Polymorphism of Dibromo-tetrakis(tetrahydrofuran-κO)magnesium(II)

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The title compound, $[MgBr_2(C_4H_8O)_4]$ (**1a**), forms twinned four-component monoclinic crystals as a new polymorph, space group $P2_1/n$ with $Z' = 2$, in addition to the already known tetragonal polymorph (**1b**). Although the molecular parameters in the two polymorphs match very well, the packing patterns are significantly different. Furthermore, the correct constitution of the mixed halide bromo-chloro-tetrakis(tetrahydrofuran-κO)magnesium(II) (**2**) could be determined.

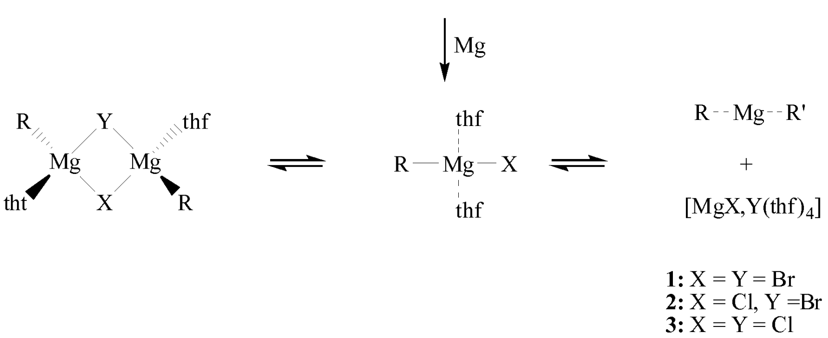
Key words: Polymorphism, Crystal Structure, Magnesium Halides, Schlenk Equilibrium, Grignard Reaction

Introduction

Since the first reports on organomagnesium compounds by Barbier [1] and Grignard [2] these highly reactive intermediates have become key reagents in synthetic chemistry [3 – 6]. Although the stoichiometry of a Grignard reagent can be expressed by the simple empirical formula RMgX (R = organic substituent, X = halide), the real composition is far more complex, both in solution and in the solid state. It can be described by the fundamental Schlenk equilibrium [7] (Scheme 1) where solvated MgX_2 (X = Cl, Br, I) is also present.

The position of the Schlenk equilibrium depends on the solvent, the concentration of the solution, the nature of the organic group and the halide, as well as the temperature. The most important factors are the solvent and the concentration [8]. Therefore, the isolation of the Grignard reagent (RMgX) itself can be exceedingly difficult and is typically hampered by the precipitation of either the magnesium dialkyl or, more frequently, the magnesium dihalide. Hence, for X-ray structural analyses the precise and reliable knowledge of the cell parameters of all possible magnesium halide complexes helps to avoid wasting valuable time.

Herein we report the crystal structures of monoclinic $[MgBr_2(C_4H_8O)_4]$ (**1a**), which is a polymorph of the already known tetragonal structure **1b** [9 – 11]. Both polymorphs could be transformed into each other by slow cooling or heating while they undergo a non-destructive phase transition which was detected by DSC and X-ray crystal structure analysis. Furthermore, we describe the structure of the mixed magnesium halide complex $[Mg(Br,Cl)(C_4H_8O)_4]$ (**2**), which was erroneously published to be a triclinic polymorph (**1c**) of **1b** [12].



Scheme 1. Formation of solvated magnesium dihalide from organomagnesium reagents in tetrahydrofuran.

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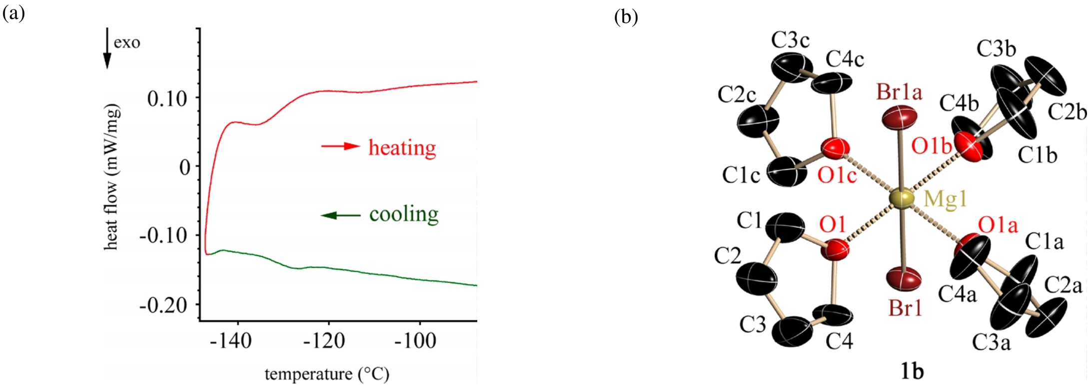


