

$\omega/2\theta$ scans
 Absorption correction:
 ψ scan (XEMP; Siemens, 1989)
 $T_{\min} = 0.153$, $T_{\max} = 0.434$
 3011 measured reflections
 2162 independent reflections

$R_{\text{int}} = 0.023$
 $\theta_{\max} = 69.41^\circ$
 $h = -1 \rightarrow 8$
 $k = -1 \rightarrow 7$
 $l = -1 \rightarrow 49$
 3 standard reflections
 every 100 reflections
 intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.097$
 $S = 1.059$
 2721 reflections
 227 parameters
 H atoms constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0492P)^2 + 0.3240P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.15 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.14 \text{ e } \text{Å}^{-3}$

Extinction correction:
 SHELXL93 (Sheldrick, 1993)
 Extinction coefficient:
 0.0041 (3)
 Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)
 Absolute structure:
 Flack (1983)
 Flack parameter = -0.03 (2)

Table 2. Selected torsion angles ($^\circ$) for BRL-52781A

| | | | |
|---------------|----------|-----------------|-----------|
| C3—C4—C7—C8 | 15.9 (4) | C13—C14—C15—C16 | -73.7 (3) |
| C4—C7—C8—N10 | 77.2 (3) | N10—C15—C16—N17 | 53.4 (3) |
| O9—C8—N10—C15 | -1.3 (4) | C15—C16—N17—H17 | -65.9 |

The title structures were solved by direct methods and refined by full-matrix least squares on F^2 for all reflections. H atoms were placed geometrically, and refined with a riding model and with U_{iso} constrained to be $1.25U_{\text{eq}}$ of the carrier atom.

For both compounds, data collection: XSCANS (Siemens, 1996); cell refinement: XSCANS; data reduction: XSCANS; program(s) used to solve structures: SIR92 (Altomare *et al.*, 1994); program(s) used to refine structures: SHELXL93 (Sheldrick, 1993); molecular graphics: DIAMOND (Bergerhoff, 1996); software used to prepare material for publication: PARST (Nardelli, 1983).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1373). Services for accessing these data are described at the back of the journal.

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(4-Methoxyphenyl)diphenylmethanol, an Unusual Tetramer Containing a $D[R]$ Pattern of Hydrogen Bonds, and Tris(2-methoxyphenyl)methanol

IAIN L. J. PATTERSON,^a CHRISTOPHER GLIDEWELL^a AND GEORGE FERGUSON^b

^aSchool of Chemistry, University of St Andrews, St Andrews, Fife KY16 9ST, Scotland, and ^bDepartment of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1. E-mail: cg@st-andrews.ac.uk

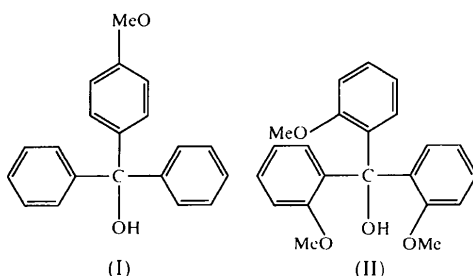
(Received 12 June 1998; accepted 9 July 1998)

Abstract

(4-Methoxyphenyl)diphenylmethanol ($C_{20}H_{18}O_2$) crystallizes with two independent molecules; the molecules are linked by O—H \cdots O hydrogen bonds into centrosymmetric tetramers in which two molecules form a cyclic $R_2^2(16)$ motif from which the other two are pendant, giving a $D_3^3(11)[R_2^2(16)]$ pattern. In tris(2-methoxyphenyl)methanol ($C_{22}H_{22}O_4$) the hydroxy H atoms are disordered over two sites; whichever site is occupied, an intramolecular O—H \cdots O hydrogen bond is formed with a methoxy O atom.

Comment

Triphenylmethanol, Ph_3COH , crystallizes as almost perfectly tetrahedral tetramers (Ferguson *et al.*, 1992), in which the four hydroxy-H atoms are mobile over 12 sites along the six O \cdots O edges of the tetrahedron (Aliev *et al.*, 1998). By contrast, tris(4-methoxyphenyl)methanol [(4-MeOC₆H₄)₃COH] forms an open dimer in which only one of the two independent hydroxy groups is involved in hydrogen bonding (Ferguson *et al.*, 1996). In view of the major differences in supramolecular aggregation between Ph_3COH and (4-MeOC₆H₄)₃COH, we have now investigated the structures of (I) (4-methoxyphenyl)diphenylmethanol [(4-MeOC₆H₄)Ph₂COH] and (II) tris(2-methoxyphenyl)methanol [(2-MeOC₆H₄)₃COH].



