

**Chemistry.** — *Investigations on Complex Salts of racemic and optically-active Cyclohexane-1-2-diamines with Trivalent Cobaltum and Rhodium. I. On trans-Cyclohexane-1-2-diamine and its Fission into optically-active Antipodes.* By F. M. JAEGER and L. BIJKERK.

(Communicated at the meeting of December 19, 1936).

§ 1. The quantity of 1-2-diamino-cyclohexane necessary for the investigations on complex salts was obtained in the way previously described<sup>1)</sup>: starting with pure cyclohexanone, first the cyclohexanone-oxalylester and then the corresponding cyclohexanone-carboxylic-ester of boilingpoint: 105°—106°.5 C. (under 12 mm. pressure) were prepared; the yield of the latter varied between 42—52 % of the theoretically expected quantity. Some cyclohexanone-oxalylic-acid of the meltingpoint: 122° C. was, as a by-product, obtained in beautiful crystals<sup>2)</sup>. The carboxylic ester was transformed into cyclohexane-dion-monoxime; the latter proved to be a viscous liquid, which could not be obtained in the crystalline state. The yield of it was about 86—87 % of the theoretical one. By means of hydroxylamine, the monoxime was transformed into the solid dioxime, which can readily be recrystallised from water and which has a meltingpoint of 187—189° C.

Cyclohexane-1-2-diondioxime crystallizes from water on slow evaporation in small colourless crystals with very lustrous faces and perfectly constant angular values. They are rhombic-bipyramidal, with:

$$a : b : c = 1.4938 : 1 : 0.9283.$$

Forms observed:  $m = \{110\}$ , predominant, highly lustrous;  $a = \{100\}$ , narrower than  $m$ , yielding good reflections, like the much narrower form  $b = \{010\}$ ;  $o = \{111\}$ , well developed and giving very sharp reflections;  $q = \{021\}$ , well reflecting, often absent, the occurrence of  $\{001\}$  as a limiting form is dubious. The habitus of the crystals is that of prismatic needles, flattened parallel to two faces of  $m$ . The crystals from acetone which are rudimentarily developed ordinarily are tables parallel to  $\{001\}$  or to two faces of  $\{111\}$ , with  $m$  predominant,  $b$  well developed,  $q$  small; moreover,  $c = \{001\}$  or two planes of  $\{111\}$ , only rudimentary and badly reflecting;  $\{100\}$  is altogether absent in this case. (Fig. 1).

<sup>1)</sup> F. M. JAEGER and J. A. VAN DIJK, Proc. Royal Acad. Amsterdam, 39, 384, 392 (1936).

<sup>2)</sup> Ibidem, loco cit. p. 391.

<i>Angular Values:</i>	<i>Observed:</i>	<i>Calculated:</i>
$a : m = (100) : (110) =$	$*56^{\circ} 12'$	—
$m : o = (110) : (111) =$	$*41 \quad 50$	—
$b : o = (010) : (111) =$	$51 \quad 46$	$51^{\circ} 44\frac{3}{4}'$
$o : o = (111) : (\bar{1}\bar{1}\bar{1}) =$	$96 \quad 20$	$96 \quad 20$
$b : m = (010) : (110) =$	$33 \quad 48$	$33 \quad 48$
$o : o = (111) : (\bar{1}\bar{1}\bar{1}) =$	$76 \quad 28$	$76 \quad 30\frac{1}{2}$
$o : o = (111) : (\bar{1}\bar{1}\bar{1}) =$	$48 \quad 56$	$48 \quad 58$
$b : q = (010) : (021) =$	$28 \quad 27$	$28 \quad 18\frac{1}{2}$

Normal extinction on  $m$ ,  $a$  and  $b$ . The plane of the optical axes is  $\{001\}$ .

