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Short intermolecular N—Br···O═C contacts in 1,3-dibromo-5,5-dimethylimidazolidine-2,4-dione

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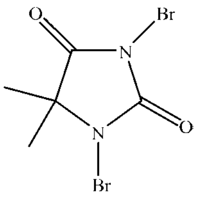
In the title compound, $C_5H_6Br_2N_2O_2$, all atoms except for the methyl group lie on a mirror plane in the space group *Pnma* (No. 62). All bond lengths are normal and the five-membered ring is planar by symmetry. Two short intermolecular N—Br···O═C contacts [Br···O = 2.787 (2) and 2.8431 (19) Å] are present, originating primarily from the O-atom lone pairs donating electron density to the antibonding orbitals of the N—Br bonds (delocalization energy transfers 3.27 and 2.11 kcal mol^{-1}). The total stabilization energies of the Br···O interactions are 3.4828 and 2.3504 kcal mol^{-1}.

Comment

In the search for uncommon intermolecular interactions in the solid state, the author's interest has focused on compounds containing short *X*···O intermolecular contacts (*X* = halogen). The structure of the title compound, dibromantin, (I), is presented here and is a unique example of short intermolecular N—Br···O═C contacts. Dibromantin (1,3-dibromo-5,5-dimethylhydantoin or 1,3-dibromo-5,5-dimethylimidazolidine-2,4-dione) is a commercially available analytical reagent used in the pharmaceutical sciences (de Bertorello *et al.*, 1967; Hilp, 2002*a*,*b*), as a brominating reagent (an alternative to *N*-bromosuccinimide and its derivatives; Jolles, 1966), as a drinking water purifier and as a popular water treatment biocide (Unhoch & Vore, 2004).



(I)

All intramolecular bond lengths and angles in (I) are normal (Fig. 1). All atoms except the methyl group lie on the special position *c* with site symmetry *m*. Thus, the five-membered ring is planar by symmetry (and without disorder).

The structure of (I) in the solid state has interesting features. There are short intermolecular N—Br···O═C contacts of 2.787 (2) (Br1···O2^{i} and O2···Br1^{ii}) and 2.8431 (19) Å (Br2···O1^{iii} and O1···Br2^{iv}), distinctly (>10%) shorter than the sum of the van der Waals radii (3.35 Å; Emsley, 1997) [symmetry codes: (i) $x - 1, y, z$; (ii) $x + 1, y, z$; (iii) $x + \frac{1}{2}, y, -z + \frac{1}{2}$; (iv) $x - \frac{1}{2}, y, -z + \frac{1}{2}$]. Moreover, although Br···O short contacts have been extensively studied over the past few decades (Hassel & Romming, 1962; Leser & Rabinovich, 1978; Ramasubbu *et al.*, 1986), only one structure with a similar N—Br···O═C short contact is known, namely *N*-bromosuccinimide, (II) (Jabay *et al.*, 1977), where the Br···O distance is 2.80 Å. Additionally, several structures have been reported with other halogen atoms involved in analogous short contacts: methyl 2-(3-oxo-1-phenylbenzo[*c*-1,5]aziodolin-2-yl)propanoate (NI···OC = 2.781 Å; Zhdankin *et al.*, 2003), 1-acetoxy-1,2-benziodazol-3(1*H*)-one (NI···OC = 2.867 Å; Zhdankin *et al.*, 1997), *N*-iodosuccinimide (NI···OC = 2.580 Å; Padmanabhan *et al.*, 1990), *N*-chlorosuccinimide, (III) (NCl···OC = 2.880 Å; Brown, 1961), *N*-chloro-*N*-(2,6-dichlorophenyl)trichloroacetamide (NCl···OC = 2.829 Å; Gowda *et al.*, 1996), 1,3-dichloro-1,3-diazetidine-2,4-dione (NCl···OC = 2.948 Å; Belaj *et al.*, 1991) and *N*-chlorophthalimide (NCl···OC = 2.946 Å; Ghassemzadeh *et al.*, 1994).

