

## 2,4-Dibromo-3-methoxy-6-nitrobenzaldehyde: effect of substituents on ring geometry

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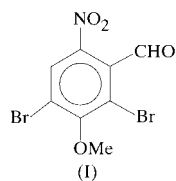
Received 24 August 2000

Accepted 19 September 2000

In the title compound, C<sub>8</sub>H<sub>5</sub>Br<sub>2</sub>NO<sub>4</sub>, the endocyclic angles of the ring deviate significantly from the ideal value of 120°. The substituents deviate from the plane of the ring, with large twist angles for the aldehyde, nitro and methoxy groups. The geometry of the molecule in the crystal is compared with that of the isolated molecule, as given by a self-consistent field molecular-orbital Hartree–Fock calculation. Only weak hydrogen bonds of the C–H···Br and C–H···O types are present in the crystal structure.

### Comment

The title compound, (I), was synthesized as a precursor in the synthesis of *meso*-aryl-substituted porphyrins, which are intermediates in the preparation of metalloporphyrins for oxidation catalysis. Hodgson & Beard (1931) studied the reaction of nitric acid with 2,4,6-tribromo-3-hydroxybenzaldehyde and found that substitution of the Br atom by the nitro group occurs at position 6, although the reaction seems equally possible at position 4. We followed the conditions described by Hodgson & Beard and confirmed by X-ray diffraction that the substitution occurs on the bromine at position 6. The X-ray study was carried out on a methoxy derivative which gave better crystals than the corresponding hydroxyl compound.



The benzene ring in (I) is planar to within 0.01 Å and the average aromatic C–C distance is 1.387 (8) Å. Bond distances within the ring range from 1.363 (7) to 1.404 (7) Å, the two shortest distances being those adjacent to the unsubstituted C atom. The internal angles of the ring deviate significantly from

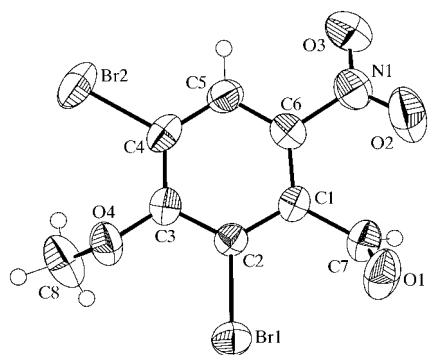
the ideal value of 120° by as much as 4.2 (4)°, although they add up to exactly 720°, as expected for an aromatic unpuckered ring. The endocyclic angles *ipso* to the Br atoms and the nitro group are larger than 120°, whereas those *ipso* to the unsubstituted C atom and the aldehyde and methoxy groups are smaller than the ideal value. This is the expected trend due to the  $\sigma$ -inductive electron-withdrawing effect of the substituents on the ring, particularly those of the NO<sub>2</sub> group and the Br atoms (Domenicano *et al.*, 1975*a,b*; Domenicano & Murray-Rust, 1979). According to these authors, the overall deviation of the endocyclic angles from 120° can be calculated, within a good approximation, as a linear combination of the individual effects of each substituent. The average deviation of the angles *ipso* ( $\alpha$ ), *ortho* ( $\beta$ ), *meta* ( $\gamma$ ) and *para* ( $\delta$ ) of monosubstituted aromatic compounds have been estimated for a number of substituents, including the nitro and methoxy groups, using linear regression upon a selection of reliable crystal data (Domenicano & Murray-Rust, 1979). To our knowledge, a similar calculation of the average distortions induced by aldehyde or bromine substituents has not yet been reported.

