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Methyl 4-bromo-3,5-dinitrobenzoate

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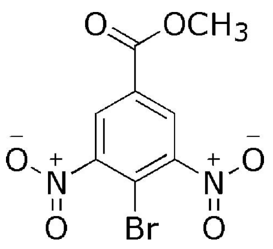
Key indicators: single-crystal X-ray study; T = 173 K; mean σ(C–C) = 0.006 Å; R factor = 0.052; wR factor = 0.179; data-to-parameter ratio = 14.5.

The title compound, $C_8H_5BrN_2O_6$, was synthesized from the nitration of 4-bromobenzoic acid with fuming nitric acid/sulfuric acid and subsequent esterification by sulfonyl chloride in dry methanol. The NO_2 groups are rotated out of conjugation with the aromatic ring, with dihedral angles of 55.6 (4) and 79.5 (3)°.

Related literature

For related literature, see: Beer & Dent (1998); Berryman *et al.* (2007); Bryantsev & Hay (2005); Demeshko *et al.* (2004); Frontera *et al.* (2005); Gale *et al.* (1996); Holman *et al.* (1996); de Hoog *et al.* (2004); Lehtonen *et al.* (1972); Lothrope & Handrick (1949); Manka *et al.* (2003); Park & Simmons (1968); Rosokha *et al.* (2004); Schottel *et al.* (2005, 2006); Staffilani *et al.* (1997); Ullman & Bielecki (1901); Yang *et al.* (1991).



Experimental

Crystal data

$C_8H_5BrN_2O_6$
M_r = 305.04
Monoclinic, $P2_1/n$
a = 9.6350 (9) Å
b = 5.0104 (5) Å
c = 21.913 (2) Å
β = 94.686 (2)°
V = 1054.31 (18) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 3.92 mm^{-1}
T = 173 (2) K
0.38 × 0.26 × 0.20 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1995)
T_{min} = 0.285, T_{max} = 0.457
3498 measured reflections
2228 independent reflections
1938 reflections with $I > 2\sigma(I)$
R_{int} = 0.012

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.052
$wR(F^2)$ = 0.179
S = 1.08
2228 reflections
154 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.83 e Å^{-3}
$\Delta\rho_{min}$ = −0.53 e Å^{-3}

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LN3050).

References

Beer, P. D. & Dent, S. W. (1998). *Chem. Commun.* pp. 825–826.
Berryman, O. B., Bryantsev, V. S., Stay, D. P., Johnson, D. W. & Hay, B. P. (2007). *J. Am. Chem. Soc.* **129**, 48–58.
Bruker (2000). *SMART* (Version 5.631), *SAINT* (Version 6.63) and *SHELXTL* (Version 6.10). Bruker AXS Inc., Madison, Wisconsin, USA.
Bryantsev, V. S. & Hay, B. P. (2005). *J. Am. Chem. Soc.* **127**, 8282–8283.
Demeshko, S., Dechert, S. & Meyer, F. (2004). *J. Am. Chem. Soc.* **126**, 4508–4509.
Frontera, A., Saczewski, F., Gdaniec, M., Dziemidowicz-Borys, E., Kurland, A., Deyá, P. M., Quiñonero, D. & Garau, C. (2005). *Chem. Eur. J.* **11**, 6560–6567.
Gale, P. A., Sessler, J. L., Kral, V. & Lynch, V. (1996). *J. Am. Chem. Soc.* **118**, 5140–5141.
Holman, K. T., Halihan, M. M., Mitchell, A. R., Burkhalter, R. S., Steed, J. W., Jurisson, S. S. & Atwood, J. L. (1996). *J. Am. Chem. Soc.* **118**, 9567–9576.
Hoog, P. de, Gamez, P., Mutikainen, I., Turpeinen, U. & Reedijk, J. (2004). *Angew. Chem. Int. Ed.* **43**, 5815–5817.
Lehtonen, K., Summers, L. A. & Carter, G. A. (1972). *Pestic. Sci.* **3**, 443–447.
Lothrope, W. C. & Handrick, G. R. (1949). *Chem. Rev.* **44**, 419–445.
Manka, J. T., Guo, F., Huang, J., Yin, H., Farrar, J. M., Sienkowska, M., Benin, V. & Kaszynski, P. (2003). *J. Org. Chem.* **68**, 9574–9588.
Park, C. H. & Simmons, H. E. (1968). *J. Am. Chem. Soc.* **90**, 2431–2432.
Rosokha, Y. S., Lindeman, S. V., Rosokha, S. V. & Kochi, J. K. (2004). *Angew. Chem. Int. Ed.* **43**, 4650–4652.
Schottel, B. L., Bacsa, J. & Dunbar, K. R. (2005). *Chem. Commun.* pp. 46–47.
Schottel, B. L., Chifotides, T. H., Shatruk, M., Chouai, A., Pérez, L. M., Bacsa, J. & Dunbar, K. R. (2006). *J. Am. Chem. Soc.* **128**, 5895–5912.
Sheldrick, G. M. (1995). *SADABS*. University of Göttingen, Germany.
Staffilani, M., Hancock, K. S. B., Steed, J. W., Holman, K. T., Atwood, J. L., Juneja, R. K. & Burkhalter, R. S. (1997). *J. Am. Chem. Soc.* **119**, 6324–6335.
Ullman, F. & Bielecki, J. (1901). *Ber. Dtsch. Chem. Ges.* **34**, 2174–2185.
Yang, X., Knobler, C. B. & Hawthorne, M. F. (1991). *Angew. Chem. Int. Ed.* **30**, 1507–1508.