In compound (I), the N—Br···O angles of 179.24 (9) and 160.70 (9)°, and the Br···O═C angles of 170.9 (2) and 148.9 (2)°, are comparable with those in (II) (169.5 and 140.9°, respectively). In both compounds, the five-membered rings are in a *trans* arrangement to the Br···O interaction, but in (I) the rings are coplanar, while in (II) they are inclined at 127°. The contacts extend molecules of (I) into a one-dimensional ladder-type double chain along the *a* axis direction (Fig. 2) with an $R_3^3(12)$ motif (Bernstein *et al.*, 1995).

The Cambridge Structural Database (Version 5.28; Allen, 2002) was searched for C—Br···O═C contacts shorter than 3.2 Å (as N—Br···O═C interactions are rare). The number of reported Br···O interactions decreases as the Br···O distance shortens, the C—Br···O angle adopts values in the range 140–180° with no single maximum, and the Br···O═C angle adopts values in the range 90–180° (maximum value 144°). Thus, the preferred angles are neither orthogonal nor

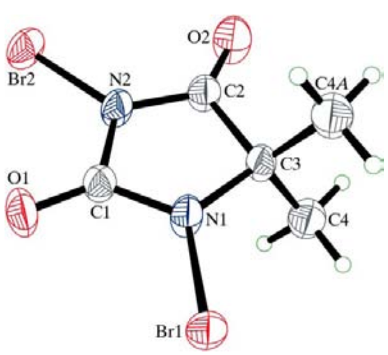


Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

linear. Examination of the two-dimensional contour plots of angle *versus* distance (Fig. 3) reveals two preferred pairs of C—Br$\cdots$O angle and Br$\cdots$O distance, 162.4°/3.167 Å and 172.0°/3.052 Å, and three preferred pairs of Br$\cdots$O=C angle and Br$\cdots$O distance, 117.7°/3.170 Å, 136.9°/3.113 Å and 141.0°/3.087 Å. The values in (I) (as + symbols in Fig. 3) have been removed from the pairs.

For compound (III) (*N*-chlorosuccinimide), it was proposed that electrostatic attraction exists between the N—Cl and O=C groups because of the large polarization of these groups (Brown, 1961) as $N^{\delta-}$—$Cl^{\delta+}\cdots O^{\delta-}$=$C^{\delta+}$. Due to the chemical similarity of the interactions in (I) and (III), electrostatic attraction can also be proposed for (I), and in order to confirm this assumption quantum mechanical calculations were performed. The molecular electronic properties have been calculated at a single point for both the diffraction-derived coordinates and the optimized structure, and these are comparable to within three standard deviations. The intermolecular interactions were calculated for sets containing between three and 23 molecules; further details are available in the archived CIF.

The calculations show that the existence of intermolecular interactions leads to a decrease of *p* character in the N,O atom hybrids and increasing *p* character in the Br,C atom hybrids. This agrees with the increased polarization of the aforementioned bonds and the larger charges on the interacting atoms (Table 2). The N, O and methyl group C atoms have δ^- charges and the remainder of the atoms have δ^+ charges, confirming the Brown (1961) postulates about polarization. The intermolecular interactions affect only the charges of the N—Br$\cdots$O=C atoms (Table 2). Additionally, it is observed that the N—Br bond in the interacting molecules is created by less electron density than in non-interacting molecules. The energies of the intermolecular interaction are 3.4828 and 2.3504 kcal mol^{-1} (1 kcal mol^{-1} = 4.184 kJ mol^{-1}) for Br1$\cdots$O2 and Br2$\cdots$O1, respectively [including the basis-set superposition error (Boys & Bernardi, 1970) of 0.1147 kcal mol^{-1}]. The second-order perturbation theory analysis of the Fock matrix in the natural bond orbital (NBO) basis sets leads to the conclusion that these interactions are formed mostly by the O-atom lone pairs donating electron density to the antibonding orbitals of the N—Br bonds, with delocalization energies of 3.27 and 2.11 kcal mol^{-1}, respectively, as above, proving that electrostatic attraction between the largely polarized groups is not responsible for these interactions. Noteworthy is the fact that, in separate molecules, there is no $2p_y$ coefficient in the $h_{C1}(\sigma$ bond) and $h_{O1}(\sigma$ bond) hybrids. This is caused by coupling of the N1 and N2 atom lone-pair electrons with the antibonding C1—O1 orbital (interaction energies of 83.39 and 54.13 kcal mol^{-1}, respectively). For the C2—O2 bond, only one such interaction is available with the N2 atom lone pair (interaction energy 76.04 kcal mol^{-1}). In sets containing the Br$\cdots$O interactions, the diminishing $2p_y$ coefficient is not observed due to the O1 atom electron-density changes (and, in consequence, changes in the natural orbital composition) caused by the intermolecular interactions.

