XXVI.—*Optical Activity and the Polarity of Substituent Groups. Part VII.* sec.-*β-Octyl Esters of* o-, m-, *and* p-*Substituted Benzoic Acids.*

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In recent years a considerable amount of attention has been directed towards the influence of substituents on the physical and chemical behaviour of a parent compound. These researches have had to do with such diverse properties as benzene substitution, velocity of reaction, optical activity, dielectric constants, and physical state. As a result, it has been made abundantly clear that in nearly all these cases the main influence at work falls into one of two categories.

The first and most commonly observed influence is that usually described as the *general effect* of the substituent, which is regarded as being due to a general shift of the valency electrons away from an electropositive group such as CH_3, and towards an electronegative one such as NO_2, CO_2H, or Cl. This influence leads to a series of the following kind (I) representing a progressive change

$$NO_2,\ CO_2H,\ \text{halogens},\ OMe,\ H, Me, \quad . \quad . \quad . \quad (I)$$

as we pass from NO_2 to Me. An excellent example of this type has been furnished by Olivier (*Rec. trav. chim.*, 1923, **42**, 516, 775) in the velocity of hydrolysis of substituted benzyl chlorides, for which the above sequence (omitting OMe) has been found to hold, irrespective of the position of the substituent in the nucleus. Apart from occasional minor deviations, the same order of the groups is repeated in their influence on the velocity of a number of other reactions, on the dissociation of acids, and on the dielectric constants of aromatic and aliphatic compounds (Rule and Paterson, J., 1924, **125**, 2155; Höjendahl, *Nature*, 1926, **117**, 896; Errera, *Compt. rend.*, 1926, **182**, 1623). In addition, the general effect of substituents has been traced in their influence on the optical activity of menthyl and *sec.*-β-octyl esters of monosubstituted acetic acids (Rule and Smith, J., 1925, **127**, 2188; Rule and Mitchell, J., 1926, 3202).

The group effect of the second type is represented by a series such as

$$(NH_3{}^+),\ NO_2,\ CO_2H, CH_3{\cdot}CO, H,\ CH_3,\ I,\ Br,\ Cl,\ O{\cdot}CH_3,\ (CO{\cdot}O^-) \quad (II)$$

which indicates the relative influence of the substituents on the nitration of a monosubstituted benzene, and on the optical rotatory powers of the menthyl esters of *o*-substituted benzoic acids. An effect of this type, however, is not peculiar to benzene compounds, as it is also exhibited in the rotatory powers of the *d*-amyl derivatives, $C_4H_9\cdot CH_2X$, and in certain chemical reactions in which those groups which are *m*-directive in benzene substitution produce an effect in the opposite sense to those which are *o,p*-directive (Henderson and Macbeth, J., 1922, **121**, 892; Hirst and Macbeth, *ibid.*, p. 904). The actual positions of the electrically charged ionic complexes $-NH_3^+$ and $\cdot CO\cdot O^-$ in this series are somewhat indefinite, but there appears to be no doubt that the former is to be ranged on the left hand side of hydrogen and the latter on the right (Rule, J., 1927, 54).

In connexion with the directive powers of these groups on the course of benzene substitution, it has been suggested that the differences are related to the residual valency of the substituent atom, leading in some cases to actual or incipient electron-sharing between it and the attached carbon atom (Robinson, *J. Soc. Chem. Ind.*, 1925, **44**, 456; Allan, Oxford, Robinson, and Smith, J., 1926, 401; Ingold and Ingold, *ibid.*, p. 1310).

The present communication deals with the optical rotatory powers of a number of *sec.*-β-octyl esters of *o*-, *m*-, and *p*-substituted benzoic acids. In Table I will be found a summary of the values of $[M]_D^{20^\circ}$ obtained for the *o*-derivatives, together with those observed by Cohen (J., 1914, **105**, 1892) for the corresponding menthyl esters, and figures illustrating the influence of the substituents on benzene substitution. Table II records the rotatory powers of *sec.*-β-octyl esters of *m*- and *p*-substituted benzoic acids and the data referring to other properties mentioned above.

