333. *Studies in Solvent Influence. Part V. Dipole Moment of Solvents and the Rotatory Power of Dissolved Menthyl Dialkylmalonates.*

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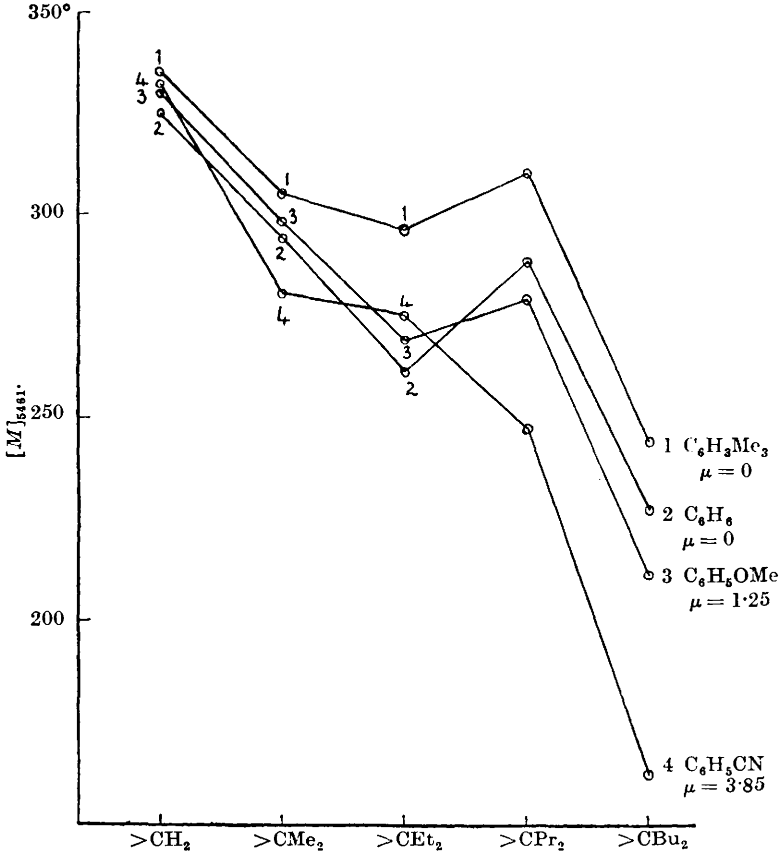
IN a former communication the optical properties of *l*-menthyl malonates of the general type $C_{10}H_{19}O_2C{\cdot}CR_2{\cdot}CO_2M$ were discussed, (R = H, Me, or Et; M = H, Na, or *l*-menthyl) (Rule and Harrower, J., 1930, 2319). It was found that, as the bulk of R increased, the rotatory power of the menthyl hydrogen malonates (M = H) rose steadily, but that a continuously greater fall in rotation occurred when the free acids were converted into their sodium salts. Among the dimenthyl malonates, the rotatory powers decreased as R became larger. All these changes are analogous to those taking place in the substituted menthyl benzoates, $X{\cdot}C_6H_4{\cdot}CO_2C_{10}H_{19}$, as the substituent group X (CO_2H, CO_2Na, or $CO_2C_{10}H_{19}$) is moved from the *p*- to the *o*-position, and on the basis of the Thorpe–Ingold valency deflexion hypothesis it was suggested that they may be related to the diminishing distance between the two carboxylic complexes as the bulk of the alkyl group increases.

In the present paper this comparison has been extended to the malonic derivatives in which R is a propyl or butyl radical, and a comparative examination of the rotatory powers of the whole series of di-esters has been made in various solvents, with a view to determine whether any definite connexion exists between the observed magnitudes and the polar nature of the solvent medium. Polar regularities of this kind have previously been noted only in the case of aromatic compounds of the type of menthyl 8-substituted-1-naphthoates and β-octyl *o*-substituted benzoates, in which there is a close spatial relationship between the two groups attached to the aromatic nuclei (Rule and McLean, J., 1931, 674; this vol., pp. 1400, 1409; Rule and Hill, J., 1931, 2652; Rule and Tod, J., 1931, 1932).

