Crystal structure studies of 4-ethylpiperazinium-1-ium 3,5-dinitrobenzoate, 4-methylpiperazinium-1-ium 3,5-dinitrobenzoate and 4-methylpiperazinium-1-ium 4-iodobenzoate

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As part of our ongoing investigation on the chemical and biological properties of piperazinium salts, we synthesized three novel compounds: 1-ethylpiperazinium 3,5-dinitrobenzoate (I), 1-methylpiperazinium 3,5-dinitrobenzoate (II) and 1-methylpiperazinium 4-iodobenzoate (III). The crystal structures of these compounds are built up of organic layers formed by the strong connection between the molecules by hydrogen bonds of type N—H/C1/C1/C1 O. These layers are linked through N—H/C1/C1/C1 O hydrogen bonds and C—H/C1/C1/C1 O interactions or C—I/C1/C1/C1 N halogen bonding, leading to the formation of a three-dimensional network.

1. Chemical context

Piperazines and substituted piperazines are important pharmacophores that can be found in many biologically active compounds across a number of different therapeutic areas (Berkheij, 2005) such as antifungal (Upadhayaya et al., 2004), anti-bacterial, anti-malarial and anti-psychotic agents (Choudhary et al., 2006). A valuable insight into recent advances on antimicrobial activity of piperazine derivatives has been reported (Kharb et al., 2012).

Piperazines are among the most important building blocks in today’s drug discovery efforts and are found in biologically active compounds across a number of different therapeutic areas (Brockunier et al., 2004; Bogatcheva et al., 2006). A review of the current pharmacological and toxicological information for piperazine derivatives is given by Elliott (2011).

1-Ethylpiperazine is used in the synthesis of 2-{2-methoxy-5-[(4-methylpiperazin-1-yl)sulfonyl]phenyl}-1H-benzo[d]-imidazole hydrochloride and 2-{5-[(4-ethylpiperazin-1-yl)sulfonyl]-2-methoxyphenyl}-1H-benzo[d]-imidazole hydrochloride as benzimidazole analogs of sildenafil, which is marketed for the treatment of erectile dysfunction (Qandil, 2012). It is also employed as an intermediate in veterinary medicine and serves as a precursor in the preparation of dyes.

N-Ethyl piperazine is used in the synthesis of enrofloxacin, which is an antibiotic used to treat bacterial infections. It is also used in the synthesis of dyes, agrochemicals and other pharmaceutical compounds. The crystal structures of compounds derived from 1-ethylpiperazine, viz., chlorobis-
(2-chlorobenzyl)(4-ethylpiperazine-1-dithiocarbamato-\(x^2S, S\))tin(IV) (Li & Li, 2007), 1-diphenylmethyl-4-ethylpiperazine-1,4-diium dichloride (Qiao et al., 2010), (S)-3-chloro-4-(4-ethylpiperazin-1-yl)-5-\{(1R,2S,5R)-5-isopropyl-5-methylcyclohexyl\}furan-2(5H)-one (Fu et al., 2010), 4-\{5-(4-chlorophenyl)-1-(4-fluorophenyl)-1H-pyrazol-3-yl\}carbonyl-N-ethylpiperazine-1-carboxamide (Shahani et al., 2011), 2-[4-(2-methoxyphenyl)piperazin-1-yl]-N-(pyridin-2-yl)acetamide (Lu & Jiang, 2011), N-(4-chlorophenyl)-4-ethylpiperazine-1-carboxamide (Li, 2011) and trichlorido(1-ethylpiperazin-1-ium)cobalt(II) (Dhieb et al., 2014) have been reported.