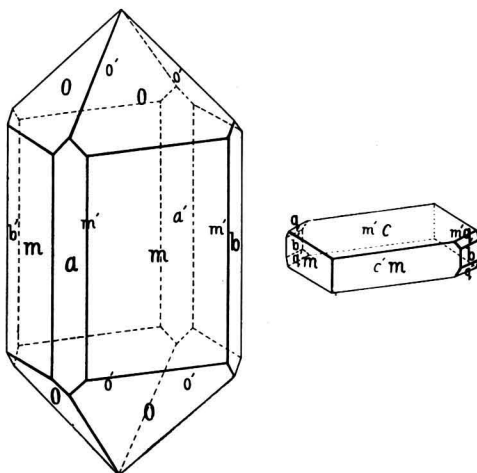


Fig. 1. *Crystalform of Cyclohexane-1-2-dion-dioxime.*

The compound forms complex *nickel*-salts which are characterized by their beautiful, deep violet-red colour. This *dioxime* was finally reduced by means of an excess of sodium and absolute alcohol in the way previously described; the different bases generated in this process were isolated in the form of their hydrochlorides and subsequently set free from those by means of caustic potash. The liquid mixture, after having carefully been dried over potassiumhydroxide and metallic sodium, then was subjected to a fractionated vacuum-distillation. Three different fractions could be isolated:

The first fraction yields a colourless base, which boils at  $37^{\circ}$  C. under a pressure of 15 mm. and at  $134^{\circ}$ — $135^{\circ}$  C. under the ordinary pressure. This substance proved to be *monobasic*; it is the *mono-amino-cyclohexane*:  $C_6H_{11} \cdot NH_2$  and forms a *benzoyl*-derivative, which melts at  $146^{\circ}$ — $147^{\circ}$  C.

The second fraction consists of the *diamino-cyclohexane* itself; this base boils at  $80^{\circ}$ — $82^{\circ}$  C. under a pressure of 12 mm. and melts at  $14^{\circ}.8$  C. With *benzoylsulfochloride* it forms a derivative melting at  $153^{\circ}$ — $155^{\circ}$  C.

The third fraction boiled at 100°—105° C. under 12 mm. pressure: it unexpectedly, however, did *not* consist of the *phenazine*-base already previously isolated by WALLACH <sup>1)</sup>. The substance readily crystallizes from a number of organic solvents and also very beautifully from water. We found a meltingpoint considerably higher than that of WALLACH's base: 138° C., in stead of 106°—108° C., as mentioned by this author. Its analysis yielded the following results: C: 74.05 %; H: 11.32 %; N: 14.31 %; calculated for  $C_{12}H_{22}N_2$ : 74.2 % C; 11.34 % H and 14.43 % N. The base: a *tetradecahydrophenazine* is identical with the  *$\alpha$ -bistetramethylenepiperazine* described by GODCHOT and MOUSSERON <sup>2)</sup>. It crystallizes from water with 1  $H_2O$ , which *cannot* be removed in vacuo, but only by dissolving the substance in anhydrous ether and thoroughly drying the solution over metallic sodium. It is very volatile, sublimes rapidly and can be distilled with water-vapour. The meltingpoint of 132° C. mentioned by the French authors is that of the *hydrate*; the *anhydrous* base melts at 137°—138° C. The *hydrochloride* crystallizes with 3  $H_2O$ ; analysis yields: 16.82 %  $H_2O$ ; 8.57 % N and 22.14 % Cl; calculated: 16.82 %  $H_2O$ ; 22.12 % Cl and 8.72 % N.

The *hydrochloride*:  $C_{12}H_{22}N_2, 2HCl + 3H_2O$ , crystallizes from its aqueous solutions on slow evaporation in small, thin, hexagonally-bordered tables, which are semi-transparent and have a mother-of-pearl-like luster. The crystals are *rhombic-bipyramidal*, with  $a : b : c = 2.115 : 1 : 0.782$ .

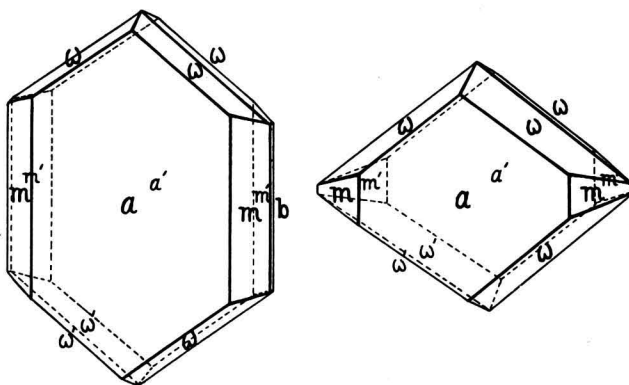


Fig. 2. Crystalform of  $\alpha$ -Bistetramethylenepiperazine-hydrochloride (+ 3 $H_2O$ ).