Influence of the Alkyl Group on the Rotatory Power.—As may be seen from Fig. 1 and Table I, the general tendency already noted for the dimenthyl esters of dialkylmalonic acids to give lower rotatory powers as the bulk of the alkyl group increases is maintained in the dipropyl and dibutyl derivatives, except that a temporary break in the downward movement occurs with some solvents at the dipropyl compound. Dimenthyl dipropylmalonate is also abnormal in a number of other ways; *e.g.*, it has a higher m. p. and lower solubility than any of the other homologues so far examined. With the dibutylmalonate the magnitude of the depression is remarkable in view of the almost negligible differences observed among the rotatory powers of the corresponding esters of monobasic aliphatic acids. In the malonic esters, however, the probability of the ends of the propyl or butyl chains returning at any given instant to the neighbourhood of the carboxylic oxygen atoms is greatly increased, owing to the fact that both chains are attached to the central malonic carbon atom. Their positions relative to the ester groupings are thus to some extent fixed, and their areas of movement restricted.

FIG. 1.

Rotatory powers of di-l-menthyl malonate and dialkylmalonates dissolved in benzene derivatives.

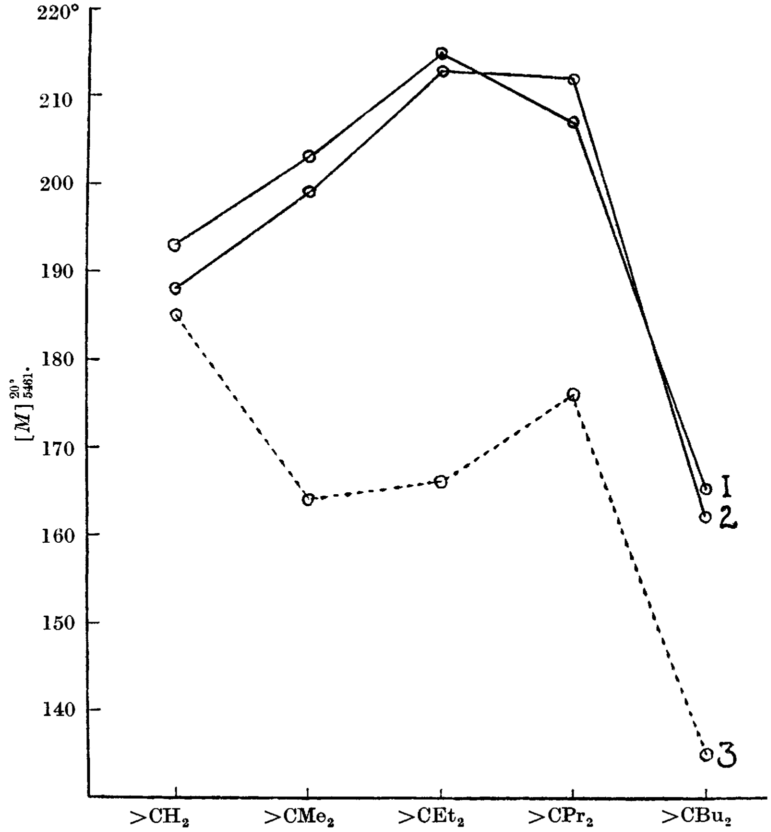


(CH_2 = *malonate*, CMe_2 = *dimethylmalonate, etc.*)

The data obtained for the menthyl hydrogen malonates and their sodium salts are summarised in Fig. 2, from which it is seen that these compounds also exhibit maxima, the one for the salts occurring at the dipropylmalonate and that for the free ester-acid extending over the diethyl and dipropyl derivatives. Despite their general dissimilarity, therefore, the optical diagrams of the di-esters, ester-acids, and ester-salts resemble one another in showing maxima at or about the dipropylmalonates, followed by a sudden fall to the dibutylmalonates. This point of resemblance is in all probability connected with the growing alkyl chains, which are here of the critical length.

