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Crystal structure and Hirshfeld surface analysis of a supramolecular aggregate of 4-formyl-*N*,*N*-dimethylanilinium bromide with tetrabromomethane

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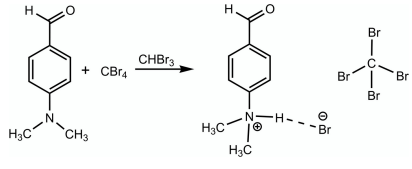
The title compound, $C_9H_{12}NO^+\cdot Br^-\cdot CBr_4$, consists of one 4-formyl-*N*,*N*-dimethylbenzenaminium bromide and a tetrabromomethane molecule. In the crystal, the bromide ions link 4-formyl-*N*,*N*-dimethylbenzenaminium moieties through intermolecular C—H···Br and N—H···Br hydrogen bonds, while intermolecular C—H···O hydrogen bonds link 4-formyl-*N*,*N*-dimethylbenzenaminium cations, enclosing $R_2^2(18)$ ring motifs, into a di-periodic network structure. The tetrabromomethane molecules fill the spaces between the layers. Neither π–π nor C—H···π(ring) interactions are observed. A Hirshfeld surface analysis of the crystal structure indicates that the most abundant contacts contributing to the crystal packing are from H···Br/Br···H (56.0%), Br···Br (12.1%), H···O/O···H (9.7%) and H···H (9.5%) interactions.

1. Chemical context

Aldehydes are versatile compounds for the synthesis of organic acids, dyes, drugs, perfumes, detergents, soaps, *etc*. In the synthesis of those compounds the aldehydes undergo many different nucleophilic addition reactions. In order to increase the electrophilicity of the carbon atom at the C=O group of the aldehyde molecule, metal complexes or organocatalysts are commonly used (Ma *et al.*, 2017, 2021; Mahmudov & Pombeiro, 2023). Following crystal engineering principles (Gurbanov *et al.*, 2020; Mahmoudi *et al.*, 2018; Velásquez *et al.*, 2019), weak interactions, halogen bonds, and other interactions, have been used in the activation of aldehydes towards the synthesis of various classes of organic compounds (Gurbanov *et al.*, 2022; Sutar & Huber, 2019). We found that weak interactions can be formed with substituents at the aldehyde molecules instead of with the oxygen atom of the C=O group.



Herein, we provide details of the synthesis and an examination of the molecular and crystal structures, together with a Hirshfeld surface analysis, of the title compound (I).

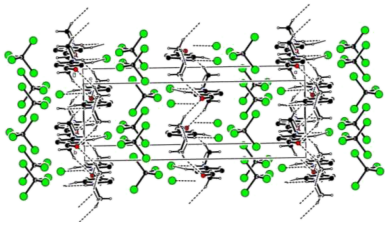


Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1*N*···Br4	0.85	2.37	3.221 (4)	175
C6—H6*A*···Br4	0.95	2.91	3.698 (4)	141
C7—H7*A*···O1^{iii}	0.98	2.52	3.424 (5)	153
C7—H7*B*···O1^{iv}	0.98	2.47	3.390 (5)	157

Symmetry codes: (iii) $x, y, z+1$; (iv) $-x+1, -y+1, -z+1$.

2. Structural commentary

The title compound, (I), consists of one 4-formyl-*N*,*N*-dimethylbenzenaminium bromide unit and a tetrabromomethane solvent molecule (Fig. 1). The C—C and C—C—C bond lengths and angles of ring *A* are in the ranges 1.366 (7) to 1.3998 (10) Å and 118.6 (4) to 121.8 (4)° with average values of 1.388 (8) Å and 120.0 (4)°, respectively. These values are reported as 1.375 Å and 119.9° in *p*-dimethylamino-benzaldehyde hydrobromide, (II) (Dattagupta & Saha, 1973). Both of the N—C bonds between the methyl carbon and amino nitrogen atoms are 1.497 (4) Å, and the corresponding ones in compound (II) are 1.51 (4) and 1.43 (4) Å. The C=O bond length in the aldehyde group is 1.198 (7) Å, and its corresponding value is 1.18 (4) Å in compound (II). The dihedral angle between ring *A* and the plane of atoms (O1/C4/C8) is 0.00 (2)° while the corresponding value in compound (II) is 1.39°. The C4—C8 [1.467 (7) Å] bond length is in good agreement with the theoretically calculated single-bond lengths between trigonally linked (sp^2) carbon atoms: 1.479 Å (Dewar & Schmeising, 1959) and 1.477 Å (Cruickshank & Sparks, 1960). The corresponding exocyclic C—C bond length is reported as 1.38 (4) Å in compound (II).

