



# Crystal structure of 4-(2-methoxyphenyl)piperazin-1-ium 3,5-dinitrosalicylate

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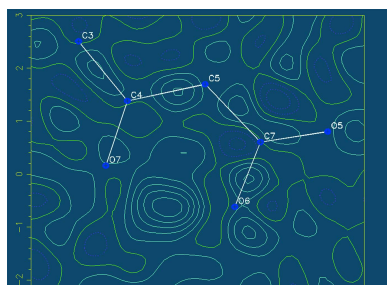
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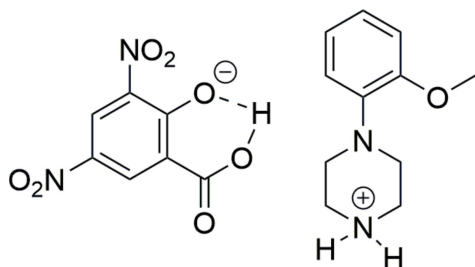
The title salt [systematic name: 4-(2-methoxyphenyl)piperazin-1-ium 2-carboxy-4,6-dinitrophenolate],  $C_{11}H_{17}N_2O^+ \cdot C_7H_3N_2O_7^-$ , exhibits secondary nitrogen atoms (N—H) in the 2-methoxyphenylpiperazine (2MeOPP) cation, which is protonated with a phenolic hydrogen atom of 3,5-dinitrosalicylic acid (DNSA). One of the oxygen atoms of the nitro group in the 3,5-dinitrosalicylate anion is disordered over two orientations with occupancy factors of 0.65 (7) and 0.35 (7). The 2-methoxyphenylpiperazinium cation and 3,5-dinitrosalicylate anion are linked in the asymmetric unit by a bifurcated N—H...O hydrogen bond, which formed is between the H atom in the protonated piperazinium unit of the cation and the carboxylic acid group in the anion. The piperazine ring adopts a chair conformation. The crystal structure features N—H...O and C—H...O hydrogen bonds interactions, which lead to the formation of a sandwich-like arrangement. Hirshfeld surface analysis was used to determine the relative contributions of various intermolecular interactions, indicating that that H...O/O...H (38.3%) and H...H (31.8%) contacts are the major contributors.

## 1. Chemical context

1-(2-Methoxyphenyl)piperazine is a substituted cyclo aliphatic amine with two nitrogen atoms at opposite positions of the six-membered ring. A substituent 2-methoxyphenyl group is attached to one of the nitrogen atoms while the other has one attached hydrogen atom (*i.e.* the secondary nitrogen atom, N—H). Piperazine and substituted piperazine derivatives are often used as intermediates for a wide range of pharmaceuticals, polymers, dyes, corrosion inhibitors and surfactants. In particular, (2-methoxyphenyl)piperazine derivatives are used as 5-HT<sub>1A</sub> receptor ligands with reduced  $\alpha$ 1-adrenergic activity (Raghupathi *et al.*, 1991; Orjales *et al.*, 1995; Zhuang *et al.*, 1998). 1-(2-Methoxyphenyl)piperazine-impregnated filters have been used for the detection of isocyanates in air (Sennbro *et al.*, 2004). 1-Cinnamyl-4-(2-methoxyphenyl)piperazine derivatives are used as ligands for D<sub>2</sub> and D<sub>3</sub> dopamine and serotonin 5-HT<sub>1 $\alpha$</sub>  receptors (Penjišević *et al.*, 2007). The crystal structure of eleven protonated 4-(2-methoxyphenyl)piperazin-1-ium salts with eleven different substituted benzoic acids (namely, 4/2-chlorobenzoic acid, 4/2-bromobenzoic acid, 4/2-iodobenzoic acid, 2-fluorobenzoic acid, 2-methylbenzoic



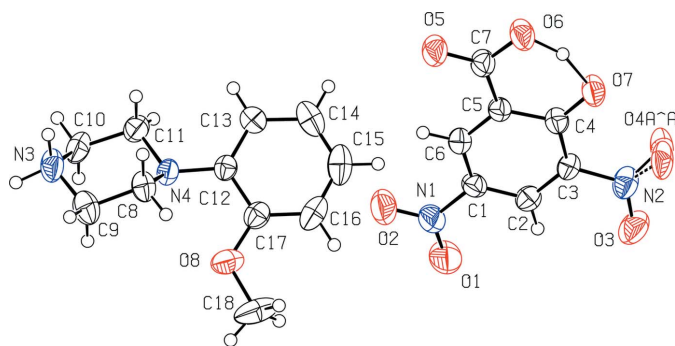
acid, 4-amino/4-nitro-benzoic acid, 3,5-dinitrobenzoic acid and picric acid) and three aliphatic dicarboxylic acid [maleic acid, fumaric acid and (2*R*,3*R*)-tartaric acid] salts and their supramolecular features have been reported (Harish Chinthala *et al.*, 2020).



As a continuation of our earlier study on the crystal structure and supramolecular analysis of a monohydrated 1:1 adduct of bis(piperazine-1,4-dium), 3,5-dinitro-2-oxido-benzoate and piperazine, we have now investigated the crystal structure of 1-(2-methoxyphenyl) piperazinium 3,5-dinitrosalicylate (I). In this study, the crystal structure, Hirshfeld surface (HS) analysis, structural features and various intermolecular interactions that exist in the title protonated salt are reported.

