Acta Cryst. (1976). B**32**, 431

The Crystal and Molecular Structure of 2-Hydroxy-4-methoxy-4′-chlorobenzophenone (HMCB)

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(*Received* 2 *June* 1975; *accepted* 12 *June* 1975)

$C_{14}H_{11}O_3Cl$, monoclinic, $C2/c$, $a=25{\cdot}04$ (2), $b=3{\cdot}935$ (5), $c=29{\cdot}53$ (2) Å, $\beta=122{\cdot}0$ (1)°, $U=2467{\cdot}4$ Å^3, $Z=8$, $M=262{\cdot}7$, $D_x=1{\cdot}416$ g cm^{-3}, $F(000)=1088$. Counter technique, direct methods, least-squares refinement, $R=5{\cdot}0\%$ for 1268 reflexions measured at 20°C ($R_w=2{\cdot}5\%$). An asymmetrical hydrogen bond with O(1)···O(2) 2·540 Å is present. Comparison with 2-hydroxy-4-methoxybenzophenone (HMB) is made and similarities and differences discussed. HMB and HMCB are non-planar and in both cases the crystal is composed of pairs of centrosymmetrically related molecules. The short intermolecular Cl···Cl distances for HMCB and the presence of pairs of molecules for both compounds are important features. The present results may also add to the knowledge of the optical filter effect of this family of substances.

Introduction

We present the crystal and molecular structure of 2-hydroxy-4-methoxy-4′-chlorobenzophenone (HMCB), and a comparison of HMCB with 2-hydroxy-4-methoxybenzophenone (HMB) (Liebich & Parthé, 1974*a*).

A study has been made of the complexes formed between HMCB and trace amounts of H_3BO_3 in concentrated sulphuric acid and the fluorescence of this reaction used to determine accurately 10^{-9} g of B in water (Liebich, Monnier & Marcantonatos, 1970), soil and plants (Liebich, 1971). More recently it was observed that HMB, used on an industrial scale as an ultraviolet absorber, reacted in a similar way.

The molecular conformation and structure of HMCB and HMB are of interest since they possess photochemical stability and a good filter effect, whereas other benzophenone derivatives are photochemically unstable.

It has been noticed that there are distinct similarities in the molecular geometries of HMB and salicylic acid (Liebich & Parthé, 1974*b*). The structure of the latter was first reported (Cochran, 1953) and later refined (Sundaralingam & Jensen, 1964) and subsequently compared with acetylsalicylic acid (aspirin) (Wheatley, 1964). It appears that similarities between the bond lengths and angles of HMB, HMCB, and salicylic acid can partly be explained by the presence of a similar intramolecular hydrogen bond associated with an aromatic ring, a feature which is not present in acetylsalicylic acid; however intermolecular hydrogen bonds exist both in salicylic and acetylsalicylic acid but not in HMB and HMCB.

Table 1. *Positional and thermal parameters of the heavy atoms of* HMCB ($\times 10^4$)

