Chemistry. — *"On Crystalforms of Derivatives of Ethoxy- and Trimethyl-Benzophenone"*. By Prof. F. M. JAEGER.

(Communicated at the meeting of January 30, 1926).

In the following paper are published the results of a series of crystal-measurements with some derivatives of *Benzophenone*. They were given to me, as already many others of this kind, for this purpose by Dr. P. J. MONTAGNE of Leyden, and they are the last members of the long series of compounds synthesized by this author in the course of his investigations, which a short time ago were suddenly ended by his too early death.

A. 4-Ethoxy-Benzophenone[1]: $C_6H_4(OC_2H_5).CO.C_6H_5$; Mpt.: 42°—46°,5 C.

From benzene + ligroine this compound is obtained in big, flat, colour-

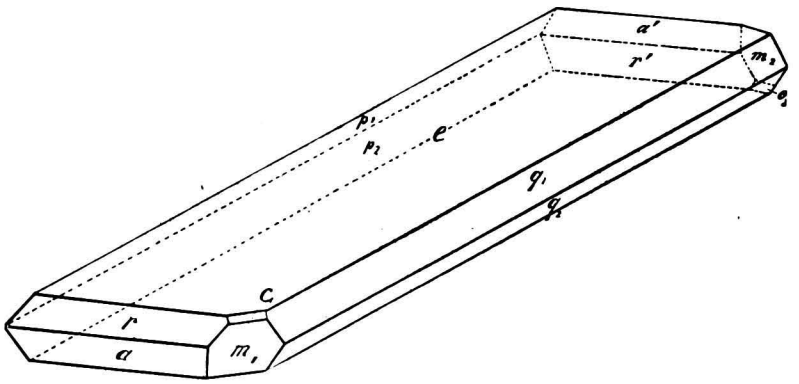

Fig. 1.

less crystals, which have meltingpoints situated between 42° C. and 46°,5 C., without being, however, different in any other respect. (Fig. 1).

Monoclinic-sphenoidal.

$a : b : c = 0{,}7427 : 1 : 1{,}6049$;

$\beta = 87°\ 58'$.

Forms observed: $c = \{001\}$, predominant, very lustrous, but often yielding multiple reflections and occasionally striated parallel to the *a*-axis; $q = \{011\}$, well developed, in most cases giving dull images, equally large as $p = \{0\bar{1}1\}$, which form, however, possesses lustrous faces; $r = \{101\}$,

[1] P. J. MONTAGNE, Receuil d. Trav. d. Chim. Pays-Bas, **41**, 709, (1922).

very lustrous and well developed, broader than $a = \{100\}$; $m = \{110\}$, distinct, very lustrous and yielding sharp reflections; $o = \{111\}$, narrow, well reflecting, but often absent.

Angular values:	*Observed:*	*Calculated:*
$c : a = (001) : (100) =$	* 87° 58′	—
$c : q = (001) : (011) =$	* 58 3½	—
$a : m = (100) : (110) =$	36 35	—
$c : r = (001) : (101) =$	63 37	63° 30′
$r : a = (101) : (100) =$	24 20	24 28
$q : q = (011) : (01\bar{1}) =$	63 53	63 53
$c : m = (001) : (110) =$	88 19	88 20
$c : o = (001) : (111) =$	68 20	68 10½
$o : m = (111) : (110) =$	19 49	19 47½
$p : r = (0\bar{1}1) : (101) =$	76 13	76 20½
$r : m = (101) : (110) =$	42 52	43 2
$m : q = (110) : (01\bar{1}) =$	60 51	60 37½
$a : p = (100) : (0\bar{1}\bar{1}) =$	91 6	91 4½
$a : q = (100) : (011) =$	88 54	88 5½
$c : p = (001) : (0\bar{1}1) =$	58 3½	58 3½
$m : q = (110) : (011) =$	58 45	58 39

Distinct cleavage parallel to {001}.

The plane of the optical axes is {010}; inclined dispersion.

