CCLXXX.—*Optical Activity and the Polarity of Substituent Groups.*[*] *Part IV.* sec.-*β-Octyl Esters of* o-, m-, *and* p-*Methoxy- and Nitro-benzoic Acids.*

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In previous communications it has been shown that the rotatory powers of derivatives of optically active alcohols reveal the existence of at least two distinct types of substituent effect. Among *l*-menthyl esters of mono-substituted acetic acids (Rule and Smith, J., 1925, **127**, 2188) the influence of a number of simple substituents agrees closely with what has been termed the *general polar effect* of the groups, as observed in their influence on acidity, reaction velocity, and molecular inductive capacity (Rule and Paterson, *ibid.*, p. 2159).

Among the numerous menthyl esters of *o*-, *m*-, and *p*-substituted benzoic acids examined by Cohen, however, this relationship does not hold. In this case Cohen (J., 1914, **105**, 1895) observed that the facts could not be explained on the basis of Frankland's lever-arm theory, and drew the conclusion that the element or group lying nearest to the asymmetric atom produces the greatest effect, which according to the nature of the group may be an increase or decrease in rotation value, and that this value approaches the normal for the unsubstituted compound the further the substituent is removed from its proximity to the asymmetric group. It has recently been pointed out (Rule, J., 1924, **125**, 1122) that those *o*-substituents which raise the rotation of menthyl benzoate are *m*-directive in their effect on substitution in benzene, while those which depress the rotation are *o*-, *p*-directive, and that the relative effect of different substituents is in agreement with their relative polarity as deduced from the views of Sir J. J. Thomson and with their relative influence on benzene substitution as we pass from the strongly *m*-directive or positive nitro-group to the strongly *o*-, *p*-directive or negative fluoro-group (see also Rule and Smith, this vol., p. 553). A similar group effect appears to exist among certain simple aliphatic derivatives of active amyl alcohol.

Generally speaking, the esters of the cyclic alcohol, menthol, behave in a remarkably regular manner when examined from the point of view of optical activity. The majority of these compounds exhibit normal and apparently simple dispersion over the usual working range of wave-length, and their rotation undergoes little alteration with change of solvent and temperature. It was therefore considered of interest to investigate the influence of substituents on certain esters of *sec.*-β-octyl alcohol, since these compounds are known to be much more sensitive to alterations in molecular structure and external conditions (compare Pickard and Kenyon, J., 1914, **105**, 837; Hunter, J., 1924, **125**, 1389).

Esters of active octyl alcohol with *o*-, *m*-, and *p*-methoxybenzoic and nitrobenzoic acids have now been prepared, and their rotatory powers in the homogeneous state determined at temperatures between 20° and 95°. In the case of the methoxybenzoates, the values were measured for the D line and for the yellow, green, and violet mercury lines. Owing to the yellow colour of the nitro-derivatives, it was not found possible to obtain satisfactory readings for these compounds with the violet line, but readings over the range λ_D to λ_{vi} were also taken using a 5% alcoholic solution. The values of $[M]_D$ and α_{vi}/α_D found for the esters at different temperatures are summarised in the following tables.* Figures referring to light of other wave-lengths and to other rotations in solution are given in the experimental portion of this paper.

I. *Molecular Rotations and Dispersion Ratios of the Homogeneous Esters.*

d-*β-Octyl Methoxybenzoates.*

	o-Compound.		*m*-Compound.		*p*-Compound.	
Temp.	$[M]_D$.	α_{vi}/α_D.	$[M]_D$.	α_{vi}/α_D.	$[M]_D$.	α_{vi}/α_D.
20°	+33·27°	1·513	+93·73°	2·084	+113·3°	2·147
40	37·31	1·663	92·77	2·086	112·2	2·149
60	40·82	1·770	91·61	2·090	111·0	2·150
80	44·00	1·852	90·42	2·096	110·0	2·149
90	45·38	1·895	89·82	2·097	109·4	2·151

$[M]_D$ for d-*β-Octyl Nitrobenzoates.*

	o-Compound.	*m*-Compound.	*p*-Compound.
Temp.	$[M]_D$.	$[M]_D$.	$[M]_D$.
20°	+121·6°	+107·8°	(30°) 117·8°
40	119·6	104·2	115·9
60	117·6	101·0	112·3
80	116·1	98·2	109·6
90	115·4	97·0	108·8

For *d*-β-octyl benzoate Pickard and Kenyon (J., 1915, **107**, 122) find $[M]_D^{20°} = +77·84°$.