Fig. 1 (color online). (a) DSC curves in the temperature window of −90 to −145 °C at a cooling rate (ν_c) of 10 °C min^{-1} and a warming rate (ν_w) of 10° min^{-1}; (b) molecular graph of tetragonal **1b** showing the atom numbering scheme. Anisotropic displacement parameters are drawn at the 50 % probability level, and H atoms are omitted for clarity (symmetry codes: (a) $-x+2$, $-y$, z; (b) $y+1$, $x-1$, $-z$; (c) $-y+1$, $-x+1$, $-z$).

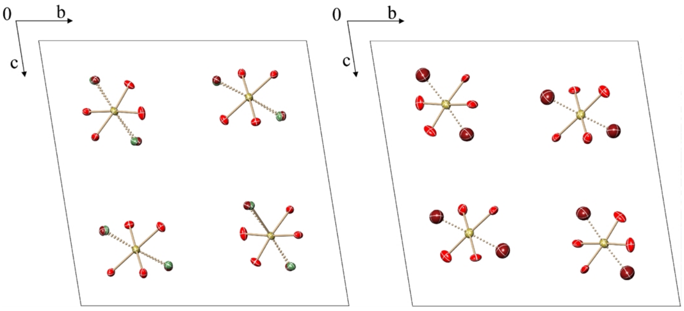


Fig. 2 (color online). A packing diagram for [Mg(Br,Cl)(C_4H_8O)$_4$] (left) and the correctly assigned [$MgBr_2$(C_4H_8O)$_4$] 'polymorph' (right), viewed in the crystallographic *bc* plane. Anisotropic displacement parameters are drawn at the 50 % probability level. C and H atoms are omitted for clarity. Color coding: Mg atoms are golden, Br atoms are brown, Cl atoms are green and O atoms are red.

Results and Discussion

The crystals analyzed were repeatedly obtained by preparing anthrylmagnesium bromides (**1a**), treating MeMgBr with S(N^{t}Bu)$_3$ (**1b**) or 2-thiophenylmagnesium bromide with phosphanyl chlorides (**2**) in THF but can of course also be prepared much more easily by reacting magnesium turnings with elemental halogens in THF [13].

Magnesium dibromide crystallizes from THF solution as dibromido-tetrakis(tetrahydrofuran)magnesium in the tetragonal space group $P4_22_12$ (**1b**) which was first described by Schröder and Spandau [9]. Redeterminations (all at room temperature) of this structure were described by Le Bihan and coworkers [10], Metzler *et al.* [11] and later by Heeg *et al.* [14]. Another supposed polymorph (triclinic space group $P\bar{1}$) **1c** was published by Bolte *et al.* [12].

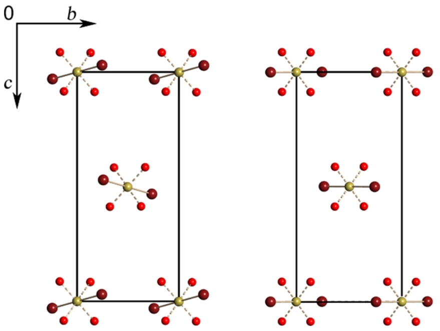


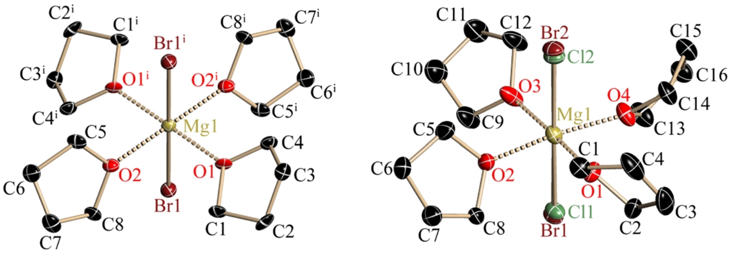
Fig. 3 (color online). Packing diagram for **1a** (left) and **1b** (right), viewed in the *bc* plane. C and H atoms have been omitted for clarity. Color coding: Mg atoms are golden, Br atoms are brown and O atoms are red.