3. Supramolecular features

In the crystal, intermolecular C—H···Br and N—H···Br hydrogen bonds link the bromide ions and the 4-formyl-*N*,*N*-dimethylbenzenaminium moieties (Table 1 and Fig. 2*a*). At the same time, intermolecular C—H···O hydrogen bonds (Table 1) link pairs of molecules through $R_2^2(18)$ hydrogen-bonding motifs, into a di-periodic network structure (Fig. 2*a*).

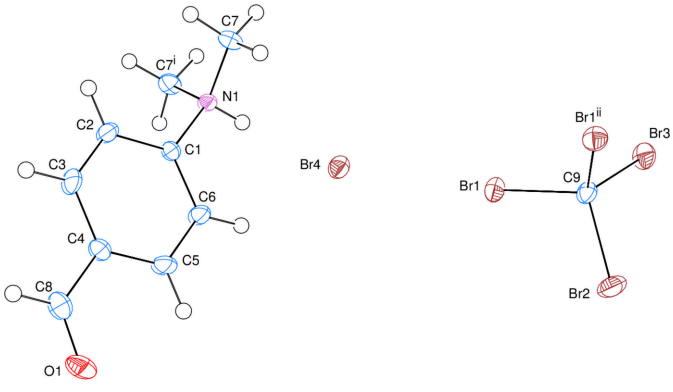


Figure 1
The title compound with atom-numbering scheme and 50% probability ellipsoids. Symmetry codes: (i) $x, -y+\frac{1}{2}, z$; (ii) $x, -y+\frac{3}{2}, z$.

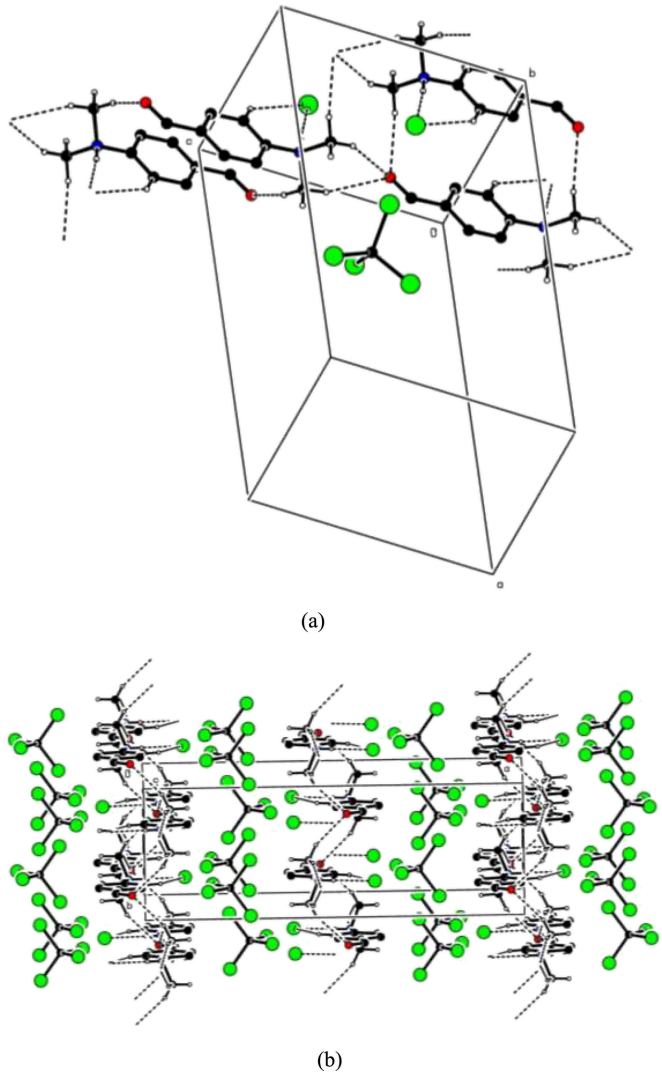


Figure 2
(*a*) A partial packing diagram showing the presence of an $R_2^2(18)$ ring motif (upper right). (*b*) A packing diagram viewed approximately down the *c*-axis direction. Intermolecular C—H···Br, N—H···Br and C—H···O hydrogen bonds are shown as dashed lines. Hydrogen atoms not involved in hydrogen bonds have been omitted for clarity.