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supplementary materials

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Methyl 4-bromo-3,5-dinitrobenzoate

J. S. Meisner, O. B. Berryman, L. N. Zakharov and **D. W. Johnson**

Comment

In the field of anion recognition, host-architectures often incorporate various types of supramolecular interactions. Hydrogen-bonding (Bryantsev & Hay, 2005; Gale *et al.*, 1996), metal coordination (Yang *et al.*, 1991), and electrostatic ion-pairing (Beer & Dent, 1998) or their combination (Park & Simmons, 1968) can be used to form primary binding motifs to target desired guest molecules. Recently, it has been shown that substituted nitro- and cyanobenzenes interact with halides in solution and in the solid state (Berryman *et al.*, 2007; Rosokha *et al.*, 2004). Anions have also been observed to interact with other electron-deficient systems (de Hoog *et al.*, 2004; Demeshko *et al.*, 2004; Frontera *et al.*, 2005; Holman *et al.*, 1996; Schottel *et al.*, 2005; 2006; Staffilani *et al.*, 1997). It is hypothesized that the substitution pattern and combination of electron withdrawing groups heavily govern the strength of the interaction. However, the attractive forces between anions and electron-deficient aromatic systems are not fully understood. Observed and calculated binding geometries contradict purposed electrostatic models and provide support for charge transfer complexes (Berryman *et al.*, 2007; Rosokha *et al.*, 2004).

One challenge in investigating the strength of anion/arene interactions lies in the synthesis of increasingly electron-deficient anionophore architectures. Highly electron-deficient arenes become non-reactive to electrophilic aromatic substitution and may become hazardous and unstable (Lothrope & Handrick, 1949). The synthesis of charge-neutral, electron-deficient arenes likely will aid in developing the supramolecular host–guest chemistry of anions. Herein we report the molecular and crystal structure of the title compound, (2), –an example of an electron-deficient arene– which offers a route to further modification through its aryl halide functionality. Compound (2) has been exploited as an antifungal agent (Lehtonen *et al.*, 1972) and efficiently undergoes homo-coupling in the presence of copper (Ullman & Bielecki, 1901) leading to synthesis of new liquid crystalline materials (Manka *et al.*, 2003).

Compound (2) is a planar molecule (Fig. 2) obtained from the nitration of 4-bromobenzoic acid with fuming nitric acid and sulfuric acid followed by esterification to the methyl ester with sulfonyl chloride and dry MeOH. The deviations of the Br1, N1 and N2 atoms from the average plane of the central 6-membered aromatic ring are 0.026 (6), 0.004 (7) and -0.095 (6) Å, respectively. The nitro groups are rotated out of conjugation with the aromatic ring due to steric constraints imposed by the large bromine atom. The dihedral angles between the N1/O2/O3 and N2/O3/O4 planes and the average plane of the aromatic ring are 55.6 (4)° and 79.5 (3)°, respectively. The ester —C═OOCH$_3$ group is rotated out this plane by 17.5 (4)°. There are no π···π intermolecular interactions due to NO$_2$ groups in the aromatic ring, but the short intermolecular Br1···O1(1.5-*x*,-1.5+*y*,0.5-*z*) and O3···C7(1-*x*,1-*y*,-*z*) contacts, 2.999 (5) and 3.013 (5) Å, respectively, indicate that intermolecular interactions in the crystal structure are relatively strong. The molecules of (2) form a centrosymmetrical pair *via* weak C—H···O interactions; the C5···O5(1 - *x*,2 - *y*,-*z*) distance is 3.173 (6) Å (Fig. 3), and pairs are stacked into one-dimensional columns in the crystal structure (Fig. 4).

