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CXX.—*The Relation of Position Isomerism to Optical Activity. IV. The Rotation of the Menthyl Esters of the Isomeric Nitrobenzoic Acids.*

By JULIUS BEREND COHEN and HENRY PERCY ARMES.

IN continuation of former work on this subject (Trans., 1903, **83**, 1213; 1904, **85**, 1262, 1271), we have examined the menthyl esters of the three nitrobenzoic acids.

The esters were obtained by the method previously described in former papers, namely, by converting the acid into the acid chloride and combining the latter with menthol.

Menthyl o-*Nitrobenzoate.*—Twenty grams of nitro-acid were heated with 26·5 grams of phosphorus pentachloride on the water-bath until further action had ceased. The product was heated to 110° *in vacuo* to remove the greater part (17 grams) of the phosphorus oxychloride. The residue was then frozen in ice and extracted with light petroleum to remove the remainder of the oxychloride. When the whole of the oxychloride is removed, the *o*-nitrobenzyl chloride remains solid at the ordinary temperature, and is not a liquid as described by previous observers. It is a colourless, crystalline compound, which melts at 21—23°. Fifteen grams of the pure acid chloride were heated in the oil-bath with an equal weight of menthol. The action set in vigorously at 110—120°, and when the evolution of hydrogen chloride ceased the product was made alkaline with sodium carbonate and distilled in steam until every trace of free menthol was removed. The residue was extracted with ether, dehydrated, and the ether removed by distillation. The light brown, solid residue, when crystallised from alcohol, formed large, colourless prisms which melted at 62—64°; 20 grams of acid yielded 21 grams of ester. A second preparation was made in the same way, and the product was found to be identical with the first.

0·5115 gave 31 c.c. moist nitrogen at 15° and 746 mm. N = 4·81.

$C_{17}H_{23}O_4N$ requires N = 4·59 per cent.

The following rotations were observed: (l = 30·2 mm.).

Preparation I.

Temperature.	Rotation.	Density.	$[\alpha]_D^{t^\circ}$.	$[M]_D^{t^\circ}$.
100°	−38·422°	1·050	−121·2°	−369·5°
80	39·952	1·058	125·0	381·5
70	40·380	1·073	124·6	380·3
65	40·622	1·078	124·8	380·9

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Preparation II.

Temperature.	Rotation.	Density.	$[\alpha]_D^{t°}$.	$[M]_D^{t°}$.
100°	−38·511°	1·050	−121·4°	−370·5°
80	39·770	1·058	124·4	379·7
70	40·210	1·073	124·0	378·4
65	40·680	1·078	125·0	381·5

Menthyl m-*Nitrobenzoate.*—This substance was prepared by heating together equal parts of *m*-nitrobenzoyl chloride (Kahlbaum) and menthol, the reaction beginning at 115—120°. The purification of the ester was conducted in the manner described under the ortho-compound. The substance is a viscid liquid, having a light brown colour, no doubt due to traces of impurity. A second preparation gave a similar product. Neither substance showed any signs of crystallisation even in a mixture of ice and salt.

0·4914 gave 20·8 c.c. moist nitrogen at 17·5° and 744 mm. N = 4·9.
$C_{17}H_{23}O_4N$ requires N = 4·59 per cent.

The following rotations were observed :

Preparation I.

Temperature.	Rotation.	Density.	$[\alpha]_D^{t°}$.	$[M]_D^{t°}$.
100°	25·980°	1·049	−82·04°	−250·3°
80	26·450	1·056	82·92	253·1
70	26·674	1·071	82·54	252·0
65	26·784	1·081	82·06	250·4
40	27·266	1·097	82·17	250·8
20	27·885	1·118	82·52	251·9

Preparation II.

100	25·972	1·049	82·00	250·2
80	26·520	1·056	83·14	253·7
70	26·757	1·071	82·71	252·4
65	26·920	1·081	82·49	251·8
40	27·430	1·097	82·71	252·4
20	27·933	1·118	82·77	252·6

Menthyl p-*Nitrobenzoate.*—The method used in the preparation of this substance was the same as that previously described. In one case, 5 grams of acid chloride gave 9 grams of ester, and in another, 20 grams of acid chloride gave 27 grams of ester. The ester when pure is a colourless solid which crystallises from alcohol in long prisms and melts at 61—63°. Both preparations had the same melting point.