The shock cooling of a single crystal of **1b** from r. t. to 100 K results in a sample showing a multicomponent defractrogram caused by a destructive phase transition. At an elevated data collection temperature of 170 K the integrity of the single crystal is maintained, and the structure analysis shows it to be the known tetragonal polymorph **1b**. This behavior indicates a phase transition from one crystalline state to another. Fig. 1A presents the DSC curves in the temperature window of −90 to −145 °C, obtained from a microcrystalline sample of **1a** cooled at a rate (ν_c) of 10 °C min^{-1},

Table 1. Comparison of the crystallographic data and structure refinement parameters for the two polymorphs of $[MgBr_2(C_4H_8O)_4]$ (**1a** and **1b**), the published erroneous polymorph **1c** and $[MgBr,Cl(C_4H_8O)_4]$ [12] (**2**), identical to **1c**.

	1a	**1b**	**1c**	**2**
	X = Y = Br	X = Y = Br	"X = Y = Br"	X = Cl, Y = Br
Crystal system	monoclinic	tetragonal	triclinic	triclinic
Space group	$P2_1/n$	$P4_22_12$	$P\bar{1}$	$P\bar{1}$
CSD	770832	770833	645523	770831
Temperature, K	100(2)	170(2)	173(2)	100(2)
Empirical formula	$MgBr_2(C_4H_8O)_4$	$MgBr_2(C_4H_8O)_4$	$MgBr_2(C_4H_8O)_4$	$MgBrCl(C_4H_8O)_4$
Z	2	2	4	4
Formula mass	472.55	472.55	472.55	428.09
Cell constants				
a, Å	7.965(2)	7.7652(4)	8.6620(9)	8.5929(5)
b, Å	7.3950(19)	7.7652(4)	15.6820(12)	15.4662(9)
c, Å	16.965(4)	16.9908(19)	15.6910(13)	15.5008(9)
α, deg	90	90	80.501(9)	80.717(2)
β, deg	99.005(3)	90	85.131(11)	85.304(2)
γ, deg	90	90	85.190(11)	85.276(2)
Volume, Å	3986.9(4)	1024.52(14)	2089.3(3)	2021.2(2)
ρ_{calc}, g cm^{-3}	1.59	1.53	1.50	1.41
F (000), e	484	484	968	896
θ range, deg	2.43 – 26.17°	2.40 – 26.74°	2.37 – 25.03°	1.74 – 28.28°
No. of coll. reflns.	11600	21837	22055	99174
No. of indep. reflns.	2388	1088	7347	10048
R_{int}	0.0283	0.0228	0.0804	0.0289
Data / restraints / ref. params.	2388 / 0 / 109	1088 / 23 / 55	7347 / 0 / 416	10048 / 28 / 448
$R1$, $wR2$ $[I \geq 2\sigma(I)]^a$	0.0509, 0.1317	0.0265, 0.0676	0.0872, 0.1163	0.0215, 0.0528
$R1$, $wR2$ (all data)	0.0579, 0.1384	0.0299, 0.0702	0.2321, 0.2211	0.0232, 0.0535
g_1 / g_2^{b}	0.0511 / 5.1094	0.0313 / 0.8033	0.091 / –	0.0253 / 0.6804
Goodness-of-fit^c	1.12	1.044	1.438	1.078
Largest diff. peak / hole, e Å^{-3}	1.03 / −0.83	0.27 / −0.26	0.97 / −1.11	0.33 / −0.29
av. Mg–X,Y, Å	2.6572(8)	2.6552 (3)	2.583(4)	2.488(8), 2.602(3)
av. Mg–O, Å	2.135(5)	2.0990 (15)	2.108(9)	2.0964(14)
U_{iso}	Mg1 = 0.0160(8) Br1 = 0.0209(2)	Mg1 = 0.0292(3) Br1 = 0.04351(15)	Mg1 = 0.0296(9) Br2 = 0.0814(7)	Mg1 = 0.02135(11) Br1 = 0.02792(25)