B. 3-Bromo-4-Ethoxy-Benzophenone[1]: $C_6H_3Br.(OC_2.H_5).CO.C_6H_5$; Mpt.: 102°,2 C.

From benzene + ligroine this substance was obtained in rectangular and beautifully crystallized plates, which are colourless, perfectly transparent and well developed.

Rhombic-bipyramidal.

$$a : b : c = 0{,}7935 : 1 : 0{,}2691.$$

Forms observed: $a = \{100\}$, predominant, very lustrous, but giving mostly double images; $m = \{110\}$, $r = \{101\}$ and $b = \{010\}$, all about equally large, yielding sharp reflections; $s = \{102\}$, very narrow, but well measurable; $o = \{121\}$, extremely small and faint, often totally absent. (Fig. 2).

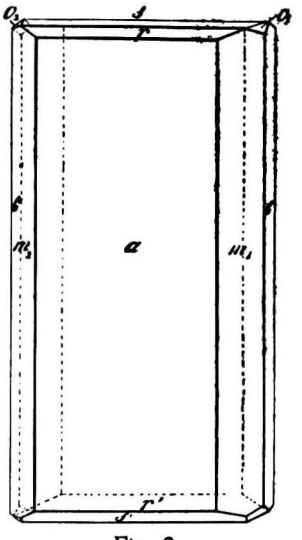

Fig. 2.

[1]) P. J. MONTAGNE, loco cit., p. 714.

Angular values:	*Observed:*	*Calculated:*
$a : m = (100) : (110) =$	* 38° 26′	—
$a : r = (100) : (101) =$	* 71 16	—
$m : b = (110) : (010) =$	51 34	51° 34′
$r : s = (101) : (10\bar{2}) =$	9 2	9 5
$s : s = (10\bar{2}) : (\bar{1}02) =$	19 25	19 17½
$r : m = (101) : (110) =$	75 27	75 26
$r : o = (101) : (121) =$	27 6	27 1½
$a : o = (100) : (121) =$	73 35	73 22
$b : o = (010) : (121) =$	62 51	62 58½

Perfectly cleavable parallel to {100}.

The plane of the optical axes is {001}, with the *a*-axis as first bisectrix; feeble birefringence, small optical axial angle.

The isomeric *2-Bromo-4′-Ethoxy-Benzophenone*: $C_6H_4Br \,.\, CO \,.\, C_6H_4(OC_2H_5)$, Mpt.: 79°,5 C. has already been described before [1]). Although this compound has the same symmetry, its crystals show no distinct crystallographical relation with those here described, neither in their angular values nor in their parameters.

C. *3-5-Dibromo-Ethoxy-Benzophenone*[2]): $C_6H_2Br_2(OC_2H_5).CO.C_6H_5$; Mpt.: 83°,5 C.

From ligroine in big colourless, strongly refracting and very lustrous crystals (Fig. 3).

Monoclinic-prismatic.

$a : b : c = 1{,}0901 : 1 : 0{,}8561$;

$\beta = 59°{,}41'$

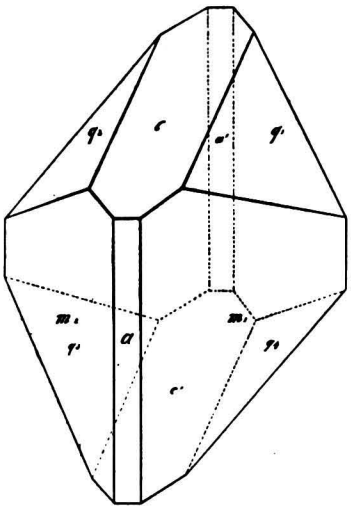

Fig. 3.