The *ab initio* calculations prove that the N—Br$\cdots$O=C interaction is bonding in character, but it is weak and its

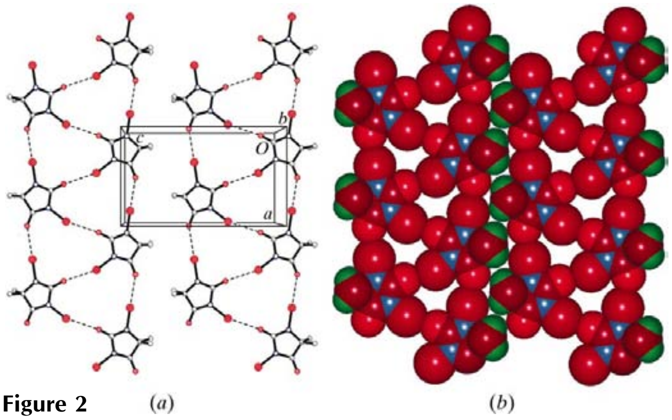


Figure 2 (*a*) (*b*)
Part of the molecular packing of (I), showing (*a*) the short intermolecular contacts (dashed lines) and (*b*) the overlapping of the van der Waals spheres.

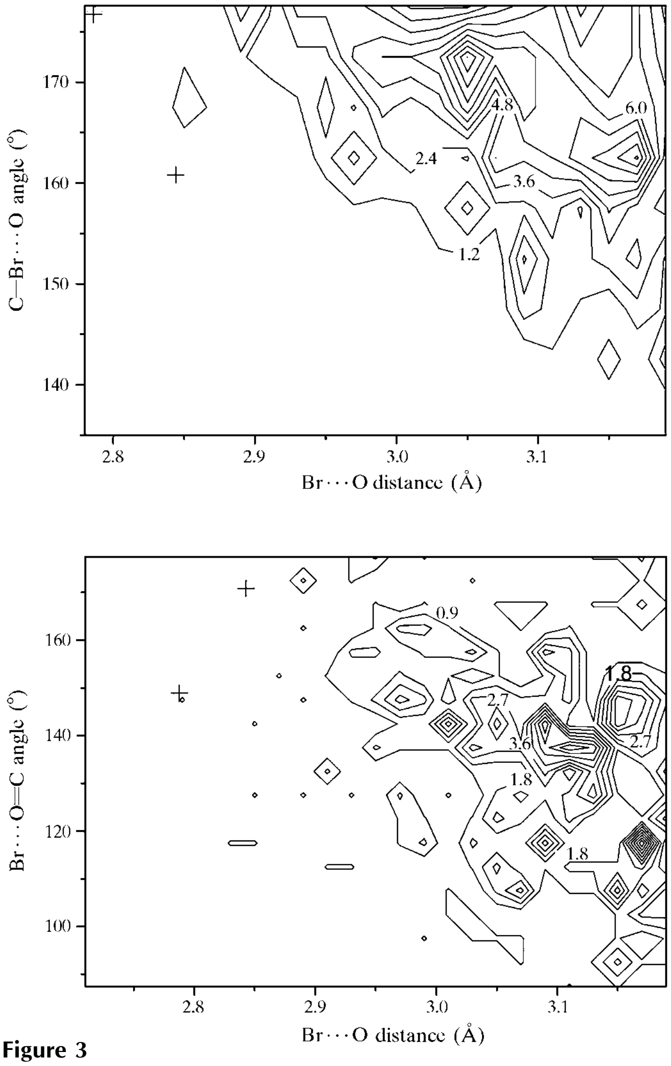


Figure 3
(*a*) Contour plot showing the relationship between the C—Br$\cdots$O angle and the Br$\cdots$O distance. (*b*) Contour plot showing the relationship between the Br$\cdots$O=C angle and the Br$\cdots$O distance. In both plots, the values for (I) are indicated by + symbols.

energy is comparable with weak C—H···O hydrogen bonds (Desiraju & Steiner, 1999).