^{a} $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$; ^{b} $w = [\sigma^2(F_o^2)+(g_1P)^2+g_2P]^{-1}$, where $P = (\mathrm{Max}(F_o^2, 0)+2F_c^2)/3$; ^{c} GoF = $[\Sigma w(F_o^2 - F_c^2)^2/(n_{obs} - n_{param})]^{1/2}$.



1a **2**

Fig. 4 (color online). Molecular graph of **1a** (left) and **2** (right) showing the atom numbering scheme. Anisotropic displacement parameters are depicted at the 50 % probability level. H atoms are omitted for clarity (symmetry code: (i) $-x+1$, $-y+1$, $-z+1$).

and then heated at a constant warming rate (ν_w) of 10 °C min^{-1}. The thermogram of the subsequent cooling shows one exothermic (−120 to −135 °C) signal that corresponds to a solid-solid transformation from the crystalline form **1a** to **1b**. Cooling down a single crystal of **1b** slowly to 100 K (ν_c = 10 K min^{-1}) leads to a crystalline sample of polymorph **1a** suitable for X-ray structure determination.

The structure determination revealed a monoclinic unit cell with almost identical parameters as for **1a** (see Table 1). A molecular graph of **1b** is given in Fig. 1b showing the central magnesium cation octahedrally coordinated by four equatorial THF molecules and the two bromide ions at the apical positions. The comparison of the data of our monoclinic polymorph with the five available datasets of **1b** suggests that the 'triclinic polymorph' **1c** published by Bolte *et al.* [12] is not made up exclusively by $MgBr_2$ but rather by a mixture of magnesium salts where the bromine atoms share their sites with the chlorine atoms. The packing pattern also differs completely from that for the tetragonal polymorph and the monoclinic polymorph described here.

The published structure of **1c** shows too large displacement ellipsoids of the bromine atoms compared to the other atoms (*e. g.* $U_{\text{iso}}(\text{Br2})/U_{\text{iso}}(\text{Mg1}) = 2.75$). The R values are too high ($wR2 = 0.232$, $R1 = 0.087$), and the goodness-of-fit value (1.44) is not close to 1.0. A redetermination of the structure of this 'polymorph' confirmed our assumption, revealing the compound to be the complex $[Mg(Br,Cl)(C_4H_8O)_4]$ (**2**). Table 1 contains crystallographic data, Fig. 2 shows the packing diagram of the incorrect (**1c**) and the correctly assigned structure of **2**. All structural quality features clearly indicate the new $[Mg(Br,Cl)(C_4H_8O)_4]$ refinement to be correct.

Unfortunately, the published crystal structures of the tetragonal polymorph could not be employed in the comparison to the new monoclinic polymorph because Schröder and Spandau published only the cell constants but not the atom coordinates. Moreover, the previous structures were determined at r. t. Therefore we re-determined the structure of the tetragonal polymorph **1b** at 170 K.

The packing pattern of the two polymorphs, monoclinic **1a** and tetragonal **1b** (Fig. 3), is slightly different. In both cases the Mg atoms are placed at the corners and in the center of the unit cell, leading to planes of molecules at $z = 0$ and $z = 1/2$ (Fig. 3, left). For **1b** the different planes of molecules have to be rotated by 90° and translated by ($1/2$, $1/2$, $1/2$) to fit each other, but due to an additional rotational symmetry element along the a axis this operation fails for **1a**.

A comparison of **1a** and **2** is given in Fig. 4. **1a** is a new polymorph of dibromido-tetrakis(tetrahydrofuran) magnesium, showing a destructive phase transition resulting in multiple domains. In Table 1 the basic crystallographic data of both polymorphs **1a** and **b**, the erroneous 'triclinic polymorph' **1c** and the mixed halogen magnesium salt complex **2** are compared. Presently no triclinic polymorph of $[MgBr_2(C_4H_8O)_4]$ is known.