0·5809 gave 23·9 c.c. moist nitrogen at 15° and 744 mm. N = 4·81.
$C_{17}H_{23}O_4N$ requires N = 4·59 per cent.

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The following rotations were observed:

Preparation I.

Temperature.	Rotation.	Density.	$[\alpha]_D^{t^\circ}$.	$[M]_D^{t^\circ}$.
100°	−23·810°	1·045	−75·48°	−230·4°
80	24·346	1·058	76·21	232·7
70	24·736	1·070	76·54	233·6
65	25·040	1·077	76·94	234·8

Preparation II.

Temperature.	Rotation.	Density.	$[\alpha]_D^{t^\circ}$.	$[M]_D^{t^\circ}$.
100	23·732	1·045	75·21	229·6
80	24·254	1·058	75·93	231·8
70	24·742	1·070	76·49	233·4
65	25·010	1·077	76·88	234·7

Conclusions.—The results of the above investigation confirm our previous observations on the effect of position isomerism on rotation. The *p*-nitro-group has the least and the *o*-nitro-group the greatest effect on the rotation, whilst the *m*-nitro-group occupies an intermediate position, having a specific rotation about 20° higher than the para compound. The main difference between the effect of the nitro-group and that of the halogens previously studied is that whereas the ortho-chlorine or bromine atom decreases the rotation, the nitro-group enormously increases it. This may be seen from the following table:

Menthyl Benzoate, $[M]_D^{20^\circ} = 236·3^\circ$ (Tschugaeff).

Menthyl nitro-benzoate (C. and A.).	$[M]_D^{t^\circ}$.	Menthyl chloro-benzoate (C. and B.).	$[M]_D^{20^\circ}$.	Menthyl bromo-benzoate (Tschugaeff).	$[M]_D^{20^\circ}$.
ortho-	−381·2 (65°)	ortho-	−195·0°	ortho-	−205·0°
meta-	251·1 (65)	meta-	236·9	meta-	238·7
para-	234·8 (65)	para-	237·3	para-	238·8

In the above table, the constants for the *o*- and *p*-nitrobenzoic esters are taken at 65°, that is, the lowest temperature at which the substances remained fused.

In regard to the effect of temperature on the constants for the three nitro-esters, it will be seen that in the case of the para-ester the rotation increases steadily with decreasing temperature.

The meta-ester fluctuates in a somewhat remarkable manner; the rotation increases as the temperature falls from 100° to 80°, and it then diminishes until the temperature passes 65°, when it again increases slightly as the temperature falls to 20°. The ortho-ester behaves

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similarly. The differences are not great in the present case, but they serve to illustrate the uncertainty of the method of extrapolating from a few observations within limited ranges of temperature.

The authors hope to publish shortly their results on the rotation of the ten isomeric chloronitrobenzoic esters.

APPENDIX.—By R. P. D. GRAHAM, B.A.

Note on the Crystallographic and Optical Properties of the Menthyl Esters of ortho- and para-Nitrobenzoic Acids.

Menthyl o-*Nitrobenzoate.*—About twelve of these crystals, obtained from solution in alcohol, were received from Prof. Cohen for measurement and optical determination. The crystals were well developed, having in general bright, smooth faces, and some of them were more than 15 mm. long and 5 mm. across; they are quite transparent, the faces having a somewhat brilliant lustre; the hardness is rather more than 2 in Mohs' scale; the crystals are very brittle, and show a tendency to break somewhat easily at right angles to the prism faces with a flat-conchoidal fracture; there is a perfect cleavage parallel to $A(100)$.

The crystals belong to the orthorhombic system, and are prismatic in habit; they all exhibited the forms $A\{100\}$, $M\{110\}$, $D\{011\}$, but were of two quite distinct habits. In the first of these, the crystals are flattened parallel to $A(100)$, as represented in the figure, and in the second this form is represented by a pair of narrow faces, whilst the rhombic prism $M\{110\}$ predominates.

In the case of many of the crystals of habit (1), the faces A were drusy, being composed in reality of a polysynthetic growth of the prism $M\{110\}$.