Experimental

4-bromo-3,5-dinitrobenoic acid (**1**). Fuming nitric acid (5 ml) was added slowly to a stirring solution of concentrated sulfuric acid (20 ml) at 273 K. 4-bromobenzoic acid (4.00 g, 9.05 mmol) was slowly added to the solution. The suspension was heated to 373 K for 10 h. The solution was cooled to room temperature and poured over cracked ice. A white precipitate was filtered off, washed with cold water and dried to yield a fine yellowish crystalline powder (5.69 g, 98.3%). M.p. 454.4–456.6 K; ^{1}H-NMR (DMSO-*d*6, 300 MHz) δ 8.51 (s, 2H). ^{13}C-NMR (DMSO-*d*6, 300 MHz) δ 169.08, 156.78, 138.47, 133.35, 116.86.

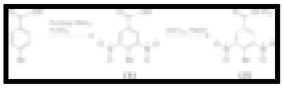
Methly 4-bromo-3,5-dinitrobenzoate (**2**). Sulfonyl chloride (4.0 ml, 58 mmol) was added dropwise to 10 ml of dry methanol stirring at 273 K. After 5 minutes at 273 K, 4-bromo-3,5-dinitrobenzoic acid (0.500 g, 1.72 mmol) was added. The suspension was heated at reflux (*ca* 338 K) for 24 h. The reaction mixture was cooled to room temperature and the off-white solid was filtered and washed with cold methanol. Subsequent recrystallization from hot methanol yielded long white needles (0.280 g, 53.4%). Further product was obtained by evaporation of the remaining mother liquor. The resulting solid was dissolved in ethyl acetate and washed with 4% aqueous sodium hydrogen carbonate (3 *x* 10 ml) followed by water (10 ml) to remove residual starting material. The organic layer was dried over magnesium sulfate and evaporation of the solvent produced an off-white solid. Recrystallization from hot methanol gave the title compound (0.201 g, 38.4%) as long white needles. (Total yield: 91.8%). M.p. 393.9–394.3 K; ^{1}H-NMR ($CDCl_3$, 300 MHz) d 8.51 (s, 2H), 4.02 (s, 3H). ^{13}C-NMR (DMSO-*d*6, 500 MHz) δ 168.2, 156.86, 137.0, 133.2, 117.4, 58.8.

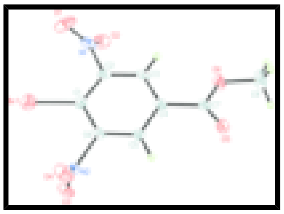
Single crystals suitable for X-ray diffraction were prepared by slow evaporation of a concentrated solution of (2) in tetrahydrofuran at room temperature. After three days crystals appeared as colorless needles.

Refinement

The H atoms were positioned geometrically and refined in the riding model approximation, C—H = 0.95 and 0.98 Å; U_{iso}(H) = 1.2U_{eq}(C) and 1.5U_{eq}(C), respectively for aromatic and methyl H atoms.

Figures





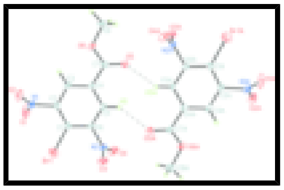
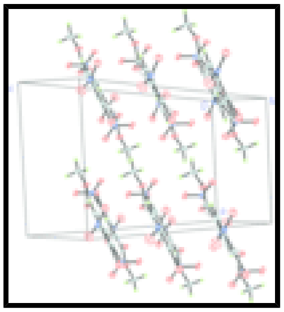


Fig. 1. Reaction scheme.