In $[MgX,Y(C_4H_8O)_4]$ (**1a** and **b**: X = Y = Br, **1c** and **2**: X = Cl, Y = Br) the magnesium atoms show octahedral coordination geometry with the two halogen atoms axially oriented. In the polymorphs **1a** and **1b** the magnesium and bromine atoms are located at special positions. Therefore the Br–Mg–Br angle is exactly 180° by symmetry requirements. However, that angle in the mixed halide complexes **1c** and **2** is marginally different (3 – 6°) from 180°. The characteristic bond lengths (Table 1) Mg–Br and Mg–O of **1a** agree well with those of **1b**.

A remarkably similar polymorphism has been described for the complex $[MgCl_2(C_4H_8O)_4]$ (**3**). Handlir *et al.* determined a tetragonal polymorph (space group $P4_22_12$) by powder diffraction [15], and additionally two monoclinic polymorphs (both space group $P2_1/c$) have been found.

The determination of the two monoclinic structures, carried out at r. t. (Huang *et al.* [16]), at 173 K (Bolte *et al.* [17]) and at 150 K (Parsons *et al.* [18]), which differ only in the choice of the unit cell, presented all massive problems indicated by large unit cells, unresolved disorder, isotropic displacement parameters and a large number of molecules in the asymmetric unit.

*Twinning of **1a**, **1b** and **2***

The twinning of **1a** was quite obvious and could be easily seen on the diffraction images. The data had to be collected because no untwinned crystals could be found in the batch. The cell determination with CELL-NOW [19] resulted in four twin domains with the major cell (1) and three twin cells (2 – 4):

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \times \begin{pmatrix} a \\ b \\ c \end{pmatrix} = \begin{pmatrix} a \\ -b \\ -c \end{pmatrix}$$

(a) 180° rotation of cell (1) about a_0 produces cell (2)

$$\begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \times \begin{pmatrix} a \\ b \\ c \end{pmatrix} = \begin{pmatrix} b \\ -a \\ c \end{pmatrix}$$

(b) 90° rotation of cell (1) about c_0 produces cell (3)

$$\begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \times \begin{pmatrix} a \\ b \\ c \end{pmatrix} = \begin{pmatrix} -b \\ a \\ c \end{pmatrix}$$

(c) −90° rotation of cell (1) about c_0 produces cell (4)

The respective twin cells could be related to the original monoclinic cell by rotating the first domain about a two-fold axis parallel to a and about a four-fold axis parallel to c ($2\|a_0$, $4\|c_0$). Data reduction with

SAINT [20] constraining the four twin cells to be equal was followed by absorption correction (TWINABS) [21] with separate parameter refinement of all four twin domains. The structural model was refined as a four-component twin using the procedure associated with the HKLF 5 format for twins and the BASF instruction in SHELXTL [22]. Fractional contributions k1, k2, k3, and k4 of the twin components refined to the values k1 = 0.373(2), k2 = 0.353(2), k3 = 0.143(3) and k4 = 0.131(2), constraining k1 = 1–k2–k3–k4.

Compound **1b** crystallizes in the chiral space group $P4_22_12$ as a racemic twin. The twinning of **1c** mentioned by Bolte *et al.* also occurred in our case. **2** crystallizes as a pseudomerohedral twin with the twin matrix:

$$\begin{pmatrix} -1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & -1 & 0 \end{pmatrix} \times \begin{pmatrix} a \\ b \\ c \end{pmatrix} = \begin{pmatrix} -a \\ -c \\ -b \end{pmatrix}$$

It describes a two-fold rotation about a_0 followed by a two-fold rotation about c_0. The axes b and c as well as the angles β and γ show almost the same values, therefore the twinning could not be detected in the reciprocal lattice. For **1b** and **2** a normal cell search with the index routine implemented in the APEX2 [23] software suite was followed by an absorption correction (SADABS) [24]. Both structural models were refined as two-component twins using the TWIN and BASF instructions in SHELXL [22]. Whereas the site occupation of the stereomers of **1b** refined to 0.50(3), the fractional contributions k1 and k2 of the twin components refined to the values k1 = 0.619(1) and k2 = 0.381(1), constraining k1 = 1–k2.

