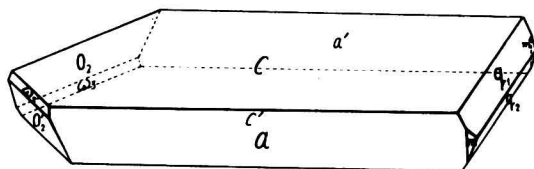


**Chemistry.** — *On the Resolution of  $\beta$ -Phenyl- $\alpha$ -Propylene-diamine into its Optically-active Components.* (3th Part.) By F. M. JAEGER and W. FROENTJES.

(Communicated at the meeting of March 29, 1941.)

§ 1. In a previous communication <sup>1)</sup> the preparation and the properties were described of  $\beta$ -phenyl- $\alpha$ -propylene-diamine:  $C_6H_5 \cdot CH(NH_2) \cdot CH(NH_2) \cdot CH_3$ ; the base has a boilingpoint of  $93^\circ C$ . under a pressure of 2 or 3 m.M. In the present paper we publish the results of our tentatives to resolve this bivalent pseudo-base into its optically-active components. Although *four* optically-active components may theoretically be expected, we up till now have only succeeded to isolate *two* enantiomorphous isomerides in a pure state. Further investigations must enable us to decide, whether in the reduction-process applied also the two other possible enantiomorphous configurations are generated or not.

§ 2. The racemic compound was combined with so much of *d*-tartaric acid as to yield the mixture of the *mono-d-tartrates*. On repeatedly recrystallizing them from an aqueous solution, — as the less soluble product, — we obtained a fraction which finally showed a *constant* specific rotation  $[\alpha]$  for sodiumlight of  $+ 25^\circ,5$ . The substance crystallizes from its aqueous solution at roomtemperature in beautiful, colourless and



*Mono-d-Tartrate of  $\beta$ -C<sub>6</sub>H<sub>5</sub>-CH(NH<sub>2</sub>)-CH(NH<sub>2</sub>)-CH<sub>3</sub>.*

Fig. 1. Crystalform of the *l*-Base-mono-*d*-Tartrate  
+ 4 H<sub>2</sub>O.

very lustrous, flat crystals, which have a typically hemimorphic aspect, as may be seen from the Fig. 1; they represent the *mono-d-tartrate* of the *levogyrotory* base and contain *four* molecules of water of crystallisation.

The crystals are *monoclinic-sphenoidal*; their axial ratio <sup>2)</sup>, as deduced from the X-ray-spectrograms is:  $a : b : c = 1,289 : 1 : 2,001$ ; with  $\beta = 74^\circ 24'$ .

Forms observed:  $c = \{001\}$ , predominant, very lustrous, occasionally finely striated parallel to the *b*-axes;  $a = \{100\}$ , smaller than *c*, but equally lustrous;  $o_2 = \{\bar{1}\bar{1}1\}$ , well developed and yielding ideal reflections;

<sup>1)</sup> F. M. JAEGER and J. A. VAN DIJK, these Proceedings, **44**, 26, 31 (1941).

<sup>2)</sup> The axial ratio directly calculated from the angular measurements is:

$$a : b : c = 1,261 : 1 : 2,003; \beta = 74^\circ 24'.$$

$q = \{011\}$ , somewhat narrower than  $o_2$ , good reflecting;  $\omega_1 = \{1\bar{1}0\}$  is ordinarily much narrower than  $o_2$  and may even be completely absent, but it also can be as broad as  $o_2$  and then yields very nice images;  $m = \{110\}$ , small but readily measurable;  $s = \{0\bar{1}1\}$ , small, yielding good reflections, but is often absent;  $u = \{0\bar{1}2\}$ , extremely small, in most cases absent. Some of the angular values appear to be rather variable ( $\pm 15'$  about their mean values). The habitus of the crystals is flat, elongated parallel to the  $b$ -axis and characteristically hemimorphic. A distinct cleavability was not observed.