Fig. 2. The molecular structure of (2), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

Fig. 3. A centrosymmetric pair of molecules. Dashed lines denote aryl C—H hydrogen-bonding associations [3.173 (6) Å]. Displacement ellipsoids are drawn at the 50% probability level. The symmetry-related fragment, labelled with the suffix A, is derived using the symmetry operator (1 - *x*, 2 - *y*, -*z*).

Fig. 4. A fragment of the crystal structure of (2), showing stacks of molecules.



Methyl 4-bromo-3,5-dinitrobenzoate

Crystal data

$C_8H_5BrN_2O_6$	$F_{000} = 600$
$M_r = 305.04$	$D_x = 1.922$ Mg m^{-3}
Monoclinic, $P2_1/n$	Melting point: 394.1 K
Hall symbol: -P 2yn	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 9.6350$ (9) Å	Cell parameters from 5682 reflections
$b = 5.0104$ (5) Å	$\theta = 2.3–27.0$º
$c = 21.913$ (2) Å	$\mu = 3.92$ mm^{-1}
$\beta = 94.686$ (2)º	$T = 173$ (2) K
$V = 1054.31$ (18) Å^3	Block, colourless
$Z = 4$	0.38 × 0.26 × 0.20 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer	2228 independent reflections
Radiation source: fine-focus sealed tube	1938 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\mathrm{int}} = 0.012$
$T = 173(2)$ K	$\theta_{\mathrm{max}} = 27.0$º
φ and ω scans	$\theta_{\mathrm{min}} = 1.9$º
Absorption correction: multi-scan (SADABS; Sheldrick, 1995)	$h = -12 \rightarrow 3$
$T_{\mathrm{min}} = 0.285$, $T_{\mathrm{max}} = 0.457$	$k = -5 \rightarrow 6$
3498 measured reflections	$l = -25 \rightarrow 27$

Refinement

Refinement on F^2	H-atom parameters constrained
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.1272P)^2 + 2.0826P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.052$	$(\Delta/\sigma)_{\mathrm{max}} < 0.001$
$wR(F^2) = 0.179$	$\Delta\rho_{\mathrm{max}} = 0.83$ e Å^{-3}
$S = 1.08$	$\Delta\rho_{\mathrm{min}} = -0.53$ e Å^{-3}

2228 reflections

154 parameters

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

Extinction correction: none

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\mathrm{sigma}(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.73453 (5)	0.16258 (10)	0.18421 (2)	0.0323 (2)
O1	0.5247 (5)	0.3004 (9)	0.27993 (17)	0.0462 (11)
O2	0.3348 (4)	0.1773 (7)	0.23145 (17)	0.0331 (8)
O3	0.7443 (4)	0.3120 (7)	0.03565 (17)	0.0297 (8)
O4	0.8423 (3)	0.6612 (7)	0.07736 (18)	0.0343 (9)
O5	0.3398 (3)	1.1689 (6)	0.04798 (15)	0.0217 (7)
O6	0.1825 (3)	0.9699 (7)	0.10260 (15)	0.0266 (7)
N1	0.4462 (4)	0.2973 (7)	0.23679 (18)	0.0230 (8)
N2	0.7466 (3)	0.5060 (7)	0.06887 (15)	0.0189 (7)
C1	0.6013 (4)	0.4070 (8)	0.15411 (18)	0.0168 (8)
C2	0.4783 (4)	0.4520 (8)	0.18125 (17)	0.0173 (8)
C3	0.3788 (4)	0.6324 (8)	0.15781 (19)	0.0188 (8)
H3A	0.2933	0.6519	0.1761	0.023*
C4	0.4060 (4)	0.7841 (8)	0.10722 (19)	0.0164 (8)
C5	0.5278 (4)	0.7439 (8)	0.07845 (19)	0.0168 (7)
H5A	0.5462	0.8448	0.0433	0.020*
C6	0.6212 (4)	0.5548 (8)	0.10203 (17)	0.0153 (7)
C7	0.3073 (4)	0.9972 (8)	0.08195 (18)	0.0184 (8)
C8	0.0813 (5)	1.1733 (10)	0.0832 (3)	0.0348 (12)
H8A	−0.0070	1.1354	0.1007	0.052*
H8B	0.0666	1.1736	0.0384	0.052*
H8C	0.1159	1.3484	0.0974	0.052*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}