The rotatory power of *d*-β-octyl hydrogen phthalate in a number of solvents has already been determined by Pickard and Kenyon (J., 1907, **91**, 2058), who found, for example, $[M]_D^{20^\circ} = +135{\cdot}2^\circ$ in 5% alcoholic solution. The rotatory powers of this ester at different temperatures in the homogeneous state have now been measured for the purpose of discovering the sign of the temperature coefficient. The molecular rotation of the fused phthalate is $[M]_D = +91{\cdot}4^\circ$ at 90·5°, and increases slowly with fall of temperature. This value is very much lower than that quoted above for 5% alcoholic solution, and determinations were therefore made of the rotatory powers in alcohol and acetone at concentrations up to the saturation points (see Table III) in the hope of deducing the rotation corresponding to the ester in the homogeneous supercooled state at 20°. Unfortunately, the solubility of the compound proved too low for this to be accomplished. It could only be concluded from the rotation curves that the value lies between + 95° and + 117° and probably approximates to 95°. In a number of other solvents the solubility was very much lower than in alcohol and acetone.

TABLE I.

Molecular Rotatory Powers, $[M]_D^{20^\circ}$, *of Optically Active Esters of* o-*Substituted Benzoic Acids.*

Substit. X.	*l*-Octyl esters.	*l*-Menthyl esters.§	Nitration of C_6H_5X.‡ % *m*-.	% *p*-.
NO_2	−122°*	−381°	93	0·4
CO_2H	90—117	332	76	1·2
H	77·8 †	239	—	—
Me	68·1	231	3·1	41
I	44·3	237	—	66
Br	49·2	205	0·3	62
Cl	47·1	195	—	70
OMe	33·0 *	148	Chiefly *p*- and *o*-.	

TABLE II.

Molecular Rotatory Powers, $[M]_D^{20^\circ}$, *of* l-*Octyl Esters of* m- *and* p-*Substituted Benzoic Acids.*

X.	*m*-Esters.	*p*-Esters.	Dissoc. consts. of acids. 1 : 2-$C_6H_4X{\cdot}CO_2H$.	$CH_2X{\cdot}CO_2H$.	Hydrolysis of 1 : 3-$C_6H_4X{\cdot}CH_2Cl$.
NO_2	−107·8°	—119·7°*	0·62	—	0·044
CO_2H	—	119·1	0·121	0·158	0·109
OMe	93·7	113·3*	—	0·033	—
Cl	92·4	103·6	0·13	0·155	0·137
Me	94·0	103·5	0·013	0·001	1·30
H	77·8	77·8	0·007	0·002	1·00

TABLE III.

Rotatory Powers of d-*Octyl Hydrogen Phthalate.*

Solvent.	G./100 c.c.	$[M]_D^{20^\circ}$.	Solvent.	G./100 c.c.	$[M]_D^{20^\circ}$.
Alcohol (20°)	5·000	+134·0°	Acetone (20°)	5·000	+121·0°
,,	20·000	131·5	,,	20·000	120·1
,,	30·000	129·5	,,	30·000	119·6
,,	36·800	128·6	,,	35·000	119·1
Homog. (90·5°)	—	91·4 ‖			

* Rule and Numbers, J., 1926, 2116.

† Pickard and Kenyon, J., 1915, **107**, 122.

‡ Holleman, " Die direkte Einführung von Substituenten," 1910, p. 199.

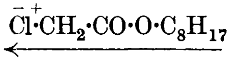
§ Cohen, *loc. cit.*

‖ This rotation increased slowly with fall of temperature. The recovered ester had a lower rotation than the initial material owing to the occurrence of slight decomposition in the fused state, hence it was not possible to obtain accurate values.