The tetrabromomethane solvent molecules occupy the spaces between the layers (Fig. 2*b*).

4. Hirshfeld surface analysis

For visualizing the intermolecular interactions in (I) a Hirshfeld surface (HS) analysis (Hirshfeld, 1977; Spackman & Jayatilaka, 2009) was carried out using *Crystal Explorer 17.5* (Spackman *et al.*, 2021). In the HS plotted over d_{norm} (Fig. 3), the white regions indicate contacts with distances equal to the sum of van der Waals radii, while the red and blue colours indicate distances shorter (in close contact) or longer (distant contact) than the sum of the van der Waals radii, respectively (Venkatesan *et al.*, 2016), where the bright-red spots indicate their roles as the respective donors and/or acceptors. There are no π–π stacking interactions between aromatic rings in the

Table 2
Selected interatomic distances (Å).

Br3···Br4^{i}	3.3403 (8)	H7*B*···O1^{iv}	2.47
H6*A*···Br3^{ii}	2.95	C2···H7*C*	2.83
O1···H5*A*	2.57	C7···H2*A*	2.96
H7*A*···O1^{iii}	2.52	H1*N*···H6*A*	2.22

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

packing of (I). Unusually, this is in spite of the presence of juxtaposed red/blue triangular regions in the HS plotted over shape-index (Fig. 4). There are also no C—H···π close contacts. According to the two-dimensional fingerprint plots (McKinnon *et al.*, 2007), the intermolecular H···Br/Br···H, Br···Br, H···O/O···H, H···H and H···C/C···H contacts make the most abundant contributions to the HS of 56%, 12.1%, 9.7%, 9.5% and 7.5% respectively (Table 2, Fig. 5). All other contact types contribute <5% to the surface. The nearest neighbour coordination environment of a molecule can be determined from the colour patches on the HS based on how close to other molecules they are. These are plotted onto the HS for the H···Br/Br···H, Br···Br, H···O/O···H and H···H interactions in Fig. 6, showing that van der Waals interactions and hydrogen bonding play the major roles in the crystal packing (Hathwar *et al.*, 2015).

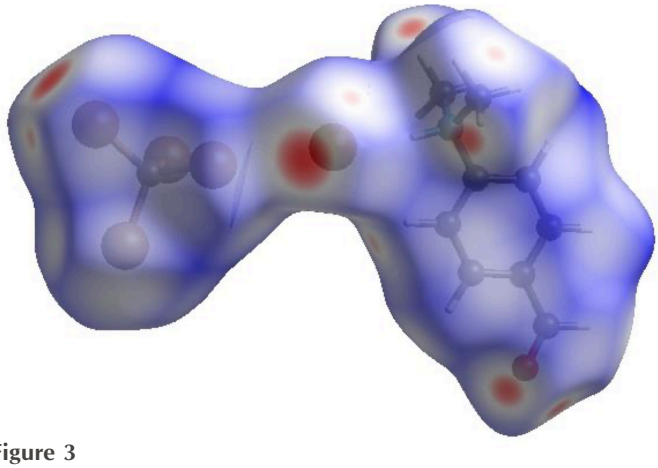


Figure 3
View of the three-dimensional Hirshfeld surface plotted over d_{norm}.

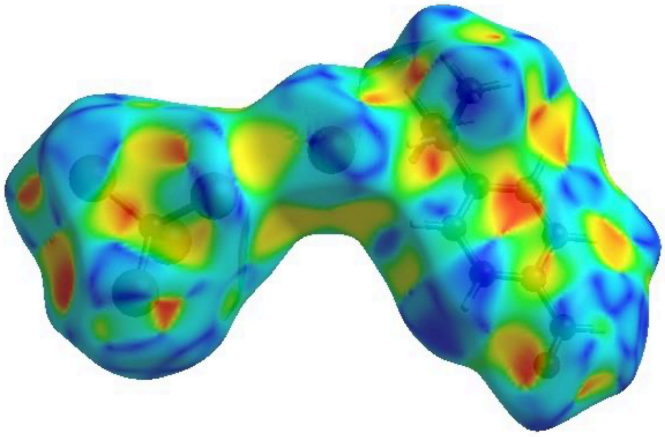


Figure 4
Hirshfeld surface of the title compound plotted over shape-index.