Forms observed: $m = \{110\}$, large and lustrous, yielding sharp reflections; $a = \{100\}$, narrower than *m*, but very lustrous; $q = \{011\}$, well developed and giving very sharp images; $c = \{001\}$, narrower than *m* and *q*, broader than *a*, often rough and yielding multiple reflections. The habit is short-prismatic, almost isometrical, occasionally with a slight elongation parallel to the *a*-axis. Some crystals show *q* predominant, *m* small, *c* narrow, thus having a distinctly flat, pyramidal shape.

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[1]) F. M. JAEGER, Zeits. f. Kryst., **56**, 59, (1921).

[2]) P. J. MONTAGNE, loco cit., p. 715.

Angular values:	*Observed:*	*Calculated:*
$q : q = (011) : (0\bar{1}1) =$	* 72° 56′	—
$m : m = (110) : (1\bar{1}0) =$	* 86 31	—
$m : c = (110) : (001) =$	* 68 26	—
$c : q = (001) : (011) =$	36 28	36° 28′
$a : m = (100) : (110) =$	43 15½	43 15½
$c : a = (001) : (100) =$	59 47	59 41
$m : m = (110) : (\bar{1}10) =$	93 29	93 29
$q : m = (011) : (\bar{1}10) =$	83 26	83 35½
$q : m = (011) : (110) =$	45 43	45 20

No distinct cleavage could be found.

The plane of the optical axes is {010}; on {100} one axis is observed at the border of the field. Inclined dispersion.

D. 4-Nitro-2′-4′-6′-Trimethylbenzophenone[1]: $C_6H_4(NO_2) . CO . C_6H_2(CH_3)_3$.

This substance crystallizes from ethyl-acetate in big, pale yellowish, strongly lustrous crystals. Occasionally individuals are met with, whose faces are less perfect, thus giving multiple images. The measurements were made with the best crystals. (Fig. 4).

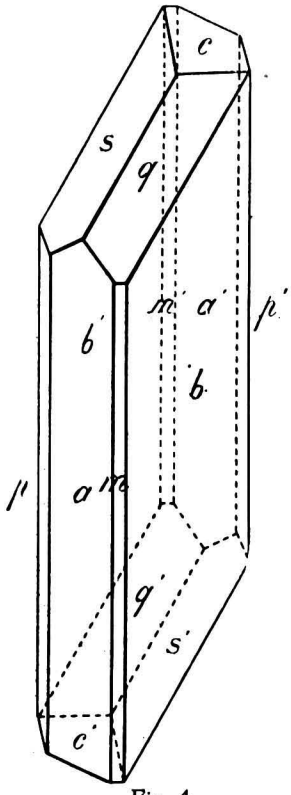

Fig. 4.

Triclinic-pinacoidal.

$a : b : c = 1{,}6303 : 1 : 0{,}6347$;
$A = 100°26′$; $\alpha = 99°41′$.
$B = 85°43$; $\beta = 91°39$.
$C = 56°33$; $\gamma = 56°45½$.

Forms observed: $b = \{010\}$, very lustrous and in most cases predominant; $a = \{100\}$, narrower, giving good reflections; $\omega = \{\bar{1}11\}$ and $o = \{111\}$, yielding excellent reflections; $c = \{001\}$, also excellently reflecting and well developed; $m = \{110\}$ and $p = \{1\bar{1}0\}$, narrow, often giving good images; $t = \{120\}$, often absent, but otherwise narrow and well reflecting. The habit of the crystals is mostly thick-prismatic and flattened parallel to b. Often, however, the crystals are peculiarly distorted: e.g. they are prismatic parallel to the edge $o : \omega$. In other individuals b and t are very narrow, but m is very large in this case.

[1]) Prepared by MONTAGNE. Although the structure mentioned here is most probable, it must yet be proved. As the author's death made this impossible, the formula given here should be considered as preliminary.