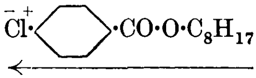
Influence of Substituents.—The values recorded in Table I show that ortho-substitution affects the rotatory power of *sec.*-β-octyl benzoate in precisely the same manner as it does that of menthyl benzoate. Substituents which are *m*-directive in type raise the rotation and those which are *o*, *p*-directive lower it. Further, the relative influence of the various substituents on rotatory power goes hand in hand with their relative influence on benzene substitution. A partial exception to this statement is found in iodine, which undergoes a small displacement in each of the columns.

On the other hand, the molecular rotations recorded for the *m*- and *p*-substituted esters reveal an influence of a totally different character. Here the *general effect* of the groups is plainly visible, the agreement, as might be expected, being more definite in the *p*- than in the *m*-series. In the *sec.*-β-octyl benzoates, therefore, we have for the first time an example of a series of optically active compounds in which both types of effect (I and II) can be clearly demonstrated.

An increase in the rotatory power of the benzoate, following on *p*-substitution by NO_2,Cl, or a similarly oriented dipole grouping, might have been anticipated from a knowledge of the rotatory powers of the substituted acetic esters. In both cases the introduction of the dipole should result in a shift of the electrons away from the asymmetric atom and hence to similar changes in rotation.



$$\underleftarrow{\overset{-\,+}{\mathrm{Cl}}\cdot\mathrm{CH_2{\cdot}CO{\cdot}O{\cdot}C_8H_{17}}}$$



A positively charged ionic complex should behave in the same manner. Nevertheless, the almost negligible change in the rotatory power of menthyl benzoate resulting from *m*- or *p*-substitution is a puzzling feature for which no adequate explanation can yet be advanced.

The general effect of a given group appears to vary somewhat with the compound and property under examination. In Table II, for instance, it is seen that the methyl group, instead of occupying its expected place below hydrogen in the series, at times falls in the position above it. Similarly, the relative positions of the three halogens among themselves are frequently found to undergo change. Variations of this kind are possibly due to a superimposed secondary influence resulting from molecular association. It is worthy of remark, however, that the general effect is a powerful one, and readily observed even when the substituent is several removes from the asymmetric carbon atom. The facility with which it is transmitted through long chains has already been commented upon by Robinson and Robinson (J., 1926, 2204).in connexion with the hydration of stearolic acid (compare also Olivier and Berger, *Rec. trav. chim.*, 1926, **45**, 710). The influence of type II, on the contrary, appears to be a comparatively local one. It cannot be traced in the menthyl or octyl esters of substituted acetic acids although it is visible in the amyl derivatives, $C_4H_9{\cdot}CH_2X$, where the substituent is only separated from the asymmetric atom by a single methylene group.

Dispersion.—Although the dispersion of most, if not all, of the homogeneous esters is probably complex, it is found that the graphs for $1/\alpha$ against λ^2, over the range λ_{5893} to λ_{4358}, approximate very closely to straight lines. The *o*-bromo- and *o*-toluic esters were examined over the range λ_{6708} to λ_{4358}, and gave linear graphs. The *o*-nitro- and *o*-methoxy-derivatives (*loc. cit.*) show definitely complex dispersion.

Values of the dispersion ratio, $\alpha_{4358}/\alpha_{5893}$, vary from 2·04 to 2·17, with abnormal values for the *o*-nitro-ester in alcohol (2·698) and for the *o*-methoxy-ester (1·51). In all cases the dispersion ratios tend to rise with temperature.

Influence of Temperature.—With one partial exception, all the octyl esters of substituted benzoic acids so far examined are affected similarly by a rise in temperature, in that the influence of the substituent—whether resulting in a depression or in an exaltation of the rotatory power of the parent compound—becomes less pronounced.

In the case of the *o*-toluic ester, however, the temperature variations are very small. Values of $[M]_{6708}$ fall slightly with increasing temperature, and those of $[M]_{4358}$ rise somewhat. For this compound there appears to be a maximum rotatory power between 20° and 90°, which occurs at a higher and higher temperature as the wave-length diminishes.