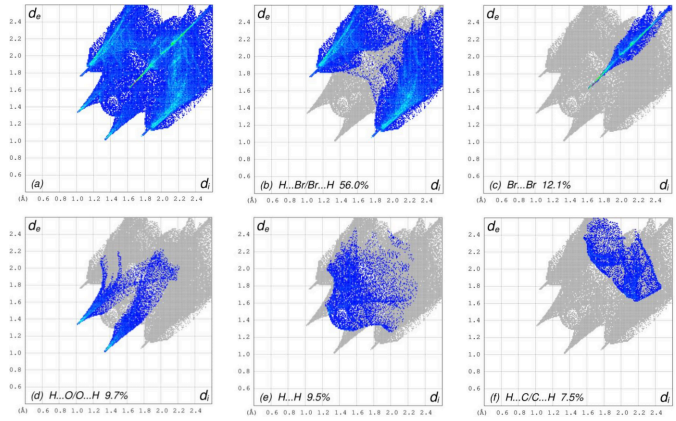


Figure 5
Two-dimensional HS-fingerprint plots showing, (*a*) all interactions, and those delineated into (*b*)H···Br/Br···H, (*c*) Br···Br, (*d*) H···O/O···H, (*e*) H···H, (*f*) H···C/C···H interactions. The d_i and d_e values are the closest internal and external distances (in Å) from given points on the Hirshfeld surface.

5. Database survey

A substructure search of the Cambridge Structural Database [CSD Version 5.46 (November 2024); Groom, *et al.*, 2016] using the 4-formyl-*N*,*N*-dimethylanilinium moiety was carried out, and 49 similar compounds were found. Of these compounds, seven are structurally related. These include: *p*-dimethylamino-benzaldehyde hydrobromide, $C_9H_{12}NOBr$ (CSD refcode MABZAL10; Dattagupta & Saha, 1973), 4-formyl-*N*,*N*-dimethylanilinium 4-methylbenzenesulfonate monohydrate, $C_9H_{12}NO^+\cdot C_7H_7O_3S^-\cdot H_2O$ (CSD refcode QAFROH; Jin *et al.*, 2016*a*), ammonium 4-formyl-*N*,*N*-dimethylanilinium naphthalene-1,5-disulfonate ammonia, $C_9H_{12}NO^+\cdot C_{10}H_6O_6S_2^{2-}\cdot H_4N^+\cdot H_3N$ (CSD refcode SUYYUI;

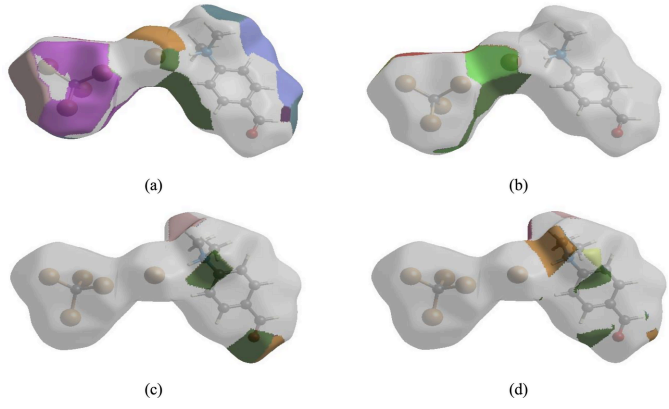


Figure 6
The Hirshfeld surface representations plotted as fragment patches for (*a*) H···Br/Br···H, (*b*) Br···Br, (*c*) H···O/O···H and (*d*) H···H interactions.