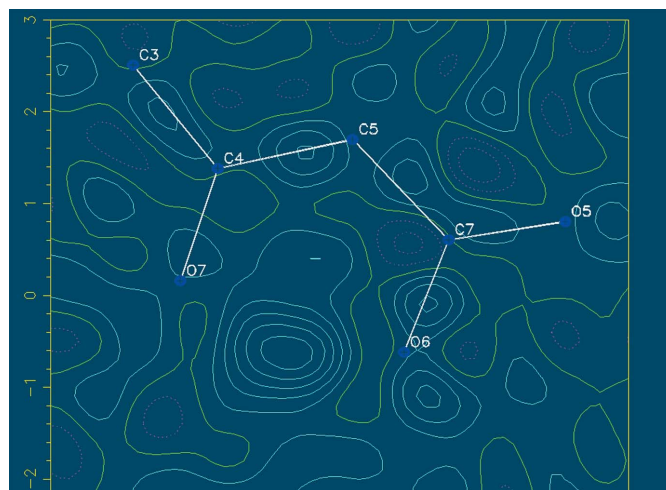
## 2. Structural commentary

The title salt crystallizes in the triclinic space group *P* $\bar{1}$  with the asymmetric unit comprising one 2-methoxyphenylpiperazinium (2MeOPP)<sup>1+</sup> cation and one 3,5-dinitrosalicylate (DNSA)<sup>1-</sup> anion (Fig. 1). The piperazine ring in the cation adopts a chair conformation with puckering parameters  $Q = 0.582$  (3) Å,  $\theta = 176.3$  (3)°,  $\varphi = 338$  (4)°. One of the oxygen atoms of the nitro group (atom O4) in the 3,5-dinitrosalicylate anion is disordered over two orientations with occupancy factors of 0.65 (7) and 0.35 (7). Both nitro groups, the phenoxylate oxygen atom and a carboxylic acid group in the anion are coplanar with an r.m.s. deviation of 0.0074 Å. A bifurcated intermolecular N—H...O hydrogen bond [N3—H3A...O5 = 2.936 (3) Å and N3—H3A...O6 = 3.153 (3) Å] links the cation and anion in the asymmetric unit.



**Figure 1**  
The molecular structure of the title molecular salt, (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

In the DNSA molecule, deprotonation of the —COOH group ( $pK_a$  COOH = 2.2) is easier than that of the phenolic —OH group ( $pK_a$  OH = 6.8). 62 carboxylate moiety structures (COO<sup>−</sup>) and 70 phenolate anion structures (O<sup>−</sup>) were found in a search of the Cambridge Structural Database (CSD, Version 5.43, update of March 2020; Groom *et al.*, 2016), which is perhaps unexpected because the number of crystal structures containing phenolate anions is larger than those containing carboxylate anions. These conflicting results may suggest that the formation of protonated salts of the DNSA molecule with phenolate ions is favoured by the thermodynamic stability and the intermolecular interactions between the phenolate anion and counter-ions in the respective crystal structures. The crystal structure of (I) suggests that the title salt was formed by deprotonation of the phenolic group in the DNSA molecule. In order to better understand the deprotonation of the phenolic group in DNSA molecule, the H-atom electron density in the difference-Fourier electron-density maps was calculated as they can yield additional insight into the proton-transfer behaviour. From Fig. 2, the electron density associated with atom H6 is shown to be smeared out between the O6 and O7 atoms, with the maximum lying closer to O6 atom than O7. It suggests that the H6A atom is attached to the carboxylic acid group and that deprotonation occurs through the phenolic group. As a result, the strong intramolecular O6—H6A...O7 hydrogen bond formed. The interatomic distance between the phenolate oxygen atom, O7, and the O6 atom in the carboxylic acid group is 2.448 (2) Å, which also indicates that the strong intramolecular hydrogen bond between the O6 and O7 atoms. Similar types of intramolecular hydrogen bonds were observed in salicylic acid with a distance of 2.62 Å (Woińska *et al.*, 2016; Montis & Hursthouse *et al.*, 2012) and in other proton-transfer salts of DNSA in the range 2.409–2.540 Å (Smith *et al.*, 1995, 1996, 1997, 2000, 2001*a,b,c,d,e*, 2002, 2006). The proton in the carboxylic acid group is located between the carboxyl-O atom [O6 at



**Figure 2**  
Difference-Fourier electron-density map showing the electron density associated with the H atom involved in the O6—H6...O7 hydrogen bond.

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

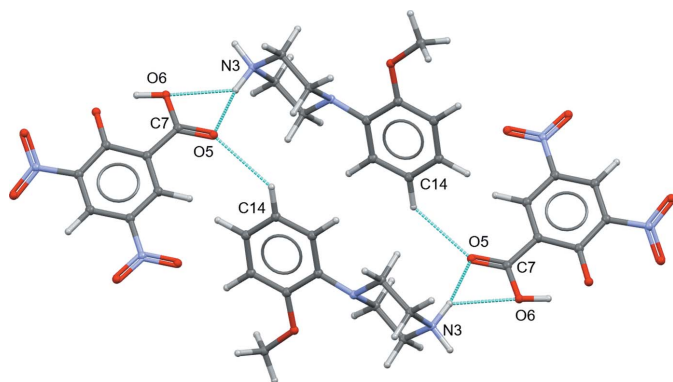
<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O6—H6A···O7	1.14 (3)	1.37 (3)	2.448 (2)	154 (3)
N3—H3A···O5	0.94 (4)	2.02 (4)	2.936 (3)	165 (3)
N3—H3A···O6	0.94 (4)	2.44 (3)	3.153 (3)	133 (2)
N3—H3B···O7 <sup>i</sup>	0.97 (3)	1.83 (3)	2.787 (3)	166 (3)
C2—H2···O1 <sup>ii</sup>	0.93	2.66	3.581 (3)	174
C9—H9A···O3 <sup>iii</sup>	0.97	2.44	3.254 (4)	141
C10—H10B···O2 <sup>iv</sup>	0.97	2.43	3.319 (3)	152
C10—H10A···O4A <sup>i</sup>	0.97	2.50	3.118 (10)	122
C14—H14···O5 <sup>v</sup>	0.93	2.74	3.481 (3)	137
C18—H18C···N4 <sup>vi</sup>	0.96	2.74	3.552 (4)	143

Symmetry codes: (i)  $-x+2, -y+1, -z$ ; (ii)  $-x, -y, -z$ ; (iii)  $-x+1, -y+1, -z$ ; (iv)  $x+1, y, z$ ; (v)  $-x+1, -y+1, -z+1$ ; (vi)  $-x+2, -y+2, -z+1$ .