EXPERIMENTAL.

The active *sec.*-β-octyl alcohol required for the following preparations was obtained by the method of Pickard and Kenyon as modified by Kenyon (J., 1922, **121**, 2540). It had a rotation of $\alpha_D^{15^\circ} = \pm 8{\cdot}22^\circ$ ($\pm 0{\cdot}04^\circ$) in a 1-dcm. tube.

Special care was taken to ensure the purity of the initial materials. In the majority of cases the acids, as purchased or prepared, were purified by repeated crystallisation. Terephthalic acid was obtained from redistilled diethyl terephthalate by hydrolysis. Acid chlorides were prepared by means of purified thionyl chloride and were fractionated before use.

Unless otherwise stated, all the following esters were obtained in the form of colourless, odourless liquids.

d-β-*Octyl Hydrogen Terephthalate.*—Terephthalic acid was converted into the diacid chloride by treatment with phosphorus pentachloride and the acid chloride was recrystallised from benzene until pure, m. p. 75—78°.

Terephthalyl chloride (21 g.) was mixed with *d*-β-octyl alcohol

(26 g.) and pyridine (32 g.), and heated under reflux for 4 hours at 120°. The di-ester, which cannot be distilled without decomposition, was separated in the usual way; yield, 33—34 g. of crude product.

Earlier attempts to carry out the half hydrolysis of dioctyl terephthalate in methyl or ethyl alcoholic solution, with or without the addition of water, resulted only in the formation of methyl or ethyl hydrogen terephthalate. The crude ester (33 g.) was therefore made into an emulsion with a solution of potassium hydroxide (5·1 g.) in water (5 c.c.) and pure *d*-β-octyl alcohol (43 g.). After 2 days, the thick, creamy mixture was heated on the water-bath till nearly neutral. The product was diluted with water and any free alcohol and unchanged ester were extracted with ether. The aqueous solution was made acid and the precipitated octyl hydrogen terephthalate removed in ether. The washed and dried ethereal solution gave on distillation of the solvent 17 g. of crude ester, which readily solidified. After crystallisation from ligroin, it melted at 95—96° and had $[\alpha]_D^{19°} = + 45·17°$ in acetone ($l = 2$, $c = 5·004$). The rotatory power was not changed by three further recrystallisations. d-β-*Octyl hydrogen terephthalate* crystallises in large, transparent plates. It is readily soluble in ligroin and even more soluble in acetone (Found : C, 69·0; H, 8·2. $C_{16}H_{22}O_4$ requires C, 69·0; H, 8·0%).

d-β-*Octyl* o-*chlorobenzoate* was prepared in the usual way from *o*-chlorobenzoyl chloride (12 g.), *d*-β-octyl alcohol (9 g.), and pyridine (12 g.). Yield 16·0 g.; b. p. 180°/14 mm. The rotatory power did not change on further fractionation (Found : Cl, 13·4. $C_{15}H_{21}O_2Cl$ requires Cl, 13·2%). d-β-*Octyl* m-*chlorobenzoate* from *m*-chlorobenzoyl chloride is a liquid, b. p. 175°/12 mm. (Found : Cl, 13·3%). d-β-*Octyl* p-*chlorobenzoate* from *p*-chlorobenzoyl chloride boils at 177—178°/12 mm. (Found : Cl, 13·5%). d-β-*Octyl* o-*bromobenzoate* from *o*-bromobenzoic acid (m. p. 148·5—149°) is a colourless liquid, b. p. 175°/9 mm. (Found : Br, 25·3. $C_{15}H_{21}O_2Br$ requires Br, 25·5%). d-β-*Octyl* o-*iodobenzoate* from *o*-iodobenzoic acid (m. p. 162·5—163°) was obtained as a liquid, b. p. 202°/12 mm., which was coloured yellow owing to a trace of free iodine (Found : I, 35·3. $C_{15}H_{21}O_2I$ requires I, 35·25%).