Experimental

Compound (I) was synthesized according to the method of Markish & Arrad (1995). To an aqueous solution (200 ml) containing NaOH (5.00 g) and 5,5-dimethylhydantoin (8.40 g), Br_2 (22.050 g) was added dropwise over a period of 1 h. The reaction temperature was kept at 284.4 (3) K and the reagents were stirred for 2 h. The resulting precipitate was filtered off using a Buchner funnel and washed with cold water [275 (1) K] until bromine was not detected in the filtrate. The resulting fine crystalline dibromantin was dried in a vacuum desiccator for 24 h (yield 97.3%; purity 99.8%, determined by the iodometric method). Colourless crystals of (I) suitable for X-ray diffraction were obtained by recrystallization from a saturated solution in water (0.22 g in 100 g H_2O) at 297 (1) K (7 weeks). This may seem to be a poor solvent as dibromantin has a low solubility in water, but usage of organic solvents (especially alcohols) causes dibromantin to decompose to 5,5-dimethylhydantoin before crystals can be obtained. Attempts to recrystallize (even from water) commercially available dibromantin always led to growth of 5,5-dimethylhydantoin. This was probably caused by decomposition catalyzed by small amounts of decomposition products always present in commercial dibromantin (3% *w*/*w* Fluka and 2% *w*/*w* Aldrich).

Crystal data

$C_5H_6Br_2N_2O_2$	$V = 841.06$ (4) Å^3
$M_r = 285.94$	$Z = 4$
Orthorhombic, *Pnma*	Mo $K\alpha$ radiation
$a = 7.9749$ (2) Å	$\mu = 9.59$ mm^{-1}
$b = 7.9205$ (2) Å	$T = 291.0$ (3) K
$c = 13.3152$ (3) Å	0.12 × 0.08 × 0.06 mm

Data collection

Kuma KM-4 CCD area-detector diffractometer	8337 measured reflections
Absorption correction: numerical (*X-RED*; Stoe & Cie, 1999)	815 independent reflections
$T_{\min} = 0.399$, $T_{\max} = 0.558$	750 reflections with $I > 2\sigma(I)$
	$R_{\rm int} = 0.017$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.016$	65 parameters
$wR(F^2) = 0.040$	H-atom parameters constrained
$S = 1.12$	$\Delta\rho_{\max} = 0.27$ e Å^{-3}
815 reflections	$\Delta\rho_{\min} = -0.56$ e Å^{-3}

The H atoms were placed in calculated positions and were refined as riding on their parent C atoms, with C—H = 0.96 Å and $U_{\rm iso}$(H) = $1.5U_{\rm eq}$(C). The methyl groups were allowed to rotate about their local threefold axis [using AFIX 137 (*SHELXL97*; Sheldrick, 1997)].

Data collection: *CrysAlis CCD* (Kuma, 2000); cell refinement: *CrysAlis RED* (Kuma, 2000); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL*/*PC* (Sheldrick, 1990*b*), *Mercury* (Version 1.4; Macrae *et al.*, 2006) and *VICS-II* (Izumi & Dilanian, 2005); software used to prepare material for publication: *SHELXL97*.

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Table 1

Natural atomic charges (a.u.) for one molecule (column A) and for sets of interacting molecules (column B).

Standard deviations originate from differences in the values obtained from different numbers of molecules used in the calculations.

Atom	A	B
N1	−0.67729	−0.69853 (6)
Br1	0.28887	0.32537 (7)
N2	−0.69288	−0.70957 (5)
Br2	0.32643	0.36190 (7)
C1	0.99779	1.01303 (3)
O1	−0.68595	−0.71403 (5)
C2	0.84446	0.86462 (4)
O2	−0.67184	−0.70829 (6)
C3	0.15930	0.15918 (11)
C4	−0.45606	−0.45629 (11)
H4*A*	0.16808	0.16846 (14)
H4*B*	0.17763	0.17725 (14)
H4*C*	0.16591	0.16583 (14)

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG3081). Services for accessing these data are described at the back of the journal.

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