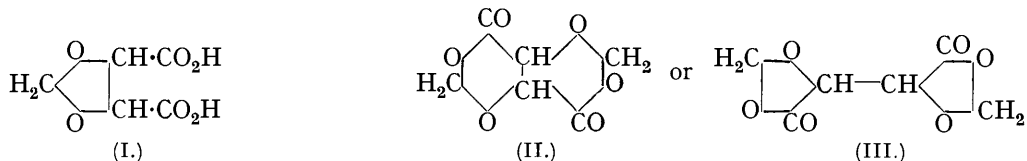


**239.** *Studies in Solvent Action. Part X. Rotatory Powers of Dimethylene Tartrate, Methylenetartronic Acid and its Dimethyl Ester, in the Presence of Added Solvents and Salts.*

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AUSTIN and CARPENTER (J., 1924, **125**, 1939) showed that methylenetartronic acid (I) and dimethylene tartrate (II or III) exhibit simple dispersion under varying solvent conditions and over a wide range of wave-length. These properties have been ascribed to the rigidity of the molecular structure, which (unless dimethylene tartrate is represented by formula III) is such that no appreciable modification in the configuration can result from the spatial rotation of one part of the molecule with respect to another.



The present communication deals with the manner in which the rotatory powers vary with the polarity of the solvent and the nature of added salts. It had also been intended to examine the influence of concentration and temperature upon the compounds in polar and in non-polar solvents, but this was not practicable owing to their extremely low solubility in the latter. These effects were, however, successfully determined by using the more readily soluble *dimethyl* ester of methylenetartronic acid. In view of the comprehensive dispersion data obtained by Austin and Carpenter, the rotatory powers in the present work were measured only for the one wave-length,  $\lambda_{5461}$ . Observed values are summarised in Table I, the solvents being arranged in diminishing order of the rotatory powers of the solutions.

TABLE I.

*Molecular rotations of dimethylene tartrate in solution.*

Solvent.	$\mu \times 10^{18}$ .	$[M]_{5461}^{20^\circ}$ .	Solvent.	$\mu \times 10^{18}$ .	$[M]_{5461}^{20^\circ}$ .
$C_6H_5 \cdot NO_2$ .....	3·89	+213°	$CH_3 \cdot NO_2$ .....	3·78	+240°
$C_6H_5 \cdot CN$ .....	3·85	188·5	$CH_3 \cdot CHO$ .....	2·71	235
$C_6H_5 \cdot CHO$ .....	2·75	173	$CH_3 \cdot OH$ .....	1·73	232
<i>o</i> - $C_6H_4Cl_2$ .....	2·24	173	$CH_2Cl_2$ .....	1·61	221·5
$C_6H_5Br$ .....	1·50	156	$CHCl_3$ .....	1·10	220
$C_6H_5Cl$ .....	1·52	154	$CH_3 \cdot CN$ .....	3·05	219
$C_6H_5 \cdot NH_2$ .....	1·60	144	$CH_3 \cdot CO_2H$ .....	1·73	218
$C_6H_5 \cdot OCH_3$ .....	1·25	142	$CH_3I$ .....	1·66	172
$C_6H_5I$ .....	1·25	129			
$C_6H_6$ .....	0	129			
$C_6H_5 \cdot CH_3$ .....	0·4	126			

*Concentration.* Where possible, a concentration  $c = 1$  was used, but in some cases, notably *o*- $C_6H_4Cl_2$  ( $c = 0\cdot192$ ),  $C_6H_5I$  ( $c = 0\cdot202$ ), and  $C_6H_5Br$  ( $c = 0\cdot254$ ), a lower value had to be adopted, on account of the small solubility. Observed rotations varied from  $0\cdot300^\circ$  (average of 10 readings) for  $l = 2$  in  $C_6H_5I$  to  $5\cdot52^\circ$  for  $l = 4$  in  $CH_3 \cdot NO_2$ . Values of  $\mu$  are from Smyth ("Dielectric Constants and Molecular Structure," 1931).

Rotatory powers of dimethylene tartrate in *aromatic* solvents are closely related to the dipole moments of the solvents, the more polar the medium the higher being the dextro-rotation of the solution. The rotations in benzene and toluene are somewhat higher than might have been expected, probably owing to the tendency of the solute molecules to associate with one another in these solvents. This hypothesis is further supported by the extremely low solubility of the ester in hydrocarbon media, a property which precluded confirmation by molecular-weight determinations.