The temperature factors are in the form $\exp[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{23}klb^*c^*+2U_{13}hla^*c^*)]$. E.s.d.'s are in parentheses.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	1593 (2)	8489 (12)	593 (2)	303 (30)	395 (30)	324 (29)	30 (25)	177 (24)	7 (24)
C(2)	1921 (2)	9678 (12)	361 (2)	276 (30)	406 (32)	437 (32)	27 (25)	191 (25)	−12 (25)
C(3)	1675 (2)	9397 (13)	−185 (2)	374 (35)	475 (35)	443 (34)	41 (28)	283 (28)	53 (27)
C(4)	1099 (2)	7818 (12)	−500 (2)	424 (33)	434 (33)	342 (31)	128 (26)	216 (27)	36 (26)
C(5)	767 (2)	6517 (12)	−283 (2)	375 (34)	500 (34)	323 (33)	−24 (29)	185 (28)	−40 (28)
C(6)	1012 (2)	6839 (12)	253 (2)	325 (32)	423 (33)	506 (36)	−31 (27)	282 (28)	46 (27)
C(7)	1873 (2)	8853 (12)	1173 (2)	381 (33)	469 (33)	455 (34)	55 (28)	256 (29)	28 (28)
C(8)	1096 (3)	8910 (19)	−1300 (2)	720 (51)	744 (55)	445 (38)	100 (44)	361 (37)	10 (40)
C(1′)	1510 (2)	8068 (12)	1429 (2)	329 (33)	459 (33)	314 (29)	−31 (26)	170 (26)	−34 (24)
C(2′)	1834 (2)	6514 (13)	1933 (2)	297 (34)	589 (36)	375 (31)	27 (30)	170 (26)	−5 (27)
C(3′)	1547 (2)	5963 (14)	2211 (2)	383 (35)	615 (39)	338 (31)	38 (31)	140 (27)	43 (29)
C(4′)	933 (2)	7058 (13)	1997 (2)	540 (35)	554 (37)	404 (28)	−85 (30)	332 (26)	−45 (27)
C(5′)	595 (2)	8632 (13)	1501 (2)	333 (36)	581 (37)	432 (35)	37 (31)	243 (29)	−9 (29)
C(6′)	891 (2)	9126 (12)	1225 (2)	369 (38)	519 (34)	305 (30)	52 (29)	160 (28)	12 (27)
O(1)	2489 (1)	11219 (10)	653 (1)	396 (22)	833 (29)	451 (22)	−126 (21)	240 (18)	−50 (24)
O(2)	2424 (1)	9896 (10)	1464 (1)	356 (20)	1101 (33)	400 (19)	−210 (22)	156 (16)	−57 (21)
O(3)	814 (1)	7358 (9)	−1037 (1)	551 (21)	697 (27)	339 (20)	25 (19)	253 (17)	−6 (19)
Cl	562 (1)	6377 (4)	2347 (1)	812 (10)	1088 (14)	664 (9)	25 (11)	569 (8)	94 (10)

Experimental

Pale yellow needles of HMCB were grown from 96% alcohol solutions (Aldrich & Co.). Photographs of a crystal (0·4 × 0·12 × 0·08 mm) permitted the determination of the centrosymmetric space group $C2/c$ (No. 15) with systematic absences hkl with $h+k \neq 2n$, $h0l$ with $l \neq 2n$. 1683 intensities ($1268 \geq 3\sigma$) were collected at 20 °C on a Philips PW 1100 automatic diffractometer (ω–2θ scan, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}7107$ Å, graphite monochromator).

The structure was solved by direct methods with *LSAM* (Main, Woolfson & Germain, 1972). Refinement was carried out with *CRYLSQ* (X-RAY system, 1972). The function minimized was $\sum w(\Delta F^2)$ where $w = 1/\sigma^2(F_o)$.

Scattering factors were from Cromer & Mann (1968).*

In the preliminary stage of refinement the data set was limited to $\sin\theta/\lambda \leq 0{\cdot}3$ Å^{-1}. Later, atomic positions and anisotropic thermal parameters of the heavy atoms (Table 1) were refined by full-matrix least-squares calculations with all the data. The H atoms were located from a difference map and their positions and isotropic thermal parameters (Table 2) refined. The final cycle gave an $R = [\sum|\Delta F|/\sum|F_o|]$ of 5·0% ($R_w = 2{\cdot}5$%) for 1268 reflexions with $I \geq 3\sigma$.

Table 2. *Positional and thermal parameters of the hydrogen atoms of* HMCB (× 10^3)

Isotropic temperature factors are expressed as $\exp[-8\pi^2 U(\sin\theta/\lambda)^2]$. E.s.d.'s are in parentheses.

	x	y	z	U
H(O1)	259 (2)	1120 (11)	95 (1)	56 (15)
H(C3)	190 (1)	1039 (10)	−32 (1)	20 (15)
H(C5)	35 (1)	517 (9)	−52 (1)	43 (12)
H(C6)	77 (1)	579 (10)	40 (1)	5 (14)
H(C2′)	229 (1)	566 (9)	207 (1)	38 (12)
H(C3′)	179 (1)	484 (9)	257 (1)	59 (12)
H(C5′)	13 (1)	935 (9)	136 (1)	65 (14)
H(C6′)	65 (1)	1039 (9)	88 (1)	50 (12)
H′(C8)	84 (1)	827 (11)	−165 (1)	69 (14)
H″(C8)	151 (1)	787 (10)	−118 (1)	71 (14)
H‴(C8)	113 (2)	1141 (10)	−125 (1)	76 (14)

Discussion

The bond distances and angles calculated with *BONDLA* (X-RAY system, 1972) are given in Fig. 1.