FIG. 2.

-Menthyl hydrogen esters of dialkylmalonic acids, $C_{10}H_{19}O_2C{\cdot}CR_2{\cdot}CO_2H$.
1. *In alcohol*; 2. *in benzene*; 3. *sodium salts in alcohol* ($c = 5$).



(CH_2 = *malonate*, CMe_2 = *dimethylmalonate, etc.*)

Variation of Rotatory Power with Polarity of Solvent.—The complete data for the rotatory powers of the dimenthyl esters of this group when dissolved in a variety of solvents are contained in Table

TABLE I.

I. *Rotatory Powers*, $[M]_{5461}$, *of Neutral* l-*Menthyl Esters* (c = 5, t = 20°).

		Dialkylmalonates, $CR_2(CO_2C_{10}H_{19})_2$.							
Solvent.	$\mu \times 10^{18}$.	R=H.	R=Me.	R=Et.	R=Pr.	R=Bu.	Oxalate.	Phthalate.	Acetate.
*cyclo*Hexane	0	−331°	−294°	−292°	−314°	−262°	− 411°	−497°	−189°
Mesitylene	0	335	305	296	310	244	415	496	185
Benzene	0	325	294	261	288	227	433	504	191
Toluene	0·4	322	288	257	280	215	—	494	185
Anisole	1·25	330	298	269	279	211	417	482	185
Chlorobenzene	1·55	—	—	—	271	200	437	475	184
Bromobenzene	1·55	—	287	—	266	194	—	477	184
Iodobenzene	1·50 (?)	326	293	263	260	180	—	479	—
Benzaldehyde	2·75	—	—	—	256	177	—	467	183
Benzonitrile	3·85	332	280	275	247	162	446	459	179
Nitrobenzene	3·89	324	290	282	254	165	432	442	175
Maximum range		*13*	*25*	*35*	*67*	*100*	*35*	*62*	*16*

Note.—In order to save space, no experimental details are quoted. The majority of the rotations were determined in a 2-dm. tube, giving an observed α_{5461} which varied from 3·24° for the dibutylmalonate (in $C_6H_5{\cdot}CN$) to about 9—12° for the malonate, acetate, phthalate, and oxalate.

I. In view of the very low solubility of certain of the di-esters in aliphatic solvents and the fact, already established in earlier investigations, that aromatic solvents are more regular in their action than those of simple aliphatic type, the present examination was limited to solvents derived from benzene. Apart from one or two exceptions, the same solvents were employed for each ester; they ranged from the non-polar *cyclo*hexane, mesitylene, toluene, benzene, and the weakly polar anisole and halogenated benzenes, to the strongly polar benzaldehyde, benzonitrile, and nitrobenzene.

Two main generalisations emerge. Among individual esters the maximum observed variation in molecular rotatory power is very small (13°) for the unsubstituted dimenthyl malonate; but the differences are greater for the dimethylmalonic ester (25°) and increase steadily in the higher homologues until in the dibutylmalonate they exceed 100°. Further, the only compounds which reveal any simple relationship between the magnitude of the rotatory power and the dipole moment of the solvent are the dipropyl- and dibutylmalonates, in which the variation is large. With these esters there is a remarkable parallelism between the two properties, the highest rotations being given in non-polar solvents and the lowest in those of a strongly polar nature. As in previous communications, it is assumed that the changes are due to the internal electrical field of the polar groups in the active solute becoming neutralised, to a smaller or greater extent, by dipole association with the polar solvent. The general behaviour of the malonic derivatives under discussion is illustrated in Fig. 1, in which, owing to the necessarily small scale of reproduction, only four typical solvents have been included. This diagram clearly shows the growing sensitivity towards solvent influence as the length of the alkyl chain increases, and also indicates the irregularities encountered among the three lower homologues.