The rather short aldehyde C7=O1 distance [1.196 (6) Å] is consistent with the fact that the O1 atom is not strongly involved in hydrogen bonding (see below). The methoxy group is twisted around the O4–C<sub>aryl</sub> bond by 77.5 (7)°. Bond distances and angles are typical of this functional group (Allen *et al.*, 1987). The two Br atoms are significantly tilted out of the least-squares plane, Br1 by –0.121 (6) Å and Br2 by 0.116 (7) Å. The N1 and O4 atoms of the nitro and methoxy groups also deviate from the plane of the ring, although by smaller distances [N1 0.033 (8) Å and O4 0.058 (7) Å]. The aldehyde and nitro groups are twisted around the C1–C7 and C6–N1 single bonds by 58.5 (7) and 17.9 (7)°, respectively, probably as a result of molecular overcrowding at the C1 position.

In order to gain a better insight into the electronic and steric factors determining the geometry of the molecule, we have performed an *ab initio* self-consistent field molecular-orbital (SCF-MO) Hartree–Fock calculation using the quantum-mechanical package GAMESS (Schmidt *et al.*, 1993). A good quality 6-31G(*d,p*) basis set was chosen for the C, N, O and H atoms. For the Br atom, the ‘double zeta’ basis set (14s,11p,5d)/[6s,4p,1d] of Binning & Curtiss (1990) was chosen. The equilibrium geometry of the isolated molecule was located starting from the X-ray geometry without imposing any symmetry constraint. Tight conditions were applied for convergence of the SCF cycles and for location of the equilibrium geometry ( $\Delta\rho$  at the end of the SCF cycle = 10<sup>–6</sup> bohr<sup>–1</sup>; maximum gradient at the end of geometry optimization = 10<sup>–5</sup> hartree bohr<sup>–1</sup> or hartree rad<sup>–1</sup>).

The calculated equilibrium geometry reproduces well the observed geometric features of the ring, in particular the distortions of the endocyclic bond angles. The observed and calculated deviations, respectively, of the endocyclic angles from the ideal value of 120° are: C1 –4.2 (4) and –2.9, C2 2.7 (4) and 1.91, C3 –2.5 (4) and –1.4, C4 1.5 (4) and 0.8, C5 –1.4 (4) and –1.1, and C6 3.9 (4) and 2.6°. In all cases, the

correct sign of the deviation is reproduced, although the absolute values of the calculated deviations are always smaller than observed. The calculated twist angles for the aldehyde and nitro groups compare well with the the observed values. The largest difference between the calculated geometry of the free molecule and that measured in the crystal concerns the twist angle of the methoxy group. The equilibrium position calculated for this group corresponds to a symmetrical position with respect to the two Br atoms, with a C8—O4—C3—C4 torsion angle of 90°. Thus, the large deviation of the methoxy group from the symmetric position [C8—O4—C3—C4 77.5 (7)°] and the slight bending out of the plane of the ring appear to be due to intermolecular interactions involving the methoxy group.



**Figure 1**  
ORTEP (Johnson, 1976) plot of (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

There are no classical hydrogen bonds in the structure, due to the fact that the molecule lacks a strong hydrogen-bond donor. However, it is worth mentioning a possible C—H...O intermolecular interaction [C7...O1<sup>i</sup> 3.187 (6) Å; symmetry code: (i)  $x - 1, y, z$ ] bridging the aldehyde groups of two neighbouring molecules. One H atom of the methyl group (H8A) appears to be involved in a weak intramolecular interaction [C8...Br2 3.406 Å] and another H atom of the same group (H8B) is favourably positioned to interact with the aldehyde group of a neighbouring molecule.

### Experimental

A sample of 2,4-dibromo-3-hydroxy-6-nitrobenzaldehyde (2.5 g) was dissolved in acetone (25 ml), and potassium carbonate (1.6 g) and dimethyl sulfate (0.81 ml) were added. The mixture was refluxed for 4 h. After evaporation of the solvent, the residue was treated with dichloromethane. The organic extracts were washed and dried (Na<sub>2</sub>SO<sub>4</sub>). Evaporation of the solvent and recrystallization (water/ethanol) gave 1.7 g (yield 65%) of brown crystals of (I) (m.p. 384 K).

