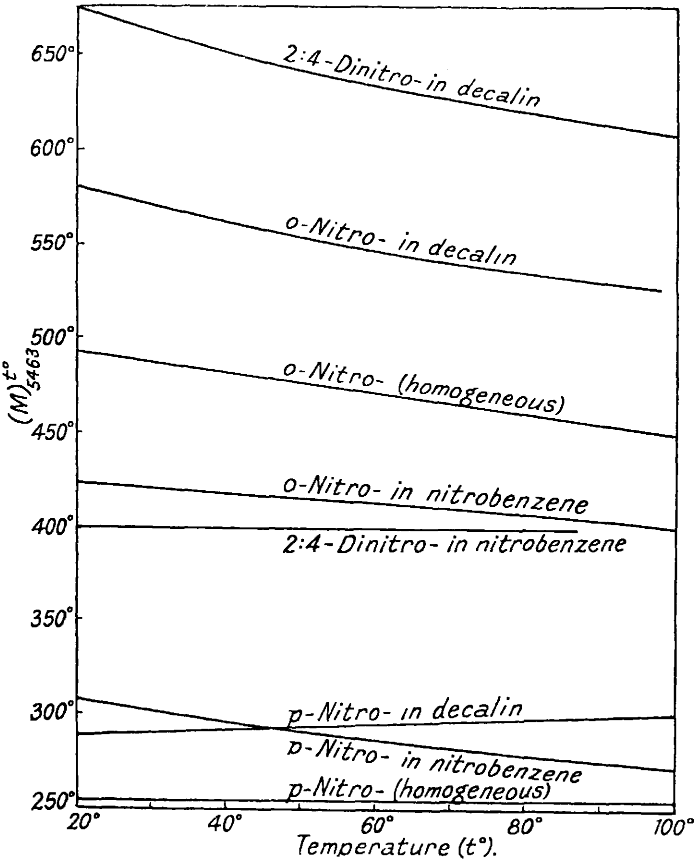
Solvent.	$d_{4°}^{t°}$.	Temp.	α_{6708}.	α_{4358}.	$[M]_{6708}$.	$[M]_{6563}$.	$[M]_{5893}$.	$[M]_{5463}$.	$[M]_{4861}$.	$[M]_{4358}$.
Decalin ...	0·8870	21·0	1·96	4·08	197·5	205·5	248·8	289·2	354·6	411·2
,, ...	0·8732	40·0	1·94	4·12	198·5	207·7	250·8	291·7	360·2	421·7
,, ...	0·8594	58·8	1·93	4·17	200·7	210·1	253·7	294·3	366·0	433·6
,, ...	0·8439	80·0	1·91	4·22	202·2	212·9	255·2	297·5	373·9	446·9
,, ...	0·8298	99·5	1·88	4·30	202·5	213·2	256·3	300·5	382·3	463·1
$C_6H_5{\cdot}NO_2$...	1·1993	20·0	2·63	* 5·27	200·1	209·9	261·0	308·1	400·8	—
,, ...	1·1794	40·75	2·48	* 4·96	191·9	201·1	249·1	295·5	383·7	—
,, ...	1·1624	58·5	2·35	* 4·76	184·5	193·0	241·8	287·2	373·6	—
,, ...	1·1435	78·5	2·25	* 4·55	179·4	188·2	236·0	279·9	362·8	—
,, ...	1·1251	97·8	2·16	* 4·37	175·2	183·2	227·9	272·4	354·4	—

* α_{4861}. † α_{5463}.

Fig. 1 summarises the results of experiments with the three esters now under consideration for $\lambda = 5463$. The values of the homogeneous *o*- and *p*-nitrobenzoates are due to Kenyon and Pickard (*loc. cit.*).

The curves for the *o*-nitrobenzoate, converging as they do at higher temperatures, are clearly in agreement with the predictions of the dipole association hypothesis and, although no values for the homogeneous 2 : 4-dinitrobenzoate are available, there is little reason to doubt that the same is true of this compound. In the light of Patterson's conclusions, however, the nitrobenzene solution is abnormal, and this is probably also the case with the 2 : 4-dinitrobenzoate in this solvent. With the *p*-nitrobenzoate there is no regularity in the solvent series, and both nitrobenzene and decalin raise the rotation above the value for the pure ester; but, with rising temperature, $[M]_{5463}$ decreases for the first solution and rises slowly for the second. Both of these observations are in agreement with Patterson's generalisation.

Fig. 1.