Angular Values:	Observed:	Calculated:
$a : c = (100) : (001) =$	*74° 24'	—
$c : q = (001) : (011) =$	*62 36	—
$o_2 : o'_2 = (\bar{1}\bar{1}1) : (1\bar{1}\bar{1}) =$	*80 32	—
$a : o'_2 = (100) : (1\bar{1}\bar{1}) =$	58 31	58° 31'
$c : o_2 = (001) : (\bar{1}\bar{1}1) =$	76 55	76 55
$o'_2 : \omega_1 = (1\bar{1}\bar{1}) : (1\bar{1}0) =$	22 58	22 56
$c : \omega_1 = (001) : (1\bar{1}0) =$	80 10	80 9½'
$a : q = (100) : (011) =$	97 14	97 6½'
$a : m = (100) : (110) =$	50 38	50 31
$q_1 : q_2 = (011) : (01\bar{1}) =$	54 48	54 48
$c : s = (001) : (0\bar{1}1) =$	62 36	62 36
$s : u = (0\bar{1}1) : (0\bar{1}2) =$	18 36	18 38
$u : c = (0\bar{1}2) : (001) =$	44 0	43 58

The axial plane is parallel to  $\{010\}$ .

From rotation-spectrograms round the  $a$ - $b$ - and  $c$ -axis respectively, with  $Fe_\alpha$ -radiation, the dimensions of the elementary cell were determined to be:  $a_0 = 9,25 \text{ \AA}$ ;  $b_0 = 7,30 \text{ \AA}$ ;  $c_0 = 14,60 \text{ \AA}$  (the latter controlled by Dr. TERPSTRA). The elementary cell contains the mass of *two* tetrahydrated molecules. The density of the crystals at 17° C. was found to be: 1,304; calculated: 1,293. The spectrogram round the  $c$ -axis showed 6 spectra, that round the  $a$ -axis 5 spectra and round the  $b$ -axis equally so.

A SAUTER-spectrogram under 45° round the  $a$ -axis showed the following indices-triplets (TERPSTRA): (001), (003), (004), (005), (006); (011), (012), (013); (020), (021), (022), (023), (024), (025), (026); (031), (032); (040), (041); (044)

and one round the  $b$ -axis:

(001), (003), (004), (005), (006); (100), (101), (102); (104); (200), (201), (202), (206); (300), (301); (400), (401).

As  $(h + k)$ ,  $(k + l)$ ,  $(h + l)$  and also  $(h + k + l)$ , appear to be even, as well as odd, *no* faces of the elementary cell are centred. According to

Dr. TERPSTRA, only the space-groups  $C_2^1$  and  $C_2^2$  can here be present; as (010) and (030) really occur,  $C_2^2$  (resp.  $P_2^2$ ) is here the only possible space-group. It is characterized by the presence of a single binary screw-axis; which is in accordance with the presence of 2 molecules in the cell, — the molecules being themselves asymmetrical.

The *d-tartrate* of the *l-base* yielded the following specific rotations in an aqueous solution of 2 % (see Table I).

Wavelength in Å:	Specific rotation $[\alpha]$ :
6480	+21.0
6074	+23.2
5893	+25.5
5463	+30.3
5224	+33.1
5126	+34.8
4950	+37.0
4793	+41.8
4724	+42.5

§ 3. From the final mother-liquors the base was set free, the liquid distilled in vacuo and subsequently treated with *levogyrotary* tartaric acid and the mixture of the *l-tartrates* thus obtained subjected to fractional crystallisations in aqueous solutions, till a product was obtained which showed a *constant* specific rotation for sodium-light of  $[\alpha]_D = -25^\circ.5$ . The crystals obtained had the same form of those just described; but they showed exactly the *enantiomorphous* development.  $(c : q = (001 : 011) = 62^\circ 37'$ ;  $c : a = (001) : (100) = 74^\circ 20'$ ;  $q : q = (011) : (0\bar{1}1) = 54^\circ 47'$ ;  $c : o = (001) : (111) = 76^\circ 57'$ . Axial plane =  $\{010\}$ .

Also their rotations were practically the same as those mentioned above, but with the opposite algebraic sign: the base set free from the *l-tartrate* is *dextrogyrotary*  $\beta$ -*phenyl- $\alpha$ -propylene-diamine*. The anhydrous tartrates melt at  $201^\circ \text{C}$ .

The *d-* and *l-bases* thus obtained boiled at  $110^\circ$ — $111^\circ \text{C}$ . under a pressure of 8 mm. Their specific rotations at different wave-lengths are collected in the following table II.

The curves for the rotatory dispersion of the two pure bases are i.a. graphically represented in Fig. 2.

TABLE IIA.  
Specific Rotations of the Optically-active  $\beta$ -Phenyl- $\alpha$ -Propylene-diamines.