Jin *et al.*, 2016*b*), 4-formyl-*N*,*N*-dimethylanilinium tetrafluoroborate, $C_9H_{12}NO^+\cdot BF_4^-$ (CSD refcode VOJMEO; Froschauer *et al.*, 2013) and 4-formyl-*N*,*N*-dimethylanilinium 2,4,6-trinitrophenolate, $C_9H_{12}NO^+\cdot C_6H_2N_3O_7^-$ (CSD refcodes VUWLIJ: Thakuria *et al.*, 2007; VUWLIJ01: Jin *et al.*, 2016*a;* VUWLIJ02: Prasad, 2016). It is worth mentioning that the last three entries report different colours for the crystals (brown, colourless and metallic dark red).

6. Synthesis and crystallization

4-(Dimethylamino)benzaldehyde (5 mmol) and tetrabromomethane (5 mmol) were dissolved in 25 ml of $CHBr_3$, and left for slow evaporation. Orange crystals (suitable for X-ray analysis) of the product started to form after 1 d at room temperature; they were then filtered off and dried in air. Yield 59% (based on tetrabromomethane), orange powder soluble in methanol, ethanol and DMSO. Analysis calculated for $C_{10}H_{12}Br_5NO$ (M_r = 561.73): C, 21.38; H, 2.15; N, 2.49. Found: C, 21.36; H, 2.13; N, 2.47. ^{1}H NMR (DMSO-d^6), δ: 5.13 (–$NHMe_2$), 9.67 (CHO), 7.70 and 7.68 (2H Ar), 6.80 and 6.78 (2H Ar), 3.05 (6H, $2CH_3$). ^{13}C NMR (DMSO-d^6), −29.2 (CBr_4), 43.6 ($2CH_3$), 111.2 ($2C_{Ar}$), 124.4 (CCHO), 133.6 ($2C_{Ar}$), 155.1 ($CNMe_2$), 190.0 (C═O).

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. The N- and C-bound hydrogen-atom positions were calculated geometrically at distances of 0.85 Å (for NH), 0.95 Å (for CH) and 0.98 Å (for CH_3) and refined using a riding model by applying the constraint $U_{iso} = kU_{eq}$ (C, N), where k = 1.2 for NH and CH hydrogen atoms and k = 1.5 for CH_3 hydrogen atoms.

Table 3
Experimental details.

Crystal data	
Chemical formula	$C_9H_{12}NO^+\cdot Br^-\cdot CBr_4$
M_r	561.76
Crystal system, space group	Orthorhombic, *Pnma*
Temperature (K)	150
a, *b*, *c* (Å)	21.1900 (7), 7.4114 (2), 10.2297 (4)
V (Å^3)	1606.55 (9)
Z	4
Radiation type	Mo *Kα*
μ (mm^{-1})	12.49
Crystal size (mm)	0.32 × 0.18 × 0.12
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.086, 0.254
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	9073, 1649, 1462
R_{int}	0.027
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.611
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.026, 0.064, 1.06
No. of reflections	1649
No. of parameters	98
No. of restraints	6
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.79, −1.21

Computer programs: *APEX3* and *SAINT* (Bruker, 2014), *SHELXT2019/1* (Sheldrick, 2015*a*), *SHELXL2019/1* (Sheldrick, 2015*b*) and *SHELXTL* (Sheldrick, 2008).