Since solutions of menthyl *o*-nitrobenzoate in various solvents are optically active, it became a matter of interest to observe whether the crystals themselves exhibit hemihedrism of a right- and left-handed character; and evidence that such actually is the case was found in the occurrence on two of the crystals of the bisphenoid $O\{111\}$, truncating alternate edges $[AD]$, so that the substance belongs to the bisphenoidal class of the orthorhombic system. Further, as would be expected in crystals taken from the same solution, the orientation of the bisphenoid was the same on both specimens. All the crystals examined were single individuals—there were no twin crystals. The measurement of the crystals gave the following results:

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System: Orthorhombic.
Symmetry: Digonal holoaxial (bisphenoidal class).
$a : b : c = 1{\cdot}4568 : 1 : 0{\cdot}8532$.
Observed forms: $A\{100\}$, $M\{110\}$, $D\{011\}$, $O\{111\}$.

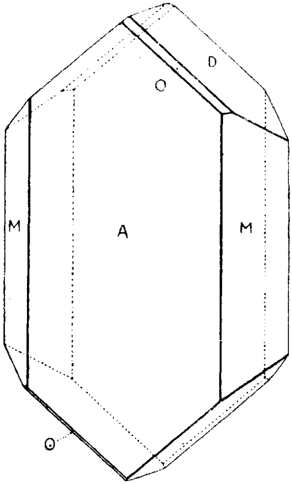

FIG. 1.—*Menthyl* o-*nitrobenzoate*.

Angle.	No.	Limits.	Mean.	Calculated.
*$AM = 100 : 110$	19	55°12′ — 55°42′	55°32′	—
$MM = 110 : \bar{1}10$	9	68 21 — 69 24½	68 54	68°56′
$AO = 100 : 111$	4	65 56½ — 66 6	66 0	65 59¼
$OD = 111 : 011$	5	23 48 — 24 3½	23 56½	24 0¾
$MO = 110 : 111$	—	—	—	44 1¼
$MD = 110 : 011$	32	57 12 — 58 1	57 37½	57 38¾
*$DD = 011 : 0\bar{1}\bar{1}$	20	80 41 — 81 8	80 56½	—
$OO = 111 : \bar{1}\bar{1}1$	—	—	—	91 57½
$OO = 111 : 1\bar{1}\bar{1}$	—	—	—	131 58½
$DD = 011 : 01\bar{1}$	13	98 30 — 99 23	99 2	99 3½
$MD = 110 : 0\bar{1}1$	33	121 17 —122 59	122 23	122 21¼
$101 : \bar{1}01$	—	—	—	60 42¾

* Angles used for calculations.

Optical Properties.

Viewed between crossed nicols in parallel light, the cleavage fragments show straight extinction with the prism edges, and in convergent light a symmetrical figure is obtained, but no optic axes are visible, the cleavage being perpendicular to the obtuse bisectrix.

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Compensation takes place when the quartz wedge is inserted over the crystal with its axis along the prism edges.

As already mentioned, the crystals break rather easily in a direction at right angles to the prism faces, and sections cut in this direction exhibit the acute bisectrix emerging normally. The biaxial interference figure obtained is symmetrical, but broad fringes of colour take the place of the usual black hyperbolic brushes, owing to the strong dispersive power of the substance; the fringes are blue on the convex side and red on the concave ($\rho < v$). The extent of the dispersion was measured by determining the refractive indices of the substance for red, yellow, and green light, and is given below. The birefringence is strong and negative.

The optic axial angle (for sodium light) was determined both in air ($2E$) and also when the crystal was immersed in oil ($2H$); the results are given below, together with the true (internal) angle between the optic axes ($2V$) as calculated from the observed angles $2H_a$ and $2H_o$ (for cedar oil).

The angle $110 : 1\bar{1}0$ for this substance being not far removed from 60°, renders a natural prism very convenient for the measurement of the refractive indices, double refraction, and dispersion; and in such a prism, used to determine the indices by the method of minimum deviation, the light travels through the crystal along the crystal-axis b, which is perpendicular to the plane of the optic axes, so that the two indices obtained correspond to the maximum and minimum refraction (γ and α), and their difference gives a true measure of the double refraction ($\gamma - \alpha$). The remaining index, β, is calculated from the optic axial angle by the formula $\beta = \frac{\mu . \sin H_a}{\sin V_a}$, μ being the refractive index of the oil in which the crystal was immersed to give H_a.

All the above optical characters are tabulated below.

Birefringence, negative, strong.