A comparison of the values obtained for HMB (Liebich & Parthé, 1974*a*) where H replaces Cl, in the 4′ position can be made. In Table 3 we see the differences between distances and angles of atoms round the hydrogen bond. O(1)–O(2), C(7)–O(2), and O(1)–H(O1) are slightly shorter in HMCB whereas C(1)–C(7) is significantly longer. C(3)–C(2)–O(1) and C(1)–C(7)–O(2) are also slightly smaller, whereas C(1′)–C(7)–O(2) is larger. The differences observed for distances and angles including H(O1) are more difficult to evaluate. The angles and distances of the two methoxy groups are of the same order. The distance of 1·740 Å for C(4′)–Cl for HMCB lies within the expected range. In both HMCB and HMB the distances of about 1·37 Å for C(3)–C(4) and C(5)–C(6) are significantly shorter than the normal C–C distance found for aromatic rings. A similar shortening of C–C bonds in comparable positions was observed in salicylic acid (Cochran, 1953) and suggests the contribution of a quinoid tautomer to the overall state of resonance. The O–H distances in the O(1)···O(2) hydrogen bond indicated in Fig. 1 and Table 3 were obtained after isotropic refinement, and from a maximum in the difference map the most probable position of the H atom is near O(1).

In the benzene ring [C(1) to C(6)] in HMB and HMCB, the angles at C(2), C(4) and C(6) are about 2° larger whereas the angles at C(1), C(3) and C(5) are about 1·5° smaller than 120°. Similar deviations were found in genisteine (Breton, Precigoux, Courseille & Hospital, 1974).

Table 4 gives the torsion angles for HMB and HMCB. The values for C(6)–C(1)–C(7)–O(2) and C(6)–C(1)–C(2)–O(1) are of the same order of magni-

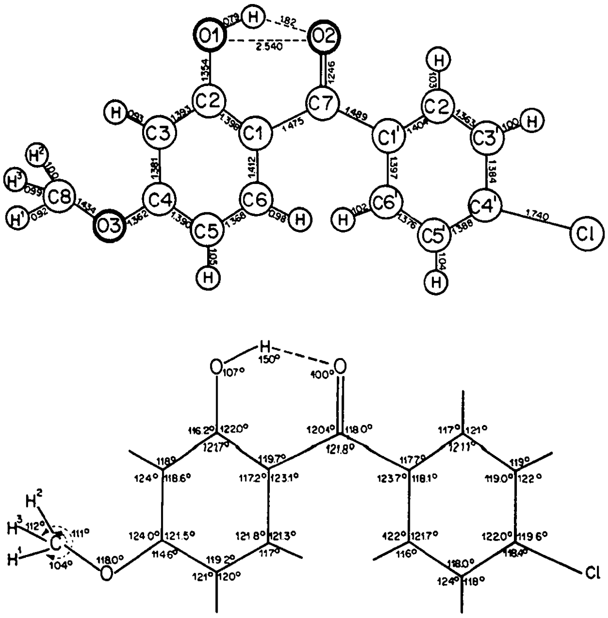

Fig. 1. The molecule, the numbering scheme, the intramolecular distances and the angles in HMCB. The estimated standard deviations for the distances between heavy atoms are 0·007 Å and for bonds to H, 0·04 Å. The estimated standard deviations for the angles are 0·4°, except for those including H where the value is 2°.

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* A table of observed and calculated structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31195 (17 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Angles and distances around the intramolecular hydrogen bond of* HMCB *and* HMB

The estimated standard deviations for the distances between the heavy atoms are 0·007 Å for HMCB and 0·005 Å for HMB but 0·05 Å for the bonds including H. The e.s.d.'s in the angles between heavy atoms are 0·4° for HMCB and 0·3° for HMB, but those including H, 2°.