Compound (I) crystallizes in space group $P\bar{1}$, with $Z' = 2$ (Wilson, 1993; Brock & Dunitz, 1994). The hydrogen-bonding characteristics of the two independent molecules (Fig. 1) are quite different. Pairs of molecules of type A (containing O1) form cyclic centrosymmetric dimers characterized by an $R_2^2(16)$ motif (Bernstein *et al.*, 1995); in these dimers the hydroxy-O atom O1 at (x, y, z) acts as donor to the methoxy-O atom O14 at $(1 - x, 1 - y, 1 - z)$. This association results in a 3.481 (2) Å plane-to-plane separation of the C111–C116 aromatic rings at (x, y, z) and $(1 - x, 1 - y, 1 - z)$. Molecules of type B (containing O2) are attached to this dimer by means of O—H...O hydrogen bonds involving the hydroxy groups only (Fig. 1, Table 2); the overall supramolecular aggregate is thus a centrosymmetric tetramer. The first-level graph set for this tetramer is thus $N_1 = DR_2^2(16)$; the combination of the two types of hydrogen bond (Table 2) described by N_1 provides a

finite pattern of type $D_3^3(11)$, so giving $D_3^3(11)[R_2^2(16)]$ as the overall pattern descriptor (Bernstein *et al.*, 1995). The $D[R]$ pattern has been noted (Bernstein *et al.*, 1995) as very common in centrosymmetric structures having $Z' > 1$. This pattern is absent in $(4\text{-MeOC}_6\text{H}_4)_3\text{COH}$, where $Z' = 2$ in the non-centrosymmetric space group $P2_1$ (Ferguson *et al.*, 1996).

The supramolecular aggregation in (I) is thus wholly different from the patterns observed in Ph_3COH (Ferguson *et al.*, 1992) and $\text{Ph}_3\text{CCH}_2\text{OH}$ (Ferguson *et al.*, 1994), where the tetramers are respectively tetrahedral and almost square planar. Moreover, it differs significantly from the patterns found in compounds analogous to (I), having a single hydrogen-bond acceptor function in one of the substituents only. Thus in diphenyl(4-pyridyl)methanol $[(\text{NC}_5\text{H}_4)\text{Ph}_2\text{COH}]$; Glidewell & Ferguson, 1994) and 3-(hydroxydiphenylmethyl)-3H-azepine $[(\text{NC}_6\text{H}_6)\text{Ph}_2\text{COH}]$; Lindner & von Gross, 1973], the molecules are linked by O—H...N hydrogen bonds into continuous chains: a $C(7)$ chain generated by translation and a $C(6)$ chain generated by the action of a 2_1 axis, respectively. In 4,4-dimethyl-5-(hydroxydiphenylmethyl)-4,5-dihydroisoxazole $[(\text{C}_5\text{H}_8\text{NO})\text{Ph}_2\text{COH}]$ the molecules are linked by O—H...N hydrogen bonds into $R_2^2(12)$ dimers (Armesto *et al.*, 1990); although these dimers bear some resemblance to the dimeric unit in (I) formed from type A molecules only, they do not have