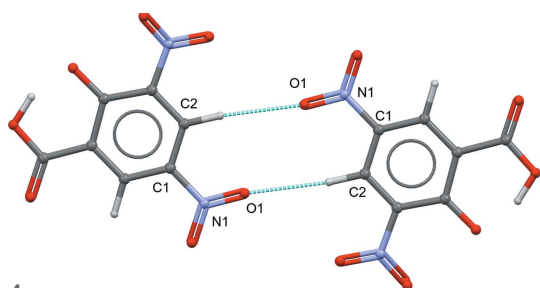
1.14 (3) Å] and the phenolate oxygen atom, [O7 at 1.37 (3) Å]. A similar trend was found in the various proton-transfer salts of DNSA (Smith *et al.*, 2002).

### 3. Supramolecular features

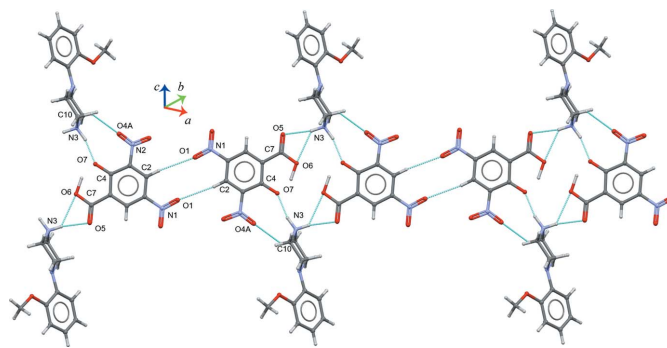
The oxygen atoms in both nitro groups (O1–O4), the carboxylic acid group (O5 and O6) and a phenolate moiety (O7) in the DNSA anion all act as acceptors for various intermolecular N—H···O and C—H···O interactions, except for atom O4 (Table 1). In the cation, the O8 atom of the methoxy group is not involved in intermolecular interactions. The



**Figure 3**  
The bifurcated intermolecular N3—H3A···(O5,O6) hydrogen bond and the C14—H14···O5 interaction linking the 2MeOPP<sup>+</sup> cation and (DNSA)<sup>-</sup> anion into a centrosymmetric tetramer architecture with an R<sub>2</sub><sup>2</sup>(20) motif.

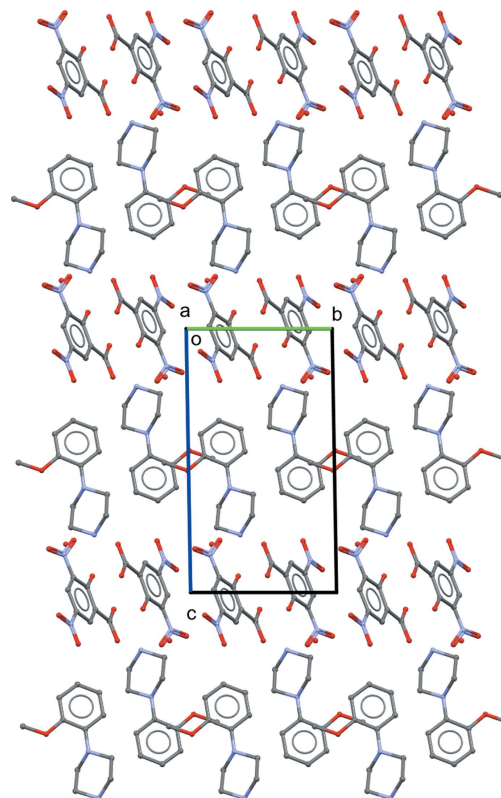


**Figure 4**  
Part of the crystal structure of (I) showing the centrosymmetric dimer motif with the R<sub>2</sub><sup>2</sup>(10) motif formed by the C2—H2···O1 interaction.



**Figure 5**  
Part of the crystal structure of (I) showing the layered molecular architecture formed by the N3—H3A···(O5,O6), N3—H3B···O7 and C10—H10···O4A interactions, which propagates parallel to the *b* axis.

oxygen atoms of the carboxylic acid group (O5 and O6) act as acceptors for a bifurcated N3—H3A···(O5,O6) interaction, which links two neighbouring cations and anions into a centrosymmetric tetrameric architecture, which is further stabilized by the C14—H14···O5<sup>v</sup> interaction [3.481 (3) Å] and yields a macrocyclic ring structure with an R<sub>2</sub><sup>2</sup>(20) motif (Fig. 3). Atom O1 of the nitro group is involved in the centrosymmetric C2—H2···O1<sup>ii</sup> interaction [3.581 (3) Å], which links two neighbouring (DNSA)<sup>-</sup> units with an R<sub>2</sub><sup>2</sup>(10) motif (Fig. 4). Neighbouring dimeric DNSA<sup>-</sup> units are further linked through the previously mentioned bifurcated N3—H3A···(O5,O6) interaction and the N3—H3B···O7<sup>i</sup> [2.787 (3) Å], C10—H10A···O4A [3.118 (10) Å] interactions