Rotations of Nitrobenzoic Esters in 5% *Alcoholic Solution* (*at about* 20°).

o-Compound.		*m*-Compound.		*p*-Compound.	
$[M]_D$.	α_{vi}/α_D.	$[M]_D$.	α_{vi}/α_D.	$[M]_D$.	α_{vi}/α_D.
155·8°	2·698	103·1°	2·047	120·2°	2·123

Dispersion.

When the reciprocal of the rotation is plotted against the square of the wave-length, a straight line is obtained for the homogeneous *m*-methoxy-compound at all temperatures and for the *p*-methoxy-compound at the two lower temperatures of experiment. It may therefore be concluded that the dispersion of these esters under the conditions stated is normal and apparently simple. The *o*-methoxy-ester exhibits complex dispersion, which is especially

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* These values are read off from the smooth curves drawn from the experimental figures. In every instance the sign of the rotation is the same as that of the active alcohol from which the ester is derived, and to avoid confusion certain values determined for *l*-esters are here tabulated—with change of sign—under the corresponding *d*-compounds.

marked at the lower temperatures employed, and the dispersions of the *o*-nitro-compound also are complex, although the graphs of $1/\alpha$ against λ^2 for the *m*- and *p*-isomerides in alcoholic solution approximate very closely to straight lines.

Both *o*-derivatives have abnormal dispersion ratios, the value of α_{vi}/α_D for the *o*-methoxy-ester being below and that for the *o*-nitro-ester above the value for the respective *m*- and *p*-compounds.

Influence of Substituents.

As may be seen from the above figures, the introduction of a methoxy-group into the *o*-position in the benzene nucleus leads to a marked depression in the rotatory power of octyl benzoate, whereas a nitro-group in the same position results in a considerable increase. As in the case of menthyl benzoate,* therefore, the *o*-, *p*-directive group produces a depression and the *m*-directive group an exaltation of rotatory power.

In the *m*- and *p*-positions both substituents bring about a rise in the rotatory power of the octyl ester, thus contrasting strongly with their behaviour in the menthyl compound, in which the effect of *m*- and *p*-substituents is in most cases negligible.

The values for the *o*-, *m*-, and *p*-derivatives are neither in agreement with Frankland's lever-arm hypothesis nor with the electrostatic modification of the latter suggested by one of us; nor do they lend support to the conclusion arrived at by Cohen (*loc. cit.*) from a study of the menthyl benzoates. It might be expected that the close relationship existing in certain cases between the influence of substituents on optical activity and acidity (Betti, *Gazzetta*, 1923, **53**, 417; Rule and Smith, *loc. cit.*) would also be evident in the octyl benzoates, particularly among the *m*- and *p*-derivatives, in which the strong specific effect of the *o*-group is absent. A comparison of the rotatory powers of the esters with the dissociation constants of the corresponding nitro- and methoxy-benzoic acids (quoted below) shows that the powerfully acidic nitro-group affects rotation and acidic strength qualitatively in the same manner, *viz.*, $o\text{-NO}_2 > p\text{-NO}_2 > m\text{-NO}_2 > \text{H}$, although for the resemblance to be complete the rotation of the *o*-nitro-ester should be much higher

	o.	*m.*	*p.*
NO_2	0·62	0·035	0·040 (benzoic acid, $k = 0{\cdot}0068$).
OMe	0·0082	—	0·0033

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* The rotations of the menthyl esters of α- and β-naphthoic acids are depressed in a similar manner by the introduction of a methoxy-group in the *o*-position to the carboxylic complex (compare Cohen and Dudley, J., 1910, **97**, 1750).

than that found.* This agreement does not extend to the very weakly acidic methoxy-group, which gives for rotatory powers the sequence *p*-OMe>*m*-OMe>H>*o*-OMe and for acidic strength *o*-OMe>H>*p*-OMe. It is remarkable that in the *p*-position the otherwise dissimilar nitro- and methoxy-groups produce the same pronounced increase in rotation.