1-Methylpiperazine is used in the preparation of 2-(4-methyl-1-piperazinylmethyl)acrylophenone as an antimicrotubular drug (Mallevais et al., 1984). It is involved in the preparation of 1-(4-methoxyphenyl)-4-methylpiperazine by reaction with 1-chloro-4-methoxy-benzene. It acts as an intermediate in the synthesis of active pharmaceutical ingredients such as ofloxacin, rifampicin, clozapine, sildenafil, trifluoperazine and zopiclone. The crystal structures of 1-methylpiperazine-1,4-diium 4-nitrophthalate(2\(\frac{1}{2}\)) 4-nitrophthalic acid monohydrate (Guo, 2004), (−)-2-methylpiperazin-1-ium perchlorate (Peng, 2010), 1-methylpiperazine-1,4-diium dipicrate (Dutkiewicz et al., 2011), 1-methylpiperazine-1,4-diium bis(hydrogen oxalate) (Essid et al., 2014), 2-methylpiperazine-1,4-diium bis(hydrogen maleate) (Wecharine et al., 2015) and 2-methylpiperazine-1,4-diium bis(hydrogen maleate) (Wecharine & Arto, 2015), have been reported.

2. Structural commentary

The molecular structures of the title salts (I), (II) and (III) are illustrated in Figs. 1, 2 and 3, respectively. The asymmetric unit of compound (I) is composed of one 1-ethylpiperazinium cation and one 3,5-dinitrobenzoate anion while (II) consists of a 1-methylpiperazinium cation and a 3,5-dinitrobenzoate anion. Compound (III) crystallizes with one 1-methylpiperazinium cation and one 4-iodobenzoate anion in the asymmetric unit. In all compounds, the piperazine rings have a
chair conformation with a positively charged protonated N atom with a maximum deviation from their mean plane of 0.239 (2), 0.258 (2) and 0.238 (2) Å at atom N1, for the three title compounds, respectively. The benzene rings are almost planar, with maximum deviations of 0.010 (2), 0.006 (2) and 0.006 (3) Å at atoms C8, C10 and C8 for (I), (II) and (III) respectively. The substituents of the benzene rings in all compounds are approximately in the same plane and do not deviate significantly from planarity.

3. Supramolecular features

In the crystal of (I), the cation and anion are linked by N2—H21···O1 hydrogen bonds, forming layers extending along the
Table 4
Experimental details.

|       | (I)                                  | (II)                                  | (III)                                 |
|-------|--------------------------------------|---------------------------------------|---------------------------------------|
|       | C₆H₁₃N₂⁺·C₇H₄IO₂⁻                     | C₆H₁₃N₂⁺·C₇H₂NO₆⁻                    | C₆H₁₃N₂⁺·C₇H₂NO₆⁻                    |
| Mᵣ    | 326.31                               | 312.29                                | 348.17                                |
| Crystal system, space group | Monoclinic, C2/c                      | Triclinic, Pₜ                         | Triclinic, Pₜ                         |
| Temperature (K) | 293                                  | 293                                   | 293                                   |
| a, b, c (Å)  | 19.362 (1), 8.6279 (7), 19.318 (1)    | 7.8023 (6), 10.3920 (8), 10.4770 (8) | 7.3578 (8), 74.289 (8), 71.828 (7)    |
| α, β, γ (°) | 90, 97.261 (8), 90                    | 75.489 (11)                           | 78.249 (11)                           |
| Z      | 8                                    | 2                                     | 2                                     |
| Radiation type | Mo K                                 | Mo K                                  | Mo K                                  |
| χ (mm⁻¹) | 0.11                                 | 0.11                                  | 2.34                                  |
| Crystal size (mm) | 0.46 × 0.28 × 0.24                    | 0.48 × 0.48 × 0.44                    | 0.48 × 0.48 × 0.44                    |

