
Comparison of halogen bonding and van der Waals and π - π interactions in 4,5-dibromo-2-hexyloxyphenol

Cukiernik *et al.*

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Comparison of halogen bonding and van der Waals and π - π interactions in 4,5-dibromo-2-hexyloxyphenol

Fabio D. Cukiernik,^{a,b} Florencia Cecchi^a and Ricardo Baggio^{c*}

^aINQUIMAE, Departamento de Química Inorgánica, Analítica y Química Física, Facultad de Ciencias Exactas y Naturales, UBA, Buenos Aires, Argentina, ^bInstituto de Ciencias, Universidad Nacional de General Sarmiento, Buenos Aires, Argentina, and ^cDepartamento de Física, Centro Atómico Constituyentes, Comisión Nacional de Energía Atómica, Buenos Aires, Argentina
Correspondence e-mail: baggio@cnea.gov.ar

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The title compound, C₁₂H₁₆BrO₂, is an interesting case of a simple organic molecule making use of five different types of intra- and intermolecular interactions (*viz.* conventional and nonconventional hydrogen bonds, and π - π , Br \cdots Br and Br \cdots O contacts), all of them relevant in the molecular and crystal structure geometry. The molecules are strictly planar, with an intramolecular O—H \cdots O hydrogen bond, and associate into two-dimensional structures parallel to ($\bar{2}01$) through two different types of halogen bonding. The planar structures, in turn, stack parallel to each other interlinked by C—H \cdots π and π - π contacts. Also discussed are the relevant structural features leading to the rather low melting point of the compound.

Comment

Noncovalent interactions have been the subject of both theoretical and experimental studies for many years and they continue to receive increasing attention. Hydrogen bonding was certainly the first such interaction to be extensively studied, followed by π - π and C—H \cdots π interactions. The so-called 'halogen bond', where the main feature is a highly polarized halogen species (Desiraju & Parthasarathy, 1989; Metrangolo *et al.*, 2007; Metrangolo *et al.*, 2008), has also been known for decades, but was 'rediscovered' only recently. In fact, the number of studies dealing with halogen bonds has increased rapidly in the last five years (Metrangolo & Resnati, 2008). In spite of some controversy about the fundamental nature of some of these noncovalent interactions (Palusiak & Grabowski, 2008; Rissanen, 2008) and the lack of a deep understanding of some of them (Sinnokrot & Sherrill, 2006; Zhang *et al.*, 2007), they are all currently and successfully used as tools in crystal engineering, in biomimetic processes involving molecular recognition and in the molecular design of

advanced materials, including magnetic materials and liquid crystals.

The relative strengths of these interactions are neither predictable nor understandable in a straightforward manner. Several authors have tried to establish, for a given compound (or series of compounds), which of these interactions is ultimately responsible for the resulting structure (Gavezzotti, 2008). In other cases, the simultaneous presence of different types of noncovalent interactions has been viewed as a competitive process (Csoregh *et al.*, 2001), and the underlying question was which of the interactions would prevail over the others, thus determining the supramolecular arrangement.

Among the interactions we shall deal with in the present paper, the least common are those of the C—X \cdots O and C—X \cdots X—C types (X is a halogen). The main aspects of the former are quite close to those of a conventional hydrogen bond and, accordingly, its most conspicuous geometric characteristics are a rather large C—X \cdots O angle (>150°) and an X \cdots O distance shorter than the sum of the van der Waals radii. The second type, instead, is rather more complex from a descriptive point of view, but the main aspects could be summarized as follows. If θ_1 is the larger of the two C—X \cdots X angles and θ_2 the smaller, then two kinds of C—X \cdots X—C interactions can be envisaged (Desiraju & Parthasarathy, 1989): the (so-called) I1 interactions have $\theta_1 = \theta_2$, while those of type I2 have $\theta_1 \sim 180^\circ$ and $\theta_2 \sim 90^\circ$. In both cases, the X \cdots X distance is shorter than the sum of the van der Waals radii.

The title compound, (I), presents an interesting case of a simple organic molecule displaying a range of different types of intra- and intermolecular interactions, *viz.* Br \cdots Br and Br \cdots O contacts, conventional and nonconventional hydrogen bonds, π - π interactions and extremely weak (though non-negligible) van der Waals interactions maximized by the parallel array of hydrophobic alkyl chains. We have found all of them to be relevant to a greater or lesser degree for the molecular and crystal structure geometry of (I).