#### Crystal data

|   |   |
|---|---|
| C <sub>8</sub> H <sub>5</sub> Br <sub>2</sub> NO <sub>4</sub> | $D_x = 2.180 \text{ Mg m}^{-3}$           |
| $M_r = 338.95$  | Mo $K\alpha$ radiation                    |
| Monoclinic, $P2_1/n$  | Cell parameters from 25 reflections       |
| $a = 4.3048 (10) \text{ \AA}$                                 | $\theta = 9.27\text{--}15.75^\circ$       |
| $b = 18.108 (3) \text{ \AA}$                                  | $\mu = 7.843 \text{ mm}^{-1}$             |
| $c = 13.3152 (17) \text{ \AA}$                                | $T = 293 (2) \text{ K}$                   |
| $\beta = 95.847 (13)^\circ$                                   | Plate, colourless                         |
| $V = 1032.5 (3) \text{ \AA}^3$                                | $0.44 \times 0.22 \times 0.17 \text{ mm}$ |
| $Z = 4$   |   |

#### Data collection

|   |                                     |
|---|-------------------------------------|
| Enraf–Nonius CAD-4 diffractometer                               | $R_{\text{int}} = 0.043$            |
| Profile data from $\omega$ -2 $\theta$ scans                    | $\theta_{\text{max}} = 27.47^\circ$ |
| Absorption correction: $\psi$ scan (North <i>et al.</i> , 1968) | $h = 0 \rightarrow 5$               |
| $T_{\text{min}} = 0.486, T_{\text{max}} = 0.955$                | $k = 0 \rightarrow 23$              |
| 2524 measured reflections                                       | $l = -17 \rightarrow 15$            |
| 2255 independent reflections                                    | 3 standard reflections              |
| 1238 reflections with $I > 2\sigma(I)$                          | frequency: 180 min                  |
|   | intensity decay: 4.7%               |

#### Refinement

|                                 |  |
|---------------------------------|--|
| Refinement on $F^2$             | $w = 1/[\sigma^2(F_o^2) + (0.0436P)^2 + 1.3920P]$    |
| $R[F^2 > 2\sigma(F^2)] = 0.035$ | where $P = (F_o^2 + 2F_c^2)/3$                       |
| $wR(F^2) = 0.099$               | $(\Delta/\sigma)_{\text{max}} < 0.001$               |
| $S = 0.981$                     | $\Delta\rho_{\text{max}} = 0.43 \text{ e \AA}^{-3}$  |
| 2255 reflections                | $\Delta\rho_{\text{min}} = -0.58 \text{ e \AA}^{-3}$ |
| 137 parameters                  |  |
| H-atom parameters constrained   |  |

**Table 1**  
Hydrogen-bonding geometry (Å, °).

| $D\text{--}H\cdots A$     | $D\text{--}H$ | $H\cdots A$ | $D\cdots A$ | $D\text{--}H\cdots A$ |
|---------------------------|---------------|-------------|-------------|-----------------------|
| C7—H7...O1 <sup>i</sup>   | 0.93          | 2.52        | 3.187 (6)   | 130                   |
| C8—H8A...Br2              | 0.96          | 2.85        | 3.406 (7)   | 118                   |
| C8—H8B...O2 <sup>ii</sup> | 0.96          | 2.55        | 3.397 (8)   | 147                   |

Symmetry codes: (i)  $x - 1, y, z$ ; (ii)  $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$ .

The methyl group was refined as a rotating rigid group. Examination of the structure with PLATON (Spek, 1995) showed that there are no solvent-accessible voids in the crystal lattice.

Data collection and cell refinement: CAD-4 Software (Enraf–Nonius, 1989); data reduction: HELENA (Spek, 1997); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEPII (Johnson, 1976).

This work was supported by Fundação para a Ciência e Tecnologia (FCT).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1420). Services for accessing these data are described at the back of the journal.

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