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References

Bruker (2014). *APEX3* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Cruickshank, D. W. J. & Sparks, R. A. (1960). *Proc. Roy. Soc.* A**258**, 270–285.
Dattagupta, J. K. & Saha, N. N. (1973). *Acta Cryst.* B**29**, 1228–1233.
Dewar, M. J. S. & Schmeising, H. N. (1959). *Tetrahedron* **5**, 166–178.
Froschauer, C., Weber, H. K., Kahlenberg, V., Laus, G. & Schottenberger, H. (2013). *Crystals* **3**, 248–256.
Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* B**72**, 171–179.
Gurbanov, A. V., Kuznetsov, M. L., Karmakar, A., Aliyeva, V. A., Mahmudov, K. T. & Pombeiro, A. J. L. (2022). *Dalton Trans.* **51**, 1019–1031.
Gurbanov, A. V., Kuznetsov, M. L., Mahmudov, K. T., Pombeiro, A. J. L. & Resnati, G. (2020). *Chem. A Eur. J.* **26**, 14833–14837.
Hathwar, V. R., Sist, M., Jørgensen, M. R. V., Mamakhel, A. H., Wang, X., Hoffmann, C. M., Sugimoto, K., Overgaard, J. & Iversen, B. B. (2015). *IUCrJ* **2**, 563–574.
Hirshfeld, H. L. (1977). *Theor. Chim. Acta* **44**, 129–138.
Jin, S., Wang, L., Liu, H., Liu, L., Zhang, H., Wang, D., Li, M., Guo, J. & Guo, M. (2016*a*). *J. Mol. Struct.* **1116**, 155–164.
Jin, S., Wang, L., Lou, Y., Liu, L., Li, B., Li, L., Feng, C., Liu, H. & Wang, D. (2016*b*). *J. Mol. Struct.* **1108**, 735–747.
Krause, L., Herbst-Irmer, R., Sheldrick, G. M. & Stalke, D. (2015). *J. Appl. Cryst.* **48**, 3–10.
Ma, Z., Gurbanov, A. V., Sutradhar, M., Kopylovich, M. N., Mahmudov, K. T., Maharramov, A. M., Guseinov, F. I., Zubkov, F. I. & Pombeiro, A. J. L. (2017). *J. Mol. Catal.* **428**, 17–23.
Ma, Z., Mahmudov, K. T., Aliyeva, V. A., Gurbanov, A. V., Guedes da Silva, M. F. C. & Pombeiro, A. J. L. (2021). *Coord. Chem. Rev.* **437**, 213859.
Mahmoudi, G., Afkhami, F. A., Castiñeiras, A., García-Santos, I., Gurbanov, A. V., Zubkov, F. I., Mitoraj, M. P., Kukułka, M., Sagan, F., Szczepanik, D. W., Konyaeva, I. A. & Safin, D. A. (2018). *Inorg. Chem.* **57**, 4395–4408.
Mahmudov, K. T. & Pombeiro, A. J. L. (2023). *Chem. A Eur. J.* **29**, e202203861.
McKinnon, J. J., Jayatilaka, D. & Spackman, M. A. (2007). *Chem. Commun.* pp. 3814–3816.
Prasad, A. A. (2016). *CSD Communication* (Refcode VUWLIJ02). CCDC, Cambridge, England.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Sheldrick, G. M. (2015*a*). *Acta Cryst.* A**71**, 3–8.
Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3–8.
Spackman, M. A. & Jayatilaka, D. (2009). *CrystEngComm* **11**, 19–32.
Spackman, P. R., Turner, M. J., McKinnon, J. J., Wolff, S. K., Grimwood, D. J., Jayatilaka, D. & Spackman, M. A. (2021). *J. Appl. Cryst.* **54**, 1006–1011.
Sutar, R. L. & Huber, S. M. (2019). *ACS Catal.* **9**, 9622–9639.
Thakuria, H., Borah, B. M., Pramanik, A. & Das, G. (2007). *J. Chem. Crystallogr.* **37**, 807–816.
Velásquez, J. D., Mahmoudi, G., Zangrando, E., Gurbanov, A. V., Zubkov, F. I., Zorlu, Y., Masoudiasl, A. & Echeverría, J. (2019). *CrystEngComm* **21**, 6018–6025.
Venkatesan, P., Thamotharan, S., Ilangovan, A., Liang, H. & Sundius, T. (2016). *Spectrochim. Acta A Mol. Biomol. Spectrosc.* **153**, 625–636.

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Computing details

4-Formyl-*N*,*N*-dimethylanilinium bromide–tetrabromomethane (1/1)

Crystal data

$C_9H_{12}NO^+·Br^-·CBr_4$
M_r = 561.76
Orthorhombic, *Pnma*
a = 21.1900 (7) Å
b = 7.4114 (2) Å
c = 10.2297 (4) Å
V = 1606.55 (9) Å^3
Z = 4
F(000) = 1048
D_x = 2.323 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 4744 reflections
θ = 2.8–25.7°
μ = 12.49 mm^{-1}
T = 150 K
Plate, orange
0.32 × 0.18 × 0.12 mm

Data collection

Bruker APEXII CCD diffractometer
φ and *ω* scans
Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)
T_{min} = 0.086, T_{max} = 0.254
9073 measured reflections
1649 independent reflections
1462 reflections with $I > 2\sigma(I)$
R_{int} = 0.027
θ_{max} = 25.7°, θ_{min} = 2.8°
h = −25→25
k = −9→8
l = −11→12