In *aliphatic* solvents the solubility is in general so low that only the more polar compounds could be employed. Within this restricted group the same tendency is noted for

strongly polar media to yield solutions of high dextrorotation. The polysubstituted compounds chloroform and dichloromethane occupy positions between nitromethane and acetonitrile, although their dipole moments are much less than those of the latter solvents. This displacement, taken in conjunction with the almost complete insolubility of the ester in non-polar aliphatic solvents, suggests that the degree of solute-solute association is greater in these cases than in the aromatic solvents examined.

The normal value found for the rotation of dimethylene tartrate in benzaldehyde may be contrasted with the exceptionally high dextrorotation of ethyl tartrate in this solvent, a peculiarity which has been attributed to co-ordination between the ketonic group in the aldehyde and the hydroxyl group in the ester (Rule, Barnett, and Cunningham, J., 1933, 1220). In the absence of free hydroxyl groups, the active solute behaves normally towards benzaldehyde, thus supporting the above view.

Austin and Carpenter (*loc. cit.*) examined the optical rotation of dimethylene tartrate in acetone and in ethyl acetate, and from the almost identical values concluded that, owing to its rigid cyclic structure, the ester was not sensitive to solvent influences. In the light of the more extended results now recorded, it is seen that this is not the case. The molecular rotations,  $[M]_{5461}$ , vary from a maximum of  $+240^\circ$  in nitromethane to a minimum of  $+126^\circ$  in toluene, and cover a somewhat greater range than is found for ethyl tartrate in the same series of solvents.

As in earlier communications of this series, the observed changes are assumed to be related to variations in the degree of association of the solute molecules with one another and with those of the added solvent. In the present instance solute-solvent association is the dominant factor, and the more polar the solvent the more completely does it enter into association with the effective dipoles of the optically active molecule, leading to corresponding modifications in their contributions towards the rotatory power.

In general, polysubstituted solvents have been excluded in comparisons such as the above, except in the case of the fully substituted methanes of zero dipole moment (carbon disulphide and tetrachloride) which usually exhibit normal behaviour. Displacements in the relationship between rotation and dipole moment are apt to be especially marked in the case of *m*- and *p*-disubstituted benzenes. These divergences have been explained (J., 1931, 680) on the assumption that for a compound such as *p*-dinitrobenzene the individual nitro-groups are so far apart as to function in some measure independently towards the dipoles in neighbouring molecules, although in a uniform electrical field the influence of one group completely neutralises that of the other. In this connexion the rotatory power of dimethylene tartrate has been determined by using disubstituted benzenes as solvents. These were employed mixed with benzene, in order to keep the components in solution (Table II).

TABLE II.

*Dimethylene tartrate in benzene and a second solvent* ( $c$  approx. 0.5;  $l = 4$ ;  $t = 20^\circ$ ).

Solvent.	$f_2$ .	$[M]_{5461}$ .	$\Delta$ .	Solvent.	$f_2$ .	$[M]_{5461}$ .	$\Delta$ .
$C_6H_5NO_2$	0.0134	+144.1°	15.0°	$C_6H_5Cl$	0.300	+144.2°	15.1°
<i>m</i> - $C_6H_4(NO_2)_2$	0.0134	149.9	20.8	<i>o</i> - $C_6H_4Cl_2$	0.300	153.8	24.7
<i>p</i> - $C_6H_4(NO_2)_2$	0.0134	148.8	19.7	<i>p</i> - $C_6H_4Cl_2$	0.300	146.2	17.1

In pure benzene,  $[M]_{5461} = +129.1^\circ$  ( $c = 0.612$ );  $f_2 =$  molar fraction of polar component in solvent mixture;  $\Delta =$  elevation in rotatory power compared with solution in pure benzene.

The above values show that *p*-disubstituted chloro- and nitro-benzenes, despite their zero dipole moment, exert a considerable polar influence, which in this case is less than that of the isomeric *o*- or *m*-derivatives but more than that of the corresponding monosubstituted compounds. Similar effects have previously been observed for *l*-menthyl hydrogen naphthalate, *d*-octyl hydrogen phthalate, and their methyl esters as the optically active solutes (Rule and McLean, J., 1931, 680; 1932, 1414; Rule and Hill, J., 1931, 2656).

