

**186.** *Studies in Solvent Action. Part IV. Optical Rotation of l-Menthyl Hydrogen Naphthalate in Polar and in Non-polar Solvents.*

By HAROLD GORDON RULE and ANDREW McLEAN.

*l*-MENTHYL hydrogen naphthalate, unlike its methyl ester, is a comparatively unstable substance, which develops an odour of menthol in the course of a few days owing to its tendency to revert to menthol and naphthalic anhydride (Rule and McLean, J., 1931, 669). Under certain conditions it exhibits very high dextro-rotations, a feature which is so unusual amongst derivatives of *l*-menthol that the optical properties have now been subjected to further investigation. A previous examination of the dispersion in benzene and acetonitrile solutions over the range 6708—4358 Å.U. has shown it to be normal and slightly complex in these solvents.

The rotatory powers of the acid ester were determined in the first instance in two series of solvents derived respectively from methane and benzene, a concentration of  $c = 4$  being employed where possible. Observed rotatory powers are recorded in the following tables, the values being arranged in order of increasing positive rotations. The majority of the dipole moments  $\mu$  of the solvents, which are included for the purpose of comparison, are taken from Debye's "Polare Molekeln."

As with the corresponding menthyl methyl derivative, the rotatory power of the acid ester tends to vary with the polarity of the solvent medium, although the polar influence is here in the opposite sense. Among the methane solvents, molecular rotations  $[M]_{5461}$  approximating to  $1000^\circ$  in the dextro-direction are found in the relatively non-polar compounds carbon tetrachloride and carbon disulphide. At the other end of the series, negative rotations of a magnitude normally associated with aromatic esters of *l*-menthol are observed in the strongly polar liquids acetonitrile and acetaldehyde. Unfortunately, the acid ester is too sparingly soluble in hexane and nitromethane, at the extremes of the polar scale, for the influence of these solvents to be determined at ordinary temperatures. The agreement between the rotatory powers and the dipole moments of the aliphatic solvents is somewhat less complete than was found

TABLE I.

*Molecular Rotations of l-Menthyl Hydrogen Naphthalate.*(i) *In Solvents of Methane Type.*

Solvent.	c.	l.	$\alpha_{5461}^{20^\circ}$ .	$[M]_{5461}^{20^\circ}$ .	$\mu \times 10^{18}$ .
CH <sub>3</sub> ·OH	4·014	2	- 4·94°	- 218°	1·64
CH <sub>3</sub> ·CHO	2·008	2	- 2·43	- 214	2·71
CH <sub>3</sub> ·CN	4·008	2	- 4·47	- 198	3·05
CH <sub>3</sub> ·CO <sub>2</sub> H	4·008	2	- 2·60	- 115	(0·75, 1·4)
C(NO <sub>2</sub> ) <sub>4</sub>	1·040	2	- 0·64	- 109	0
CHBr <sub>3</sub>	4·016	1	+ 3·23	+ 285	1·3
CH <sub>2</sub> Cl <sub>2</sub>	4·020	2	+ 8·46	+ 372	1·61
CHCl <sub>3</sub>	4·022	2	+ 9·50	+ 418	1·10
CH <sub>2</sub> Br <sub>2</sub>	3·784	2	+ 9·10	+ 426	1·89
CH <sub>3</sub> I	3·992	2	+ 14·85	+ 658	1·66
CS <sub>2</sub>	4·028	2	+ 21·01	+ 923	0
CCl <sub>4</sub>	1·998	2	+ 11·16	+ 989	0

(ii) *In Solvents of Benzene Type.*

C <sub>6</sub> H <sub>5</sub> ·CHO	2·004	2	- 3·29°	- 291°	2·75
C <sub>6</sub> H <sub>5</sub> ·CN	4·010	2	- 3·22	- 142	3·85
C <sub>6</sub> H <sub>5</sub> ·NO <sub>2</sub>	2·000	2	+ 1·09	+ 96·6	3·89
C <sub>6</sub> H <sub>5</sub> ·OMe	4·012	1	+ 2·83	+ 250	1·25
<i>o</i> -C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>	2·018	1	+ 2·80	+ 491	2·25
C <sub>6</sub> H <sub>5</sub> Br	2·004	2	+ 6·13	+ 541	1·50
C <sub>6</sub> H <sub>5</sub> Cl	2·000	2	+ 6·41	+ 568	1·52
C <sub>6</sub> H <sub>5</sub> I	2·006	2	+ 6·61	+ 583	1·50
C <sub>6</sub> H <sub>6</sub>	4·014	2	+ 16·32	+ 720	0
C <sub>6</sub> H <sub>5</sub> ·CH <sub>3</sub>	4·000	2	+ 18·03	+ 798	0

for *l*-menthyl methyl naphthalate, prominent exceptions being methyl alcohol, acetic acid and tetranitromethane. These abnormalities are discussed below in connexion with the benzene solvents. Several minor inversions also occur among the halogen derivatives.