Wave-lengths in Å:	Specific Rotations $[\alpha]$ of the				Mean Values: (+ or -)
	Levogyrotory Base:		Dextrogyrotory Base:		
8050	-24.8	—	—	—	(24.8)
7607	-24.3	—	—	—	(24.3)
7280	-23.3	—	—	—	23.3
6980	-23.8	—	+24.0	—	23.9
6730	-25.8	-26.0	+25.4	+25.8	25.8
6480	-28.1	—	+28.2	—	28.2
6262	-30.4	-30.4	+30.0	+30.3	30.3
6074	-32.6	—	+32.7	—	32.7
5893	-34.7	-34.9	+34.6	+35.0	34.8
5735	-37.1	—	+37.1	—	37.1
5592	-39.2	-39.3	+39.5	+39.7	39.5
5463	-41.5	—	+41.6	—	41.6
5340	-43.7	-43.7	+43.1	+44.2	43.7
5224	-45.8	—	+45.5	—	45.6
5126	-48.0	-48.1	+47.8	+48.6	48.1
3036	-50.2	—	+49.9	—	50.1
4950	-52.3	-52.9	+52.1	+53.1	52.6
4861	-54.4	—	+53.9	—	53.7
4793	-56.5	—	—	—	56.5
4724	-58.6	—	+58.2	—	58.4
4658	-60.5	—	+60.3	—	60.4
4596	-62.7	—	+62.6	—	62.7
4537	-64.9	—	+64.8	—	64.9
4483	-66.8	—	+66.8	—	66.8
4430	-68.9	—	+68.9	—	68.9
4380	-70.2	—	—	—	70.2
4335	-72.6	—	—	—	72.6
4290	-74.5	—	—	—	74.5
4248	-76.3	—	—	—	76.3

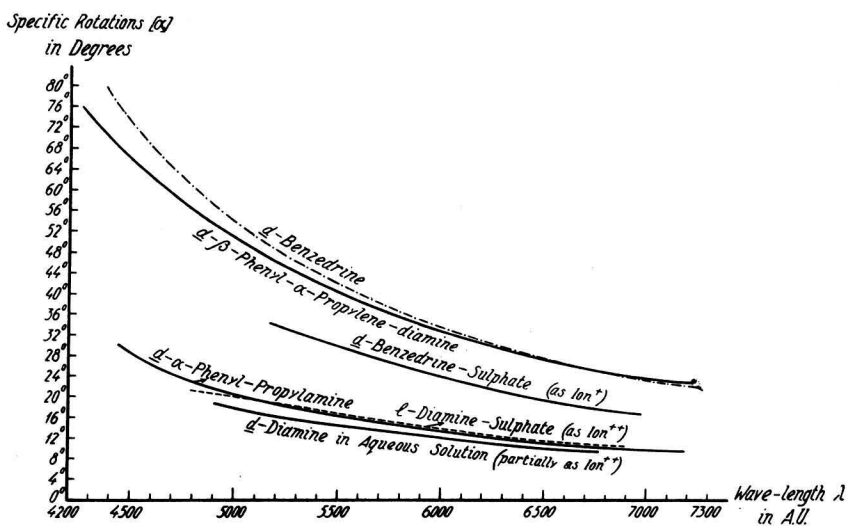


Fig. 2. Rotatory Dispersion of  $\beta$ -Phenyl- $\alpha$ -Propylene-diamine and its Ions; etc.

Simultaneously both pseudo-bases were also studied when dissolved in water; the measurements were made with solutions of 2,5 % of the *levo*- and of 2,1 % of the *dextro*-gyratory diamine (length of the tube: 20 cm). The specific rotations  $[\alpha]$  thus observed were:

Wave-lengths in Å:	Levogyrotary Base: [ $\alpha$ ]:	Dextrogyrotary Base: [ $\alpha$ ]:	Mean Values of [ $\alpha$ ]:
6730	- 9.4	+ 9.5	9.5
6480	-10.2	+10.2	10.2
6262	-11.2	+11.4	11.3
6074	-12.0	+11.9	11.9
5893	-12.8	+12.6	12.7
5735	-13.2	+13.3	13.3
5592	-13.8	+14.2	14.0
5463	-14.4	+14.7	14.6
5340	-15.2	+15.5	15.4
5224	-16.0	+16.2	16.1
5126	-16.4	+17.1	16.8
5036	-17.2	+17.9	17.6
4950	-18.0	+18.6	18.3

A comparison of these values with the corresponding ones of the former table proves, that the rotations of the pseudo-bases in aqueous solution are for the same wavelengths only 0,4 to 0,33 of those of the pure bases themselves.