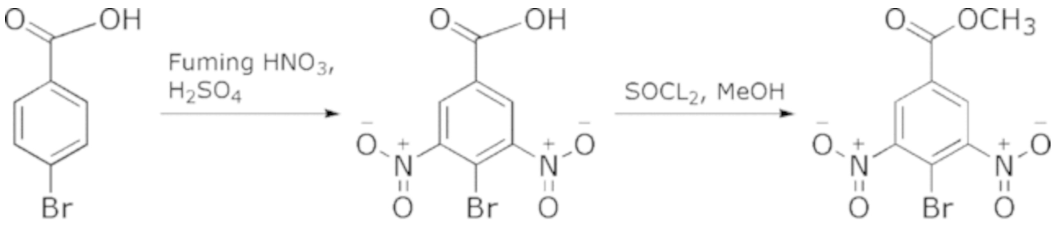
Br1	0.0381 (4)	0.0299 (4)	0.0282 (4)	0.00590 (17)	−0.0007 (2)	0.00055 (17)
O1	0.059 (3)	0.060 (3)	0.0201 (18)	−0.014 (2)	0.0071 (18)	0.0135 (17)
O2	0.0378 (19)	0.032 (2)	0.0309 (19)	−0.0103 (14)	0.0125 (15)	0.0035 (14)
O3	0.0306 (16)	0.0285 (18)	0.0316 (18)	0.0057 (13)	0.0110 (14)	−0.0095 (14)
O4	0.0213 (16)	0.040 (2)	0.043 (2)	−0.0047 (13)	0.0103 (14)	−0.0078 (16)
O5	0.0199 (14)	0.0210 (16)	0.0248 (17)	0.0025 (10)	0.0056 (12)	0.0026 (11)
O6	0.0141 (13)	0.0338 (18)	0.0330 (17)	0.0068 (12)	0.0081 (12)	0.0073 (14)
N1	0.0278 (19)	0.0154 (17)	0.028 (2)	−0.0036 (14)	0.0162 (16)	−0.0050 (15)
N2	0.0141 (14)	0.0261 (19)	0.0170 (16)	0.0059 (13)	0.0041 (12)	0.0025 (14)
C1	0.0208 (17)	0.0140 (18)	0.0156 (19)	−0.0002 (15)	0.0008 (14)	−0.0022 (15)
C2	0.0237 (18)	0.0165 (19)	0.0121 (18)	−0.0031 (15)	0.0043 (14)	−0.0002 (15)
C3	0.0173 (17)	0.023 (2)	0.017 (2)	−0.0018 (15)	0.0067 (14)	−0.0042 (16)
C4	0.0134 (17)	0.0180 (19)	0.0182 (19)	0.0009 (14)	0.0034 (14)	−0.0013 (16)
C5	0.0167 (17)	0.0182 (19)	0.0163 (17)	0.0003 (15)	0.0055 (14)	−0.0007 (15)
C6	0.0133 (16)	0.0187 (19)	0.0141 (18)	0.0002 (14)	0.0037 (13)	−0.0022 (15)
C7	0.0163 (17)	0.023 (2)	0.0163 (19)	0.0026 (15)	0.0024 (14)	−0.0050 (16)
C8	0.0150 (19)	0.040 (3)	0.049 (3)	0.0105 (18)	0.0040 (19)	0.008 (2)

Geometric parameters (Å, °)

