CCCXXXV.—*Optical Activity and the Polarity of Substituent Groups. Part XIII. Note on the Direct Space Effect in* d-*Amyl Derivatives.*

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In view of the conclusions as to the nature and incidence of the space effect arrived at in the preceding communication, it is of interest to examine whether this type of influence has any bearing on the optical properties of *d*-amyl derivatives.

As might be expected, chemical changes involving the hydroxyl groups of different optically active alcohols lead in general to similar changes in rotatory power. This has been established for a number of homologous series by Pickard and Kenyon and their co-workers and may be illustrated further by the figures in the following table, recorded in the literature for derivatives of the dissimilar alcohols *l*-menthol, *d*-*sec*.-β-octyl alcohol, and *d*-amyl alcohol. Despite the variety of the structural changes, the rotatory powers are similarly affected in each case.

Molecular Rotations, $[M]_D$.

R =	*l*-Menthyl.	*d*-Octyl.	*d*-Amyl.*
R·OH	− 78°	+ 11·99°	− 5·2°
R·OMe	−163	+ 12·5	+ 0·4
R·O·COMe	−154	+ 13·0	+ 3·2
R·O·CO·CH_2Cl	−171	+ 17·9	+ 5·1
R·Br	—	+ 53·1†	+ 5·6
R·O·CO·C_6H_4Me (*o*-)	−231	+ 68·1	+ 9·4
R·O·CO·C_6H_5	−239	+ 78	+ 9·5
R·O·CO·C_6H_4Me (*p*-)	−246	+103	+10·7

* The majority of these values are taken from Landolt's "Das optische, Drehungsvermögen."

† Pickard and Kenyon, *Ber.*, 1912, **45**, 1592; Houssa, Kenyon, and Phillips, this vol., p. 1700.

Now among the *l*-menthyl (I) and *sec.*-β-octyl esters (II) of monosubstituted acetic acids it has been shown that the predominant substituent influence is of the *general polar* type, which is also apparent in the dissociation constants (III) of the free acids (J., 1925, **127**, 2188; 1926, 3202). Data for the corresponding *d*-amyl derivatives are lacking, but from the similar properties of the

I. CN>Cl>Br>OH,OMe>Me>H
II. Br>Cl>OMe>Me>H
III. CN>Cl>Br>OMe,OH>H>Me

l-menthyl, β-octyl, and *d*-amyl series evident in the above table, coupled with the fact that *d*-amyl chloroacetate has a higher positive rotation than the unsubstituted ester, it may be deduced that the *general polar* effect operates in the same sense among *d*-amyl acetic esters. Hence substituents such as carboxyl and methoxyl, which also increase the dissociation constant of acetic acid, would be expected to resemble chlorine in raising the positive rotatory power.

On the other hand, *d*-amyl derivatives of the formula $C_4H_9\cdot CH_2X$, in which a simple highly polar substituent is only separated from the asymmetric centre by a single carbon atom, do not show any trace of the *general polar* effect. In this case the substituent influence, as has already been pointed out (J., 1927, 54), approximates to that observed among the ortho-substituted benzoic esters. Taking the indifferent group $X = C_2H_5$ as standard, the relative changes in positive rotation are given by

$$CO_2H > Et > Br > Cl > OMe > NH_2$$

as compared with $CO_2H > H > Me > Br > Cl > OMe > NH_2$ for the *d*-octyl *o*-substituted benzoates (Rule, Miles, and MacGillivray, this vol., p. 2274). In these series of compounds the ionisation of the amino- or carboxyl groups also leads to similar changes. Amylamine, like *d*-octyl anthranilate, has an increased positive rotation in the form of its hydrochloride; and from the behaviour of similar aliphatic acids, it may be concluded (*loc. cit.*) that the sodium salt of *d*-$C_4H_9{\cdot}CH_2{\cdot}CO_2H$ will resemble sodium *d*-octyl phthalate in having a diminished positive, or even a negative rotatory power. It is therefore very probable that these parallel changes arise from the same cause, namely, the overwhelming influence of the direct effect of the substituents propagated through space.

In the preceding communication it has been found that the direct space effect due to a positive pole or other *m*-directive substituent alters the rotation in the same direction as the general polar effect of the group, both tending to raise the rotatory power, whereas the direct effect due to a negative pole or *o,p*-directive substituent tends to lower the value. These findings are in agreement with the assumption of a direct effect in the *d*-amyl derivatives $C_5H_{11}X$. The positive pole $\overset{+}{N}H_3$ and the *m*-directive CO_2H give high positive values as compared with the relatively indifferent ethyl group, and the substituent influence is in the same direction as would have been predicted from the known *general polar* effect of chlorine in the chloroacetic ester. Low positive or negative values are given by *d*-amyl halides (as in many other cases, iodine is anomalous), the methyl ether, and the amine, in all of which X is an *o,p*-directive group. All the available evidence therefore supports the view that in these *d*-amyl derivatives the dominant substituent effect is identical with the direct space effect observed in ortho- and peri-substituted aromatic esters.

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