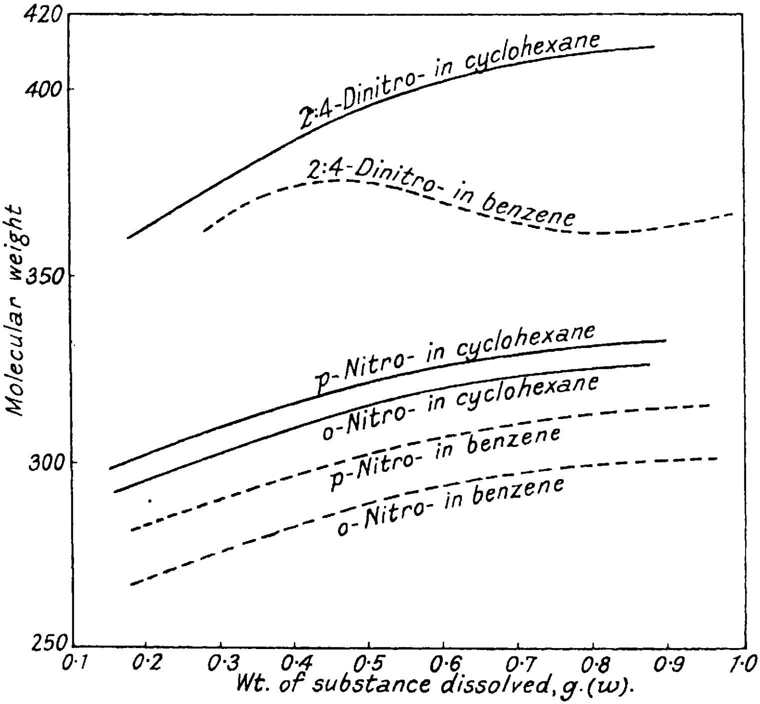
Variation of rotatory power of l-*menthyl nitrobenzoates with temperature.*

A theoretical explanation of the observed facts is readily afforded by the dipole association hypothesis, at least in so far as the solutions in non-polar solvents are concerned. In this connexion it was thought that molecular-weight measurements of the optically active substances concerned in various solvents would furnish data for a more convincing argument and accordingly the determinations embodied in Table VII were made. Owing to its low f. p. and high b. p., decalin is not a suitable solvent for molecular-weight measurements, but an examination of the foregoing tables shows that *cyclo*hexane is roughly similar to decalin in its effects on the rotatory powers of the esters under consideration.

TABLE VII.

o-Nitro-ester.			2 : 4-Dinitro-ester.			*p*-Nitro-ester.		
M, calc. = 305.			M, calc. = 350.			M, calc. = 305.		
Solvent, *cyclo*hexane; ebullioscopic weight constant (k) = 28·6.								
W = 20·04; b. p. = 80·5°.			W = 19·90; b. p. = 81·3°.			W = 19·76; b. p. = 81·0°.		
w.	e.	M.	w.	e.	M.	w.	e.	M.
0·1961	0·095°	295	0·1662	0·067°	357	0·1615	0·079°	296
0·4049	0·186	311	0·3346	0·125	385	0·3302	0·150	319
0·5879	0·264	318	0·5018	0·183	394	0·5499	0·246	324
0·7597	0·335	324	0·6584	0·233	406	0·6935	0·307	327
			0·8690	0·303	412	0·7925	0·346	332
Solvent, benzene; ebullioscopic weight constant (k) = 26·1.								
W = 22·65; b. p. = 79·5°.			W = 22·82; b. p. = 80·5°.			W = 23·14; b. p. = 80·1°.		
0·1731	0·076	262	0·3070	0·096	366	0·2148	0·085	285
0·3642	0·149	282	0·4576	0·139	377	0·4224	0·161	296
0·5457	0·213	295	0·6126	0·190	369	0·5994	0·220	307
0·7444	0·291	295	0·7589	0·238	365	0·8134	0·293	313
0·9264	0·359	297	0·9106	0·286	364	0·9526	0·340	316
			1·0600	0·330	367			

FIG. 2.



Variation of molecular weight of l-*menthyl nitrobenzoates with concentration.*

Benzene and *cyclo*hexane were therefore employed as solvents for ebullioscopic determinations (cf. Menzies and Wright, *J. Amer. Chem. Soc.*, 1921, **43**, 2314).

The relationship between the degrees of association of the individual esters is emphasised in Fig. 2, in which the weight of ester is plotted against the molecular weight calculated by means of the formula $M = kw/eW$.