An example of a different type which exhibits some points in common with the above is that of the substituted benzoylcarvoximes (Goldschmidt and Freund, *Z. physikal. Chem.*, 1894, **14**, 398).

Molecular Rotations of Substituted Benzoylcarvoximes (*in chloroform solution*).

Substit.	*o*-.	*m*-.	*p*-.	Substit.	*o*-.	*m*-.	*p*-.
Br	90·3	63·5	51·8	H	—	71·7	—
Me	76·6	76·0	66·3	NO_2	0	64·9	54·4

Here the *m*-directive nitro-group lowers the rotation when introduced into the *o*-position, and the *o*-, *p*-directive bromo- and methyl groups raise the value. The methyl group also increases the rotation in the *m*-position, but otherwise all *m*- and *p*-substituents depress the rotatory power. The case is thus closely analogous to that of the octyl benzoates, except that the changes are in the reverse direction. In passing, it may be noted that the relative influence of the different *o*-substituents, Br>Me>H>NO_2, is in agreement with their relative polarity and their relative influence on the substitution of benzene.

In general, the molecular rotations of the octyl esters fall with rise of temperature, as may be seen from the figures given in Table I. An exception is found in the *o*-methoxy-ester, the rotation of which increases with rise of temperature.

EXPERIMENTAL.

The active *sec.*-β-octyl alcohol required for this investigation was prepared from the racemic alcohol by the method of Pickard and Kenyon (J., 1907, **91**, 2058) as modified later by Kenyon (J., 1922, **121**, 2540). It had $[\alpha]_D^{16} = \pm 8{\cdot}14°$.

The esters were obtained from the corresponding acids by way of the acid chlorides, the combination of the latter with active alcohol being carried out in the presence of pyridine as a condensing agent. Purification was effected by fractionating the crude esters until of constant rotatory power. In general it was found that no further change in rotation occurred after the first fractionation.

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* The relatively high rotation of the *o*-isomeride is much more evident in alcoholic solution, especially when values for λ_{vi} are compared.

l-β-*Octyl* o-*methoxybenzoate* was prepared from *o*-methoxybenzoic acid obtained by the oxidation of pure *o*-tolyl methyl ether. It is a colourless, odourless liquid, b. p. 187·5°/13 mm. (Found : C, 72·6; H, 9·2. $C_{16}H_{24}O_3$ requires C, 72·7; H, 9·2%).

l-β-*Octyl* m-*methoxybenzoate* was obtained in a similar manner to the *o*-compound from *m*-tolyl methyl ether, which was oxidised to *m*-methoxybenzoic acid at the ordinary temperature by a 2½% solution of potassium permanganate (compare Oppenheim and Pfaff, *Ber.*, 1875, **8**, 887). The acid was purified by repeated crystallisation from ligroin till it melted sharply at 106°. The ester is a colourless, odourless liquid, b. p. 187·5°/12 mm. (Found : C, 72·6; H, 9·3. $C_{16}H_{24}O_3$ requires C, 72·7; H, 9·2%).

l-β-*Octyl anisate* (from anisic acid) is a colourless, odourless liquid, b. p. 189°/13 mm. (Found : C, 72·5; H, 9·2. $C_{16}H_{24}O_3$ requires C, 72·7; H, 9·2%).

l-β-*Octyl* o-*nitrobenzoate* was prepared from *o*-nitrobenzoyl chloride (Kahlbaum). The pale yellow ester is odourless, and boils at 204°/15 mm. (Found : C, 64·5; H, 7·8; N, 5·2. $C_{15}H_{21}O_4N$ requires C, 64·5; H, 7·6; N, 5·0%).

l-β-*Octyl* m-*Nitrobenzoate*.—The starting point in the preparation of this ester was *m*-nitrobenzaldehyde, which was purified by recrystallisation from ligroin. The *m*-nitro-ester was obtained as a pale yellow, odourless liquid, b. p. 212°/18 mm. (Found : C, 64·6; H, 7·6; N, 5·3. $C_{15}H_{21}O_4N$ requires C, 64·5; H, 7·6; N, 5·0%).

l-β-*Octyl* p-*nitrobenzoate* (from Kahlbaum's *p*-nitrobenzoyl chloride) is a pale yellow solid at the ordinary temperature. It was recrystallised from alcohol till of constant rotation. M. p. 29·5—30° (Found : C, 64·5; H, 7·7; N, 5·3%).