*Forms observed*:  $a = \{100\}$ , predominant, finely vertically-striated;  $\omega = \{111\}$ , about as broad as  $m = \{210\}$ ; but more lustrous than the latter

<sup>1)</sup> O. WALLACH, Lieb. Ann. d. Chem., **437**, 177 (1924): the dioxime was here reduced by means of  $KOH$  and  $Zn$ . Although the properties of this base are in some respects comparable with those of our base, the two substances yet were proved to be quite different ones.

<sup>2)</sup> M. GODCHOT and M. MOUSSERON, Compt. rend. Paris, **190**, 442 (1930); Bull. Soc. Chim., (4), **51**, 360 (1932).

form;  $b = \{010\}$ , very narrow, often absent. The habitus is thinly-tabular parallel to  $\{100\}$ :

Angular Values:	Observed:	Calculated:
$\omega : \omega = (111) : (\bar{1}\bar{1}\bar{1}) =$	$^*72^\circ 24'$	—
$a : \omega = (100) : (111) =$	$^*73 47$	—
$a : m = (100) : (210) =$	46 44	$46^\circ 36'$
$m : \omega = (110) : (111) =$	51 23	$51 36\frac{1}{2}$
$\omega : \omega = (111) : (\bar{1}\bar{1}\bar{1}) =$	32 26	32 26
$\omega : \omega = (111) : (\bar{1}\bar{1}\bar{1}) =$	98 20	98 25

The crystals are perfectly cleavable parallel to  $\{100\}$ .

The plane of the optical axes is  $\{001\}$ , with the  $a$ -axis as the first bisectrix. The double refraction is negative. The apparent angle of the optical axes is rather small; but the dispersion is very strong. Probably the axial planes for violet and yellow are perpendicular to each other.

From the higher boiling fraction (about  $100^\circ \text{C}$ . under 14 mm. pressure)

also a very small quantity of a *hydrochloride* was obtained, which from an aqueous solution containing an excess of hydrochloric acid crystallizes in small, apparently trigonal pyramids. In reality they prove to be rhombic bisphenoids, truncated by small faces of a prism. (Fig. 3).

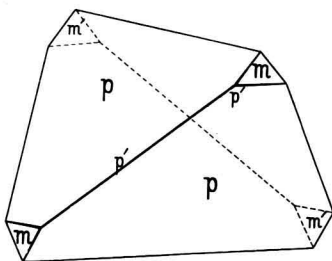


Fig. 3. *Crystal form of l-Cyclohexanediamine-hydrochloride.*

The crystals are anhydrous; analysis yielded: 37.81 % Cl; 14.27 % N; calculated: 37.97 % Cl and 14.9 % N.

Although the nitrogen-value is too low, there is no doubt as to the substance being the hydrochloride of the base mentioned.

*Rhombic-bisphenoidal.* Axial ratio:  $a : b : c = 0.6831 : 1 : 0.7935$ .

*Forms observed:*  $p = \{1\bar{1}1\}$ , predominant, lustrous, but often yielding somewhat oscillating angular values;  $m = \{110\}$ , much smaller than  $p$ , but giving splendid reflections.

Angular Values:	Observed:	Calculated:
$m : m = (110) : (\bar{1}\bar{1}0) =$	$^*68^\circ 35'$	—
$m : p = (\bar{1}\bar{1}0) : (\bar{1}\bar{1}\bar{1}) =$	$^*54 42$	—
$p : p = (\bar{1}\bar{1}\bar{1}) : (\bar{1}\bar{1}\bar{1}) =$	109 24	$109^\circ 24'$
$m : p = (110) : (\bar{1}\bar{1}\bar{1}) =$	73 1	$72 45\frac{1}{2}$
$p : p = (\bar{1}\bar{1}\bar{1}) : (\bar{1}\bar{1}\bar{1}) =$	95 30	95 24

No distinct cleavability could be stated.

It is quite inconceivable in what way the crystals of this antipode have been formed. Originally we thought that the hydrochloride perhaps would manifest the phenomenon of a fission by spontaneous crystallization. For this reason the solubilities as well of the racemic as of the optically-active base were gravimetrically determined between 20° and 34° C.

