

Citation:

F.M.Jaeger, On benzylphtalimide and benzylphtal-isoimide, in:
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$$R_{b,h}(x) + S_{b,h}(x) = \sum_{k=1}^x \mu^2(k) = Q_{b,h}(x),$$

so

$$\frac{R_{b,h}(x)}{x} = \frac{1}{2} \left(\frac{Q_{b,h}(x)}{x} + \frac{P_{b,h}(x)}{x} \right) \dots \dots \dots (23)$$

and

$$\frac{S_{b,h}(x)}{x} = \frac{1}{2} \left(\frac{Q_{b,h}(x)}{x} - \frac{P_{b,h}(x)}{x} \right) \dots \dots \dots (24)$$

As now according to (17) (after substitution of $n = 0$)

$$\lim_{x=\infty} \frac{P_{b,h}(x)}{x} = 0$$

and on the other hand according to (21) and (22) when the limit is put equal to $L_{b,h}$,

$$\lim_{x=\infty} \frac{Q_{b,h}(x)}{x} = L_{b,h} > 0,$$

we find from (23) and (24)

$$\lim_{x=\infty} \frac{R_{b,h}(x)}{x} = \frac{1}{2} L_{b,h},$$

$$\lim_{x=\infty} \frac{S_{b,h}(x)}{x} = \frac{1}{2} L_{b,h},$$

so

$$\lim_{x=\infty} \frac{R_{b,h}(x)}{S_{b,h}(x)} = 1.$$

This confirms the supposition expressed by Mr. KLUYVER at the conclusion of his paper:

If we divide the integers $mb + h$ without quadratic factors into two classes according to their consisting of an even or an odd number of prime factors, the ratio of the numbers of integers minor to x of both classes converges for $x = \infty$ towards the limit unity.

Berlin, May 23rd 1904.

Crystallography. — “On Benzylphthalimide and Benzylphthal-isoimide.” By Dr. F. M. JAEGER. (Communicated by Professor A. P. N. FRANCHIMONT.

(Communicated in the meeting of May 28, 1904).

Some time ago a preparation was forwarded to me by Prof. Dr. GABRIEL of Berlin, of a Benzylphthalimide¹⁾: $C_6H_4(CO)_2N(CH_2C_6H_5)$ melting point $115^{\circ},5$, which he had obtained by synthesis. A short time afterwards, through the kindness of Prof. HOOGWERFF, at Delft,

¹⁾ Berl. Ber. 20. 2227.

I obtained some crystals of *Benzylphthal-iso-imide*¹⁾ melting point 82°,5. As both isomeric compounds are, structurally, closely related, I thought it a matter of importance to investigate their crystallographical symmetry.

a). *Benzylphthalimide*. (m.p. 115¹/₂°).

From a mixture of ether and alcohol I obtained this compound in large, very transparent and lustrous crystals of a somewhat rhombohedral habitus. In many cases they are more flattened. The power of crystallising from the said solvent is extraordinarily great.

The symmetry is *trichlino-pinacoidal*; the axial elements are:

$$a : b : c = 0,8443 : 1 : 1,3600$$

$$A = 101^{\circ} 51'. \quad \alpha = 108^{\circ} 24'.$$

$$B = 116^{\circ} 51\frac{1}{2}'. \quad \beta = 120^{\circ} 7'.$$

$$C = 80^{\circ} 45\frac{1}{2}'. \quad \gamma = 73^{\circ} 8'.$$

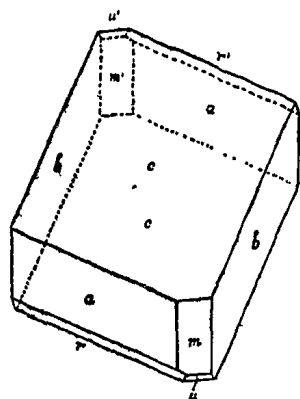


Fig. 1.