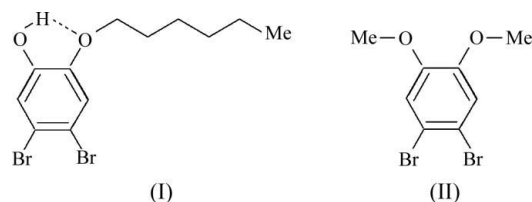


Fig. 1 shows a molecular view of (I), displaying the labelling scheme and the intermolecular interactions (to be discussed below). Bond distances and angles are unexceptional and comparable with the recently reported related structures 1,2-dibromo-4,5-dimethoxybenzene, (II), and 1,2-diiodo-4,5-dimethoxybenzene (Cukiernik *et al.*, 2008). The most conspicuous characteristic of the molecule is its overall planarity (average deviation from the least-squares plane = 0.032 Å, with a maximum deviation of 0.092 Å for atom C7), a property enhanced by the intramolecular O2—H2A \cdots O1 bond (Table 1 and Fig. 1). This least-squares plane almost contains a centre of symmetry (0.124 Å away from the plane), which in turn generates a planar dimer through a head-to-

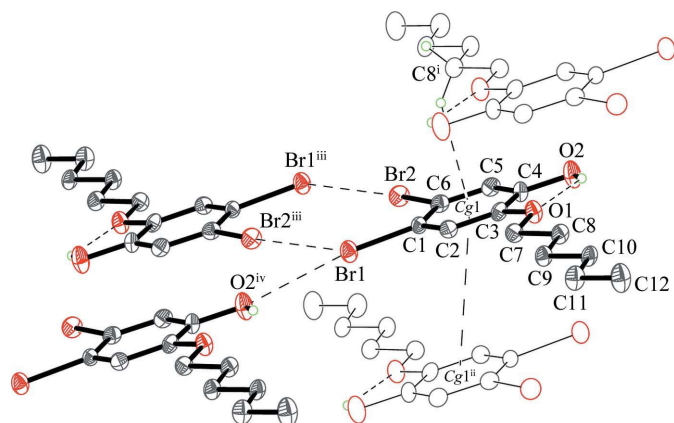


Figure 1

A molecular view of (I), showing the atom-labelling scheme. **Displacement ellipsoids are drawn at the XX% probability level [Please complete]** and H atoms have been omitted for clarity. Dashed lines indicate the intra- and intermolecular interactions present. Heavy lines denote molecules in the reference plane and lighter lines denote molecules in the planes above and below the reference plane. [Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $2-x, 1-y, 1-z$; (iii) $2-x, 1-y, 2-z$; (iv) $x, 1+y, z$.]

head C—Br \cdots Br—C type I2 interaction (Table 3 and Fig. 1). The Br \cdots Br distance [3.676 (1) Å] indicates this interaction to be rather weak; a survey of similar contacts in the Cambridge Structural Database (CSD; 2009 Version; Allen, 2002) showed 511 cases reported, covering a range from 3.30 to 3.70 Å, with a median (maximum occurrence) at 3.62 Å.

In addition, the dimers are laterally linked to each other through a C—Br \cdots O bond (Table 4 and Fig. 1) to which a similar analysis can be applied. A CSD search provided some 1400 cases covering (with a significant population) the range 2.90–3.37 Å, with a median of 3.20 Å, a value significantly shorter than the Br \cdots O distance in (I) [3.28 (1) Å]. The interaction serves to form planar strips two molecules wide, with the hydrophobic organic tail oriented outwards in a comb-like structure. These combs interdigitate in a classical packing array of parallel hydrophobic alkyl chains, thus maximizing the van der Waals interactions, with minimum C \cdots C approach distances in the range 3.86 (1)–3.90 (1) Å.

The outcome of these interactions is the formation of planar two-dimensional structures parallel to (201) (Fig. 2). These structures in turn interact with their nearest neighbours, 3.60 (5) Å apart, through two different types of interactions, also shown in Fig. 1, namely a C—H \cdots π bond (Table 1 and the upper portion of Fig. 1) and a π – π contact (Table 2 and the lower portion of Fig. 1).

Thus, the crystal structure of (I) is the result of an intricate balance between a diversity of interactions covering a vast range, from medium strength (halogen bonding) down to weak (interchain van der Waals contacts).