Temperature t in °C	Grammes of the Salt in 100 Gr. of the Solution:		Grammes of the Salt in 100 Gr. of the Solute:	
	Racemic:	Opt. active:	Racemic:	Opt. active:
20°	45.35	46.72	82.99	87.69
26.1	46.41	47.54	86.60	90.62
30	47.14	48.17	89.19	92.94
33.7	47.86	48.70	91.78	94.93

From this follows that the racemic salt, being the more stable one, is less soluble than the optically-active; moreover, from the course of the solubility-lines it is seen that *no* intersection of them takes place at the ordinary and even much higher temperatures. The occurrence of a spontaneous fission, therefore, seems highly improbable.

The total yield of the racemic *cyclohexane-1-2-diamine* thus prepared (630 Gr.), calculated with respect to the quantity of the cyclohexanone used, does not exceed 23 % of the theoretically expected quantity.

§ 2. The base obtained possesses the *trans*-configuration, as is proved by its resolvability into optically-active components. This fission was performed by means of *d-tartaric acid*, — just as in the case of *1-2-diamino-cyclopentane*<sup>1)</sup>. Whilst in the latter case, however, the *acid d-tartrates* proved to be most suited for this purpose, here we got better results by using the *neutral d-tartrates*. If the inactive base be combined with the calculated quantity of *d-tartaric acid*, the *neutral d-tartrate* of the *levorotatory* component for the greater part immediately falls out. After recrystallisation and fractionating, easily fractions are obtained with a specific rotation for sodiumlight of 11°, from which the pure lefthanded base can be separated, which has a specific rotation  $[\alpha]_D$  of  $-36^\circ$  and a boilingpoint of 82° C. under a pressure of 14 mm. At ordinary temperatures the base readily crystallizes and then has a meltingpoint of 42°.7 C.

Because the inactive base melts at 14°.8 C., the latter remains liquid at room-temperature. It is not possible to isolate the *dextrogyratory* component in a pure state from the mother-liquor of the *d-tartrates*, because, on evaporation, the solution gradually assumes the consistency of a glassy

<sup>1)</sup> F. M. JAEGER and H. B. BLUMENDAL, Zeits. f. anorg. Chem., 175, 161 (1928).

mass, without the very soluble tartrate separating from it. By fractional precipitation by means of absolute alcohol, a considerable quantity of the dextrogyratory component, could, however, be obtained, the latter showing a specific rotation  $[\alpha]_D$  of  $32^\circ$ — $34^\circ$ .

Therefore, the remaining *d*-component was isolated in still another way: to the concentrated mother-liquor now so much *d*-tartaric acid was added, as necessary to form the *bitartrate*. Soon a white precipitate appears, which has a specific rotation of about  $+27^\circ$  and from which the dextrogyratory base can be obtained, showing an only slightly weaker positive rotation, than the negative one of the lefthanded component.

§ 3. The *hydrochloride of rac. Cyclohexanediamine* is highly soluble and usually crystallizes from its mother-liquors in featherlike aggregations of only approximately measurable crystals. Sometimes the hydrochloride is deposited from its aqueous solutions in rather poorly developed, long needles, ordinarily united in cross-shaped aggregations. The angular values are strongly oscillating, more especially in the zone of the prism, so that only approximate measurements can be made. *Monoclinic-prismatic*, with the axial ratio:

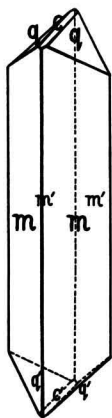


Fig. 4. *Crystal form of rac. Cyclohexanediamine-hydrochloride.*

$$a : b : c = 1.061 : 1 : 0.895 \text{ and } \beta = 78^\circ 44'.$$

Forms observed:  $m = \{110\}$ , large, but with curved planes and yielding multiple reflections;  $q = \{011\}$ , small, well measurable; sometimes  $c = \{001\}$ , very narrow. The habitus is prismatic parallel to the *c*-axis. (Fig. 4).

Most of the crystals are crossing twins, with  $\{\bar{1}01\}$  as the twinning plane.

Angular Values:	Observed:	Calculated:
$m : m = (110) : (\bar{1}10) =$	$*87^\circ 42'$	—
$q : q = (011) : (0\bar{1}1) =$	$*82 \quad 28$	—
$q : m = (011) : (110) =$	$*54 \quad 45$	—
$q : m = (011) : (\bar{1}10) =$	$67 \quad 54$	$68^\circ 4'$
$c : q = (011) : (011) =$	$41 \quad 14$	$41 \quad 14$

No distinct cleavability was observed.