Forms observed are $c = \{001\}$, predominating; $a = \{100\}$ and $b = \{010\}$, about equally much developed; $m = \{110\}$, narrow; $r' = \{\bar{1}01\}$ small and narrow, sometimes a little broader; $u = \{\bar{1}\bar{1}1\}$, small and much less conspicuous.

The crystals are represented in fig. 1; the measured and calculated angles are annexed:

	Measured :	Calculated :
* $a : b = (100) : (010) = 99^{\circ} 14\frac{1}{2}'$		—
* $a : c = (100) : (001) = 63^{\circ} 8\frac{1}{2}'$		—
* $b : c = (010) : (001) = 78^{\circ} 9'$		—
* $m : b = (110) : (010) = 58^{\circ} 19\frac{1}{2}'$		—
* $c : r' = (001) : (\bar{1}01) = 78^{\circ} 59'$		—
$a : m = (100) : (110) = 40^{\circ} 55'$		40° 55'
$c : m = (001) : (110) = 58^{\circ} 22\frac{1}{2}'$		58 17
$a : r' = (100) : (10\bar{1}) = 37^{\circ} 55'$		37 55
$b : r' = (010) : (\bar{1}01) = 71^{\circ} 35'$		71 28
$m : r' = (110) : (10\bar{1}) = 61^{\circ} 53'$		62 1

The crystals cleave quite parallel $\{100\}$ and $\{010\}$.

¹⁾ Recueil d. Trav. Chim. d. Pays-Bas, T. XIII, 99.

When recrystallised from ether, very strongly refractive, hexagonally bounded little plates are obtained. On investigation it appears that these are *twin* crystals: {001} is the twin-plane with a twin-axis standing normally on it.

In addition to $c = \{001\}$, $b = \{010\}$, $r' = \{\bar{1}01\}$ and $w' = \{1\bar{1}\bar{1}\}$, I noticed a form $q = \{01\bar{1}\}$; c is strongly developed, b and q are narrow, r' and w' are equally broad and well-formed. The planes of cleavage are the same as above.

There were also measured:

$$q : b = (01\bar{1})_{(2)} : (010)_{(1)} = 23^{\circ}58' ; \text{calculated} : 23^{\circ}42'$$

$$b : b = (010)_{(1)} : (010)_{(2)} = -19^{\circ}23' ; \text{calculated} : -19^{\circ}28'$$

$$r : r = (10\bar{1})_{(1)} : (10\bar{1})_{(2)} = 21^{\circ}45' ; \text{calculated} : 22^{\circ}2'$$

$$c : q = (00\bar{1}) : (01\bar{1}) = 58^{\circ}21' ; \text{calculated} : 58^{\circ}9'$$

The nature of the twin-formation has, therefore, been sufficiently explained.

On {001}, the direction of the optical elasticity-axis is orientated nearly perpendicularly on the sides (001):(010); an axial image could not be observed.

The specific gravity of the crystals was determined by means of a THOULET's solution; $d = 1.343$, at 16° and consequently the topical axes, calculated according to the formule:

$$\chi = \left(\frac{a^2 V}{c \sin \beta \sin \gamma \sin A} \right)^{1/3}; \psi = \left(\frac{V}{ac \sin \beta \sin \gamma \sin A} \right)^{1/3};$$

$$\omega = \left(\frac{c^2 V}{a \sin \beta \sin \gamma \sin A} \right)^{1/3},$$

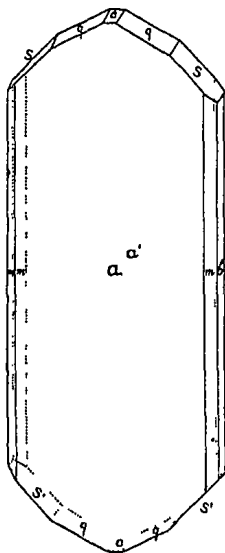


Fig. 2.

in which $V = \frac{M}{d}$, if M represents the molecular weight, are equal to:

$$\chi : \psi : \omega = 4,8513 : 5,7458 : 7,8145.$$

b.) During a cold winter night, I once obtained from a solution of the compound in *benzene* a second, *less stable* modification.