Such a pronounced modification of the solvent effect following a relatively small change in the alkyl group was unexpected and led to similar determinations being made with dimenthyl oxalate and dimenthyl phthalate, both of which bear a structural resemblance to the malonates. Menthyl acetate was also examined, as representing the simple mono-ester type. Molecular rotations for these compounds are given in Table I, from which it is seen that for the same series of solvents the values for the oxalate only vary over 35° and exhibit little or no regularity in their arrangement. In this particular case the highest rotation is given in nitrobenzene and the lowest in *cyclo*hexane, an inversion of the usual order of influence for menthyl esters. On the other hand, with dimenthyl phthalate and menthyl acetate the agreement is excellent, least polar solvents again yielding the most highly active solutions.

The case of menthyl acetate is of particular interest, not only because the maximum variation in rotatory power is so small (16°), but also because the regularity of the solvent effect indicates that polar influences may be observed with comparatively simple types of active esters, and are not therefore limited to molecular structures containing two polar groups in close spatial proximity, such as the higher malonic esters and ortho- and peri-derivatives of aromatic hydrocarbons. We are also led to infer that the absence of any definite solvent relationship in the oxalate, malonate, and the dimethyl- and diethyl-malonic esters is due to the operation of some disturbing factor, and that this either disappears in the dipropyl and dibutyl derivatives or becomes subordinated to a new influence which is again responsive to the polarity of the surrounding medium.

Optical differences of the type under discussion would be anticipated if the esters varied in their degree of association in non-polar solvents, so that the oxalate and malonate were relatively strongly associated and the two highest homologues existed largely in the unimolecular state. In this case molecular association in hydrocarbon solvents would depress the rotation, for the same reason that a diminished rotatory power is found in highly polar media owing to association between solute and solvent. The result would be a general flattening out of the solvent effect and an absence of regularities. Esters, however, do not as a class undergo appreciable association, and no support for the foregoing supposition is to be found in the following values (cryoscopic) of molecular weights for 5% solutions in benzene :

Ester.	*M*, calc.	*M*, found.
Dimenthyl oxalate	366	343
Dimenthyl dibutylmalonate	492	469

A possible explanation of the observed solvent effects is that the polar groups in di-esters such as menthyl oxalate and malonate differ from those in the acetate in being more effectively screened by the bulky menthyl radicals, and hence are not readily approached by the solvent dipoles. In this case the regularities among the two higher dialkyl derivatives may be ascribed to secondary influences exerted through the medium of the growing chains, which are of the critical length.

It may be noted, in this connexion, that the maximum rotatory power exhibited by the dipropylmalonate (see Fig. 1 and Table I) is very pronounced when the ester is dissolved in non-polar solvents, less marked in weakly polar solvents such as anisole, and disappears altogether in nitrobenzene and benzonitrile, which are strongly polar. These changes throw an interesting light on the suggestion of Frankland (J., 1912, **101**, 660) that " some solvents should permit a more unrestricted development of the rotatory effect of the homologous group than is the case when the same compounds are examined in the liquid condition." The correctness of this view was established by the work of Pickard and Kenyon, more especially on secondary alcohols of the type CH(OH)EtR (see also Kenyon, *Trans. Faraday Soc.*, 1930, 439), the effects being considerably accentuated in benzene or alcoholic solution. From the standpoint of the present series of communications, the spatial influence of the returning alkyl chain on the ester grouping may be compared to that exerted by an ortho- or peri-substituent in menthyl benzoate or naphthoate, which has been shown in various cases to attain a maximum in non-polar or weakly polar solvents. No detailed examination has been made of the influence of aliphatic solvents on the rotatory powers of the di-esters, but the diagram for ethyl alcohol, if inserted in Fig. 1, would run approximately parallel to that of benzene and about 50° above it. In the case of the homologous menthyl hydrogen carboxylates of the type $C_{10}H_{19}O_2C{\cdot}[CH_2]_n{\cdot}CO_2H$, where the returning chain ends in a carboxyl group, it has been found that the periodical deviations are small in alcohol as solvent but large when benzene is employed (Rule, Hay, and Paul, J., 1928, 1350, 1353). Hence it may be concluded that in general these effects are most pronounced in solvents of low polarity.