On  $\{110\}$  oblique extinction, under about  $14^\circ$  with the direction of the vertical axis.

The plane of the optical axes is perpendicular to  $\{010\}$ , with the *b*-axis as the first bissectrix of negative character. On  $\{110\}$  one axis is visible; there is a very strong crossed dispersion, the orange and blue colours being

visible in adjacent quadrants; for red the axial plane is almost parallel to  $\{001\}$ .

§ 4. The corresponding *nitrate*, on the other hand, is much less soluble than the hydrochloride and can easily be obtained in clear, colourless crystals.

They are *anhydrous*, as was proved by their analysis.

Racemic *Cyclohexanediamine-nitrate*:  $C_6H_{10}(NH_2)_2, 2HNO_3$  crystallizes from its acid aqueous solutions in beautiful, colourless, kite-shaped crystals.

*Rhombic-bipyramidal*:  $a : b : c = 0.9110 : 1 : 1.0612$ .

*Forms observed*:  $c = \{001\}$ , well developed, very lustrous;  $o = \{111\}$ , large, yielding good reflections. The habitus is thick-tabular parallel to  $\{001\}$ . (Fig. 5).

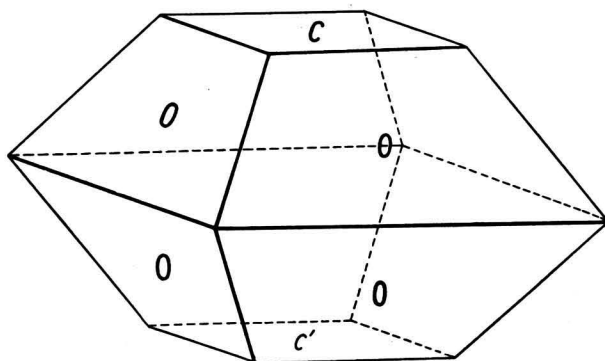


Fig. 5. Crystalform of *r*-Cyclohexanediamine-nitrate.

Angular Values:	Observed:	Calculated:
$c : o = (001) : (111) =$	$^*57^\circ 36'$	—
$o : o = (111) : (\bar{1}\bar{1}\bar{1}) =$	$^*77 14$	—
$o : o = (111) : (1\bar{1}\bar{1}) =$	$68 58$	$69^\circ 19'$

No distinct cleavability was observed.

Optically biaxial. The axial plane is parallel to  $\{100\}$ ; the  $c$ -axis is the first bisectrix of negative character. On  $\{001\}$  a rather large apparent axial angle is observed; rhombic dispersion, with  $\rho > \nu$ .

#### § 5. The Optically-active Components.

I. The *hydrochloride* of the *dextrogyratory cyclohexanediamine* crystallizes from its hydrochloric acid containing or pure aqueous solutions in beautiful, colourless and highly lustrous crystals. They are *rhombic-bisphenoidal* with the axial ratio:  $a : b : c = 0.6831 : 1 : 0.7935$ .

*Forms observed*:  $q = \{011\}$ , predominant;  $o = \{111\}$ , large and very lustrous;  $p = \{1\bar{1}\bar{1}\}$ , very small, well reflecting;  $c = \{001\}$ , narrow, but

well measurable. The habitus is prismatic parallel to the  $a$ -axis, usually somewhat flattened parallel to two opposite faces of  $q$ . (Fig. 6).

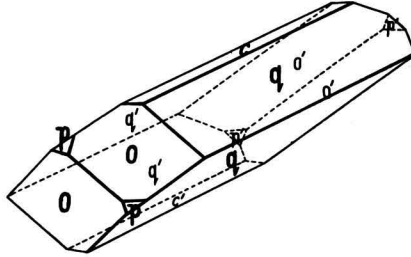


Fig. 6. *Crystalform of d-Cyclohexanediamine-hydrochloride.*

Angular Values:	Observed:	Calculated:
$q : o = (011) : (111) =$	$42^{\circ} 18'$	—
$c : q = (010) : (011) =$	$38 \quad 26$	—
$o : o = (111) : (\bar{1}\bar{1}\bar{1}) =$	$95 \quad 24$	$95^{\circ} 24'$
$q : q = (011) : (0\bar{1}\bar{1}) =$	$103 \quad 8$	$103 \quad 28$
$q : o = (0\bar{1}\bar{1}) : (111) =$	$80 \quad 25$	$80 \quad 19\frac{1}{2}$
$c : o = (001) : (111) =$	$54 \quad 42$	$51 \quad 35\frac{1}{2}$
$a : o = (100) : (111) =$	—	$47 \quad 42$
$b : o = (010) : (111) =$	—	$62 \quad 38$

No distinct cleavability was observed.