The acid naphthalate resembles the other compounds previously examined in that the relationship between the rotatory power of the solution and the polar character of the solvent appears to be exhibited more definitely among aromatic solvents than among those of aliphatic type. This is clearly visible in the figures recorded in Table I (ii), which are on the whole in good agreement. Values of  $[M]_{5461}$  in aromatic solvents vary from +798° in toluene to -291° in benzaldehyde, a maximum range which is somewhat smaller than that given by the corresponding series of methane derivatives.

*Mechanism of the Solvent Influence.*—Earlier examples of solvent influence of this nature have been explained on the assumption that polar solvents may enter into dipole association with the optically active solute, thus lowering the internal electrical field of the latter (Rule and McLean, J., 1931, 678, 686). In the cases of *l*-menthyl methyl naphthalate, octyl hydrogen phthalate, and octyl methyl phthalate (Rule and Hill, J., 1931, 2651), the introduction of the second polar substituent, CO<sub>2</sub>Me or CO<sub>2</sub>H, brings about an increase in rotatory power as compared with the unsubstituted naphthoate

or benzoate. When dissolved in a liquid such as benzene, a solute of this type will exist largely in the unimolecular condition, thus allowing the substituent to exert its maximum electrical influence on the molecule to which it is attached, and yielding a solution of high activity. Association with a polar solvent, however, will diminish the internal field due to the substituent group, and in the above esters the result will be a fall in rotatory power.

*l*-Menthyl hydrogen naphthalate represents an example of a different character, in which the introduction of a carboxyl group into the parent ester *l*-menthyl naphthoate leads to a strongly *diminished* laevorotation. This is readily seen on comparing the rotatory powers given in Table I with the extreme values of  $[M]_{5461}$  previously found for the naphthoate in benzene ( $-325^\circ$ ) and acetonitrile ( $-249^\circ$ ) respectively (Rule and McLean, *loc. cit.*, p. 686). Hence it follows that the influence of polar solvents upon the rotation of the acid naphthalate, leading to an increased displacement in a laevo-sense, is in complete harmony with the explanation previously adopted. In acetonitrile solution, the high laevo-activity of *l*-menthyl methyl naphthalate is reduced to  $-239^\circ$ , and the high dextro-activity of *l*-menthyl hydrogen naphthalate is lowered, with change of sign, to  $-198^\circ$ . These values approximate in order of magnitude to the figure given above ( $-249^\circ$ ) for the unsubstituted *l*-menthyl naphthoate when dissolved in the same solvent.

*Irregularities in Solvent Effect.*—Several of the solvents listed in Table I exert an influence which is not in agreement with their polar character, as determined by the value of their dipole moments. Among these, methyl alcohol, acetic acid, and tetranitromethane are outstanding exceptions. Acetaldehyde and benzaldehyde also yield more highly active solutions than would be anticipated on the above basis.

On several grounds, however, it is to be expected that the influence of solvents on the rotatory power of menthyl hydrogen naphthalate will be more irregular than in the case of the menthyl methyl ester. In the latter compound, the additional polar groups which are introduced into the active molecule during the conversion of menthol into menthyl naphthoate and thence into menthyl methyl naphthalate are each of such nature and orientation as to produce successive increments in the laevorotatory power. Consequently, no matter which of these groups in the diester enters into dipole association with the solvent, the result will be a fall in laevorotation. In the acid ester the normal tendency for the carbomethoxy-group to exhibit a relatively high laevorotation is largely masked by the powerful dextro-influence of the free carboxyl in close proximity to it. Thus the optical effects, whether originating directly from the substituent

groups in the solute molecule or from the secondary influences exerted upon them by a solvent, are no longer cumulative but operate in reverse directions. In addition, the ease with which a given dipole in the active solute can be approached by the dipoles in the solvent molecules will depend upon a number of factors, such as dipole strength, the structure of the groups concerned, and the screening influence of other groups in their immediate neighbourhood. It therefore follows that this condition of affairs must give rise to less regular solvent influence.