Angular values:	*Observed:*	*Calculated:*
$a : m = (100) : (110) =$	* 86° 19′	—
$m : b = (110) : (010) =$	* 37 8	—
$c : b = (001) : (010) =$	* 79 34	—
$a : c = (100) : (001) =$	* 94 17	—
$\omega : b = (1\bar{1}1) : (0\bar{1}0) =$	* 52 7	—
$b : p = (0\bar{1}0) : (1\bar{1}0) =$	20 36	20° 42½′
$p : a = (1\bar{1}0) : (100) =$	35 56	35 50½
$b : o = (010) : (111) =$	57 15	57 12
$o : \omega = (111) : (1\bar{1}1) =$	70 38	70 41
$a : \omega = (100) : (1\bar{1}1) =$	53 27	53 33½
$a : o = (100) : (111) =$	88 31	88 21
$m : o = (110) : (111) =$	51 5	51 7½
$c : o = (001) : (111) =$	29 30	29 35
$c : \omega = (001) : (1\bar{1}1) =$	52 12	52 10
$b : t = (010) : (120) =$	16 50	16 51
$t : m = (120) : (110) =$	20 18	20 17
$c : m = (001) : (\bar{1}10) =$	99 25	99 17½
$c : p = (001) : (\bar{1}10) =$	80 59	80 50
$p : \omega = (1\bar{1}0) : (1\bar{1}1) =$	46 49	47 0

No distinct cleavage was found. The extinction on {010} is almost normally orientated, i. e. almost parallel and perpendicular to the edge $b : m$.

E. 3-5-Dibromo-2′-4′-6′-Trimethyl-Benzophenone[1]: $C_6H_3Br_2 . CO . C_6H_2(CH_3)_3$.

From ligroine large, very lustrous and almost colourless crystals were obtained, which show a strong variation of their habit. Also the angular values appear to oscillate not inappreciably with different individuals. The following data were obtained by means of the best developed crystals. (Fig. 5).

Monoclinic-prismatic.

$a : b : c = 0{,}5291 : 1 : 0{,}5873$;

$\beta = 70°\ 14\frac{1}{2}'$.

Forms observed: $c = \{001\}$, broad and lustrous, ordinarily predominant, but occasionally showing also smaller dimensions; $o = \{121\}$ and $m = \{110\}$, both generally equally large

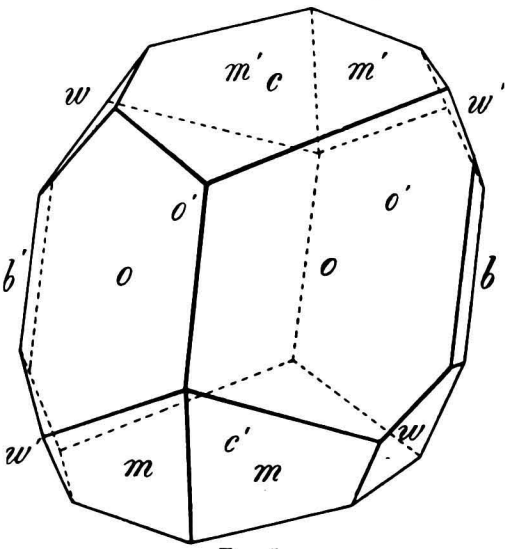

Fig. 5.

[1]) P. J. MONTAGNE: Also the paper concerning this and the following substance has not been published. However, the constitution of both these compounds has been made certain.

and very lustrous, but occasionally o is strongly predominant and *m* very narrow; $\omega = \{\bar{1}41\}$, smaller than *o*, exceptionally even very insignificant, but always yielding good reflections; $b = \{010\}$, very narrow, often absent, but e. g. in the needle-shaped crystals very well reflecting; $q = \{011\}$, rather small, giving good images, but often absent. The habit is thick and tabular parallel to {001} or elongated in the direction of an edge *b* : o. Also other combinations occur.