EXPERIMENTAL.

The solvents employed for the optical measurements were purified by the methods described by Rule and McLean (J., 1931, 689).

Di-l-*menthyl dipropylmalonate*, after five recrystns. from EtOH, was isolated in the form of fine monoclinic crystals, m. p. 94°, having a constant rotation of $[M]_{5461}^{20^\circ}$ − 288° in C_6H_6 (c = 5) (Found : C, 74·6; H, 11·1. $C_{29}H_{52}O_4$ requires C, 74·9; H, 11·3%).

l-*Menthyl hydrogen dipropylmalonate* was the only acid ester of this group to be isolated as a solid. It was prep. and purified in the same manner as the corresponding hydrogen diethylmalonate (*loc. cit.*) and formed a white powder, m. p. 41—42°, $[M]^{20°}_{5461}$ − 207° in EtOH ($c = 5$) (Found : C, 70·2; H, 10·7. $C_{19}H_{34}O_4$ requires C, 69·9; H, 10·5%). The solutions of the Na salts of this and the following hydrogen dibutylmalonate required for the optical measurements were obtained by adding the calc. amounts of alc. EtONa to the ester-acids dissolved in EtOH.

*Di-*l*-menthyl dibutylmalonate* separated from EtOH in fine monoclinic needles, m. p. 58°, $[M]_{5461}$ − 227° in C_6H_6 ($c = 5$) (Found : C, 75·8; H, 11·5. $C_{31}H_{56}O_4$ requires C, 75·5; H, 11·5%).

l*-Menthyl hydrogen dibutylmalonate* resembled the majority of the earlier homologues in being a viscous syrup at room temp.; $[M]^{20°}_{5461}$ − 162° in C_6H_6 ($c = 5$) (Found : C, 70·8; H, 10·6. $C_{21}H_{38}O_4$ requires C, 71·1; H, 10·8%).

l-Menthyl acetate (B.D.H.) was fractionated under reduced pressure, the main fraction giving $[\alpha]^{19°}_{D}$ − 79·45°. Tschugaeff (*Ber.*, 1898, **31**, 364) records $[\alpha]^{20°}_{D}$ −79·42°.

The samples of dimenthyl malonate, dimethylmalonate, and diethylmalonate used were those prep. by Rule and Harrower (*loc. cit.*), and the following esters were prep. by the sodium menthoxide catalytic method employed by those authors.

Dimenthyl phthalate was prepared by Arth (*Ann. Chim. Phys.*, 1886, **7**, 485) and later by Cohen (J., 1916, **109**, 232), who obtained a product of different m. p. and rotatory power. Phthalic anhydride (29·6 g.) and menthol (62·4 g.) were heated together at 135—140° for 40 hrs. The reaction mixture gave the neutral di-ester (15 g.; 17%) and a larger amount (45 g.) of acid ester. The m. p. and rotatory power of the former were as follows, the values recorded by Arth and Cohen being also given for comparison.

	R. & R.	A.	C.
M. p.	133°	133°	99°
$[\alpha]_D$ in C_6H_6	−96·5° (c=5)	−94·7°	−100·5°

Dimorphism of Menthyl Oxalate.—This compound had previously been prep. by Tschugaeff (*Ber.*, 1902, **35**, 2474), Zelnikoff (*Ber.*, 1904, **37**, 1378) and Hilditch (J., 1909, **95**, 1579), either by heating menthol and oxalic acid for several hours under reflux or by treating oxalyl chloride with menthol. In each case firm octahedra of m. p. 68° were obtained.