It was impracticable to determine the influence of homogeneous solvents upon the rotatory power of methylenetartronic acid (I), for this compound is almost insoluble in the majority of organic liquids at ordinary temperatures. The solvents were therefore employed in admixture with ethanol. The rotatory power  $[M]_{5461}$  in pure ethanol was  $-190^\circ$ .

Table III reveals no definite relationship between the rotatory power of the solution and the polarity of the primary solvent. The variations are irregular, and, more particularly

TABLE III.

*Methylenetartaric acid in mixtures of ethanol (1 mol.) with other solvents (2 mols.).*

Solvent.	$\mu \times 10^{18}$ .	$[M]_{5461}^{20}$ .	Solvent.	$\mu \times 10^{18}$ .	$[M]_{5461}^{20}$ .
C <sub>5</sub> H <sub>12</sub> .....	0	-184.9°	C <sub>6</sub> H <sub>6</sub> .....	0	-180.7°
CS <sub>2</sub> .....	0	184.0	C <sub>6</sub> H <sub>5</sub> Cl .....	1.52	179.6
CH <sub>3</sub> ·OH .....	1.73	180.3	C <sub>6</sub> H <sub>5</sub> Br .....	1.50	179.2
*CH <sub>3</sub> ·CO <sub>2</sub> H .....	1.70	177.2	C <sub>6</sub> H <sub>5</sub> ·CN .....	3.85	178.5
CCl <sub>4</sub> .....	0	174.8	C <sub>6</sub> H <sub>5</sub> ·CH <sub>3</sub> .....	0.4	177.4
CH <sub>3</sub> ·CHO .....	2.71	172.1	C <sub>6</sub> H <sub>5</sub> ·NO <sub>2</sub> .....	3.89	174.9
CHCl <sub>3</sub> .....	1.10	167.8	C <sub>6</sub> H <sub>5</sub> ·OMe .....	1.25	173.9
CH <sub>3</sub> ·CN .....	3.05	166.2	For aliphatic solvents $c = 1$ , aromatic solvents $c = 2$ . In all cases $t = 20^\circ$ , $l = 4$ . Limiting values of $a_{5461}$ were $-3.74^\circ$ in CH <sub>3</sub> I and $-8.95^\circ$ in C <sub>6</sub> H <sub>6</sub> mixtures.		
CH <sub>3</sub> ·NO <sub>2</sub> .....	3.78	164.4			
CH <sub>2</sub> Cl <sub>2</sub> .....	1.61	164.3			
CH <sub>3</sub> I .....	1.66	150.8			

\* In a mixture of acetic acid and ethyl alcohol the molecular rotation rose gradually during 15 minutes to the final value of  $-190^\circ$ .

in the aromatic group, limited in magnitude. In both these respects the behaviour of methylenetartaric acid resembles that of other optically active solutes possessing a strong tendency towards self-association, such as *d*- $\beta$ -nitro-octane and  $\alpha$ -methyl-*n*-hexoic acid (Rule, Smith, and Harrower, J., 1933, 376). With such compounds the optical influence of a given solvent depends on its dual capacity to break down the solute complexes and to enter into solute-solvent association with the individual molecules.

In dealing with irregular solvent effects of this kind, it is often difficult to determine in which direction the rotatory power is displaced by an increase in the degree of association of the active solute with itself or with the solvent. Molecular-weight determinations were not attempted in the present case owing to the low solubility of the compound. As a typical carboxylic acid, however, it may be concluded that methylenetartaric acid tends to exist mainly in bimolecular form when dissolved in mixtures of alcohol with the non-polar solvents pentane, carbon disulphide, and carbon tetrachloride, under which conditions it exhibits high lævorotations. In agreement with this view, strongly lævorotatory solutions are also found in mixtures containing acetic acid, which in disrupting some of the solute-solute complexes must, as a carboxylic acid, replace them with a very similar state of solute-solvent association. Among the aromatic solvents, the low value in anisole also supports the conclusion that increasing association of the active compound displaces the rotation in a lævorotatory direction, since ethers are known to be peculiarly effective in breaking down associated carboxylic complexes.

In general, the behaviour of an optically active hydroxylic compound is not fundamentally changed by methylation, and the values given in Table IV for the dimethyl ester

TABLE IV.