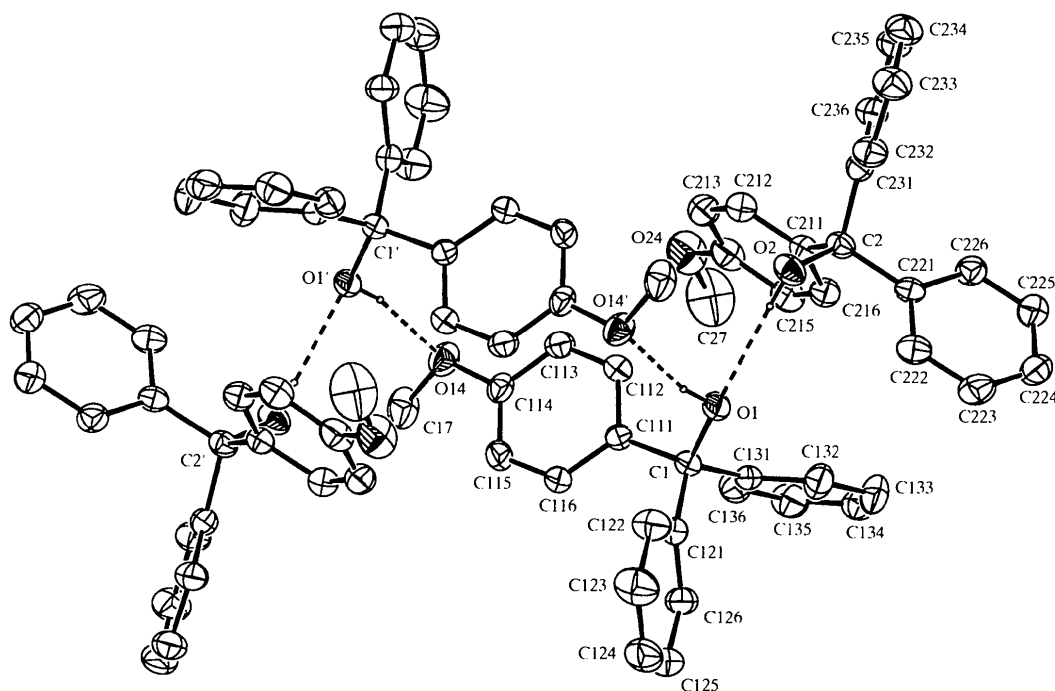


Fig. 1. A view of the centrosymmetric tetrameric aggregate in compound (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. Atoms O1', C1' etc., are at equivalent position $(1 - x, 1 - y, 1 - z)$. For clarity, the only H atoms shown are those involved in the hydrogen bonding.

pendant components comparable to the type *B* molecules in (I).

As well as having different hydrogen-bonding properties, the two independent molecules in (I) also have significantly different conformations (Table 1): in molecule *A* the conformation of the triarylmethyl fragment, ignoring the hydroxy and methoxyl groups, is not far from *C*₃ symmetry, whereas in molecule *B* the corresponding O—C—C torsion angles for the three rings are very different. In addition, the C—O—C torsion angles indicate near coplanarity of the exocyclic group with its aryl ring only in molecule *B*.

Compound (II) exhibits no intermolecular hydrogen bonding; instead, the hydroxy-H atom, which is essentially equally disordered over two sites (Fig. 2), engages in intramolecular hydrogen bonding, forming puckered *S*(6) rings with two of the three methoxyl groups. In this respect the hydrogen-bonding pattern is reminiscent of that in (2-pyridyl)diphenylmethanol, where an *S*(5) ring is formed (Ferguson *et al.*, 1995).

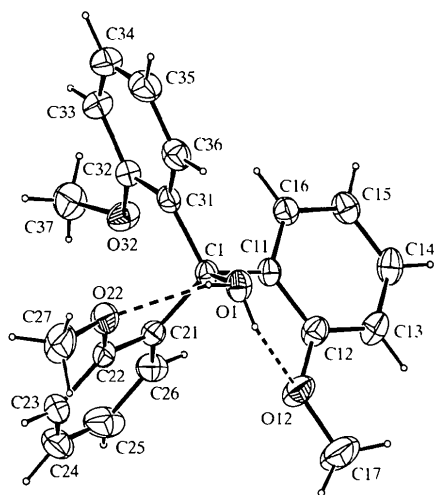


Fig. 2. The asymmetric unit in compound (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

The geometries of the CH₃—O—C—C fragments in the two independent molecules of (I) (Table 1) and in (II) (Table 3) exhibit the same patterns as found both in (4-MeOC₆H₄)₃COH and in anisole (Seip & Seip, 1973): the exocyclic C—O—C angles are significantly larger than tetrahedral, while the O—C—C angles, respectively *cisoid* and *transoid* to the methoxy substituent, lie in the ranges 121.9(2)–124.9(2)° and 115.7(2)–117.2(1)°, consistent with previous observations. The bond distances are all typical of their types (Allen *et al.*, 1987).