Axial plane, $B(010)$; Ac. Bis. $\perp$ $C(001)$.

Refractive indices:

	Red (Li).	Yellow (Na).	Green (Tl).
α	1·49270	1·49657	1·50033
β	—	1·5203	—
γ	1·56591	1·57219	1·57812
$\gamma - \alpha$.........	0·07321	0·07562	0·07779

Dispersion, very strong, $\rho < v$.

Axial angle narrow; for sodium light:

$$2V = 30°32' : 2E = 47°24'.$$

$$2H_a = 31°55' \text{ (Olive oil, } \mu = 1·4707).$$

$$\left.\begin{array}{l} 2H_a = 30°25' \\ 2H_o = 148°1' \end{array}\right\} \text{(Cedar oil, } \mu = 1·526).$$

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Pleochroism slight; the crystal is pale brown when the short axis of the nicol is parallel to the crystallographic axis *C*, darker when it is parallel to *B*, and a still deeper brown when it coincides with *A*.

Menthyl p-*Nitrobenzoate.*—These are pale yellow crystals, obtained from solution in alcohol; they are of prismatic habit and vary in length from 1 or 2 mm. to about 5 mm. They are extremely soft and easily break, either with a conchoidal to uneven fracture, or else along the face *B*(010), parallel to which there is a perfect cleavage The more perfect crystals are transparent, and the faces in the prism zone, especially the cleavage surfaces, have a brilliant lustre suggestive of a high refractive power. The following geometrical relations were calculated from measurements made on 15 crystals:

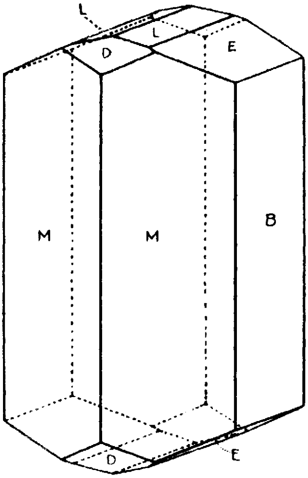

FIG. 2.—*Menthyl* p-*nitrobenzoate.*

System: Orthorhombic.

Symmetry: ? Holosymmetric (Bipyramidal).

$a:b:c = 0{\cdot}46622:1:0{\cdot}43349$.

Observed forms: *B*{010}, *M*{110}, *H*{210}, *K*{230}, *D*{101}, *E*{011}, *L*{012}.

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Angle.	No.	Limits.	Mean.	Calculated.
**MM* = $110 : 1\bar{1}0$	8	49°56½′ — 50° 4½′	49°59½′	—
HH = $210 : 2\bar{1}0$	—	—	—	26°14½′
KK = 230 : 280	—	—	—	69 56
EE = $011 : 0\bar{1}1$	—	—	—	46 52½
LL = $012 : 0\bar{1}2$	8	24 6½ — 24 47½	24 30	24 27½
DD = $101 : \bar{1}01$	4	85 37 — 86 3	85 51	85 50
BM = 010 : 110	18	64 57 — 65 4	65 0¼	65 0¼
**BE* = 010 : 011	16	66 20½ — 66 48	66 33¾	—
EL = 011 : 012	12	11 0 — 11 36½	11 11½	11 12½
BK = 010 : 230	4	54 27 — 55 27½	55 4	55 2
KM = 230 : 110	5	9 37½ — 10 30	10 0	9 58¼
HM = 210 : 110	3	11 45 — 12 2	11 53	11 52½
ME = 110 : 011	13	80 0 — 80 34	80 19½	80 19½
MD = 110 : 101	8	51 38 — 52 2	51 52½	51 53½
DE = 101 : 011	13	47 32 — 48 1½	47 48½	47 47

* Angles used for calculations.

The majority of the crystals were prisms terminated at each end by a broken surface; but a number were picked out bearing faces at the ends which gave good images of the collimator slit; most of the latter exhibited faces of the domes *E*{011} and *L*{012}; *D*{101} was less common, and the forms *H*{210} and *K*{230} were only found as narrow faces in a few cases. These crystals were in many cases doubly terminated, and were found to bear the same forms at each end; the usual habit is represented in the figure. Some of the crystals, however, were extremely thin plates with bevelled edges; the measurement of these showed that in all cases the flattening is parallel to *B*{010}.