*Molecular rotations of dimethyl methylenetartrate in solution (l = 4).*

Solvent.	$\mu \times 10^{18}$ .	$[M]_{5461}^{20}$ .	Solvent.	$\mu \times 10^{18}$ .	$[M]_{5461}^{20}$ .
CH <sub>3</sub> ·OH .....	1.73	-245°	C <sub>6</sub> H <sub>5</sub> ·CN .....	3.85	-235°
CH <sub>3</sub> ·CHO .....	2.71	241	C <sub>6</sub> H <sub>5</sub> ·NO <sub>2</sub> .....	3.89	227
CH <sub>3</sub> ·CN .....	3.05	238	C <sub>6</sub> H <sub>5</sub> ·CHO .....	2.75	221
CH <sub>3</sub> ·CO <sub>2</sub> H .....	1.70	228	C <sub>6</sub> H <sub>5</sub> ·NH <sub>2</sub> .....	1.60	220
CH <sub>3</sub> ·NO <sub>2</sub> .....	3.78	223	C <sub>6</sub> H <sub>5</sub> ·OMe .....	1.25	218
CH <sub>2</sub> Cl <sub>2</sub> .....	1.61	208	C <sub>6</sub> H <sub>5</sub> Cl .....	1.52	214
C <sub>6</sub> H <sub>14</sub> .....	0	204	C <sub>6</sub> H <sub>6</sub> .....	0	213
CS <sub>2</sub> .....	0	204	C <sub>6</sub> H <sub>5</sub> Br .....	1.50	212
CCl <sub>4</sub> .....	0	200	C <sub>6</sub> H <sub>5</sub> I .....	1.50	209
CH <sub>3</sub> I .....	1.66	199	C <sub>6</sub> H <sub>5</sub> ·CH <sub>3</sub> .....	0.40	207
CHCl <sub>3</sub> .....	1.10	199			

For aliphatic solvents,  $c = 1$  (approx.) except in hexane, for which  $c = 0.493$ . Limiting values of  $a_{5461}$  are  $-5.20^\circ$  (methyl alcohol) and  $0.49^\circ$  (hexane). For aromatic solvents,  $c = 2$  (approx.), and  $a_{5461}$  varies from  $-8.74^\circ$  (toluene) to  $-9.95^\circ$  (benzonitrile).

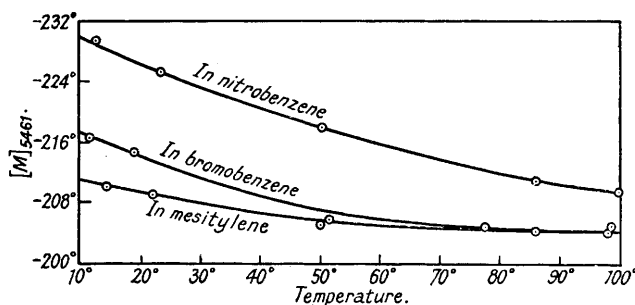
of methylenetartaric acid support this statement. On esterification of the two carboxyl groups, however, the strong tendency of the free acid to undergo association is considerably reduced. Hence the rotatory powers of the ester in solution indicate a more definite agreement between  $\mu$  and  $[M]$ , in that an increase in the polarity of the solvent corresponds to a higher lævorotation. Certain minor irregularities also occur, such as the relatively high rotations found for the ester in non-polar media, especially benzene, hexane, and carbon disulphide. These abnormalities, when considered in the light of the very low solubility of the compound in such solvents, suggest that methylenetartaric ester still retains an appreciable tendency to associate with itself, thus displacing the rotation in a lævorotatory sense.

*Concentration Effect.*—The above conclusions as to the optical changes produced by association are confirmed by the variations observed in the rotatory powers of the ester when examined at increasing concentrations in benzene as solvent ( $t = 20^\circ$ ,  $l = 4$ ):

$c$ .....	2.002	5.261	10.04	19.78
$[M]_{5461}$ .....	$-212.8^\circ$	$213.9^\circ$	$215.3^\circ$	$216.5^\circ$

(Limiting values of  $\alpha_{5461}$ :  $-8.96^\circ$  and  $-90.12^\circ$ .)

It was not possible to obtain higher concentrations than  $c = 20$ , but up to this value an increase in concentration corresponds to a rise in the lævorotation, a change in the direction to be anticipated on the assumption of a greater degree of association of the active molecules at the higher concentrations.



Temperature-rotation diagram for dimethyl methylenetartarate in solution.