The plane of the optical axes is  $\{100\}$ ; on  $\{011\}$  and  $\{0\bar{1}\bar{1}\}$  one of the axes is visible excentrically. Probably the first bissectrix is parallel to the  $c$ -axis.

II. The *hydrochloride* of the *levogyrotory* base shows the same angular values as the previous crystals, but here  $p = \{\bar{1}\bar{1}\bar{1}\}$  is predominant and  $o = \{111\}$  very small. Moreover, the form  $m = \{110\}$  is here observed, small but very lustrous. The habitus (Fig. 7) is analogous to that of the

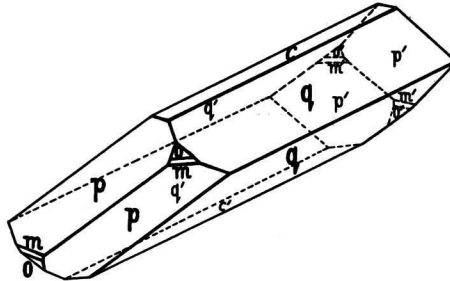


Fig. 7. *Crystalform of l-Cyclohexanediamine-hydrochloride.*



dextrogyratory salt or, — as formerly (Fig. 3) was described, to that of the bisphenoid  $p$ , truncated by small faces of  $m$ .

Besides the angular values previously mentioned, also the following angles were measured:

$$\begin{array}{ll} m : m = (110) : (\bar{1}\bar{1}0) = 68^\circ 35' & 68^\circ 40\frac{1}{2}' \\ p : p = (11\bar{1}) : (\bar{1}\bar{1}1) = 109 \ 24 & 109 \ 11 \\ m : p = (110) : (\bar{1}\bar{1}1) = 73 \ 0 & 72 \ 45\frac{1}{2}' \end{array}$$

The optical orientation is the same as in the case of the other compound. The two kinds of crystals are perfect mirror-images of each-other.

§ 6. The optically-active *nitrates* are less soluble than the hydrochlorides.

I. The *nitrate* of the *dextrogyratory* base crystallizes from dilute nitric acid in colourless, well built, lustrous crystals. They are anhydrous.

*Rhombic-bisphenoidal*:

$$a : b : c = 0.9620 : 1 : 0.4725.$$

Forms observed:  $o = \{111\}$  and  $p = \{1\bar{1}1\}$ , equally large and well reflecting;  $m = \{110\}$ , broad and lustrous;  $a = \{100\}$ , small but very lustrous;  $\omega = \{2\bar{1}1\}$ , very small, but well measurable;  $r = \{101\}$ , broader than  $q = \{011\}$ , both yielding feeble

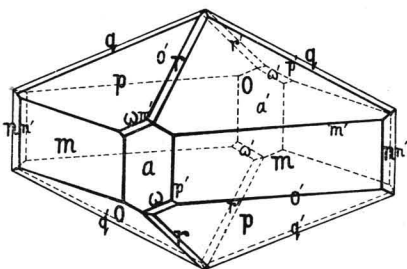


Fig. 8. The Crystalform of *d-Cyclohexanediamine-nitrate*.

reflections;  $n = \{120\}$ , broader than  $r$ , well reflecting. The habitus (Fig. 8) is usually flattened parallel to two faces of  $\{111\}$ .