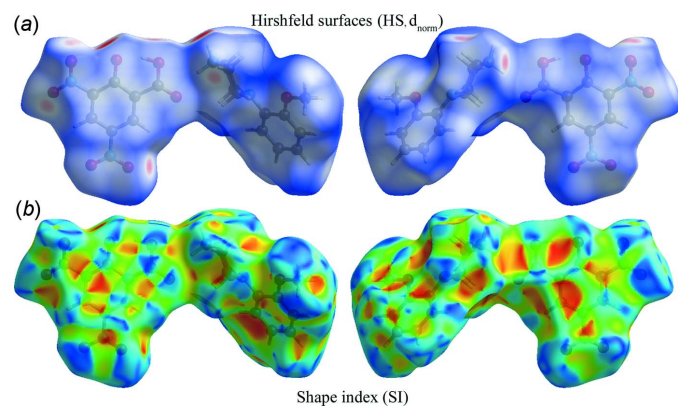
**Figure 6**  
Overall packing diagram for the title salt (I)



into a layered structure propagating parallel to the  $b$  axis (Fig. 5). Of the above three  $N-H\cdots O$  interactions [ $N3-H3A\cdots(O5,O6)$ , and  $N3-H3B\cdots O7$ ], the  $N3-H3B\cdots O7$  interaction is stronger [ $D\cdots A = 2.787(3) \text{ \AA}$ ] than the other two, which is due to the fact that two charged components are involved in this interaction, *i.e.* the phenolate  $O7$  atom in  $DNSA^{1-}$  and the protonated  $N3-H3B$  unit in  $2MeOPP^{+1}$ . All of the above interactions facilitate the arrangement of the  $DNSA^{1-}$  ions in a layered molecular structure. The top and bottom sides of the  $DNSA^{1-}$  layers are stabilized by the two adjacent cationic layers. As a result, a sandwich-like arrangement is observed. Briefly, the layered  $DNSA^{1-}$  units form the core with the top and bottom sides of the cation layers arranged facing. An overall packing diagram is shown Fig. 6.

#### 4. Hirshfeld surface analysis

*Crystal Explorer 17.5* (Turner *et al.*, 2017) was used to calculate the Hirshfeld surfaces (HS; McKinnon *et al.*, 1998, 2004; Spackman & Jayatilaka, 2009) of the title protonated salt and generate two-dimensional fingerprint plots (full and decomposed, 2D-FP; Spackman & McKinnon, 2002) in order to investigate and quantify the different intermolecular interactions. Distinct colours and intensities indicate short and long contacts, as well as the relative contribution of the different interactions in the solid state (Venkatesan *et al.*, 2015, 2016). Two views of the HS mapped with  $d_{\text{norm}}$  in the range  $-0.6295$  to  $1.3240$  a.u. (front and back) are shown in Fig. 7. Bright red spots on the surface near  $O2$ ,  $O3$ ,  $O4A$ ,  $O7$ ,  $O6$ ,  $H10B$  and  $H3B$  suggest that these atoms participate in hydrogen-bonding interactions (see Table 1). No significant pattern of convex blue and concave red triangles are observed in the shape-index (SI) diagram, indicating the absence of  $\pi$ -stacking interactions in the title salt. The 2D-FP plots show the relative contributions of the various non-covalent contacts (Fig. 8), indicating that intermolecular  $O\cdots H$  contacts [sharp symmetrical spikes are observed in the FP plot at  $d_e + d_i = 1.8 \text{ \AA}$ ] make the most significant contribution (38.3%), followed by  $H\cdots H$  contacts [symmetrical blunt spikes at  $d_e + d_i = 2.4 \text{ \AA}$ ],



**Figure 7**  
Two different orientations of the Hirshfeld surface of the title salt mapped with (a)  $d_{\text{norm}}$  and (b) shape index.

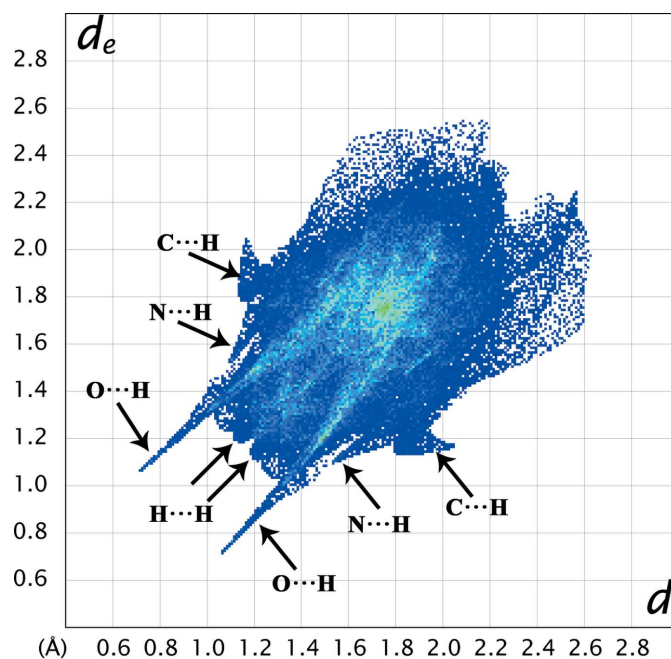
which contribute 31.8%, while  $C\cdots H$ ,  $N\cdots H$ ,  $C\cdots O$ ,  $O\cdots N$ ,  $C\cdots N$  and  $C\cdots C$  contacts contribute 11.6%, 1.7%, 6.7%, 2.7%, 1.9%, 0.5% and 2.8%, respectively. Other significant peaks for various non-covalent contacts are indicated in the FP plot (Fig. 8).

#### 5. Database survey

A search of the Cambridge Structural Database (CSD, Version 5.43, update of March 2020; Groom *et al.*, 2016) using *Conquest* (Bruno *et al.*, 2002) for 1-(2-methoxyphenyl)-piperazine gave 111 hits, of which seven hits were for the protonated piperazinium unit. In particular, the crystal structure of 1-(2-methoxyphenyl) piperazin-4-ium picrate, which like the title compound has a phenolate anion, has been reported (CSD refcode NEBGIK; Verdonk *et al.*, 1997). In the case of the  $DNSA$  molecule, 21 hits were observed for neutral  $DNSA$  molecules and 65 and 71 hits for  $DNSA$  carboxylate and  $DNSA$  phenolate, respectively.