Densities and Rotatory Powers of the Esters in the Homogeneous State.

All rotations were measured in a 50 mm. tube. Densities were determined with the aid of a pyknometer holding between 3 and 4 c.c.

Observed Densities and Rotations.

l-*β*-Octyl *o*-methoxybenzoate.

$D_{4^\circ}^{t^\circ}$ 1·0004 at 20·3°; 0·9824 at 42·4°; 0·9699 at 57·9°; 0·9513 at 81·35°.
α_D 6·48° at 24·4°; 6·94° at 39·6°; 7·38° at 55°; 8·14° at 92·1°.
α_{ye} 6·60° at 24·4°; 7·14° at 39·6°; 7·67° at 55°; 8·49° at 92·1°.
α_{gr} 7·32° at 24·4°; 7·95° at 39·6°; 8·58° at 55°; 9·51° at 92·1°.
α_{vi} 10·01° at 24·4°; 11·45° at 39·6°; 12·95° at 55°; 15·48° at 92·1°.

l-*β*-Octyl *m*-methoxybenzoate.

$D_{4^\circ}^{t^\circ}$ 0·9939 at 20·42°; 0·9771 at 41·6°; 0·9641 at 58·2°; 0·9464 at 80·45°.
α_D 17·63° at 20·4°; 17·24° at 37·1°; 16·44° at 68·5°; 15·90° at 92·9°.
α_{ye} 18·43° at 20·4°; 18·03° at 37·1°; 17·17° at 68·5°; 16·59° at 92·9°.
α_{gr} 21·04° at 20·4°; 20·62° at 37·1°; 19·64° at 68·5°; 19·02° at 92·9°.
α_{vi} 36·76° at 20·4°; 36·05° at 37·1°; 34·52° at 68·5°; 33·33° at 92·9°.

l-β-Octyl *p*-methoxybenzoate.

$D_{4^\circ}^{t^\circ}$ 0·9940 at 23·9°; 0·9807 at 41°; 0·9677 at 57·9°; 0·9488 at 81·8°.
α_D 21·33° at 21·5°; 20·87° at 39°; 20·22° at 65·4°; 19·42° at 93·7°.
α_{ye} 22·33° at 21·5°; 21·88° at 39°; 21·08° at 65·4°; 20·23° at 93·7°.
α_{gr} 25·56° at 21·5°; 25·05° at 39°; 24·16° at 65·4°; 23·21° at 93·7°.
α_{vi} 45·81° at 21·5 ; 44·80° at 39°; 43·26° at 65·5°; 41·75° at 93·7°.

l-β-Octyl *o*-nitrobenzoate.

$D_{4^\circ}^{t^\circ}$ 1·0701 at 24·2°; 1·0560 at 41·8°; 1·0407 at 61·1°; 1·0234 at 82·5°.
α_D 23·26° at 23·5°; 22·70° at 38·3°; 21·77° at 65°; 20·98° at 92·2°.
α_{ye} 24·54° at 23·5°; 23·90° at 38·3°; 22·96° at 65°; 21·97° at 92·2°.
α_{gr} 28·88° at 23·5°; 28·07° at 38·3°; 26·92° at 65°; 25·90° at 92·2°.

d-β-Octyl *m*-nitrobenzoate.

$D_{4^\circ}^{t^\circ}$ 1·0725 at 24·1°; 1·0587 at 41°; 1·0453 at 57·4°; 1·0238 at 83·8°.
α_D 20·77° at 20·0°; 19·81° at 39°; 19·07° at 55·7°; 17·53° at 94°.
α_{ye} 21·68° at 20·0°; 20·76° at 39°; 20·00° at 55·7°; 18·40° at 94°.
α_{gr} 24·88° at 20·0°; 23·63° at 39°; 22·79° at 55·7°; 21·01° at 94°.

d-β-Octyl *p*-nitrobenzoate.