There were formed transparent hexagonal bounded little plates; the crystals were single and not twin crystals as in the former case. The melting point was situated at 115° ; the little crystals, however, soon became opaque so that on warming a molecular transformation probably takes place. But I have only once succeeded in obtaining this modification.

It is *monoclinic-prismatic*; the crystal parameters were calculated to be:

$$a : b : c = 0,8476 : 1 : 0,5092$$

$$\beta = 70^{\circ}42'.$$

Forms observed: $a = \{100\}$, strongly predominating; $m = \{110\}$ and $b = \{010\}$, very narrow; $c = \{001\}$, very small and less conspicuous; $q = \{011\}$ and $s = \{021\}$ equally broadly developed.

$$\begin{aligned} *a : m &= (100) : (110) = 38^{\circ} 39\frac{1}{2}' & - \\ *a : q &= (100) : (011) = 72 \quad 40 & - \\ *c : q &= (001) : (011) = 25 \quad 40 & - \\ s : q &= (021) : (011) = 18 \quad 18 & 18^{\circ} 12' \\ b : m &= (010) : (110) = 51 \quad 20 & 51 \quad 20\frac{1}{2}'. \end{aligned}$$

A distinct cleavability was not found.

Therefore, *benzylphthalimide* is *dimorphous*. As regards the remarkable connection of this β -modification with the crystalline form of the *iso-imide* and with that of the α -modification, see the end of this article.

c). *Benzylphthal-iso-imide*. (m.p. $82\frac{1}{2}^{\circ}$).

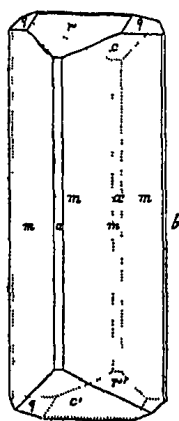


Fig. 3.

The crystals represented in Fig. 3 have been obtained from *anhydrous* ether; they are long-prismatic and here and there of a porcelain white. After some time, even if kept in the dark, they become quite opaque and look as if they were effloresced. The crystals, however, do not contain any co-crystallised solvent; probably some transformation as yet unknown, has taken place here.

The symmetry is *monoclinic-prismatic*; the axial elements, when choosing the following elementary forms, are calculated to be:

$$a : b : c = 1,2303 : 1 : 0,5932$$

$$\beta = 71^{\circ}46'.$$

Forms observed: $m = \{110\}$, strongly predominating; $c = \{\bar{2}01\}$, also well developed; $r = \{001\}$, fairly strongly; $q = \{011\}$, very plain; $a = \{100\}$ narrower; $b = \{010\}$ very narrow; between r and c there is still an orthodoma $\{h0k\}$, which was very little developed and could not be measured. I have retained the above letters for the notation of the forms, because the habitus of the crystal renders,

at first sight, the use of $c = \{001\}$, $r = \{\bar{2}01\}$ and $q = \{\bar{2}11\}$, in many respects more obvious.

	<i>Measured:</i>	<i>Calculated:</i>
* $a : m = (100) : (110) = 49^\circ 26\frac{2}{3}'$		—
* $c : m = (\bar{2}01) : (110) = 68 25\frac{1}{2}$		—
* $q : q = (011) : (0\bar{1}1) = 58 47\frac{1}{2}$		—
$c : r = (\bar{2}01) : (001) = 52 32\frac{1}{2}$		$52^\circ 40\frac{1}{2}'$
$c : a = (\bar{2}01) : (100) = 55 42\frac{1}{2}$		$55 33\frac{1}{2}$
$r : a = (001) : (100) = 71 44$		$71 46$
$c : q = (\bar{2}01) : (011) = 58 9\frac{1}{2}$		$58 7$
$q : r = (011) : (001) = 29 24$		$29 24$
$m : b = (110) : (010) = 40 49$		$40 33$
$m : m = (110) : (\bar{1}10) = 81 7$		$81 7$
$q : m = (011) : (\bar{1}10) = 53 34$		$53 28$

A distinct cleavability was not found; perhaps q is a plane of cleavage. The symmetrical extinction on the planes of $\{110\}$ amounts to about 3° with regard to the vertical axis; a further optical investigation was excluded.