#### 6. Synthesis and crystallization

The title protonated salt was synthesized using 1-(2-methoxyphenyl)piperazine (Sigma Aldrich, 99%) and 3,5-dinitrosalicylic acid (Merck India, 99.5%) in an equimolar ratio. The stoichiometrically (1 mmol) weighed starting materials were completely dissolved in 50 mL of methanol at room temperature and stirred continuously for 3 h. The homogeneous solution was filtered using Whatmann filter paper and placed in a dust-free atmosphere, and allowed to evaporate



**Figure 8**  
Two-dimensional fingerprint plots for the complete unit of the title salt indicating the various types of contacts.

**Table 2**  
Experimental details.

Crystal data	
Chemical formula	$C_{11}H_{17}N_2O^+ \cdot C_7H_3N_2O^{7-}$
$M_r$	420.38
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	296
$a, b, c$ (Å)	7.3729 (6), 8.4842 (7), 15.5411 (13)
$\alpha, \beta, \gamma$ (°)	88.954 (4), 81.333 (4), 89.352 (3)
$V$ (Å <sup>3</sup> )	960.85 (14)
$Z$	2
Radiation type	Mo $K\alpha$
$\mu$ (mm <sup>-1</sup> )	0.12
Crystal size (mm)	0.18 × 0.15 × 0.10
Data collection	
Diffractometer	Bruker Kappa APEXII
Absorption correction	Multi-scan (SADABS; Bruker, 2012)
$T_{\min}$ , $T_{\max}$	0.608, 0.745
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	24028, 3513, 2035
$R_{\text{int}}$	0.084
$(\sin \theta/\lambda)_{\text{max}}$ (Å <sup>-1</sup> )	0.602
Refinement	
$R[F^2 > 2\sigma(F^2)]$ , $wR(F^2)$ , $S$	0.048, 0.140, 1.02
No. of reflections	3513
No. of parameters	294
No. of restraints	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}$ , $\Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	0.23, -0.21

Computer programs: APEX2, SAINT and XPREP (Bruker, 2012), SHELXT2014/5 (Sheldrick, 2015a), SHELXL2018/3 (Sheldrick, 2015b), ORTEP-3 for Windows (Farrugia, 2012), Mercury (Macrae et al., 2020) and PLATON (Spek, 2020).

slowly at room temperature. A suitable single crystal was harvested after a growth period of 25 days.

## 7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The amine H atoms and O-bound H atoms were located in a difference-Fourier map and refined freely along with their isotropic displacement parameters. C-bound H atoms were included in calculated positions and treated as riding atoms [C–H = 0.93–0.98 Å, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ ].

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## supporting information

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## Crystal structure of 4-(2-methoxyphenyl)piperazin-1-ium 3,5-dinitrosalicylate

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## Computing details

Data collection: *APEX2* (Bruker, 2012); cell refinement: *APEX2* and *SAINT* (Bruker, 2012); data reduction: *SAINT* and *XPREF* (Bruker, 2012); program(s) used to solve structure: *SHELXT2014/5* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015b); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *Mercury* (Macrae *et al.*, 2020); software used to prepare material for publication: *PLATON* (Spek, 2020).

## 4-(2-Methoxyphenyl)piperazin-1-ium 2-carboxy-4,6-dinitrophenolate

## Crystal data

$C_{11}H_{17}N_2O^+ \cdot C_7H_3N_2O_7^-$

$M_r = 420.38$

Triclinic,  $P\bar{1}$

$a = 7.3729$  (6) Å

$b = 8.4842$  (7) Å

$c = 15.5411$  (13) Å

$\alpha = 88.954$  (4)°

$\beta = 81.333$  (4)°

$\gamma = 89.352$  (3)°

$V = 960.85$  (14) Å<sup>3</sup>

$Z = 2$

$F(000) = 440$

$D_x = 1.453$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 3479 reflections

$\theta = 2.7\text{--}21.4^\circ$

$\mu = 0.12$  mm<sup>-1</sup>

$T = 296$  K

BLOCK, yellow

$0.18 \times 0.15 \times 0.10$  mm

## Data collection

Bruker Kappa APEXII

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

$\omega$  and  $\varphi$  scan

Absorption correction: multi-scan

(SADABS; Bruker, 2012)

$T_{\min} = 0.608$ ,  $T_{\max} = 0.745$

24028 measured reflections

3513 independent reflections

2035 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.084$

$\theta_{\max} = 25.4^\circ$ ,  $\theta_{\min} = 2.4^\circ$

$h = -8 \rightarrow 8$

$k = -10 \rightarrow 10$

$l = -18 \rightarrow 18$

## Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.048$

$wR(F^2) = 0.140$

$S = 1.02$

3513 reflections

294 parameters

1 restraint

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0588P)^2 + 0.1844P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.23$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.21$  e Å<sup>-3</sup>

Extinction correction: SHELXL-2018/3  
 (Sheldrick 2015b),  
 $F_c^* = kF_c [1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$   
 Extinction coefficient: 0.050 (4)