Experimental

Compound (I) was prepared by hydrolysis of chloro-(4-methoxyphenyl)diphenylmethane with dilute aqueous sodium carbonate; the crude product was an oil, which was repeatedly crystallized from light petroleum. Analysis: found C 82.7, H 6.2%; C₂₀H₁₈O₂ requires C 82.7, H 6.3%. Compound (II) was prepared by reaction of 2-methoxyphenylmagnesium bromide with diethyl carbonate, followed by acid work-up and recrystallization, firstly from acetone/dichloromethane and secondly from methanol (m.p. 454 K, literature value 454 K; Morton & Brachman, 1954). Analysis: found C 75.2, H 6.2%; C₂₂H₂₂O₄ requires C 75.4, H 6.3%. For both compounds, crystals suitable for single-crystal X-ray diffraction were selected directly from the analytical samples.

Compound (I)

Crystal data

C₂₀H₁₈O₂
M_r = 290.36
 Triclinic
P $\bar{1}$
a = 10.1013 (9) Å
b = 11.820 (1) Å
c = 14.1077 (11) Å
 α = 77.388 (7)°
 β = 85.339 (7)°
 γ = 74.803 (6)°
V = 1585.8 (2) Å³
Z = 4
D_s = 1.216 Mg m⁻³
D_m not measured

Mo *K* α radiation
 λ = 0.7107 Å
 Cell parameters from 25 reflections
 θ = 9.49–18.81°
 μ = 0.077 mm⁻¹
T = 294 (1) K
 Plate
 0.41 × 0.41 × 0.21 mm
 Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
 $\theta/2\theta$ scans
 Absorption correction: none
 5901 measured reflections
 5901 independent reflections
 3323 reflections with $I > 2\sigma(I)$

θ_{\max} = 25.5°
h = -11 → 12
k = 0 → 14
l = -16 → 17
 3 standard reflections
 frequency: 120 min
 intensity decay: no decay, variation 0.4%

Refinement

Refinement on *F*²
 $R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.102$
S = 1.008
 5901 reflections
 402 parameters
 H atoms constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0536P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.156 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.134 \text{ e } \text{Å}^{-3}$
 Extinction correction: *SHELXL97* (Sheldrick, 1997a)
 Extinction coefficient: 0.0131 (15)
 Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °) for (I)

| | | | |
|---------|-------------|---------|-------------|
| O1—C1 | 1.4460 (17) | O2—C2 | 1.4349 (17) |
| C1—C11 | 1.525 (2) | C2—C21 | 1.529 (2) |
| C1—C12 | 1.532 (2) | C2—C22 | 1.532 (2) |
| C1—C13 | 1.537 (2) | C2—C23 | 1.533 (2) |
| C11—O14 | 1.3809 (18) | C21—O24 | 1.370 (2) |
| O14—C17 | 1.435 (2) | O24—C27 | 1.426 (5) |

| | | | | | | | |
|-------------------|-------------|---------------|-------------|-----------------|-------------|-------------|--------------|
| O14—C114—C113 | 116.33 (15) | O24—C214—C213 | 115.65 (18) | O12—C12—C11 | 116.95 (14) | C22—O22—C27 | 118.75 (17) |
| O14—C114—C115 | 123.74 (15) | O24—C214—C215 | 124.87 (19) | O12—C12—C13 | 122.14 (15) | O32—C32—C31 | 117.23 (13) |
| C114—O14—C17 | 116.95 (13) | C214—O24—C27 | 117.10 (18) | C12—O12—C17 | 117.75 (16) | O32—C32—C33 | 122.24 (15) |
| O1—C1—C111—C112 | | | 45.24 (18) | O22—C22—C21 | 116.97 (13) | C32—O32—C37 | 118.62 (15) |
| O1—C1—C121—C122 | | | 33.9 (2) | O22—C22—C23 | 121.87 (17) | | |
| O1—C1—C131—C132 | | | 43.94 (18) | O1—C1—C11—C12 | | | 57.28 (18) |
| C113—C114—O14—C17 | | | 146.21 (15) | O1—C1—C21—C22 | | | 47.98 (17) |
| O2—C2—C211—C212 | | | 60.34 (17) | O1—C1—C31—C32 | | | -175.41 (12) |
| O2—C2—C221—C222 | | | 7.34 (19) | C11—C12—O12—C17 | | | 174.0 (2) |
| O2—C2—C231—C232 | | | 41.26 (19) | C21—C22—O22—C27 | | | -173.21 (15) |
| C213—C214—O24—C27 | | | -179.9 (2) | C31—C32—O32—C37 | | | 164.71 (16) |