It is well known that amongst aromatic isomerides the *o*-substituted compound is least and the *p*-substituted compound most associated (Turner, "Molecular Association," 1915, p. 26). Furthermore, it is to be expected that the dinitrobenzoate will be more associated than the mononitrobenzoates, and that all these compounds will be more associated in a saturated non-polar solvent such as *cyclo*hexane (or decalin) than in an aromatic non-polar solvent such as benzene. The curves of Fig. 2 show that at concentrations comparable with those employed in the polarimetric measurements, these assumptions are valid, the molecular association being considerable even at the b. p. of the solution. Taken in conjunction with the established fact that lowering of temperature increases the complexity of molecular aggregates (Turner, *op. cit.*, p. 14), this allows a partial explanation of the trend of the temperature–rotation curves in Fig. 1. For instance, as the temperature of the decalin solution of the *p*-nitrobenzoate is raised, the rotatory value tends to that for single molecules; an indication as to whether this should result in a rise or a fall in rotation is furnished by a comparison of the values of $[M]_{5463}^{20^\circ}$ for solutions in benzene at $c = 4$ ($-$ 316·9°) and $c = 48$ ($-$ 303·9°) and of the molecular-weight values in benzene, for, as shown in Fig. 2, the state of aggregation of the *p*-nitrobenzoate is more complex in more concentrated solutions. Evidently, therefore, the hypothesis predicts a rise in rotation as the decalin solution of the *p*-nitrobenzoate is raised in temperature, in agreement with observation.

It might be thought that the same result should be obtained with the *o*-nitro- and the 2 : 4-dinitro-benzoate in decalin solution, and, indeed, there is little doubt that association will also be less in non-polar solutions of these compounds at higher temperatures. There is reason to believe, however, that the predominant factor influencing the rotatory power in these two cases is the spatial proximity of the *o*-nitro-group to the asymmetric centre, as distinct from its proximity through the chain of carbon atoms (Rule, *Trans. Faraday Soc.*, 1930, **26**, 332), and as the temperature is raised the distance between the two *o*-groups will increase (cf. Ebert, *op. cit.*, p. 43), so the total effect of increase of temperature with these two compounds will probably be a fall in rotation, which again is in agreement with observation.

The systems nitrobenzene–optically active solute will probably admit of no such simple treatment as the above, and in the absence of reliable data as to the molecular state of the components under different conditions, theoretical considerations have little value.

The Rotatory Power of l-*Menthyl* 2 : 4-*Dinitrobenzoate.*—The abnormally low rotatory power of the 2 : 4-dinitrobenzoate (compared with the *o*-nitrobenzoate) in benzenoid solvents has already been commented upon. The fact that in saturated non-polar solvents, such as *cyclo*hexane and decalin, the dinitrobenzoate has higher rotations than the *o*-nitrobenzoate indicates that the abnormality has its origin in some influence exerted between the dinitrobenzoate and benzoid solvents. Consideration of the molecular weight–concentration curves for the dinitrobenzoate shows that, whereas the curve for *cyclo*hexane pursues a smooth upward course, that for benzene after a preliminary rise falls to a minimum and rises again. According to Turner (*op. cit.*, p. 38), this shape of curve is to be expected where there is combination between solvent and solute accompanying increasing molecular association of the solute. The effect of this phenomenon on rotatory power is being investigated in greater detail with the *l*-menthyl esters of *m*-nitrobenzoic acids, in which it seems to be a more predominant factor; meanwhile, it may be noted that it appears to cause a comparatively great fall in rotation. Thus, although the 2 : 4-dinitrobenzoate aggregates are simpler in benzene than in *cyclo*hexane, the rotatory powers of the solutions are almost identical because there is no combination with the latter solvent. If, as is probable, combination between 2 : 4-dinitrobenzoate and benzenoid solvent is general, then the abnormally low rotatory powers of this ester in such solvents are explicable, for there is no evidence that this phenomenon takes place with the *o*-ester.

Optical Rotatory Dispersion.—Relevant studies of the effect of solvent on the rotatory dispersion of an optically active solute have been made by a number of authors. Tschugaeff and Ogoronikoff (*Z. physikal. Chem.*, 1912, **79**, 471) investigated certain xanthates and substituted thiourethanes of borneol, menthol, and fenchol in toluene and acetone solution; these compounds in general formed coloured solutions, which showed anomalous rotatory dispersion, and in every case the dispersion curve of the toluene solution was displaced towards the red end of the visible spectrum relative to the acetone curve, and the absorption maximum was displaced in a similar way. More recently, Owen (*Trans. Faraday Soc.*, 1930, **26**, 423) has studied the effect of change of concentration and of solvent on the rotatory dispersion of camphor, with reference especially to the value of the dispersion and rotation constants in the Drude equation.

In no case, however, does a series of related solvents appear to have been employed, and in view of the regularities which have already been discovered under those conditions, it was thought of interest to extend the present work to a short investigation of rotatory dispersion. In many respects nitro-compounds, although excellent for the study of solvent influences when green or yellow light is employed, are by no means ideal for dispersion work, the solutions usually being slightly yellow, thus considerably increasing the experimental error in the blue and violet regions of the spectrum. This is especially the case with nitrobenzene solutions, and at higher concentrations in colourless solvents. One compensating factor is the comparatively high values of the observed rotations. From amongst the solutions prepared, only the data for those in which the observational error did not exceed ± 0·03° were employed to calculate the constants tabulated below. There is no regularity apparent in the effect of solvents on *l*-menthyl *p*-nitrobenzoate and no calculations were made from the data for this compound.