### 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 ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
C1	0.2780 (3)	0.2159 (3)	0.07284 (15)	0.0394 (6)	
C2	0.3262 (3)	0.1599 (3)	−0.00995 (15)	0.0403 (6)	
H2	0.245907	0.096812	−0.034491	0.048*	
C3	0.4942 (3)	0.1982 (3)	−0.05608 (14)	0.0381 (6)	
C4	0.6246 (3)	0.2917 (3)	−0.02095 (15)	0.0386 (6)	
C5	0.5670 (3)	0.3451 (3)	0.06598 (14)	0.0357 (6)	
C6	0.3973 (3)	0.3079 (3)	0.11071 (15)	0.0402 (6)	
H6	0.362307	0.344693	0.166821	0.048*	
C7	0.6924 (4)	0.4410 (3)	0.10897 (16)	0.0437 (6)	
C8	0.7613 (3)	0.7961 (3)	0.32628 (14)	0.0453 (7)	
H8A	0.714529	0.899464	0.344577	0.054*	
H8B	0.659791	0.734255	0.312652	0.054*	
C9	0.9053 (4)	0.8122 (3)	0.24697 (16)	0.0547 (8)	
H9A	0.851985	0.862088	0.199882	0.066*	
H9B	1.003753	0.878425	0.260013	0.066*	
C10	1.0516 (4)	0.5698 (3)	0.29246 (16)	0.0528 (7)	
H10A	1.157647	0.624708	0.306580	0.063*	
H10B	1.090079	0.464033	0.274758	0.063*	
C11	0.9068 (4)	0.5609 (3)	0.37158 (15)	0.0449 (7)	
H11A	0.804693	0.498591	0.359076	0.054*	
H11B	0.957081	0.510002	0.419258	0.054*	
C12	0.7467 (3)	0.7377 (3)	0.48169 (14)	0.0349 (6)	
C13	0.6760 (3)	0.6130 (3)	0.53447 (15)	0.0438 (6)	
H13	0.686122	0.511151	0.513072	0.053*	
C14	0.5896 (4)	0.6383 (4)	0.61938 (17)	0.0586 (8)	
H14	0.542766	0.553503	0.654172	0.070*	
C15	0.5738 (4)	0.7860 (4)	0.65120 (17)	0.0644 (9)	
H15	0.514640	0.802436	0.707561	0.077*	
C16	0.6448 (4)	0.9121 (4)	0.60065 (18)	0.0572 (8)	
H16	0.634257	1.013138	0.623208	0.069*	
C17	0.7317 (3)	0.8895 (3)	0.51661 (15)	0.0418 (6)	
C18	0.7951 (4)	1.1646 (3)	0.4922 (2)	0.0782 (10)	
H18A	0.667923	1.193863	0.505074	0.117*	
H18B	0.855921	1.233884	0.447752	0.117*	
H18C	0.851231	1.172510	0.543815	0.117*	

N1	0.0996 (3)	0.1758 (3)	0.12107 (14)	0.0552 (6)	
O4A	0.6481 (12)	0.2063 (16)	-0.1968 (8)	0.079 (3)	0.65
N3	0.9804 (4)	0.6538 (3)	0.21950 (15)	0.0557 (7)	
N4	0.8428 (3)	0.7185 (2)	0.39644 (11)	0.0368 (5)	
O1	-0.0033 (3)	0.0951 (3)	0.08644 (13)	0.0810 (7)	
O2	0.0596 (3)	0.2239 (3)	0.19541 (13)	0.0777 (7)	
O3	0.4386 (3)	0.0337 (3)	-0.16524 (12)	0.0699 (6)	
O5	0.6514 (3)	0.4920 (2)	0.18265 (11)	0.0597 (6)	
O6	0.8538 (2)	0.4713 (2)	0.06426 (11)	0.0584 (6)	
O7	0.7832 (2)	0.3284 (2)	-0.06190 (10)	0.0530 (5)	
O8	0.8105 (2)	1.0068 (2)	0.46251 (12)	0.0556 (5)	
N2	0.5361 (3)	0.1362 (3)	-0.14395 (14)	0.0514 (6)	
O4B	0.690 (2)	0.153 (3)	-0.1854 (16)	0.090 (7)	0.35
H3A	0.891 (5)	0.589 (4)	0.202 (2)	0.087 (11)*	
H3B	1.070 (4)	0.674 (3)	0.168 (2)	0.085 (10)*	
H6A	0.857 (5)	0.415 (4)	-0.002 (2)	0.125 (13)*	

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C1	0.0373 (14)	0.0422 (15)	0.0384 (14)	-0.0082 (11)	-0.0043 (11)	0.0015 (11)
C2	0.0411 (15)	0.0404 (15)	0.0405 (14)	-0.0013 (12)	-0.0097 (12)	-0.0042 (11)
C3	0.0407 (15)	0.0418 (15)	0.0325 (13)	0.0016 (11)	-0.0071 (11)	-0.0069 (11)
C4	0.0351 (14)	0.0442 (15)	0.0359 (14)	-0.0003 (12)	-0.0030 (11)	-0.0010 (11)
C5	0.0371 (15)	0.0383 (14)	0.0317 (13)	-0.0034 (11)	-0.0044 (11)	-0.0012 (10)
C6	0.0443 (16)	0.0433 (15)	0.0323 (13)	-0.0018 (12)	-0.0035 (11)	-0.0019 (11)
C7	0.0445 (16)	0.0525 (17)	0.0342 (14)	-0.0060 (13)	-0.0057 (12)	-0.0039 (12)
C8	0.0415 (15)	0.0600 (17)	0.0341 (14)	0.0018 (13)	-0.0045 (12)	0.0008 (12)
C9	0.0509 (18)	0.075 (2)	0.0384 (15)	-0.0005 (15)	-0.0074 (13)	0.0067 (13)
C10	0.0530 (18)	0.0567 (18)	0.0472 (16)	0.0080 (14)	-0.0015 (13)	-0.0198 (13)
C11	0.0485 (16)	0.0438 (16)	0.0425 (14)	-0.0002 (12)	-0.0063 (12)	-0.0082 (12)
C12	0.0317 (13)	0.0407 (14)	0.0329 (13)	0.0011 (11)	-0.0064 (10)	-0.0044 (11)
C13	0.0420 (15)	0.0453 (16)	0.0435 (15)	-0.0025 (12)	-0.0048 (12)	0.0021 (12)
C14	0.0474 (17)	0.082 (2)	0.0441 (17)	-0.0007 (15)	-0.0009 (13)	0.0173 (16)
C15	0.059 (2)	0.097 (3)	0.0361 (16)	0.0148 (18)	-0.0058 (14)	-0.0090 (17)
C16	0.0563 (19)	0.063 (2)	0.0547 (18)	0.0131 (15)	-0.0133 (15)	-0.0260 (15)
C17	0.0377 (15)	0.0451 (16)	0.0441 (15)	0.0018 (12)	-0.0097 (12)	-0.0086 (12)
C18	0.069 (2)	0.0371 (18)	0.135 (3)	0.0035 (15)	-0.034 (2)	-0.0234 (18)
N1	0.0508 (15)	0.0625 (16)	0.0497 (14)	-0.0172 (12)	0.0025 (12)	-0.0061 (12)
O4A	0.062 (5)	0.135 (8)	0.039 (2)	-0.029 (4)	0.005 (3)	-0.027 (4)
N3	0.0492 (15)	0.0839 (19)	0.0336 (13)	-0.0120 (14)	-0.0018 (12)	-0.0168 (12)
N4	0.0427 (12)	0.0379 (12)	0.0291 (10)	0.0057 (9)	-0.0038 (9)	-0.0034 (8)
O1	0.0652 (14)	0.1054 (18)	0.0711 (14)	-0.0428 (13)	-0.0005 (11)	-0.0193 (12)
O2	0.0637 (14)	0.1058 (18)	0.0572 (13)	-0.0293 (12)	0.0162 (11)	-0.0244 (12)
O3	0.0679 (14)	0.0792 (15)	0.0646 (13)	-0.0108 (12)	-0.0125 (11)	-0.0313 (11)
O5	0.0585 (12)	0.0813 (14)	0.0388 (10)	-0.0220 (10)	-0.0024 (9)	-0.0154 (9)
O6	0.0467 (12)	0.0858 (15)	0.0409 (11)	-0.0250 (10)	0.0027 (9)	-0.0117 (10)
O7	0.0413 (11)	0.0782 (14)	0.0374 (10)	-0.0139 (9)	0.0025 (8)	-0.0111 (9)