Br1—C1	1.856 (4)	C1—C2	1.387 (5)
O1—N1	1.162 (6)	C2—C3	1.386 (6)
O2—N1	1.227 (5)	C3—C4	1.386 (6)
O3—N2	1.214 (5)	C3—H3A	0.9500
O4—N2	1.209 (5)	C4—C5	1.392 (5)
O5—C7	1.196 (5)	C4—C7	1.505 (5)
O6—C7	1.327 (5)	C5—C6	1.378 (6)
O6—C8	1.450 (5)	C5—H5A	0.9500
N1—C2	1.496 (5)	C8—H8A	0.9800
N2—C6	1.481 (4)	C8—H8B	0.9800
C1—C6	1.387 (6)	C8—H8C	0.9800
C7—O6—C8	115.7 (3)	C3—C4—C7	121.9 (3)
O1—N1—O2	126.2 (4)	C5—C4—C7	117.8 (4)
O1—N1—C2	119.4 (4)	C6—C5—C4	118.6 (4)
O2—N1—C2	114.4 (4)	C6—C5—H5A	120.7
O4—N2—O3	125.7 (3)	C4—C5—H5A	120.7
O4—N2—C6	117.5 (3)	C5—C6—C1	123.1 (3)
O3—N2—C6	116.8 (3)	C5—C6—N2	117.6 (3)
C6—C1—C2	116.5 (4)	C1—C6—N2	119.3 (3)
C6—C1—Br1	120.5 (3)	O5—C7—O6	125.3 (4)
C2—C1—Br1	123.0 (3)	O5—C7—C4	123.4 (3)
C3—C2—C1	122.5 (4)	O6—C7—C4	111.4 (3)
C3—C2—N1	117.2 (3)	O6—C8—H8A	109.5
C1—C2—N1	120.3 (4)	O6—C8—H8B	109.5
C2—C3—C4	118.9 (4)	H8A—C8—H8B	109.5
C2—C3—H3A	120.5	O6—C8—H8C	109.5
C4—C3—H3A	120.5	H8A—C8—H8C	109.5
C3—C4—C5	120.3 (4)	H8B—C8—H8C	109.5
C6—C1—C2—C3	0.6 (6)	C4—C5—C6—N2	177.0 (4)

Br1—C1—C2—C3	−179.1 (3)	C2—C1—C6—C5	2.0 (6)
C6—C1—C2—N1	178.6 (3)	Br1—C1—C6—C5	−178.3 (3)
Br1—C1—C2—N1	−1.1 (5)	C2—C1—C6—N2	−176.7 (3)
O1—N1—C2—C3	−125.8 (5)	Br1—C1—C6—N2	3.0 (5)
O2—N1—C2—C3	53.9 (5)	O4—N2—C6—C5	80.3 (5)
O1—N1—C2—C1	56.1 (6)	O3—N2—C6—C5	−100.0 (4)
O2—N1—C2—C1	−124.2 (4)	O4—N2—C6—C1	−100.9 (5)
C1—C2—C3—C4	−3.4 (6)	O3—N2—C6—C1	78.8 (5)
N1—C2—C3—C4	178.5 (4)	C8—O6—C7—O5	−2.3 (6)
C2—C3—C4—C5	3.7 (6)	C8—O6—C7—C4	177.2 (4)
C2—C3—C4—C7	−175.7 (4)	C3—C4—C7—O5	162.8 (4)
C3—C4—C5—C6	−1.2 (6)	C5—C4—C7—O5	−16.6 (6)
C7—C4—C5—C6	178.2 (4)	C3—C4—C7—O6	−16.7 (6)
C4—C5—C6—C1	−1.7 (6)	C5—C4—C7—O6	164.0 (4)