	HMCB	HMB
O(1)—O(2)	2·540 Å	2·551 Å
C(2)—O(1)	1·354	1·355
C(7)—O(2)	1·246	1·255
C(1)—C(7)	1·475	1·447
C(2)—C(1)	1·398	1·406
O(1)—H(O1)	0·79	1·04
C(3)—C(2)—O(1)	116·2°	117·1°
C(1)—C(2)—O(1)	122·0	121·7
C(1)—C(7)—O(2)	120·1	121·0
C(1′)—C(7)—O(2)	118·0	116·1
C(2)—O(1)—H(O1)	107	102
O(1)—H(O1)-O(2)	150	154
H(O1)-O(2)—C(7)	100	100

Table 4. *Torsion angles in the two centrosymmetrically related forms of* HMCB *and* HMB

	HMCB	HMB
C(3)-C(4)-O(3)-C(8)	∓6·7°	±0·9°
C(1)-C(7)-C(1′)-C(6′)	∓47·0	∓43·8
C(6)-C(1)-C(2)-O(1)	∓178·3	∓178·3
C(6)-C(1)-C(7)-O(2)	±169·9	±168·7
C(6)-C(1)-C(7)-C(1′)	∓11·4	∓11·7
C(1)-C(2)-O(1)-H(O1)	±2·4	±7·3

tude for both HMCB and HMB, and characterize these particular intramolecular hydrogen bonds.

In HMCB there is a twist of 6·7° in O(3)–C(8) of the methoxy group away from the benzene ring. The twist between the two benzene rings in HMB and HMCB is indicated by a torsion of about 11° for C(6)–C(1)–C(7)–C(1′) and respectively a torsion of 44° and 47° for C(1)–C(7)–C(1′)–C(6′).

In Table 5 the deviations of atoms from least-squares planes are given. In HMB and HMCB the benzene rings are very nearly planar, but distinct deviations for plane 2 through the enol ring are found. The angles between planes 1 and 3 are 49·9° for HMCB and 49·0° for HMB, and between planes 1 and 2, 4·0° for HMCB and 3·6° for HMB. The dihedral angles between the benzene and enol rings also show significant distortions in the hydrogen bonds of both compounds.

According to Kitaigorodskii (1961, 1973) the presence of four centrosymmetric molecules is expected for *Pbca* and *C*2/*c*; if eight molecules are found, as for HMB and HMCB, the molecules are associated in centrosymmetrically related pairs, and take the place of the previous centrosymmetric molecules. The unit cell of the structures of HMB and HMCB, and the layered packing of the eight molecules, can be seen in Figs. 2 and 3. Cl has a distinct effect on the packing in HMCB (*C*2/*c*). Several compounds with a hydrogen bond between a hydroxyl and a carbonyl group which

Table 5. *Equations of least-squares planes through sets of atoms and distances* (Å) *of atoms from the plane* (*in square brackets*) *for* HMB *and* HMCB

System of axes used for planes: orthonormal axes with *x*(ortho) ⊥ to **b** and to **c**, *y*(ortho) ∥ to **b**, *z*(ortho) ∥ to **c**.

(*a*) Least-squares planes for HMB

Plane 1: C(1), C(2), C(3), C(4), C(5), C(6) (benzene)
[C(1) −0·014; C(2) 0·010; C(3) 0·005; C(4) −0·016; C(5) 0·011; C(6) 0·003; C(7) −0·019; C(8) −0·103; O(1) 0·030; O(2) 0·177; O(3) −0·076]
Plane 2: C(1), C(2), C(7), O(1), O(2) (enol)
[C(1) 0·020; C(2) 0·029; C(7) −0·063; O(1) −0·037; O(2) 0·052; H(O1) 0·044]
Plane 3: C(1′), C(2′), C(3′), C(4′), C(5′), C(6′) (benzene)
[C(1′) −0·001; C(2′) 0·010; C(3′) −0·010; C(4′) 0·001; C(5′) 0·009; C(6′) −0·009; C(7) 0·061]
Plane 1: $0\cdot063546x-0\cdot981723y-0\cdot179395z+2\cdot60691=0$
Plane 2: $0\cdot028021x-0\cdot970988y-0\cdot237479z+2\cdot827307=0$
Plane 3: $0\cdot412387x+0\cdot552366y+0\cdot724451z-4\cdot645746=0$