Angular Values:	Observed:	Calculated:
$a : m = (100) : (110) =$	$^*43^\circ 53\frac{1}{2}'$	—
$m : o = (110) : (111) =$	$^*55 \ 43\frac{1}{2}$	—
$o : o = (111) : (\bar{1}\bar{1}1) =$	68 33	$68^\circ 33'$
$o : r = (111) : (101) =$	22 59	22 59
$o : p = (111) : (1\bar{1}1) =$	45 58	45 58
$o : q = (111) : (011) =$	23 55	$23 \ 56\frac{1}{2}$
$o : p = (111) : (\bar{1}\bar{1}1) =$	47 50	47 53
$a : o = (100) : (111) =$	66 5	$66 \ 3\frac{1}{2}$
$m : n = (110) : (120) =$	18 33	18 39
$a : \omega = (100) : (2\bar{1}1) =$	48 18	$48 \ 23\frac{1}{2}$
$p : \omega = (1\bar{1}1) : (2\bar{1}1) =$	17 48	17 40

No distinct cleavability was observed.

The plane of the optical axes is  $\{001\}$ ; an optical axis is visible on  $m$  almost perpendicular to the prism-faces. The  $a$ -axis, of positive character, is the first bissectrix. Strong rhombic dispersion with  $\rho > v$ .

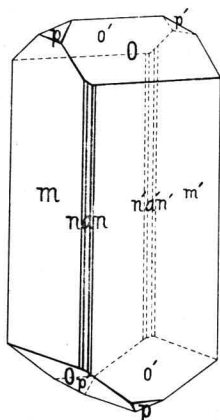


Fig. 9. The Crystalform of *l*-Cyclohexanediamine-nitrate.

II. The *nitrate* of the *levogyrotory* base is quite analogous to the former. Colourless, flat crystals, usually flattened parallel to two faces of  $\{110\}$ .

*Rhombic-bisphenoidal:*

$$a : b : c = 0.9539 : 1 : 0.4697.$$

*Forms observed:*  $m = \{110\}$ , broad and often yielding multiple reflections;  $o = \{111\}$ , large and lustrous;  $p = \{111\}$ , small, weak reflections;  $a = \{100\}$ , lustrous but narrow;  $n = \{210\}$ , broader than  $a$  and well reflecting (Fig. 9).

Angular Values:	Observed:	Calculated:
$a : m = (100) : (110) =$	$*43^{\circ} 39'$	—
$m : o = (110) : (111) =$	$*55 46$	—
$m : m = (110) : (\bar{1}\bar{1}0) =$	87 18	$87^{\circ} 18'$
$m : p = (\bar{1}\bar{1}0) : (\bar{1}\bar{1}0) =$	55 43	55 46
$a : n = (100) : (210) =$	25 38	25 30
$n : m = (210) : (110) =$	18 1	17 51
$o : o = (111) : (\bar{1}\bar{1}\bar{1}) =$	68 28	68 28

The other physical properties are the same as in the case of the *nitrate* of the *dextrogyrotory* base.

#### § 7. The rotatory dispersion of *d*- and *l*-Cyclohexanediamine.

As has already been mentioned, the optically-active antipodes of cyclohexanediamine, melting at  $42^{\circ}.7\text{C.}$ , are at ordinary temperature solid, well crystallized substances. As in aqueous solution, like the racemic base, they immediately form a strongly built *hydrate*, their rotation can only be exactly determined in the *molten* state. It may here be remarked that during our experiments with the complex salts derived from them, we more and more got the impression, that the "racemic" base actually is an equimolar *mixture* of the two antipodes and *not* a true chemical compound. The binary meltingpoint-curve, therefore, is most probably one with *two* branches, the meltingpoint of the inactive base ( $14^{\circ}.8\text{C.}$ ) being that of an *eutectic mixture*.

For the measurement of the optical rotation the molten base was enclosed

within a specially constructed polarimeter-tube (length: 19.87 cm.) which was surrounded by a wider mantle through which a steady current of the water from a thermostat was continually flowing at a carefully regulated rate. The temperature of the molten base thus was constantly held at 55° C.; the density of the liquid at that temperature was determined to be: 0.946. The tube was provided with the necessary diaphragms so as to screen-off, as completely as possible, the troublesome reflections of the light-rays at the walls of the rather thin tube.