The very high positive rotation of the acid naphthalate is an abnormal feature which it is legitimate to seek to explain in terms of the molecular structure, and more especially of the relationship existing between the two peri-substituents. All the available evidence indicates that peri-substituents in the naphthalene molecule are in much closer proximity than the corresponding ortho-substituents in a benzene nucleus (see also Rule, Spence, and Bretscher, J., 1929, 2519), so close, in fact, that the free movement of the groups may be inhibited (Mills and Elliott, J., 1928, 1291). It is not improbable, therefore, that the unusual optical properties of menthyl hydrogen naphthalate are due to the carboxyl group being present in a state of loose chemical combination with the adjoining ester radical. Similar compounds formed by union between an acid and an ester have been shown by Kendall and Booge (*J. Amer. Chem. Soc.*, 1916, **38**, 1712) to exist in non-hydroxylic solvents. On the assumption that such combination is the cause of the high dextrorotation, the diminished value resulting from the presence of a strongly polar solvent, which may break up the complex by entering into dipole association with the carboxyl group, is readily understood. Further, the dextrorotatory structure would be even more completely disrupted by solvents such as alcohol, acetaldehyde, or benzaldehyde, which can enter into co-ordination with the carboxyl group, and by acetic acid, which may combine with it to form a definite molecular compound. All these solvents, as may be seen from Table I, yield solutions having a negative rotation out of all proportion to their dipole moments.

Another source of irregularity in the present instance arises from the varying basic properties of the solvents employed. By union with the carboxyl group of the acid, a basic compound will disrupt the assumed dextrorotatory complex and shift the rotatory power in the negative direction. An examination of the influence of the typically basic solvents aniline and dimethylaniline showed the molecular rotations  $[M]_{5461}$  in these liquids to be  $-306^\circ$  and  $+71^\circ$  respectively. Both of these compounds have dipole moments approximating to 1.4, and the above values therefore represent a

strong displacement as compared with the other benzene derivatives recorded in Table I (ii). A similar explanation accounts for the relatively high positions in the series occupied by benzonitrile and anisole, each of which possesses weak basic properties. Nitrobenzene, on the other hand, has little or no basic character.

In view of the many contending influences at work, it is not possible to determine the part played in the above cases by the varying degree of ionisation of the acid in its effect upon the rotatory power. It is possible, however, that this factor may be traced in the data of Table II, which refer to the rotation of the acid ester in a number of aliphatic alcohols. Owing to its low solubility, the solute had to be used in a concentration of  $c = 2$  or less.

TABLE II.

*Rotatory Powers of l-Menthyl Hydrogen Naphthalate in Alcohols*  
( $t = 20^\circ$ ,  $l = 1$ ).

Alcohol.	$c$ .	$\alpha_{5461}$ .	$M_{5461}$ .
<i>n</i> -EtOH	1.996	-1.06°	-188°
<i>n</i> -PrOH	2.000	1.44	255
<i>n</i> -BuOH	2.000	1.49	264
<i>n</i> -AmOH	2.002	1.56	276
<i>iso</i> -BuOH	2.012	1.59	280
<i>tert.</i> -BuOH	1.495	0.78	185
<i>iso</i> -AmOH	2.010	1.70	299
<i>tert.</i> -AmOH	2.000	0.90	159

On comparing the normal homologues, it will be seen that the rotatory powers rise steadily on passing from ethyl alcohol to amyl alcohol. Lower values are observed in *tert.*-butyl and *tert.*-amyl alcohols. The figures suggest that all the normal and *iso*-alcohols enter into co-ordination with the carboxyl group, detaching it more or less completely from the ester group in the peri-position and forming a solution of relatively high lævorotation. As the molecular weight of the hydroxylic solvent decreases, however, there will be a corresponding increase in its power of ionisation. Apparently, it is this secondary effect, leading to a rise in the proportion of ionised acid present, which is responsible for the diminished rotation in the lower members. It may be noted that *l*-menthyl hydrogen naphthalate in methyl alcohol ( $c = 4$ ) possesses a molecular rotation  $[M]_{5461}$  of  $-218^\circ$ , whereas for the potassium salt under similar conditions the value is  $+12^\circ$ . The exceptionally low rotations observed in the tertiary alcohols may be due to less complete co-ordination, arising from the screening of the hydroxyl group by the alkyl radicals, in which event a larger proportion of the dextrorotatory complex will exist in solution.