(*b*) Least-squares planes for HMCB

Plane 1: C(1), C(2), C(3), C(4), C(5), C(6) (benzene)
[C(1) −0·014; C(2) 0·012; C(3) −0·001; C(4) −0·007; C(5) 0·004; C(6) 0·007; C(7) −0·001; C(8) −0·146; O(1) 0·029; O(2) 0·168; O(3) 0·005]
Plane 2: C(1), C(2), C(7), O(1), O(2) (enol)
[C(1) 0·012; C(2) 0·028; C(7) −0·051; O(1) −0·034; O(2) 0·044; H(O1) −0·044]
Plane 3: C(1′), C(2′), C(3′), C(4′), C(5′), C(6′) (benzene)
[C(1′) 0·021; C(2′) −0·009; C(3′) 0·001; C(4′) −0·003; C(5′) 0·015; C(6′) −0·024; C(7) −0·113; Cl 0·007]
Plane 1: $0\cdot448644x-0\cdot879263y+0\cdot160049z+1\cdot312678=0$
Plane 2: $0\cdot421229x-0\cdot900867y+0\cdot104905z+1\cdot577733=0$
Plane 3: $-0\cdot113421x-0\cdot885468y+0\cdot450646z+4\cdot618766=0$

(*c*) Angles between least-squares planes (centrosymmetrically related forms considered) of HMB and HMCB

	HMB	HMCB
Plane 1/Plane 3	±49·0°	±49·9°
Plane 1/Plane 2	± 3·6	± 4·0
Plane 2/Plane 3	±45·4	±45·8

participates in a system of conjugated double bonds (on, or close to, an aromatic ring) are formed of centrosymmetrically related pairs (allowed space groups $P\overline{1}$, $P2_1/c$, $C2/c$ and $Pbca$), *e.g.* salicylic acid (Cochran, 1953), dibenzoylmethane (Williams, 1966), ω-(*p*-toluoyl)-acetophenone enol (Kato, 1971), benzoylacetone (Semmingsen, 1972), genisteine (Breton *et al.*, 1974), tropolone (Shimanouchi & Sasada, 1970), and also two derivatives of tropolone (Wiehager, 1975).

The low photochemical reactivity of certain derivatives of benzophenone especially some with hydroxyl groups in the *ortho* position were studied by Beckett & Porter (1963). It was shown that, on excitation by a medium-pressure mercury arc, 2,4-dihydroxybenzophenone gave no luminescence in solution and in the

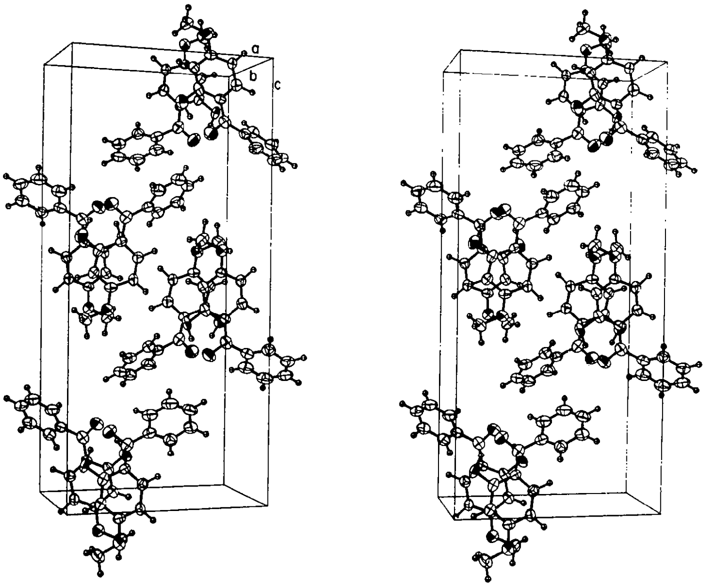

Fig. 2. Stereo view of the arrangement of HMB molecules in the (010) plane. Eight molecules with centres between $0<y<1$ are shown (*ORTEP*; Johnson, 1971).