*Temperature Effect.*—The rotatory powers of the ester in solution were determined over the range  $10$ – $100^\circ$ , the three typical aromatic solvents nitrobenzene, bromobenzene, and mesitylene being employed. Of these, the first is very strongly polar, the second of medium polarity, and the third non-polar. The results are illustrated graphically in the fig. The high rotation of a solution in nitrobenzene has been related to the high degree of dipole association existing between the dissolved ester and the strongly polar solvent molecules. On theoretical grounds it has been deduced (Rule, Barnett, and Cunningham, J., 1933, 1217) that this characteristic influence of the polar solvent should diminish with rise in temperature, as the increased molecular movement leads to a fall in the degree of solvation, and that at higher temperatures the temperature-rotation curve for a solution in a polar medium should therefore tend to approach the corresponding curve for one of non-polar type. These predictions are fulfilled in the present case for solutions in nitrobenzene and mesitylene, the curve for bromobenzene occupying an intermediate position in agreement with its weakly polar properties.

*Influence of Added Salts.*—Although extensive investigations have been carried out on the optical effects arising from the addition of inorganic salts to solutions of active acids and their salts, little information is available regarding the changes undergone by non-ionisable active compounds, probably because few of the latter are soluble in water. Patterson and Anderson (J., 1912, 101, 1833) record some observations with ethyl *d*-tartrate which indicate that, although the optical changes are smaller than those found for free malic and tartaric acids, the characteristic cationic effects are similar in each case. For

an  $M/2$ -aqueous solution of ethyl tartrate, these authors find the relative depressions in rotatory power due to the addition of various chlorides ( $2M$ ) to be given by  $\text{NH}_4 < \text{Na} < \text{K} < \text{Ba}$ .

As dimethylene tartrate was hydrolysed comparatively rapidly in aqueous solution (period of half-change about 50 hours at  $20^\circ$ ), it was examined in aqueous alcohol, prepared by diluting 50 c.c. of absolute alcohol to 100 c.c. with distilled water. In this mixture no appreciable hydrolysis occurred during the determination of the rotatory power. The observed depressions in the molecular rotation of dimethylene tartrate ( $[M]_{5461}^{20^\circ} = +240.8^\circ$ ,  $c = 0.6$ ), caused by the addition of various chlorides in  $0.5M$ -concentration, are given in line I below. The corresponding lowerings of the negative rotatory power of dimethyl methylenetartrate in pure aqueous solution ( $[M]_{5461}^{20^\circ} = -235.4^\circ$ ,  $c = 1$ ) produced by the addition of chlorides in  $2.5M$ -concentration are given in line II. In each case the

Cation.	Li.	$\text{NH}_4$ .	Na.	K.	Rb.	Cs.	Mg.	Ca.	Sr.	Ba.
I .....	1.5	2.0	4.0	4.5	6.3	6.1	—	—	6.6	*
II .....	3.3	3.6	10.1	13.4	13.6	—	9.5	11.7	19.1	29.0†

\* Larger than Sr.

† Extrapolated value.

relative effects for univalent cations are  $\text{Li} < \text{NH}_4 < \text{Na} < \text{K} < \text{Rb}, \text{Cs}$ , and for bivalent cations  $\text{Mg} < \text{Ca} < \text{Sr} < \text{Ba}$ , both series being identical with those found for malic acid by Stubbs (J., 1911, **99**, 2265) and for sodium *d*-octyl phthalate by Rule and Hill (J., 1931, 2644).

The remarkable regularity of these results proves that the effects are in no way dependent upon the presence of an ionised grouping or of hydroxyl in the optically active solute, since neither of these factors occurs in the esters under examination. Hence it may be assumed that the changes arise from the attraction of the cations to the negative ends of the dipoles in the active substance, leading to electronic deformation and consequent alteration in rotatory power, much in the same way as these dipoles may be deformed by association with a polar solvent.

#### EXPERIMENTAL.

Dimethylene tartrate was prepared by Austin and Carpenter's method (*loc. cit.*);  $m. p.$   $118.5$ — $119^\circ$ ,  $[\alpha]_{5461}^{20^\circ}$  in acetone ( $c = 4$ )  $+130.6^\circ$ . The above authors record  $m. p.$   $119^\circ$  and  $[\alpha]_{5461}^{20^\circ} +123.5^\circ$  ( $c = 5$ ).