On plotting $1/\alpha$ against λ^2, a small regular deviation from linearity was obtained in each case, indicating that the dispersion equation would probably be of the form $\alpha = k_1/(\lambda^2 - \lambda_1^2) \pm k_2/\lambda^2$. On this basis the values contained in the following table were calculated.

Dispersion and Rotation Constants for Solutions of l-*Menthyl Esters.*

Solvent.	(a) l-*Menthyl* o-*Nitrobenzoate.*				(b) l-*Menthyl* 2 : 4-*Dinitrobenzoate.*			
	c.	λ_1^2.	k_1.	k_2.	*c.*	λ_1^2.	k_1.	k_2.
C_6H_6	4·010	0·1349	0·991	0·975	3·980	0·1459	0·556	0·985
,, ...	7·980	0·1436	1·345	2·710	8·062	0·1428	1·159	1·893
,, ...	16·012	0·1438	2·903	4·805	16·072	0·1414	2·329	3·689
$C_6H_5{\cdot}CH_3$	4·000	0·1464	0·628	1·368	4·012	0·1480	0·460	1·022
$C_6H_5{\cdot}OCH_3$	4·000	0·1470	0·560	1·229	3·998	0·1504	0·383	0·933
C_6H_5Br	3·994	0·1502	0·491	1·253	—	—	—	—
$C_6H_5{\cdot}CHO$.........	4·000	0·1511	0·346	1·180	4·030	0·1501	0·316	0·950
$C_6H_5{\cdot}CN$	4·046	0·1590	0·287	1·203	3·994	0·1552	0·250	0·947
$C_6H_5{\cdot}NO_2$	—	—	—	—	4·029	0·1658	0·195	0·922

When these data are inserted in a three-constant equation of the above type, they allow the calculation of values of α, which approximate closely to the observed values, the positive and negative differences being distributed quite irregularly.

Considering, first, only those solutions in which $c = 4$, it is seen that, for both esters, the dispersion constant, λ_1^2, increases with the polarity of the solvent. If $1/\lambda_1$ is assumed to be the absorption frequency responsible for the optical rotatory power, this means that the active band moves towards the red end of the visible spectrum as the polarity of the solvent increases. As already indicated, such a movement of the absorption maximum was observed experimentally by Tschugaeff and Ogoronikoff, who, however, failed to note the regularity, probably because they used only two solvents which were of different types. Amongst the rotation constants another regularity is present : in both cases k_1 decreases rapidly with increase in polarity of the solvent, whilst k_2 remains approximately constant.

For solutions in benzene of concentration exceeding $c = 4$, the data are somewhat less extensive than was desired, owing to the fact that the observed readings above $c = 16$ are too inaccurate to give satisfactory Drude equations. The limited results available, however, present a rough parallel to those obtained by Owen (*loc. cit.*) with camphor in alcoholic solution.

A general survey of the above results suggests that for solutions of an optically active compound :

(1) The dispersion constant, λ_1^2, or, more correctly, the absorption frequency, $1/\lambda_1$, responsible for the rotatory power, is governed by the polarity of the solvent as measured by the dipole moment. Application of the hypothesis advanced in this and preceding

papers of this series further indicates that this influence is effective through the mutual interference of the polar groups in both components of the system. Such a conclusion is not incompatible with modern physical theories of the origin of optical rotatory power.

(2) The rotation constant, k_1, since it varies greatly, is dependent on the polarity of the solvent, whilst k_2, which is practically constant, is independent of the polar nature of the solvent. The dipole association hypothesis indicates that k_1 is an index of the contribution of the nitro-groups in the optically active compound to the rotatory power, whereas k_2 is an index of the contribution of the hydrocarbon part of the molecule or of some part which is screened from the influence of dipole association.

SUMMARY.

(1) Solutions of the *l*-menthyl esters of *o*-nitro- and 2 : 4-dinitro-benzoic acids in benzenoid solvents show rotatory powers which vary in a contrary sense to the dipole moment of the solvent. To a certain extent this relationship is quantitative.

(2) Solutions of the *l*-menthyl ester of *p*-nitrobenzoic acid show no regularity in solvent influence.

(3) An explanation of the effects of concentration and temperature on the rotatory powers of these esters is advanced in terms of dipole association.

(4) The effect of a series of related solvents on the constants of the Drude equation is briefly investigated.

This work was carried out in the Chemistry Department, University of Edinburgh, and was originally suggested by Dr. H. G. Rule, to whom the author wishes to express his indebtedness for interest and advice.

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