Table 2. Hydrogen-bonding geometry (\AA , $^\circ$) for (I)

| D—H...A | D—H | H...A | D...A | D—H...A |
|--------------------------|------|-------|-----------|---------|
| O1—H1...O14 ⁱ | 0.82 | 2.06 | 2.866 (2) | 166 |
| O2—H2...O1 | 0.82 | 2.12 | 2.919 (2) | 164 |

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.**Compound (II)***Crystal data*

C₂₂H₂₂O₃
M_r = 350.40
 Monoclinic
Cc
a = 11.9327 (8) \AA
b = 10.5752 (9) \AA
c = 14.6833 (11) \AA
 β = 101.857 (6) $^\circ$
V = 1813.4 (2) \AA^3
Z = 4
D_r = 1.283 Mg m⁻³
D_m not measured

Data collection

Enraf-Nonius CAD-4 diffractometer
 $\theta/2\theta$ scans
 Absorption correction: none
 3767 measured reflections
 3767 independent reflections
 2956 reflections with $I > 2\sigma(I)$

Refinement

Refinement on *F*²
 $R[F^2 > 2\sigma(F^2)] = 0.031$
 $wR(F^2) = 0.081$
S = 1.056
 3767 reflections
 241 parameters
 H atoms constrained
 $w = 1/[\sigma^2(F_o^2) + (0.045P)^2 + 0.1112P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.004$
 $\Delta\rho_{\max} = 0.130 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.126 \text{ e } \text{\AA}^{-3}$

Table 3. Selected geometric parameters (\AA , $^\circ$) for (II)

| | | | |
|---------|-------------|---------|-----------|
| O1—C1 | 1.4339 (17) | O12—C17 | 1.400 (3) |
| C1—C11 | 1.545 (2) | C22—O22 | 1.378 (2) |
| C1—C21 | 1.545 (2) | O22—C27 | 1.426 (2) |
| C1—C31 | 1.543 (2) | C32—O32 | 1.365 (2) |
| C12—O12 | 1.373 (2) | O32—C37 | 1.421 (2) |

Table 4. Hydrogen-bonding geometry (\AA , $^\circ$) for (II)

| D—H...A | D—H | H...A | D...A | D—H...A |
|--------------|------|-------|-----------|---------|
| O1—H1A...O12 | 0.82 | 2.20 | 2.782 (2) | 128 |
| O1—H1B...O22 | 0.82 | 2.08 | 2.694 (2) | 132 |

Compound (I) crystallized in the triclinic system; space group $P\bar{1}$ was assumed and confirmed by the analysis. Compound (II) crystallized in the monoclinic system; space groups *Cc* or *C2/c* were indicated by the systematic absences. Both were investigated and *Cc* shown to be correct. Although a complete set of Friedel pair reflections was collected to $\theta = 25.2^\circ$, the small anomalous scattering of C and O did not allow us to determine the direction of the polar axis in this case. Difference maps at an intermediate stage showed that the hydroxy-H atom of (II) was disordered over two adjacent sites. Refining these H-atom occupancies resulted in values of 0.56 (3) and 0.44 (3). For both compounds, H atoms were treated as riding atoms (C—H 0.93 and 0.96, O—H 0.82 \AA).

For both compounds, data collection: *CAD-4-PC Software* (Enraf-Nonius, 1992); cell refinement: *SET4* and *CELDIM* in *CAD-4-PC*; data reduction: *DATRD2* in *NRCVAX96* (Gabe *et al.*, 1989); program(s) used to solve structures: *SHELXS97* (Sheldrick, 1997b); program(s) used to refine structures: *NRCVAX96* and *SHELXL97* (Sheldrick, 1997a); molecular graphics: *NRCVAX96*, *ORTEPII* (Johnson, 1976) and *PLATON* (Spek, 1998); software used to prepare material for publication: *NRCVAX96*, *SHELXL97* and *PREP8* (Ferguson, 1998).