Although solutions of this substance exhibit optical activity, none of the crystals measured showed any indication of hemihedrism; the forms observed, lying as they do in the three principal zones only, would not be affected, so far as the number of faces they exhibit is concerned, by enantiomorphous hemihedrism.

In order to obtain evidence of the true symmetry, a number of the crystals were exposed to the action of solvents, and the minute pits etched on the faces were examined; the etching was conveniently effected by momentarily introducing a crystal just within the neck of a bottle containing benzene, when the vapour produces a number of small pits all over the previously plane surfaces; but no evidence was obtained from the examination of the etched figures which would lead to the view that the crystals are other than holosymmetric.

No evidence of twinning was found among the crystals examined.

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Optical Properties.

The crystals extinguish parallel to the prism edges when viewed through the faces *M* or *B* between crossed nicols in parallel light. That the birefringence is very strong is shown by the fact that even very thin flakes yield white of higher orders between crossed nicols, and also by the thickness of quartz required to compensate. When thin cleavage flakes, parallel to *B*(010), are examined, the quartz wedge compensates when it is placed over the crystal with its axis perpendicular to the prism edges.

In convergent light, an optic axis belonging to a biaxial interference figure emerges well within the field of view in air when the crystal is lying on a face *M*{110}, and the axial plane is seen to lie at right angles to the prism edges; the obtuse bisectrix (positive) emerges normally through cleavage flakes. To measure the acute angle between the optic axes, it is therefore necessary to cut a section at right angles to *B*(010) and parallel to *A*(100), which is not among the forms occurring on the crystals. On immersion in cedar oil, such a section gives the customary biaxial figure; the axial angle is small, and the hyperbolic brushes are replaced by very broad fringes of colour, which are tinged red on the convex and blue on the concave side ($\rho > v$), showing that the substance has a very high dispersive power. The acute angle between the optic axes, $2H_a$, was measured in cedar oil, and for sodium light is 18°20′.

The obtuse angle, $2H_o$, cannot be measured in this way by employing a cleavage flake, on account of the wide angle; the true angle, $2V_a$, was, however, calculated from the relations in $V_a = \frac{\mu}{\beta} \sin H_a$ and found to be 17°19′.

The refractive indices β and γ were determined by the method of minimum deviation, using the natural prism faces, *MM*, $110 : \bar{1}10 = 50°0'$; the remaining index, α, was obtained approximately by the use of H. Smith's total reflectometer. For yellow light, the indices are

$$\alpha = 1{\cdot}472\ ;\ \beta = 1{\cdot}6151\ ;\ \gamma = 1{\cdot}6192\ ;\ \gamma - \alpha = 0{\cdot}147.$$

The angle $2V_a$ calculated from these indices is 17°54½′, which agrees fairly well with the value 17°19′ given above, and affords a check on its accuracy.

The birefringence is thus very strong, but it is interesting to note that although there is this large difference between γ and α, yet $\gamma - \beta$ only amounts to 0·004. These differences are well brought out in determining the indices by the minimum deviation method. Using the prism $110 : 1\bar{1}0 = 50°$, the images due to the β- and γ-

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rays are almost superposed, being separated by only 0°33′; on the other hand, the prism *BM*, $010:1\bar{1}0 = 65°$, gives two widely separated readings for minimum deviation, the actual figures being $2D = 110°49'$, which gives the index $\beta = 1{\cdot}6151$, and $2D = 86°19'$, which gives an index having a value, 1·507, between those of α and γ, that is, very much less than the mean index, β.

The index β was also determined for red (lithium) light and found to be 1·6071, which, by comparison with the value for yellow light, gives an indication of the very strong dispersion of the substance.

The optical characters are tabulated below:

Birefringence, negative, very strong.

Axial plane, $C(001)$; Ac. Bis. ⊥ $A(100)$.

Refractive indices: For yellow (Na) light, $\alpha = 1{\cdot}472$; $\beta = 1{\cdot}6151$; $\gamma = 1{\cdot}6192$; $\gamma - \alpha = 0{\cdot}147$. For red (Li) light, $\beta = 1{\cdot}1071$.

Dispersion, very strong; $\beta_{Na} - \beta_{Li} = 0{\cdot}008$.

Axial angle narrow: $2V = 17°19'$. $2H_a = 18°20'$ from cedar oil, $\mu = 1{\cdot}526$.

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