O8	0.0570 (12)	0.0373 (11)	0.0730 (13)	-0.0040 (9)	-0.0105 (10)	-0.0069 (9)
N2	0.0423 (14)	0.0683 (17)	0.0439 (14)	0.0018 (12)	-0.0067 (12)	-0.0136 (12)
O4B	0.048 (7)	0.138 (16)	0.078 (12)	-0.028 (8)	0.023 (7)	-0.052 (9)

*Geometric parameters (Å, °)*

C1—C2	1.374 (3)	C11—H11B	0.9700
C1—C6	1.385 (3)	C12—C13	1.384 (3)
C1—N1	1.453 (3)	C12—C17	1.403 (3)
C2—C3	1.374 (3)	C12—N4	1.416 (3)
C2—H2	0.9300	C13—C14	1.395 (3)
C3—C4	1.429 (3)	C13—H13	0.9300
C3—N2	1.460 (3)	C14—C15	1.353 (4)
C4—O7	1.283 (3)	C14—H14	0.9300
C4—C5	1.434 (3)	C15—C16	1.376 (4)
C5—C6	1.373 (3)	C15—H15	0.9300
C5—C7	1.479 (3)	C16—C17	1.381 (3)
C6—H6	0.9300	C16—H16	0.9300
C7—O5	1.225 (3)	C17—O8	1.367 (3)
C7—O6	1.309 (3)	C18—O8	1.422 (3)
C8—N4	1.465 (3)	C18—H18A	0.9600
C8—C9	1.506 (3)	C18—H18B	0.9600
C8—H8A	0.9700	C18—H18C	0.9600
C8—H8B	0.9700	N1—O1	1.217 (3)
C9—N3	1.492 (4)	N1—O2	1.225 (3)
C9—H9A	0.9700	O4A—N2	1.225 (8)
C9—H9B	0.9700	N3—H3A	0.94 (4)
C10—N3	1.487 (3)	N3—H3B	0.97 (3)
C10—C11	1.503 (3)	O3—N2	1.215 (3)
C10—H10A	0.9700	O6—H6A	1.13 (4)
C10—H10B	0.9700	O7—H6A	1.38 (4)
C11—N4	1.452 (3)	N2—O4B	1.228 (13)
C11—H11A	0.9700		
C2—C1—C6	121.0 (2)	C13—C12—C17	118.0 (2)
C2—C1—N1	119.0 (2)	C13—C12—N4	123.3 (2)
C6—C1—N1	120.0 (2)	C17—C12—N4	118.6 (2)
C3—C2—C1	119.3 (2)	C12—C13—C14	120.8 (2)
C3—C2—H2	120.4	C12—C13—H13	119.6
C1—C2—H2	120.4	C14—C13—H13	119.6
C2—C3—C4	122.8 (2)	C15—C14—C13	120.1 (3)
C2—C3—N2	116.5 (2)	C15—C14—H14	119.9
C4—C3—N2	120.7 (2)	C13—C14—H14	119.9
O7—C4—C3	124.4 (2)	C14—C15—C16	120.4 (3)
O7—C4—C5	120.4 (2)	C14—C15—H15	119.8
C3—C4—C5	115.3 (2)	C16—C15—H15	119.8
C6—C5—C4	121.2 (2)	C15—C16—C17	120.4 (3)
C6—C5—C7	119.1 (2)	C15—C16—H16	119.8