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.026
$wR(F^2)$ = 0.064
S = 1.06
1649 reflections
98 parameters
6 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0299P)^2 + 4.3541P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.79 e Å^{-3}
$\Delta\rho_{min}$ = −1.21 e Å^{-3}

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.27771 (2)	0.53801 (5)	0.91970 (4)	0.02322 (12)
Br2	0.16582 (3)	0.750000	0.78589 (6)	0.03084 (16)
Br3	0.17920 (2)	0.750000	1.09645 (6)	0.02633 (15)
Br4	0.39332 (2)	0.250000	0.88637 (6)	0.02293 (15)
O1	0.53538 (19)	0.250000	0.1926 (4)	0.0295 (9)
N1	0.54209 (18)	0.250000	0.8217 (4)	0.0160 (9)
H1N	0.502359	0.250000	0.833231	0.019*
C1	0.55221 (17)	0.250000	0.6801 (5)	0.0158 (10)
C2	0.61354 (18)	0.250000	0.6293 (5)	0.0219 (11)
H2A	0.649120	0.250000	0.685839	0.026*
C3	0.6211 (2)	0.250000	0.4967 (5)	0.0244 (12)
H3A	0.662508	0.250000	0.460938	0.029*
C4	0.5690 (2)	0.250000	0.4127 (5)	0.0195 (11)
C5	0.5087 (2)	0.250000	0.4645 (4)	0.0247 (12)
H5A	0.473132	0.250000	0.407806	0.030*
C6	0.4998 (2)	0.250000	0.6000 (4)	0.0227 (12)
H6A	0.458558	0.250000	0.636234	0.027*
C7	0.56696 (17)	0.4161 (5)	0.8872 (3)	0.0201 (8)
H7A	0.556697	0.412102	0.980521	0.030*
H7B	0.547604	0.523040	0.847635	0.030*
H7C	0.612859	0.421721	0.876162	0.030*
C8	0.5776 (3)	0.250000	0.2704 (5)	0.0268 (13)
H8A	0.619581	0.250000	0.237724	0.032*
C9	0.2245 (2)	0.750000	0.9317 (5)	0.0193 (11)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.01931 (18)	0.0224 (2)	0.0280 (2)	0.00397 (14)	0.00079 (15)	0.00030 (15)
Br2	0.0245 (3)	0.0342 (3)	0.0338 (4)	0.000	−0.0135 (2)	0.000
Br3	0.0197 (3)	0.0320 (3)	0.0273 (3)	0.000	0.0072 (2)	0.000
Br4	0.0177 (2)	0.0244 (3)	0.0266 (3)	0.000	0.0002 (2)	0.000
O1	0.039 (2)	0.038 (2)	0.012 (2)	0.000	−0.0011 (18)	0.000
N1	0.0140 (19)	0.024 (2)	0.010 (2)	0.000	−0.0006 (16)	0.000
C1	0.015 (2)	0.020 (2)	0.012 (3)	0.000	0.0019 (19)	0.000
C2	0.013 (2)	0.036 (3)	0.016 (3)	0.000	−0.002 (2)	0.000
C3	0.013 (2)	0.038 (3)	0.022 (3)	0.000	0.006 (2)	0.000
C4	0.021 (2)	0.025 (3)	0.013 (3)	0.000	0.002 (2)	0.000
C5	0.022 (3)	0.042 (3)	0.011 (3)	0.000	−0.003 (2)	0.000

C6	0.014 (2)	0.041 (3)	0.013 (3)	0.000	0.000 (2)	0.000
C7	0.0262 (17)	0.0209 (19)	0.0132 (19)	−0.0021 (15)	−0.0019 (15)	−0.0029 (15)
C8	0.027 (3)	0.036 (3)	0.018 (3)	0.000	0.008 (2)	0.000
C9	0.013 (2)	0.022 (3)	0.022 (3)	0.000	0.001 (2)	0.000

Geometric parameters (Å, º)