d-β-*Octyl* o-*toluate* from *o*-toluic acid boiled at 154—155°/9 mm. (Found : C, 77·4; H, 10·0. $C_{16}H_{24}O_2$ requires C, 77·3; H, 9·75%). d-β-*Octyl* m-*toluate* from *m*-toluic acid boiled at 181·5—182°/17 mm. (Found : C, 77·3; H, 9·9%). d-β-*Octyl* p-*toluate* from *p*-toluic acid boiled at 184°/19 mm. (Found : C, 77·25; H, 9·9%).

Observed Densities and Rotations of the Homogeneous Esters.—The following rotations of the homogeneous esters were determined in a 1-dcm. tube, except in a few cases (marked *) where one of 0·5-dcm.

was employed. Densities were measured at four temperatures between 20° and 95°, in a pyknometer holding 3—5 c.c.

All rotations are of the same sign as that of the alcohol from which the esters are derived.

d-β-Octyl *o*-chlorobenzoate ($l = 1$).

$D_{4°}^{t°}$	1·0473 at 20°;	1·0319 at 39·0°;	1·0134 at 63°;	0·9960 at 85·0°.
α_{5893}	18·36° at 19·7°;	18·50° at 36·3°;	18·64° at 56·0°;	18·75° at 92·1°.
α_{5780}	19·17° at 19·8°;	19·27° at 36·3°;	19·64° at 55·3°;	19·54° at 95·3°.
α_{5461}	21·79° at 19·7°;	21·98° at 36·3°;	22·22° at 55·6°;	22·31° at 95·3°.
α_{4358}	36·90° at 19·8°;	37·52° at 36·3°;	38·20° at 55·3°;	38·85° at 95·6°.

d-β-Octyl *m*-chlorobenzoate ($l = 1$).

$D_{4°}^{t°}$	1·0425 at 20°;	1·0272 at 39°;	1·0087 at 63°;	0·9912 at 85°.
α_{5893}	35·87° at 20·0°;	34·89° at 35·0°;	33·39° at 61·2°;	31·87° at 94·3°.
α_{5780}	37·51° at 20·0°;	36·47° at 35·0°;	34·98° at 61·2°;	33·26° at 94·3°.
α_{5461}	42·74° at 20·0°;	41·53° at 35·0°;	39·87° at 61·2°;	37·88° at 94·3°.
α_{4358}	73·74° at 20·0°;	71·71° at 35·0°;	68·93° at 61·2°;	65·67° at 94·3°.

l-β-Octyl *p*-chlorobenzoate ($l = 1$).

$D_{4°}^{t°}$	1·0403 at 20·7°;	1·0257 at 39°;	1·0074 at 63°;	0·9902 at 85°.
α_{5893}	40·10° at 20·5°;	38·90° at 37·0°;	37·58° at 55·8°;	35·21° at 95·3°.
α_{5780}	42·02° at 20·5°;	40·72° at 37·0°;	39·33° at 55·8°;	36·66° at 95·3°.
α_{5461}	47·94° at 20·5°;	46·56° at 37·0°;	44·98° at 55·8°;	41·96° at 95·3°.
α_{4358}	83·96° at 20·5°;	81·44° at 37·0°;	78·86° at 55·8°;	73·75° at 95·3°.

d-β-Octyl hydrogen phthalate.

$D_{4°}^{t°}$ 1·027 at 72°; 1·022 at 80·6°; 1·016 at 90·5°; 1·015 at 92·5°

Rotations at 90·5° in 1-dcm. tube : $\alpha_{5893} = 33·40°$; $\alpha_{5780} = 35·02°$; $\alpha_{5461} = 40·46°$. The rotation of the fused acid falls slowly owing to decomposition. A re-examination of the same specimen gave $\alpha_{5461}^{92·5°} = 39·52°$; $\alpha_{5461}^{80·6°} = 39·99°$; $\alpha_{5461}^{72°} = 40·55°$.

d-β-Octyl *o*-bromobenzoate.