C4—C5—C7	119.7 (2)	C17—C16—H16	119.8
C5—C6—C1	120.5 (2)	O8—C17—C16	124.5 (2)
C5—C6—H6	119.8	O8—C17—C12	115.3 (2)
C1—C6—H6	119.8	C16—C17—C12	120.2 (2)
O5—C7—O6	120.0 (2)	O8—C18—H18A	109.5
O5—C7—C5	123.1 (2)	O8—C18—H18B	109.5
O6—C7—C5	116.8 (2)	H18A—C18—H18B	109.5
N4—C8—C9	109.1 (2)	O8—C18—H18C	109.5
N4—C8—H8A	109.9	H18A—C18—H18C	109.5
C9—C8—H8A	109.9	H18B—C18—H18C	109.5
N4—C8—H8B	109.9	O1—N1—O2	122.7 (2)
C9—C8—H8B	109.9	O1—N1—C1	118.9 (2)
H8A—C8—H8B	108.3	O2—N1—C1	118.4 (2)
N3—C9—C8	110.1 (2)	C10—N3—C9	110.9 (2)
N3—C9—H9A	109.6	C10—N3—H3A	107 (2)
C8—C9—H9A	109.6	C9—N3—H3A	112 (2)
N3—C9—H9B	109.6	C10—N3—H3B	115.4 (18)
C8—C9—H9B	109.6	C9—N3—H3B	104.9 (17)
H9A—C9—H9B	108.1	H3A—N3—H3B	107 (3)
N3—C10—C11	110.8 (2)	C12—N4—C11	117.54 (18)
N3—C10—H10A	109.5	C12—N4—C8	115.96 (18)
C11—C10—H10A	109.5	C11—N4—C8	110.66 (19)
N3—C10—H10B	109.5	C7—O6—H6A	106.5 (19)
C11—C10—H10B	109.5	C4—O7—H6A	102.6 (15)
H10A—C10—H10B	108.1	C17—O8—C18	118.5 (2)
N4—C11—C10	109.9 (2)	O3—N2—O4A	122.2 (7)
N4—C11—H11A	109.7	O3—N2—O4B	118.7 (15)
C10—C11—H11A	109.7	O3—N2—C3	118.5 (2)
N4—C11—H11B	109.7	O4A—N2—C3	118.2 (8)
C10—C11—H11B	109.7	O4B—N2—C3	119.7 (14)
H11A—C11—H11B	108.2		
C6—C1—C2—C3	-1.0 (4)	C15—C16—C17—C12	0.6 (4)
N1—C1—C2—C3	179.6 (2)	C13—C12—C17—O8	177.5 (2)
C1—C2—C3—C4	1.4 (4)	N4—C12—C17—O8	1.3 (3)
C1—C2—C3—N2	-179.4 (2)	C13—C12—C17—C16	-1.4 (4)
C2—C3—C4—O7	179.3 (2)	N4—C12—C17—C16	-177.7 (2)
N2—C3—C4—O7	0.2 (4)	C2—C1—N1—O1	-0.8 (4)
C2—C3—C4—C5	-0.8 (4)	C6—C1—N1—O1	179.8 (3)
N2—C3—C4—C5	-179.9 (2)	C2—C1—N1—O2	178.7 (2)
O7—C4—C5—C6	179.6 (2)	C6—C1—N1—O2	-0.7 (4)
C3—C4—C5—C6	-0.3 (3)	C11—C10—N3—C9	54.4 (3)
O7—C4—C5—C7	-0.9 (4)	C8—C9—N3—C10	-55.3 (3)
C3—C4—C5—C7	179.2 (2)	C13—C12—N4—C11	-14.9 (3)
C4—C5—C6—C1	0.7 (4)	C17—C12—N4—C11	161.1 (2)
C7—C5—C6—C1	-178.8 (2)	C13—C12—N4—C8	119.2 (3)
C2—C1—C6—C5	0.0 (4)	C17—C12—N4—C8	-64.7 (3)
N1—C1—C6—C5	179.3 (2)	C10—C11—N4—C12	-162.6 (2)

C6—C5—C7—O5	-1.3 (4)	C10—C11—N4—C8	61.0 (3)
C4—C5—C7—O5	179.1 (2)	C9—C8—N4—C12	161.0 (2)
C6—C5—C7—O6	178.9 (2)	C9—C8—N4—C11	-61.9 (3)
C4—C5—C7—O6	-0.6 (4)	C16—C17—O8—C18	-3.3 (4)
N4—C8—C9—N3	58.4 (3)	C12—C17—O8—C18	177.8 (2)
N3—C10—C11—N4	-56.8 (3)	C2—C3—N2—O3	-13.1 (3)
C17—C12—C13—C14	1.1 (4)	C4—C3—N2—O3	166.1 (2)
N4—C12—C13—C14	177.1 (2)	C2—C3—N2—O4A	155.4 (6)
C12—C13—C14—C15	0.1 (4)	C4—C3—N2—O4A	-25.4 (7)
C13—C14—C15—C16	-0.9 (4)	C2—C3—N2—O4B	-172.7 (12)
C14—C15—C16—C17	0.5 (4)	C4—C3—N2—O4B	6.4 (13)
C15—C16—C17—O8	-178.2 (2)		

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ )

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
O6—H6 <i>A</i> $\cdots$ O7	1.14 (3)	1.37 (3)	2.448 (2)	154 (3)
N3—H3 <i>A</i> $\cdots$ O5	0.94 (4)	2.02 (4)	2.936 (3)	165 (3)
N3—H3 <i>A</i> $\cdots$ O6	0.94 (4)	2.44 (3)	3.153 (3)	133 (2)
N3—H3 <i>B</i> $\cdots$ O7 <sup>i</sup>	0.97 (3)	1.83 (3)	2.787 (3)	166 (3)
C2—H2 $\cdots$ O1 <sup>ii</sup>	0.93	2.66	3.581 (3)	174
C9—H9 <i>A</i> $\cdots$ O3 <sup>iii</sup>	0.97	2.44	3.254 (4)	141
C10—H10 <i>B</i> $\cdots$ O2 <sup>iv</sup>	0.97	2.43	3.319 (3)	152
C10—H10 <i>A</i> $\cdots$ O4 <i>A</i> <sup>i</sup>	0.97	2.50	3.118 (10)	122
C14—H14 $\cdots$ O5 <sup>v</sup>	0.93	2.74	3.481 (3)	137
C18—H18 <i>C</i> $\cdots$ N4 <sup>vi</sup>	0.96	2.74	3.552 (4)	143

Symmetry codes: (i)  $-x+2, -y+1, -z$ ; (ii)  $-x, -y, -z$ ; (iii)  $-x+1, -y+1, -z$ ; (iv)  $x+1, y, z$ ; (v)  $-x+1, -y+1, -z+1$ ; (vi)  $-x+2, -y+2, -z+1$ .