Fig. 1


O
OH
Br
Fuming HNO$_3$,
H$_2$SO$_4$
O
OH
O
N
O
Br
N
O
SOCL$_2$, MeOH
O
OCH$_3$
O
N
O
Br
N
O

(1) **(2)**

Fig. 2

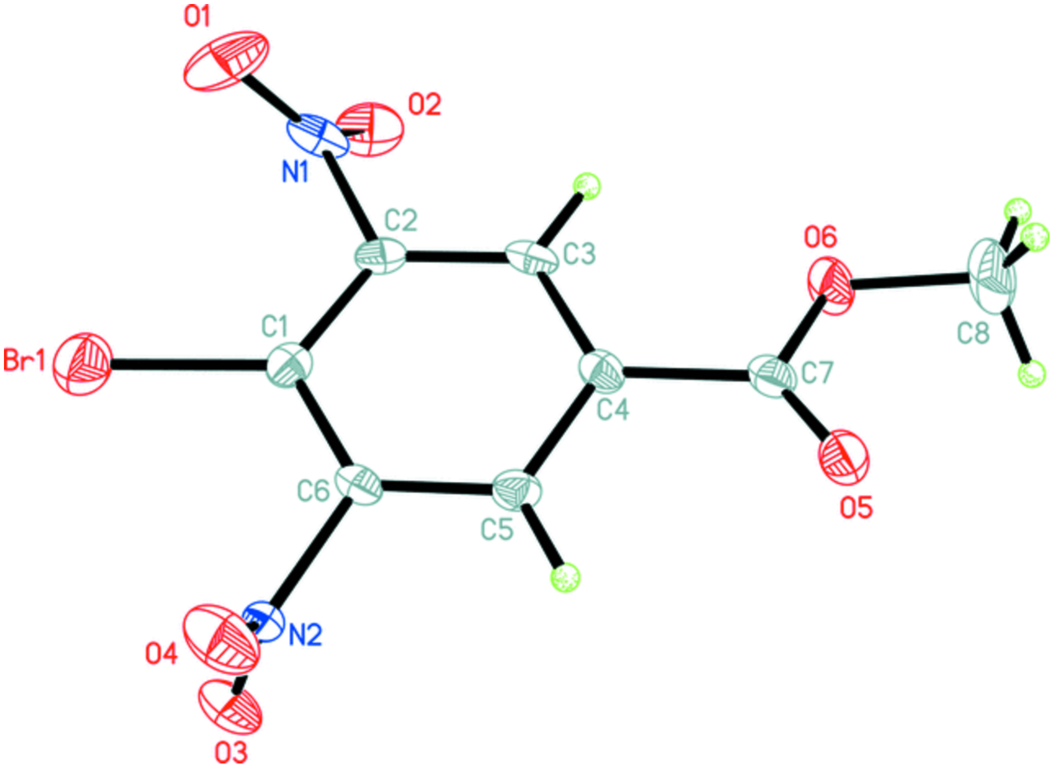


Fig. 3

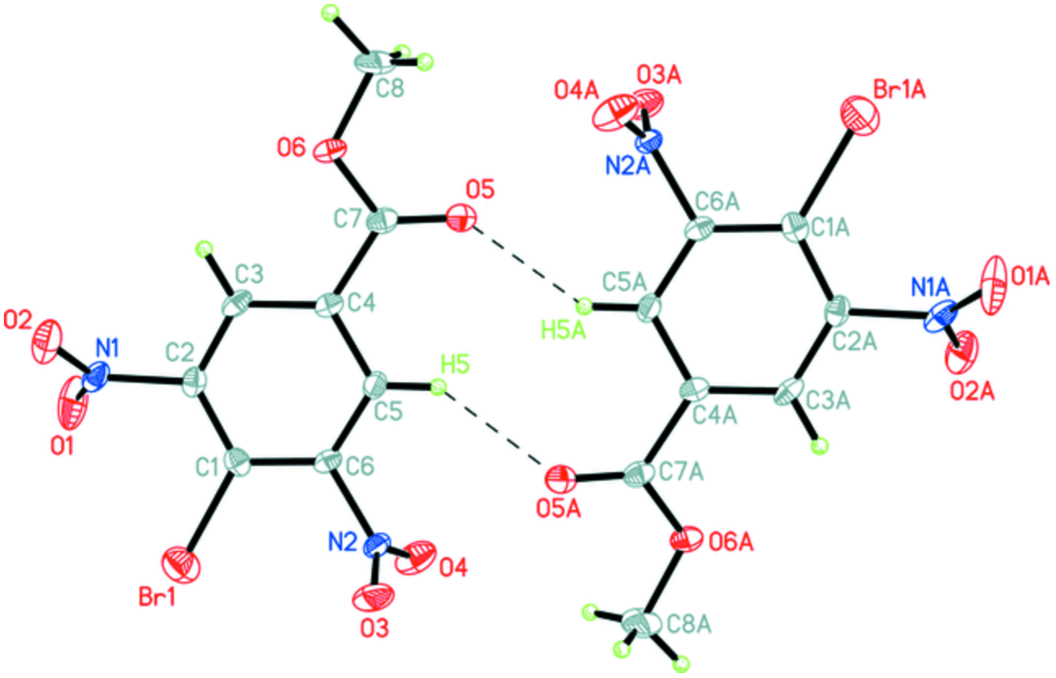

O4A
O3A
Br1A
C8
O6
N2A
O5
C7
C6A
C1A
C3
C4
C5A
N1A
O1A
O2
N1
C2
H5A
C2A
H5
C5
C4A
C3A
O2A
O1
C1
C6
C7A
O5A
N2
O6A
O4
Br1
O3
C8A

Fig. 4