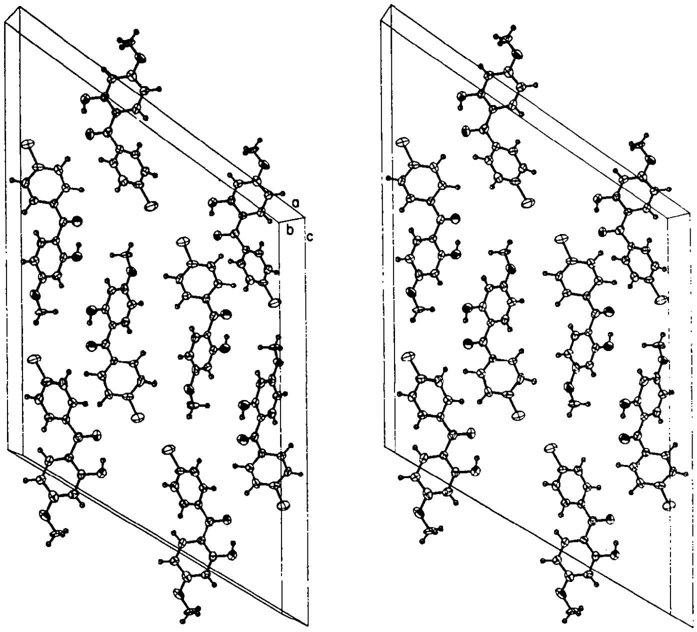

Fig. 3. Stereo view of the arrangement of HMCB molecules in the (010) plane. Eight molecules with centres between $0<y<1$ are shown (*ORTEP*; Johnson, 1971).

crystalline state at room temperature and at 77°K. To explain the dissipation of the absorbed energy, an efficient radiationless deactivation process was sought, such as aggregation in solution. No evidence of aggregation could be found in the molecular weight determination. For this reason the structure determination of HMB and of HMCB which shows the presence of dimers of centrosymmetrically related molecules is an important new element in the understanding of the photostability of these hydroxy derivatives of benzophenone.

I thank Professors E. Parthé and K. Yvon for their continued interest and support, and Dr H. D. Flack for adapting the programs.

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Crystal Structures of Acid Hydrates and Oxonium Salts. IX. *o*-Sulphobenzoic Acid Trihydrate*

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(*Received* 12 *June* 1975; *accepted* 16 *June* 1975)

The structure of $C_6H_4(COOH)SO_3H.3H_2O$ has been determined from 3180 X-ray intensities collected on an automatic diffractometer, and refined, including H atoms, to $R=0{\cdot}038$. The crystals are triclinic, space group $P\bar{1}$, with $a=6{\cdot}954$ (1), $b=11{\cdot}741$ (2), $c=7{\cdot}872$ (1) Å, $\alpha=102{\cdot}11$ (1), $\beta=111{\cdot}73$ (2), $\gamma=103{\cdot}83$ (2)°, $Z=2$. The anions, deprotonated at the sulpho group only, are stacked in layers. Successive layers are connected by the interleaving water structure, which with a short [O–O: 2·404 (2) Å] and a normal [2·714 (2) Å] hydrogen bond is $H_5O_2^+.H_2O$. There is no hydrogen bonding directly between anions.

Introduction

For investigation of higher hydrated protons in the crystalline state, the hydrates of aromatic sulphonic acids are of special interest. Mostly these hydrates contain more than one molecule of water, thus enabling the acid proton of the sulpho group to form various cationic water species. X-ray and neutron investigations show the cation $H_7O_3^+$ in the following trihydrates: 5-sulphosalicylic acid (X-ray: Mootz & Fayos, 1970; neutron: Williams & Peterson, 1972), 2,5-dichlorobenzenesulphonic acid (Lundgren & Lundin, 1972) and 2,5-dibromobenzenesulphonic acid (Lundgren, 1972*a*). The tetrahydrate of picrylsulphonic acid (X-ray: Lundgren, 1972*b*; neutron: Lundgren &

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* Part of the dissertation of R. Attig, Braunschweig, 1973. Part VIII: Attig & Mootz (1975). *Z. anorg. allgem. Chem.* In the press.