Angular values:	*Observed:*	*Calculated:*
$c : o = (001) : (12\bar{1}) =$	* 47° 53′	—
$m : m = (110) : (1\bar{1}0) =$	* 52 56½	—
$c : m = (001) : (110) =$	* 72 23	—
$o : o = (121) : (1\bar{2}1) =$	65 20	65° 14½′
$o : m = (121) : (110) =$	29 22	29 15
$o : \omega = (121) : (14\bar{1}) =$	58 40	58 38
$o : \omega = (1\bar{2}1) : (\bar{1}4\bar{1}) =$	64 25	64 22
$\omega : o = (\bar{1}4\bar{1}) : (\bar{1}2\bar{1}) =$	48 15	48 22½
$o : m = (1\bar{2}1) : (110) =$	67 12	67 16
$c : \omega = (001) : (\bar{1}4\bar{1}) =$	75 36	75 40
$c : q = (001) : (011) =$	28 59	28 56
$b : q = (010) : (01\bar{1}) =$	61 1	61 4
$o : q = (121) : (0\bar{1}1) =$	70 59	70 58
$q : \omega = (0\bar{1}1) : (\bar{1}4\bar{1}) =$	49 50	49 48
$q : o = (1\bar{2}1) : (0\bar{1}1) =$	32 4	32 1
$o : b = (121) : (010) =$	57 20	57 23

No distinct cleavage was found.

On {001} there is a diagonal extinction; on *m* and *b* it is oblique with respect to the vertical axis.

F. 4-4′-4″-4‴-*Tetrabromo-Benzopinacone* [1]: $(C_6H_4Br)_2\,C\,.\,OH\,.\,C.\,OH.\,(C_6H_4Br)_2 + 1$ *Ethyl-acetate.*

From ethylacetate this substance crystallizes in thick, colourless, prismatic crystals, containing 1 molecule of the solvent. Already at a slight increase of temperature they turn opaque by loss of ethylacetate. The clear, transparent crystals appear to be well built and show constant angles.

Monoclinic-prismatic.

$$a : b : c = 1{,}7540 : 1 : 0{,}4636;$$

$$\beta = 81° 41'.$$

[1]) Prepared by P. J. MONTAGNE; concerning this compound must be applied what has been remarked in the footnote on the preceding page.

Forms observed: $a=\{100\}$, large, often curved and yielding multiple reflections; $m=\{110\}$, somewhat broader than $b=\{010\}$, both giving very sharp images; $o=\{111\}$, broad and lustrous; $\omega=\{\bar{1}11\}$, much smaller than o, but also well reflecting. The habit is elongated parallel to the c-axis and flattened parallel to $\{100\}$. (Fig. 6).

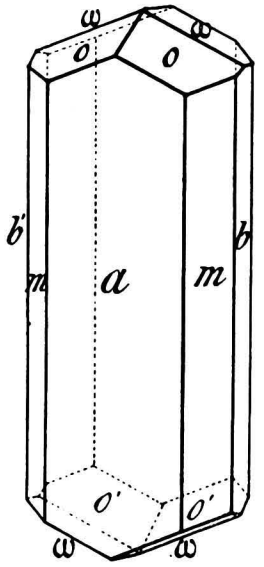

Fig. 6.

Angular values:	*Measured*:	*Calculated*:
$a:m=(100):(110)$	$=^*$ 60° 3′	—
$a:\omega=(\bar{1}00):(\bar{1}11)$	$=^*$ 83 44	—
$b:o=(010):(111)$	$=^*$ 67 18	—
$b:\omega=(010):(\bar{1}11)$	$=$ 65 23	65° 17⅓′
$o:o=(111):(1\bar{1}1)$	$=$ 45 24	45 24
$\omega:\omega=(\bar{1}\bar{1}1):(\bar{1}11)$	$=$ 49 14	49 25⅓
$b:m=(010):(110)$	$=$ 29 57	29 57
$o:\omega=(111):(\bar{1}11)$	$=$ 26 55	26 54
$a:o=(100):(111)$	$=$ 69 22	69 26

No distinct cleavage was found.

On $\{100\}$ the extinction was normal. The plane of the optical axes is $\{010\}$; on (100) and (101) one of the optical axes can be seen excentrically. The dispersion is inclined and rather strong.

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