Methylenetartronic acid was obtained by a modification of Austin and Carpenter's process. Powdered tartaric acid (150 g.) and water (3 c.c.) were mixed and heated to  $165^\circ$ , and para-formaldehyde (45 g.) was added in small portions with stirring. When the mixture had become quite liquid, the temperature was allowed to fall slowly to  $60^\circ$ , and 100 g. of oleum were added, the mixture being kept below  $72^\circ$ . The use of oleum in place of pure sulphuric acid was found to give an improved yield. The mixture was diluted with 400 c.c. of water and heated to boiling, then 215 g. of barium carbonate, sufficient to precipitate the oleum, were stirred in, and the barium sulphate filtered off. The clear filtrate was again boiled, and the organic acids neutralised by the addition of a thin paste of 203 g. of barium carbonate. At this point precipitated barium tartrate was filtered off. Since the solubility of barium methylenetartrate is low, it is essential that the following conditions be observed; the barium tartrate must be precipitated from a large volume of water, the solution should be filtered hot, and the precipitate of tartrate washed well with hot water, the total volume of solution for the above quantities being at least 3 litres. The solution was next concentrated by boiling until crystals of barium methylenetartrate began to separate; it was then allowed to cool, and the crystals filtered off. The hot filtrate was again treated with more barium carbonate to neutralise tartaric acid formed by the gradual hydrolysis of the small amount of dimethylene tartrate originally present. The mixture was again filtered and further concentrated until another crop of barium methylenetartrate was obtained. These processes were repeated, the liquid being kept neutral as far as possible, until all the methylenetartrate had been recovered from solution. The crude barium methylenetartrate (80 g.) was purified by three recrystallisations from water.

Austin and Carpenter record that the salt crystallised in long needles which were extremely hygroscopic, necessitating analyses for barium content in order to determine the amount of sulphuric acid required in the next stage. In the present work it was found that in some cases the long silky needles ( $2\text{H}_2\text{O}$ ), on standing in the solution, slowly changed into short biaxial

crystals of orthorhombic type ( $4\text{H}_2\text{O}$ ). Moreover, if the hot solution was vigorously stirred at intervals during crystallisation, a crop of very fine orthorhombic prisms was obtained. In this form the salt dried quickly and showed no trace of hygroscopy. The free acid was obtained by exact precipitation of the barium with standard sulphuric acid, the amount required being calculated directly from the weight of the tetrahydrate employed. Concentration of the filtered mixture gave methylenetartronic acid, m. p.  $164.7^\circ$  (after being dried in a vacuum for 5 days) :  $[\alpha]_{5461}^{20} = -96.8^\circ$  ( $c = 6.3$ , in water). Austin and Carpenter record  $-96.0^\circ$  ( $c = 4$ ).

*Dimethyl Methylenetartrate*.—The pure barium salt, obtained as above, was treated in boiling aqueous suspension with the calculated amount of sodium sulphate. The filtrate containing the disodium salt was concentrated, cooled, and silver nitrate solution added in slight excess. The precipitate of silver salt was dried, and shaken vigorously with excess of methyl iodide, added in portions to prevent undue rise of temperature. *Dimethyl methylenetartrate* so obtained crystallised from light petroleum in long needles, m. p.  $31.5^\circ$  (Found : C, 44.4; H, 5.6.  $\text{C}_7\text{H}_{10}\text{O}_6$  requires C, 44.2; H, 5.3%).

The solvents used in the determinations of rotatory power were purified by the methods described in earlier papers of this series.

#### SUMMARY.

(a) The characteristic rotatory powers of dimethylene tartrate and of dimethyl methylenetartrate in solution rise in magnitude as the dipole moment of the solvent increases.

(b) The rotatory power of the strongly associated methylenetartronic acid, on the other hand, varies irregularly with the solvent, and the observed changes may be interpreted on the assumption that solute-solvent and solute-solute association both raise the rotation.

(c) In agreement with the demands of the association hypothesis, the optical rotation of dimethyl methylenetartrate dissolved in a non-polar solvent increases with the concentration of the ester; and the rotatory powers of solutions in a highly polar and in a non-polar solvent approach one another as the temperature rises.

(d) The cationic effects produced by the addition of metallic chlorides to aqueous solutions of the above esters are identical with those found for optically active acids and their salts. Such effects must therefore be transmissible through the dipoles as well as through ionised groupings contained in the active solute.

One of the authors (H. G. R.) is indebted to the Carnegie Trust for a Teaching Fellowship.

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[Received, June 5th, 1935.]