Conclusion

In Grignard reactions magnesium dihalides are formed as side products. The purification of the products frequently is hampered by difficulties in the separation from these salts, which are readily soluble in donating solvents. They even tend to co-crystallize as mixed halide twinned polymorphs difficult to identify. The knowledge of the cell parameters of the potential by-products helps to recognize the target products unequivocally. With **1a** we found a new polymorph of dibromido-tetrakis(tetrahydrofuran)magnesium. Furthermore, we identified the erroneously assigned triclinic polymorph to be the mixed halide bromido-chlorido-tetrakis(tetrahydrofuran)magnesium (**2**).

Experimental Section

The syntheses were performed under an inert gas atmosphere of dry nitrogen with Schlenk techniques. All solvents were dried and purified according to standard procedures and stored under nitrogen.

*Dibromido-tetrakis(tetrahydrofuran)magnesium (**1a**)*

A solution of 9-bromoanthracene (3.00 g, 11.67 mmol) in diethyl ether (40 mL) was added dropwise to magnesium turnings (0.44 g, 12.84 mmol) previously activated with iodine. The reaction mixture was stirred for 24 h under reflux. After cooling to ambient temperature the formed precipitate was filtered off, washed with Et_2O (10 mL) and dissolved in dry tetrahydrofuran. After cooling to −30 °C colorless crystals of $[MgBr_2(thf)_4]$ suitable for X-ray crystallographic analysis were obtained.

*Dibromido-tetrakis(tetrahydrofuran)magnesium (**1b**)* [25]

$S(N^tBu)_3$ (1.25 g, 5.0 mmol) was dissolved in THF (20 mL), and MeMgBr (5.0 mmol) dissolved in tetrahydrofuran (20 mL) was added to this solution at −78 °C over a period of 15 min. The mixture was allowed to warm to r. t. and stirred overnight. The solvent was removed *in vacuo*, the residual solid was re-dissolved in a *n*-hexane/tetrahydrofuran mixture, and insoluble particles were filtered off. The resulting solution was stored at 24 °C and yielded colorless crystals suitable for X-ray crystallographic analysis after 1 – 3 d.

*Bromido-chlorido-tetrakis(tetrahydrofuran)magnesium (**2**)* [26]

A solution of 2-bromothiophene (25.00 g, 153 mmol) in tetrahydrofuran (50 mL) was added dropwise to magnesium turnings (4.2 g, 172 mmol) previously activated with iodide, to maintain a gentle reflux. After the addition was complete, the reaction mixture was stirred for 1 h at r. t. and cooled down to 0 °C before diethylphosphoramidous dichloride (12.0 g, 76.5 mmol) was added. The reaction was allowed to warm to room temperature and was stirred over night. The precipitate was filtered off through Celite, and most of the solvent was removed *in vacuo*. The resulting solution was stored at 4 °C and yielded colorless crystals suitable for X-ray crystallographic analysis after one week.

*Structure determination of **1a**, **1b** and **2***

The data for **1a** and **2** were collected from shock-cooled crystals at 100(2) K, and **1b** at 170(2) K [27]. The data of **1a** were collected on a INCOATEC Mo Microsource [28] with Quazar mirror optics and an APEX II detector with D8 goniometer. The data of **1b** and **2** were measured on a Bruker TXS-Mo rotating anode with Helios mirror optics and APEX II detector with D8 goniometer. Both diffractometers were equipped with a low-temperature device [29] and used MoK_α radiation, λ = 71.073 pm. All data were integrated with SAINT [20], and an empirical absorption correction was applied (SADABS [24]). The structures were solved by Direct Methods (SHELXS-97) and refined by full-matrix least-squares methods against F^2 (SHELXTL/SHELXL-97) [22]. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model with their U_{iso} values constrained to 1.5 times the U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms. Disordered moieties were refined using bond length restraints and isotropic displacement parameter restraints.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. The CCDC numbers, crystal data and experimental details for the X-ray measurements are listed in Table 1. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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