The density of the crystals is *approximately*¹⁾ 1,145; by putting in the above formula γ and $A = 90^\circ$ we obtain for the proportion of the topical axes:

$$\chi : \psi : \omega = 8.2234 : 6.6840 : 3.9650.$$

If we compare the crystal parameters of the two heteromorphous modifications of benzylphthalimide with the parameters of *benzylphthal-iso-imide* we at once notice an interesting relation between the crystalline forms of these substances.

<i>Compound:</i>	<i>Symmetry:</i>	<i>Crystal-parameters:</i>
<i>α-Benzylphthalimide.</i>	Triclinic-pinacoidal.	$a : b : c = 0,8443 : 1 : 1,3600. (\alpha, \beta, \gamma; \text{s.a.})$
<i>β-Benzylphthalimide.</i>	Monoclinic-prismatic.	$a : b : c = 0,8476 : 1 : 0,5092. \beta = 70^\circ 42'$
<i>Benzylphthal-iso-imide.</i>	Monoclinic-prismatic.	$a : b : c = 1,2303^2) : 1 : 0,5932. \beta = 71^\circ 46'$

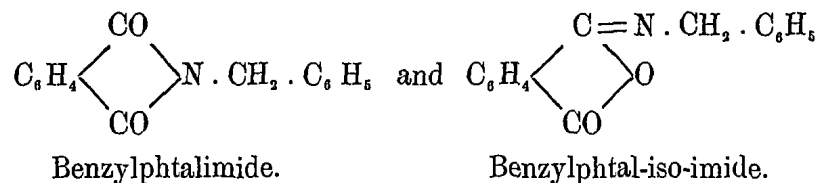
¹⁾ *Approximately*, because the opaque crystals did not give a sufficient guarantee of *homogeneity* and because the substance is attacked on the surface by contact with THOULET's solution.

²⁾ It may be observed that the proportion $a : b$ would become for $m \{230 0,8202 : 1.$

First of all the proportion $\alpha : b$ is the same in both the α - and β -modification; a proof that these crystallographical forms are closely related to each other as regards their internal structure. I have noticed more than once this equality of two parameters in different modifications of a same compound; I met lately with a striking instance in the case of the red α - and the less stable yellow β -modification of the 1-3-4-*Dinitrodiethylaniline* notwithstanding the difference in the degree of symmetry. From a crystallographical point of view such modifications *must* always be dependent on each other, although that dependence may not always be immediately noticed.

But then the very close relationship between the less stable β -modification and the crystalline form of the *iso-imide*, as is plainly shown from the analogous values for the angle β and the proportion $b : c$ is surprising in a high degree.

According to Drs. HOOGEWERFF and VAN DORP ¹⁾ the isomerism of *imides* and *iso-imides* is based on a difference in the way of combination of the N-atom on the one side and the O-atom on the other:



The heteromorphous β -modification of the first substance now appears to be extremely closely related to the crystalline form of the first one owing to desmotropical change. Both phenomena, dimorphism and desmotropism therefore cause, respectively, an analogous change in the crystal-symmetry of α -benzylphthalimide.

The presumption raised by me some time ago that *crystallographic polymorphism* in a number of organic compounds might be caused by a *chemical isomerism* ²⁾, which would then account for the temporary existence of more stable atom-configurations is again a little more justified by the fact that above connection has been found.

¹⁾ loco cit.

²⁾ Kristallografische en Moleculaire Symmetrie van plaatsings-isomere Benzol-derivaten. Proefschrift, Leiden, 1904, pag. 120, 121. Z. f. Kryst. 38. 600. (1904).