$D_{4°}^{t°}$	1·1987 at 24·6°;	1·1764 at 48·8°;	1·1623 at 64·1°;	1·1435 at 84·6°.
α_{6708}	14·09° at 21·0°;	14·23° at 38·6°;	14·34° at 65·2°;	14·32° at 89·5°.
α_{5893}	18·89° at 21·0°;	19·07° at 38·6°;	19·18° at 65·2°;	19·17° at 89·5°.
α_{5870}	19·66° at 21·0°;	19·88° at 38·6°;	20·00° at 65·2°;	20·02° at 89·5°.
α_{5461}	22·53° at 21·0°;	22·73° at 38·6°;	22·92° at 65·2°;	22·93° at 89·5°.
α_{4358}	39·23° at 21·0°;	39·74° at 38·6°;	40·33° at 65·2°;	40·47° at 89·5°.

d-β-Octyl *o*-iodobenzoate.

$D_{4°}^{t°}$	1·3522 at 18·9°;	1·3239 at 47·35°;	1·3131 at 58·3°;	1·2904 at 81·4°.
α_{6708}	12·33° at 18·3°;	12·74° at 40·4°;	13·03° at 60·5°;	13·33° at 89·0°.
α_{5893}	16·57° at 18·3°;	17·20° at 40·4°;	17·58° at 60·5°;	17·58° at 89·0°.
α_{5780}	17·33° at 18·3°;	17·95° at 40·4°;	18·38° at 60·5°;	18·70° at 89·0°.
α_{5461}	19·87° at 18·3°;	20·64° at 40·4°;	21·10° at 60·5°;	21·54° at 89·0°.
α_{4358}	Rotations could not be taken owing to the yellow colour of the ester.			

d-β-Octyl *o*-toluate.

$D_{4°}^{t°}$	0·9522 at 22·6°;	0·9345 at 45·6°;	0·9250 at 58·1°;	0·9073 at 80·9°.
α_{6708}	19·64° at 20·0°;	19·31° at 39·2°;	18·71° at 70·2°;	9·16°* at 90·3°.
α_{5893}	26·18° at 20·0°;	25·78° at 39·2°;	25·00° at 70·2°;	12·25°* at 90·3°.
α_{5780}	27·32° at 20·0°;	26·88° at 39·2°;	26·10° at 70·2°;	12·77°* at 90·3°.
α_{5461}	31·10° at 20·0°;	30·64° at 39·2°;	29·79° at 70·2°;	14·615°* at 90·3°.
α_{4358}	53·36° at 20·0°;	52·78° at 39·2°;	51·64° at 70·2°;	25·42°* at 90·3°.

l-β-Octyl *m*-toluate.

$D_{4^\circ}^{t^\circ}$ 0·9492 at 20°; 0·9245 at 52·9°; 0·8997 at 84·7°.
α_{5893} 36·09° at 17·6°; 34·38° at 48·2°; 33·31° at 66·0°; 32·94° at 74·6°; 15·91°* at 98·2°.
α_{5780} 37·72° at 17·6°; 36·18° at 43·2°; 34·82° at 66·0°; 34·41° at 74·6°; 16·64°* at 98·2°.
α_{5461} 43·04° at 17·6°; 41·36° at 43·2°; 39·74° at 66·0°; 39·32° at 74·0°; 18·96°* at 98·2°.
α_{4358} 74·97° at 17·6°; 71·89° at 43·2°; 69·20° at 66·0°; 68·72° at 73·5°; 33·10°* at 98·2°.

l-β-Octyl *p*-toluate.