Although all these interactions seem to provide the stability of (I), the geometric requirements of some of them tend to act as restraints for the others to reach more optimized geometries. For example, closer Br \cdots Br or Br \cdots O approaches would conflict with the setting up of proper π – π or aliphatic chain interactions. The resulting compromise renders the structure

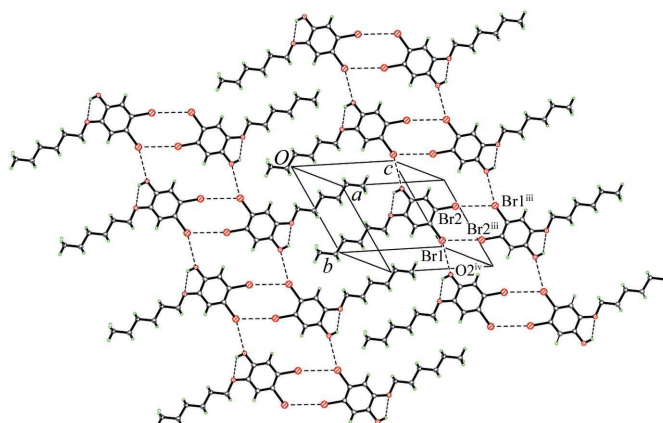


Figure 2

A packing diagram for (I), showing the (201) plane formed by the interdigitated strips. [Symmetry codes: (iii) $2-x, 1-y, 2-z$; (iv) $x, 1+y, z$.]

stable, but not as stable as might be anticipated from the presence of potentially strong C—Br \cdots Br—C and C—Br \cdots O interactions.

This relative weakness in (I) is evidenced in the rather low melting point of 326 K, well below those found in structurally analogous compounds with a similar display of nonbonding interactions, *e.g.* 1,2-dibromo-4,5-dimethoxybenzene (Cukiernik *et al.*, 2008), (II), which has a melting point in the range 362–364 K. Since the main difference between these two molecular structures lies in the lateral chain, present in (I) but lacking in (II) (see scheme), it is tempting to look in this direction to find the reasons for such a weakening. [The hydrogen bonding in (I) is intramolecular and so can be disregarded from the present analysis.]

From a structural point of view, the presence of this aliphatic chain favours a head-to-head arrangement with interdigitated tails. From an energetic point of view, the contributions of the aliphatic chains to the total melting enthalpy can be roughly estimated as 22–25 kJ mol $^{-1}$, taking 3.7–4.1 kJ mol $^{-1}$ as the melting enthalpy of one mole of CH $_2$ or CH $_3$ groups (Weast, 1986; Seurin *et al.*, 1981). This value accounts for *ca* two thirds of the measured melting enthalpy (37 kJ mol $^{-1}$; see *Experimental*), thus supporting our previous suggestion. It seems that conformational freedom at the aliphatic chain level allows the system to override the stronger interactions, thus melting at a moderate temperature. This kind of distribution analysis of the melting enthalpy is often found in the field of molecular liquid crystals (LC), materials structurally related to (I) in the sense that they also usually present ‘localized’ (stronger) and van der Waals (weaker) interactions in synergic co-operation. Indeed, the molecular description of several types of LC phases involves molten aliphatic chains and more or less oriented interacting cores. The presence in (I) of a halogen-bonding-based ‘extended core’ might in principle induce some LC character, even if, from its molecular structure, (I) is not expected to exhibit LC behaviour as its aromatic part is not long enough. As a matter of fact, we have not found any evidence of LC phases in (I), a result that can be ascribed to the previously discussed weak-

ness of the C—Br···Br—C and C—Br···O interactions. In particular, the few LC based on halogen bonding known to date are based on one of the strongest types of halogen bond, *viz.* involving N atoms as donors and I atoms bound to electron-withdrawing groups as acceptors (Bruce *et al.*, 2008).

Finally, the influence of chain length on melting point has been extensively studied in LC (Demus, 1998). Short-chain compounds usually melt at higher temperatures, since in these structures the localized interactions prevail. On increasing the chain length, it is often observed that the melting point decreases to a certain limit, rising again afterwards. The accepted explanation for this behaviour is based on the structure-disturbing effect associated with middle-length aliphatic chains, in accordance with the ideas herein suggested for (I).

Experimental

2-(Hexyloxy)phenol was synthesized under typical conditions for Williamson's etherification, following a published procedure (Wan *et al.*, 2003), and was obtained in 38% yield. The title compound, (I), was prepared by direct halogenation of 2-(hexyloxy)phenol using Br₂ in a manner exactly analogous to that described in the synthesis of 1,2-dibromo-4,5-dimethoxybenzene (Cukiernik *et al.*, 2008); full experimental details are available in the archived CIF. Crystals were obtained by slow evaporation of a solution of (I) in heptane.