As in the other examples previously examined, the rotatory powers of the acid ester were also determined in several isomeric

disubstituted benzenes. The results obtained with the chlorotoluenes, dinitrobenzenes, and dichlorobenzenes are recorded below. Except in the case of the first-named compounds, these substances were employed in admixture with benzene, as several of them are solids at the ordinary temperature.

*l*-Menthyl Hydrogen Naphthalate in Disubstituted Benzenes ( $l = 1$ ,  
 $t = 20^\circ$ ).

Solvent.	<i>c.</i>	$\alpha_{5461}$ .	$[M]_{5461}$ .	$\mu \times 10^{18}$ .
<i>o</i> -CH <sub>3</sub> ·C <sub>6</sub> H <sub>4</sub> Cl	2.012	+3.11°	+547°	1.39
<i>m</i> -CH <sub>3</sub> ·C <sub>6</sub> H <sub>4</sub> Cl	2.004	2.85	503	1.60
<i>p</i> -CH <sub>3</sub> ·C <sub>6</sub> H <sub>4</sub> Cl	2.016	2.95	522	1.70

  

Solvent.	<i>c.</i>	$f_2$ .	$\alpha_{5780}$ .	$[M]_{5780}$ .	$\Delta$ .
C <sub>6</sub> H <sub>6</sub>	1.996	—	+3.59°	+637°	—
C <sub>6</sub> H <sub>6</sub> + C <sub>6</sub> H <sub>5</sub> ·NO <sub>2</sub>	2.000	0.0146	3.39	600	37°
C <sub>6</sub> H <sub>6</sub> + <i>m</i> -C <sub>6</sub> H <sub>4</sub> (NO <sub>2</sub> ) <sub>2</sub>	2.008	0.0142	3.16	557	80
C <sub>6</sub> H <sub>6</sub> + <i>p</i> -C <sub>6</sub> H <sub>4</sub> (NO <sub>2</sub> ) <sub>2</sub>	2.012	0.0142	3.14	552	85

$f_2$  = mol.-fraction of polar solvent in benzene mixture.

$\Delta$  = depression in rotatory power as compared with the value in benzene.

In agreement with the general behaviour of the monosubstituted benzenes, it is found that among the isomeric chlorotoluenes the highest dextrorotation is given in the solvent having the lowest dipole moment. The *m*- and *p*-compounds have higher moments and yield solutions of lower activity, but in these two cases a minor inversion becomes evident.

The values observed with the dinitro- and dichloro-benzenes resemble those obtained with the other active solutes to which reference has already been made (p. 1410). When mixed with benzene in similar concentrations, the *m*- and *p*-dinitrobenzenes each produce a considerably greater depression in rotatory power than does nitrobenzene under the same conditions. Despite the fact that the dipole moment of the para-compound is zero, it behaves as a polar solvent, apparently because the two nitro-groups are so far apart that they tend to function individually. A similar tendency may be noted among the dichloro-compounds; although the influence of the *p*-derivative with its zero dipole moment is relatively much less than that of the *o*-compound ( $\mu = 2.25 \times 10^{-18}$ ), it is nevertheless not negligible and brings about a definite depression as compared with benzene.

Solvent.	<i>c.</i>	$f_2$ .	$\alpha_{5780}$ .	$[M]_{5780}$ .	$\Delta$ .
C <sub>6</sub> H <sub>6</sub> + C <sub>6</sub> H <sub>5</sub> Cl	2.004	0.4093	+3.15	+556°	81
C <sub>6</sub> H <sub>6</sub> + <i>o</i> -C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>	1.996	0.4154	+2.91	+516	121
C <sub>6</sub> H <sub>6</sub> + <i>p</i> -C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>	2.000	0.4266	+3.37	+596	41

These investigations on solvent effect lead to the conclusion that, in general, the rotatory power most characteristic of an optically active solute is exhibited when the substance is dissolved in a non-

polar solvent such as benzene or carbon tetrachloride. In aliphatic hydrocarbons like hexane there may be a tendency, even at high dilutions, for the active compound to exist in the associated state, with a consequent modification of the rotatory power. Solvents containing polar substituents, on the other hand, may affect the rotation by themselves entering into combination or dipole association with the solute. In the latter case, the influence of mono-substituted derivatives of the same parent hydrocarbon tends to be related to the dipole moments of the solvents.

The authors wish to record their indebtedness to the Carnegie Trust for a scholarship to A. McLean which has enabled him to take part in this investigation.

UNIVERSITY OF EDINBURGH.

[Received, March 16th, 1932.]

---