Data collection

| Diffractometer | Oxford Diffraction Xcalibur            | Oxford Diffraction Xcalibur            | Oxford Diffraction Xcalibur            |
|----------------|---------------------------------------|---------------------------------------|---------------------------------------|
| Absorption correction | Multi-scan (CrysAlis RED; Oxford Diffraction, 2009) | Multi-scan (CrysAlis RED; Oxford Diffraction, 2009) | Multi-scan (CrysAlis RED; Oxford Diffraction, 2009) |
| Tₓ, Tᵧ | 0.964, 0.974                           | 0.948, 0.952                           | 0.515, 0.626                           |
| No. of measured, independent and observed [I > 2σ(I)] reflections | 6345, 2943, 1968                      | 4819, 2774, 1935                      | 4189, 2492, 2324                      |
| R(int) | 0.016                                 | 0.010                                 | 0.011                                 |
| R(F²) = 0.20, 0.123, 1.04                          | 0.28, –0.15                           | 0.57, –0.95                           |
| H-atom treatment | H atoms treated by a mixture of independent and constrained refinement | H atoms treated by a mixture of independent and constrained refinement | H atoms treated by a mixture of independent and constrained refinement |

Computer programs: CrysAlis CCD (Oxford Diffraction, 2009), CrysAlis RED (Oxford Diffraction, 2009), SHELXT (Sheldrick, 2015a), Mercury (Macrae et al., 2020), SHELXL2014 (Sheldrick, 2015b), PLATON (Spek, 2020) and pubICIF (Westrip, 2010).

c-axis direction. The layers are connected via N2—H22···O2 hydrogen bonds, forming sheets lying parallel to the ac plane (Table 1 and Fig. 4). The crystal structure of compound (II) is built up of N2—H21···O2 and N2—H22···O1 hydrogen bonds that connect the molecules in strong layers along the c-axis direction. The layers are linked via weak interactions of the type C—H···O, giving a three-dimensional network along the b axis (Table 2 and Fig. 5). The molecules in the crystal of (III) are linked by N2—H21···O2, N2—H22···O1, C—H···O and C—H···π interactions, forming layers along the b axis. The layers are linked through C—I···N halogen bonding with C9—I1 and I1···N1(1 − x, 1 − y, −z) bond distances of 2.103 (2) and 3.073 (2) Å, respectively, and bond angle of 174.33 (8)°, leading to a three-dimensional structure (Table 3 and Fig. 6).

4. Database survey

A search of the Cambridge Structural Database (Version 2020.3.0, last update March 2021; Groom et al., 2016) for the piperazinium cation and benzoate anion involved in the three salts gave 62 hits, 60 of which have branched aromatic substituents either on the piperazinium cation, the benzoate anion or both, that make their structures extremely different from those of the title salts. The other two compounds are quite similar to the title molecules: 4-methylpiperazin-1-ium 2-amino-5-iodobenzoate (MAVMEC: Zhu & Guo, 2005) and 1-methylpiperazin-1,4-diium 4-nitrophthalate(2-) 4-nitrophthalic acid monohydrate (IZEFY: Guo, 2004), which share the cationic part and its chair conformation with salts (II) and (III). The crystal structures of the two compounds are based on differently sized rings formed through hydrogen-bond contacts, which then aggregate into a 3D framework.

5. Synthesis and crystallization

For the synthesis of (I), a solution of commercially available 1-ethylpiperazine (100 mg, 0.88 mol) (from Sigma-Aldrich) in methanol (10 ml) was mixed with an equimolar solution of 3,5-dinitrobenzoic acid (186.6 mg, 0.88 mol). Compounds (II) and (III) were prepared by the same method in which 1-methylpiperazine (100 mg, 1.0 mol) in methanol (10 ml) was mixed with an equimolar solution of 3,5-dinitrobenzoic acid (212 mg, 1.0 mol) for (II) or with an equimolar solution of 4-iodobenzoic acid (248 mg, 1.0 mol) for (III). The corresponding mixtures were stirred for 30 min at 323 K and allowed to stand at room temperature. X-ray quality crystals were formed upon slow evaporation in a week time (m.p. 453–455 K, 459–461 K and 410–412 K, respectively).
6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4. The H atoms bound to C were positioned with idealized geometry and refined using a riding model with aromatic C—H = 0.93 Å, 0.96 Å (methyl) or 0.97 Å (methylene). The H atoms of the N atom were located in a difference map and later restrained to the distance N—H = 0.86 (2) Å. All H atoms were refined with isotropic displacement parameters set at 1.2 $U_{eq}$ (C-aromatic, C-methylene, N) or 1.5 $U_{eq}$ (C-methyl) of the parent atom.