We thank Peter Jaspers-Fayer of the University of Guelph Computing Centre Services Division for his invaluable assistance in installing the LINUX operating system and associated graphics routines on the Dell Inspiron 3200 266 MHz Pentium-II laptop computer used for all the calculations in the analysis of compound (II).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1217). Services for accessing these data are described at the back of the journal.

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2,4,6-Halogeno-Aniline Derivatives

GEORGE FERGUSON,^a JOHN N. LOW,^b GLENN H. PENNER^a
AND JAMES L. WARDELL^c

^aDepartment of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1, ^bAMRC, Department of Applied Physics and Electronic & Mechanical Engineering, University of Dundee, Dundee DD1 4HN, Scotland, and ^cDepartment of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB9 2UE, Scotland. E-mail: j.n.low@dundee.ac.uk

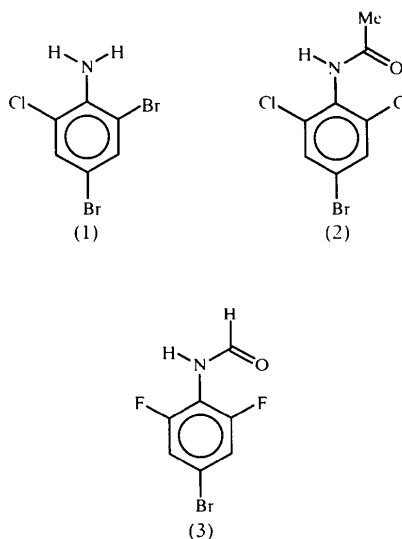
(Received 19 June 1998; accepted 9 July 1998)

Abstract

The title compounds, 2,4-dibromo-6-chloroaniline, C₆H₄-Br₂ClN, (1), *N*-acetyl-4-bromo-2,6-dichloroaniline (alternative name: 4'-bromo-2',6'-dichloroacetanilide), C₈H₆-BrCl₂NO, (2), and *N*-formyl-4-bromo-2,6-difluoroaniline [alternative name: *N*-(4-bromo-2,6-difluorophenyl)formamide], C₇H₄BrF₂NO, (3), all have at least one short cell axis (in the range 4.2–4.7 Å) and contain molecules which are linked to form infinite chains along the short-axis directions via N—H...N or N—H...O hydrogen bonds. Compound (1) has halogen disorder at the 2 and 6 positions.

Comment

The aniline derivatives (1) and (2) arose as minor by-products in a synthetic scheme; compound (3) was synthesized by an unequivocal route. The X-ray analyses were undertaken to establish their structures and to provide details of their conformation and hydrogen bonding. Molecule (1) is isomorphous with 2,4,6-tribromoaniline (Christensen & Stromme, 1969). Molecule (2) is isostructural with *N*-acetyl-2,4,6-trichloroaniline, (4) (Nyburg *et al.*, 1987).



Views of the three molecules are presented in Fig. 1. In (1), the sizes of the electron-density maxima at the *ortho* sites were consistent with an unequal disorder of Br and Cl atoms; refinement showed that the ratio was 0.639 (4)/0.361 (4). This disorder effectively precludes any meaningful discussion of ring dimensions. Compounds (2) and (3) show the typical variation in benzene ring internal angles found in polyatomic substituted benzene rings, with the rings showing *2mm* symmetry about the Cl...C₄ axis at a 3σ significance level (Domenicano, 1992); the mean internal angles at the *ortho* and *para* sites exceed 120°, while those at the 1 and *meta* positions are smaller (Table 1).

The amount by which the group at Cl is rotated out of the aromatic ring plane in each molecule is of interest. For (1), difference maps showed that the H atoms of the NH₂ group lay approximately in the aromatic ring plane. For (2), the plane of the *N*-acetyl group is rotated 60.97 (14)° from coplanarity with the aromatic ring; for (3), the corresponding value for the rotation of the *N*-formyl group is 57.3 (3)°. Details of the relevant torsion angles in (2) and (3), along with those of (4) for comparison, are given in Table 2. All three compounds adopt a conformation by which the carbonyl group is *cis* to the exocyclic C—N bond.