$D_{4^\circ}^{t^\circ}$ 0·9492 at 20°; 0·9264 at 49·5°; 0·9025 at 80·3°.
α_{5893} 39·45° at 22·2°; 38·65° at 36·6°; 37·77° at 52·4°; 17·65°* at 98·7°.
α_{5780} 41·29° at 22·0°; 40·45° at 36·6°; 39·26° at 57·2°; 18·45°* at 98·7°.
α_{5461} 47·25° at 21·8°; 46·30° at 36·6°; 45·40° at 52·4°; 21·06°* at 98·7°.
α_{4358} 82·50° at 21·8°; 81·14° at 35·4°; 79·46° at 52·4°; 37·15°* at 98·7°.

Dispersion Ratios of the Homogeneous Esters.

	d-β-Octyl *o*-chlorobenzoate.		*d*-β-Octyl *m*-chlorobenzoate.		*l*-β-Octyl *p*-chlorobenzoate.		*d*-β-Octyl *o*-bromobenzoate.	
t.	$D_{4^\circ}^{t^\circ}$.	$\frac{\alpha_{4358}}{\alpha_{5893}}$.	$D_{4^\circ}^{t^\circ}$.	$\frac{\alpha_{4358}}{\alpha_{5893}}$.	$D_{4^\circ}^{t^\circ}$.	$\frac{\alpha_{4358}}{\alpha_{5893}}$.	$D_{4^\circ}^{t^\circ}$.	$\frac{\alpha_{4358}}{\alpha_{5893}}$.
20°	1·0473	2·010	1·0425	2·055	1·0411	2·092	1·2029	2·076
40	1·0313	2·029	1·0267	2·059	1·0252	2·098	1·1845	2·084
60	1·0156	2·043	1·0111	2·064	1·0097	2·098	1·1661	2·098
80	0·9997	2·061	0·9954	2·064	0·9941	2·097	1·1477	2·109
90	0·9918	2·067	0·9914	2·062	0·9903	2·096	1·1385	2·112
	l-β-Octyl *o*-toluate.		*d*-β-Octyl *m*-toluate.		*l*-β-Octyl *p*-toluate.		*d*-β-Octyl *o*-iodobenzoate.	
20	0·9542	2·038	0·9492	2·077	0·9492	2·089	1·3511	1·200†
40	0·9388	2·047	0·9339	2·076	0·9337	2·097	1·3313	1·200†
60	0·9235	2·059	0·9187	2·078	0·9182	2·104	1·3115	1·200†
80	0·9080	2·069	0·9035	2·080	0·9028	2·108	1·2918	1·203†
90	0·9003	2·074	0·8959	2·080	0·8951	2·110	1·2819	1·207†

† $\alpha_{5461}/\alpha_{5893}$.

Rotatory Powers of *d*-β-Octyl Hydrogen Terephthalate in Solution.

t.	Solvent.	G./100 c.c.	$[M]_{5893}$.	$[M]_{5780}$.	$[M]_{5461}$.	$[M]_{4358}$.	$\alpha_{4358}/\alpha_{5893}$.
20°	Acetone	5·004	125·5°	132·5°	149·2°	265·6°	2·12
18·3	Benzene	4·304	119·0	125·3	142·1	258·6	2·17
18·0	Alcohol	5·020	119·1	126·4	145·2	253·0	2·12

Summary.

The rotatory powers of a number of octyl esters of *o*-, *m*-, and *p*-substituted benzoic acids have been determined in the homogeneous state, with the following results.

1. The relative influence of *o*-substituents is given by $NO_2 > CO_2H > H > Me > Br > Cl > I > OMe$. Except for a small displacement of I, this series also represents the influence of the substituents on the rotatory power of menthyl benzoate and on benzene substitution.

2. In the *m*- and *p*-positions the influence of the substituents accords closely with their *general effect, e.g.*, for the *p*-series $NO_2 > CO_2H > OMe > Cl > CH_3 > H$. The electron-shift theory of the general effect being assumed, the change of rotation is in the direction anticipated from a knowledge of the rotatory powers of the substituted acetic esters.

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