Br1—C9	1.937 (3)	C3—C4	1.3998 (10)
Br2—C9	1.942 (5)	C3—H3A	0.9500
Br3—C9	1.940 (5)	C4—C5	1.384 (7)
O1—C8	1.198 (7)	C4—C8	1.467 (7)
N1—C1	1.464 (6)	C5—C6	1.3995 (10)
N1—C7^{i}	1.497 (4)	C5—H5A	0.9500
N1—C7	1.497 (4)	C6—H6A	0.9500
N1—H1N	0.8501	C7—H7A	0.9800
C1—C6	1.379 (6)	C7—H7B	0.9800
C1—C2	1.3997 (10)	C7—H7C	0.9800
C2—C3	1.366 (7)	C8—H8A	0.9500
C2—H2A	0.9500		
Br3···Br4^{ii}	3.3403 (8)	H7B···O1^{v}	2.47
H6A···Br3^{iii}	2.95	C2···H7C	2.83
O1···H5A	2.57	C7···H2A	2.96
H7A···O1^{iv}	2.52	H1N···H6A	2.22
C1—N1—C7^{i}	113.0 (2)	C6—C5—H5A	119.9
C1—N1—C7	113.0 (2)	C1—C6—C5	118.8 (4)
C7^{i}—N1—C7	110.6 (4)	C1—C6—H6A	120.6
C1—N1—H1N	106.4	C5—C6—H6A	120.6
C7^{i}—N1—H1N	106.7	N1—C7—H7A	109.5
C7—N1—H1N	106.6	N1—C7—H7B	109.5
C6—C1—C2	121.8 (4)	H7A—C7—H7B	109.5
C6—C1—N1	118.0 (3)	N1—C7—H7C	109.5
C2—C1—N1	120.2 (4)	H7A—C7—H7C	109.5
C3—C2—C1	118.6 (4)	H7B—C7—H7C	109.5
C3—C2—H2A	120.7	O1—C8—C4	124.5 (5)
C1—C2—H2A	120.7	O1—C8—H8A	117.7
C2—C3—C4	121.1 (4)	C4—C8—H8A	117.7
C2—C3—H3A	119.4	Br1—C9—Br1^{vi}	108.4 (2)
C4—C3—H3A	119.4	Br1—C9—Br3	110.07 (18)
C5—C4—C3	119.6 (4)	Br1^{vi}—C9—Br3	110.07 (18)
C5—C4—C8	119.6 (4)	Br1—C9—Br2	108.90 (18)
C3—C4—C8	120.8 (5)	Br1^{vi}—C9—Br2	108.90 (18)
C4—C5—C6	120.2 (4)	Br3—C9—Br2	110.5 (2)
C4—C5—H5A	119.9		
C7^{i}—N1—C1—C6	116.7 (3)	C2—C3—C4—C8	180.000 (1)
C7—N1—C1—C6	−116.7 (3)	C3—C4—C5—C6	0.000 (1)

C7^{i}—N1—C1—C2	−63.3 (3)	C8—C4—C5—C6	180.000 (1)
C7—N1—C1—C2	63.3 (3)	C2—C1—C6—C5	0.000 (1)
C6—C1—C2—C3	0.000 (1)	N1—C1—C6—C5	180.000 (1)
N1—C1—C2—C3	180.000 (1)	C4—C5—C6—C1	0.000 (1)
C1—C2—C3—C4	0.000 (1)	C5—C4—C8—O1	0.000 (1)
C2—C3—C4—C5	0.000 (1)	C3—C4—C8—O1	180.000 (1)

Symmetry codes: (i) *x*, −*y*+1/2, *z*; (ii) −*x*+1/2, −*y*+1, *z*+1/2; (iii) −*x*+1/2, *y*−1/2, *z*−1/2; (iv) *x*, *y*, *z*+1; (v) −*x*+1, −*y*+1, −*z*+1; (vi) *x*, −*y*+3/2, *z*.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*N*···Br4	0.85	2.37	3.221 (4)	175
C6—H6*A*···Br4	0.95	2.91	3.698 (4)	141
C7—H7*A*···O1^{iv}	0.98	2.52	3.424 (5)	153
C7—H7*B*···O1^{v}	0.98	2.47	3.390 (5)	157

Symmetry codes: (iv) *x*, *y*, *z*+1; (v) −*x*+1, −*y*+1, −*z*+1.