Crystal data

C ₁₂ H ₁₆ Br ₂ O ₂	$\gamma = 64.03 (3)^\circ$
$M_r = 352.07$	$V = 673.6 (6) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 2$
$a = 8.863 (4) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 9.140 (4) \text{ \AA}$	$\mu = 6.00 \text{ mm}^{-1}$
$c = 10.148 (6) \text{ \AA}$	$T = 295 \text{ K}$
$\alpha = 65.70 (4)^\circ$	$0.22 \times 0.14 \times 0.10 \text{ mm}$
$\beta = 79.43 (5)^\circ$	

Data collection

Rigaku AFC-6S diffractometer	1775 reflections with $I > 2\sigma(I)$
Absorption correction: ψ scan (North <i>et al.</i> , 1968)	$R_{\text{int}} = 0.053$
$T_{\text{min}} = 0.40$, $T_{\text{max}} = 0.55$	3 standard reflections every 150 reflections
2800 measured reflections	intensity decay: <2%
2641 independent reflections	

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.063$	146 parameters
$wR(F^2) = 0.183$	H-atom parameters constrained
$S = 0.97$	$\Delta\rho_{\text{max}} = 1.53 \text{ e \AA}^{-3}$
2641 reflections	$\Delta\rho_{\text{min}} = -1.48 \text{ e \AA}^{-3}$

The H atom attached to atom O2 was found in a difference Fourier map, further idealized (O—H = 0.82 Å) and finally allowed to ride. H atoms attached to C atoms were placed in calculated positions [C—H = 0.93 (aromatic) or 0.96 Å (methyl)] and allowed to ride; methyl groups were allowed to rotate as well. Displacement parameters were taken as $U_{\text{iso}}(\text{H}) = xU_{\text{eq}}(\text{parent})$, where x is 1.2 (aromatic) or 1.5 (methyl and O—H).

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *MSC/AFC Diffractometer Control Software*; program(s) used to solve structure:

Table 1

Hydrogen-bond geometry (Å, °).

Cg1 is the centroid of the C1–C6 ring. [Please check added text]

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O2—H2A···O1	0.82	2.13	2.688 (7)	124
C8—H8B···Cg1 ⁱ	0.96	2.93	3.753 (8)	143

Symmetry code: (i) $-x + 1, -y + 1, -z + 1$.

Table 2

π – π interactions.

Cg1 is the centroid of the C1–C6 ring, CCD is the centre-to-centre distance (distance between ring centroids), SA is the mean slippage angle (angle subtended by the intercentroid vector to the plane normal) and IPD is the mean interplanar distance (distance from one plane to the neighbouring centroid). For details, see Janiak (2000).

Group 1/Group 2	CCD (Å)	SA (°)	IPD (Å)
Cg1/Cg1 ⁱⁱ	4.373 (5)	36.?(1)	3.60 (1)

Symmetry code: (ii) $2 - x, 1 - y, 1 - z$. [Please check angle for missing decimal place]

Table 3

C—Br···Br—C interactions (Å, °).

$\theta_1 = C'-Br'\cdots Br''$, the smaller of the two XB angles; $\theta_2 = Br'\cdots Br''-C'$, the larger of the two XB angles. Expected values: $\theta_1 \sim 90^\circ$ and $\theta_2 \sim 180^\circ$ (for I2 type contacts) or $\theta_1 \sim \theta_2$ (for I1 type contacts). For details, see Desiraju & Parthasarathy (1989).

$C'-Br'\cdots Br''-C'$	$C'-Br'$	$C''-Br''$	$Br'\cdots Br''$	θ_1	θ_2
C1—Br1···(Br2—C6) ⁱⁱⁱ	1.915 (1)	1.907 (1)	3.676 (1)	124.8 (1)	170.0 (1)

Symmetry code: (iii) $2 - x, 1 - y, 2 - z$.

Table 4

C—Br···O interactions (Å, °).

For details, see Desiraju & Parthasarathy (1989).

C—Br···O	C—Br	Br···O	C—Br···O
C1—Br1···O2 ^{iv}	1.915 (1)	3.280 (5)	158.4 (2)

Symmetry code: (iv) $x, 1 + y, z$.

SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2009).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG3087). Services for accessing these data are described at the back of the journal.

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150	172	238	332	504	198
200	214	294	410	624	246
Additional 50's	42	54	78	118	40

PAYMENT AND ORDERING

Cheques should be in **United States dollars** payable to **INTERNATIONAL UNION OF CRYSTALLOGRAPHY**. Official purchase orders should be made out to **INTERNATIONAL UNION OF CRYSTALLOGRAPHY**.

Orders should be returned by fax to:

INTERNATIONAL UNION OF CRYSTALLOGRAPHY
5 Abbey Square
Chester CH1 2HU, England. Fax: +44 1244 314888

ENQUIRIES

Enquiries concerning offprints should be sent to support@iucr.org.