During the present investigation the ester was prep. by drawing a current of air through a mixture of methyl oxalate (10 g.) and menthol (40 g.) containing a trace of sodium menthoxide (0·3 g. Na) and maintained at 90—110°. When no more MeOH distilled, the residue was cooled, taken up in light petroleum, and the solution washed successively with acid, alkali, and H_2O, and then dried over $CaCl_2$. The solvent and excess menthol were removed by distillation, eventually under reduced pressure, and the oxalate fractionated, b. p. 222—224°/11 mm. On being cooled in a bath of solid CO_2–Et_2O, dimenthyl oxalate solidified, forming octahedra, m. p. 39°, unchanged after repeated recrystns. from light petroleum or after standing in a vac. desiccator; 2 months later the m. p. had risen to 68°. Both forms had the same molecular rotation, $[M]^{20°}_{5461}$ −433°, in C_6H_6 ($c = 5$). Pickard and Kenyon, using a sample of ester prepared by Cohen, record $[M]^{20°}_{5461}$ −425° in the same solvent. It appears, therefore, that this is a case of dimorphism, but unfortunately several further preps. by each of the above methods gave only a product of m. p. 68°.

In addition to the optical data recorded for the di-esters in various solvents (Table I), determinations were also made with the neutral and acid esters in EtOH and C_6H_6 for four wave-lengths (Table II; $t = 20°$; $l = 2$).

TABLE II.

Solvent.	c.	$[M]^{20°}_{6708}$.	$[M]^{20°}_{5893}$.	$[M]^{20°}_{5461}$.	$[M]^{20°}_{4358}$.
		Di-l-*menthyl dipropylmalonate.**			
Benzene	3·996	– 189°	– 258°	– 287°	– 488°
Alcohol	2·068	– 207	– 279	– 337	– 539
		l-*Menthyl hydrogen dipropylmalonate.*			
Benzene	4·994	– 135	– 184	– 212	– 331
Alcohol	5·052	– 137	– 170	– 207	– 306
Na salt in EtOH ..	4·018	—	—	– 176	—
		Di-l-*menthyl dibutylmalonate.*			
Benzene	5·012	– 145	– 187	– 227	– 358
Alcohol	4·954	– 187	– 141	– 287	– 476
		l-*Menthyl hydrogen dibutylmalonate.*†			
Benzene	5·200	—	—	– 162	—
Alcohol	4·947	—	—	– 165	—
Na salt in EtOH ..	4·184	—	—	– 135	—

* It was not possible to obtain a concentration of $c = 5$ in this case.

† Solutions too strongly coloured to obtain satisfactory readings except for λ_{5461}.

In so far as may be judged from the limited range of wave-lengths employed, the dibutylmalonate resembles the homologues previously studied in exhibiting relatively simple dispersion. The neutral dipropylmalonate in EtOH and C_6H_6, and the corresponding acid ester in EtOH, possess definitely complex dispersion.

Summary.

An investigation of the optical properties of the menthyl esters of malonic and dialkylmalonic acids in solution leads to the following main conclusions.

(*a*) The rotatory powers of the di-esters fall as the alkyl chain increases from methyl to butyl. A temporary maximum occurs at the dipropyl derivative, which is accentuated when the ester is examined in solvents of low polarity but disappears altogether in the presence of highly polar media.

(*b*) The sensitivity of the di-esters towards solvent influence increases with the length of the alkyl chain. Using a series of eleven benzene derivatives as solvents, it is found that the molecular rotation of the dipropyl- and dibutyl-malonates varies with the dipole moment of the solvent medium. A similar relationship is exhibited by menthyl acetate and dimenthyl phthalate. No regularity could be traced in the case of the malonate, dimethyl- and diethyl-malonates, or with the oxalate.

(*c*) Dimenthyl oxalate has been obtained in a low-melting form, m. p. 39°.

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