$D_{4^\circ}^{t^\circ}$ 1·0631 at 32·9°; 1·0471 at 52·75°; 1·0384 at 63·25°; 1·0248 at 80·1°.
α_D 22·00° at 39·1°; 21·05° at 58·4°; 20·22° at 76·5°; 19·75° at 91·9°.
α_{ye} 22·99° at 39·1°; 22·02° at 58·4°; 21·21° at 76·5°; 20·64° at 91·9°.
α_{gr} 26·44° at 39·1°; 25·27° at 58·4°; 24·22° at 76·5°; 23·65° at 91·9°.

II. *Specific Rotations of the Esters in the Homogeneous State.*

(For values of $[M]_D$ and α_{vi}/α_D see Table I.)

l-β-Octyl *o*-methoxybenzoate.

t.	$D_{4^\circ}^{t^\circ}$.	$[\alpha]_D$.	$[\alpha]_{ye}$.	$[\alpha]_{gr}$.	$[\alpha]_{vi}$.
20°	1·0006	−12·59°	−12·93°	−14·23°	−19·05°
40	0·9844	14·12	14·59	16·25	23·47
60	0·9683	15·45	16·07	17·97	27·35
80	0·9523	16·66	17·37	19·45	30·85
90	0·9443	17·18	17·94	20·08	32·55

l-β-Octyl *m*-methoxybenzoate.

20	0·9945	−35·48	−37·08	−42·33	−73·97
40	0·9785	35·11	36·65	41·90	73·27
60	0·9627	34·67	36·19	41·40	72·50
80	0·9467	34·23	35·70	40·94	71·77
90	0·9389	34·00	35·47	40·67	71·32

l-β-Octyl *p*-methoxybenzoate.

20	0·9968	−42·88	−44·90	−51·38	−92·07
40	0·9814	42·47	44·43	50·89	91·26
60	0·9661	42·03	43·93	50·31	90·36
80	0·9503	41·63	43·44	49·84	89·49
90	0·9427	41·39	43·20	49·52	89·02

l-β-Octyl *o*-nitrobenzoate.

t.	$D_{4^\circ}^{t^\circ}$.	$[\alpha]_D$.	$[\alpha]_{ye}$.	$[\alpha]_{gr}$.
20°	1·0735	−43·56°	−46·00°	−54·18°
40	1·0571	42·82	45·15	52·97
60	1·0410	42·15	44·38	52·03
80	1·0251	41·60	43·68	51·33
90	1·0172	41·35	43·33	51·08

d-β-Octyl *m*-nitrobenzoate.

20	1·0758	+38·61°	+40·31°	+46·25°
40	1·0594	37·32	39·12	44·59
60	1·0430	36·18	37·97	43·17
80	1·0266	35·18	36·92	42·02
90	1·0185	34·74	36·45	41·53

d-β-Octyl *p*-nitrobenzoate.

30	1·0655	+42·20°	+44·04°	+50·94°
40	1·0573	41·52	43·43	49·88
60	1·0410	40·21	42·15	48·24
80	1·0249	39·24	41·12	47·05
90	1·0168	38·97	40·75	46·68

III. *Rotations of Octyl Nitrobenzoates in Alcoholic Solution (approx. 5%).*

	o-Ester (5·0900 g. in 100 c.c.). *l* 50 mm.		*m*-Ester (5·1436 g. in 100 c.c.). *l* 200 mm.		*p*-Ester (5·0652 g. in 100 c.c.). *l* 200 mm.	
	$\alpha^{20\cdot8°}$.	[α].	$\alpha^{20\cdot2°}$.	[α].	$\alpha^{22\cdot3°}$.	[α].
α_D	1·42°	55·80°	3·80°	36·94°	4·36°	43·04°
α_{ye}	1·69	66·40	3·99	38·79	4·60	45·41
α_{gr}	1·90	74·65	4·51	43·84	5·19	51·23
α_{vi}	3·83	150·5	7·78	75·63	9·38	92·59

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