§ 4. In this connection it seemed of interest also to investigate the rotations of the aqueous solutions of the *salts* of the two antipodes with an optically-*inactive* acid; in analogy to our similar measurements in the case of *benzedrine* and of  *$\alpha$ -phenyl-propylamine*<sup>1)</sup>, we for this purpose also here choose the neutral *sulphates*.

With respect to the fact, that from the *d-tartrate* we obtained the *levo*-pseudo-base and vice-versa, it could be expected, that also in the case of the *sulphates*, the *salts* would show rotations *opposite* to those of the pseudo-bases contained in them.

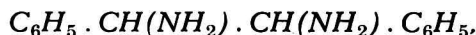
Wave-lengths in Å	Specific Rotations $[\alpha]$ of the		Mean Values of $[\alpha]$ for the Ions: (+ or -)
	Sulphate of the <i>l</i> -diamine (solution of 3.3%):	Sulphate of the <i>d</i> -diamine (solution of 2.8%):	
6730	+11.2°	-10.7°	11.0°
6480	+12.0	-11.6	11.8
6262	+12.9	-12.5	12.7
6074	+13.6	-13.4	13.5
5893	+14.6	-14.5	14.5
5735	+15.2	-15.2	15.2
5592	+16.1	-16.4	16.3
5463	+17.0	-17.1	17.1
5340	+17.6	-18.0	17.8
5224	+18.3	-19.0	18.6
5126	+19.4	-20.0	19.7
5036	+20.3	-20.5	20.4
4950	+21.3	-21.4	21.3

The data of table III corroborate this conclusion: just as in the case of  *$\alpha$ -phenyl-propylamine*, the *sulphates* derived of the optically-active *diamines* also manifest the *opposite* rotations in comparison with the pseudo-bases of which they are derivatives.

A highly curious fact is, that the rotation of the *dextro*-gyrate *sulphate*, — i.e. of the *l*-diamine-ion, — is *practically the same* as that of *d*- *$\alpha$ -phenylpropylamine* in the *undissociated* state (Fig. 2).

<sup>1)</sup> F. M. JAEGER and J. A. VAN DIJK, loco cit., p. 40; F. M. JAEGER and W. FROENTJES, these Proceed., 44, 140 (1941).

In Table IV we also have collected the data obtained in the study of the rotations of the *sulphate of dextrogyrate stilbene-diamine*:



— a base previously <sup>1)</sup> studied in this laboratory. The salt was dissolved in water (0,57 %) and, therefore, the rotations observed equally correspond to those of the corresponding *ion*.

Although the curve between 5126 and 6480 Å. runs sensibly *parallel* to that of *d-β-phenyl-α-propylene-diamine* in the pure state, — the rotatory dispersion being, therefore, quite similar, — the difference of the rotations  $[\alpha]$  between them still amounts to about 5°; the rotations themselves are about *twice* those of the *l-diamine-sulphate*.

TABLE IV. Rotatory Dispersion of <i>d</i> -Stilbenediamine-Sulphate in an aqueous Solution (0.5712%).	
Wave-lengths in Å:	Specific Rotations:
6730	+22.4
6480	+24.0
6262	+25.4
5893	+29.3
5592	+34.2
5340	+39.0
5126	+43.3

With respect to the *β-phenyl-α-propylene-diamine-sulphate* here investigated, it can, moreover, be stated that the *absolute* values of  $[\alpha]$ , — although of *opposite* algebraic sign, — evidently are only slightly different from those characteristic for the free pseudo-base when dissolved in water, in which it is present, at least partially, in a dissociated state. As to the question whether really more *quantitative* relations between these different rotations do exist, we hope to return to it afterwards, as soon as all necessary data for this discussion will completely be available. —

The final mother-liquors of the various fractional crystallisations of the *tartrates* turn into a more or less viscous mass; we now are occupied in investigating them more thoroughly with the purpose of eventually being able to isolate the other isomerides which might possibly still be present in them.

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

<sup>1)</sup> J. G. BOS, *Thesis*, Groningen, (1940), p. 23 and 24. The base, being only insignificantly soluble in water, was investigated in its ethereal solution; its meltingpoint is 87° C.