In this way the following values of the rotation at different wave-lengths were determined:

Wavelength $\lambda$ in Å.U.	Rotation $2\alpha$ observed:	Specific Rotation [ $\alpha$ ]:	Molecular Rotation [ $M$ ]. $10^{-2}$ :
6480	-55.53	-29.47	-33.61
6262	-59.84	-31.77	-36.22
6074	-63.84	-33.90	-38.64
5893	-67.90	-36.05	-41.10
5735	-71.99	-38.22	-43.57
5592	-75.93	-40.31	-45.96
5463	-79.74	-42.34	-48.26
5340	-83.44	-44.30	-50.55
5224	-87.13	-46.26	-52.74
5126	-90.70	-48.15	-54.90
5036	-94.38	-50.11	-57.12
4950	-97.30	-51.66	-58.89

In Fig. 10 these values of [ $\alpha$ ] and of [ $M$ ].  $10^{-2}$  are represented in a graph (*A* and *A'*), simultaneously those of *cyclopentanediamine* (*B* and *B'*) for the purpose of comparison<sup>1</sup>).

The *dextrogyratory* base which, as already mentioned, had a somewhat lower meltingpoint by the admixture of a small amount of the racemic one, showed rotations 2°—3° lower than the pure *levogyratory* base.

From these curves it is seen that as well the absolute magnitude of the rotation of the *cyclohexanediamine* for each wavelength, as the rotatory dispersion are less than for *cyclopentanediamine*. As we soon will see this phenomenon is in the same way revealed in the dispersion-curves of the

<sup>1</sup>) F. M. JAEGER and H. B. BLUMENDAL, Zeits. f. anorg. Chem., 175, 168. 169 (1928).

colourless rhodium- and platinum-complexes derived from these optically-active bases.

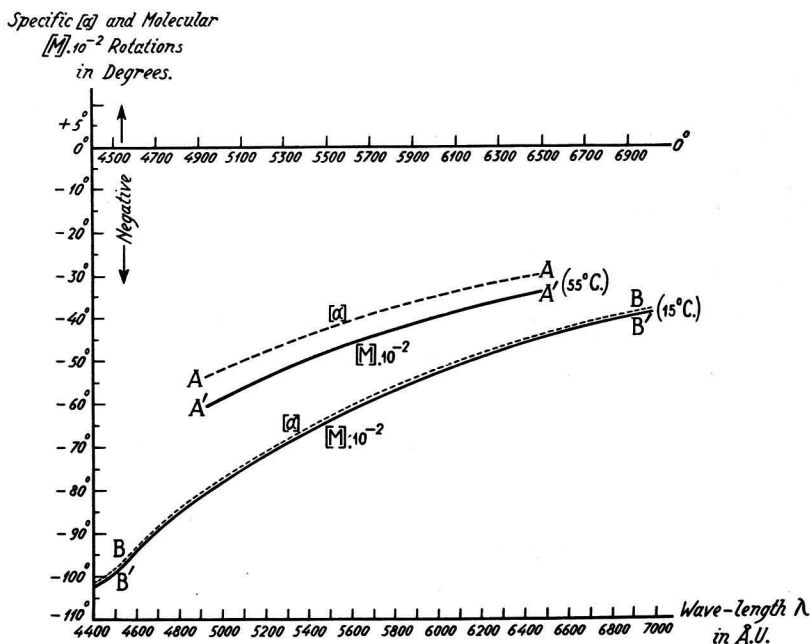


Fig. 10. The Rotatory Dispersion of the optically-active Cyclohexanediamines. (The curves B relate to the corresponding Cyclopentanediamines).

Groningen, Laboratory for Inorganic and Physical Chemistry of the University.

**Chemistry.** — *Some properties of unsaturated sulphones.* By J. BÖESEKEN and E. DE ROY VAN ZUYDEWIJN.

(Communicated at the meeting of November 28, 1936).

In a previous communication<sup>1)</sup> one of us (B) pointed out that a saturated five-ring, exclusively consisting of carbon atoms, corresponds with regard to its properties with the analogous, non-cyclic saturated compound. This applied to the  $\alpha$ -hydroxy-carbonic acids, where was stated by means of their behaviour towards boric acid that the ring closure did not alter the position of hydroxyl and carboxyl groups with respect to each other.

From measurements of the conductivity of mixtures of boric acid with cyclopentane-cis-hydroxy-carbonic acids<sup>2)</sup> it might even be concluded that in this ring there must still be some flexibility, allowing the adjacent

<sup>1)</sup> Proc. Royal Acad. Amsterdam, 39, 28 (1936).

<sup>2)</sup> J. BÖESEKEN, G. SLOOFF, J. M. HOEFFELMAN and H. E. HIRSCH, Recueil trav. chim. 52, 881 (1933).