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Computing details
For all structures, data collection: CrysAlis CCD (Oxford Diffraction, 2009); cell refinement: CrysAlis RED (Oxford Diffraction, 2009); data reduction: CrysAlis RED (Oxford Diffraction, 2009); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: SHELXL2014 (Sheldrick, 2015b); molecular graphics: Mercury (Macrae et al., 2020); software used to prepare material for publication: SHELXL2014 (Sheldrick, 2015b), PLATON (Spek, 2020) and publCIF (Westrip, 2010).

4-Ethylpiperazin-1-ium 3,5-dinitrobenzoate (I)

Crystal data

\[\text{C}_6\text{H}_{15}\text{N}_2^+ \cdot \text{C}_7\text{H}_3\text{N}_2\text{O}_6^-\]

\(M_r = 326.31\)

Monoclinic, \(\text{C}2/c\)

Hall symbol: -\(\text{C}2\) 2yc

\(a = 19.362\) (1) Å

\(b = 8.6279\) (7) Å

\(c = 19.318\) (1) Å

\(\beta = 97.261\) (8)°

\(V = 3201.3\) (4) Å³

\(Z = 8\)

Data collection

Oxford Diffraction Xcalibur diffractometer

Graphite monochromator

\(\omega\) scans

Absorption correction: multi-scans

(CrysAlis RED; Oxford Diffraction, 2009)

\(T_{\text{min}} = 0.964, T_{\text{max}} = 0.974\)

6345 measured reflections

Refinement

Refinement on \(F^2\)

Least-squares matrix: full

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

\(wR(F^2) = 0.123\)

\(S = 1.04\)

2943 independent reflections

2943 reflections with \(I > 2\sigma(I)\)

\(\theta_{\text{max}} = 25.4°, \theta_{\text{min}} = 2.6°\)

\(h = -23\rightarrow 23\)

\(k = -10\rightarrow 10\)

\(l = -9\rightarrow 23\)

214 parameters

2 restraints
0 constraints
Primary atom site location: structure-invariant
direct methods
Secondary atom site location: difference Fourier
map
Hydrogen site location: mixed

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)**

| Atom | x       | y       | z       | Uiso/*/Ueq |
|------|---------|---------|---------|------------|
| C1   | 0.18587 (15) | 0.3364 (3) | 0.30396 (15) | 0.0884 (9) |
| H1A  | 0.232834 | 0.339426 | 0.326863 | 0.133* |
| H1B  | 0.177587 | 0.424858 | 0.273903 | 0.133* |
| H1C  | 0.154108 | 0.338102 | 0.338302 | 0.133* |
| C2   | 0.17517 (12) | 0.1925 (3) | 0.26195 (13) | 0.0655 (7) |
| H2A  | 0.208261 | 0.190584 | 0.228215 | 0.079* |
| H2B  | 0.184798 | 0.103891 | 0.292568 | 0.079* |
| C3   | 0.08924 (11) | 0.2969 (3) | 0.17179 (12) | 0.0533 (6) |
| H3A  | 0.12338 | 0.291797 | 0.13919 | 0.064* |
| H3B  | 0.092984 | 0.397926 | 0.194012 | 0.064* |
| C4   | 0.01736 (11) | 0.2779 (3) | 0.13276 (13) | 0.0589 (6) |
| H4A  | −0.017049 | 0.290226 | 0.164733 | 0.071* |
| H4B  | 0.009231 | 0.357361 | 0.097152 | 0.071* |
| C5   | 0.02593 (11) | 0.0011 (3) | 0.15297 (12) | 0.0563 (6) |
| H5A  | 0.023563 | −0.099603 | 0.130507 | 0.068* |
| H5B  | −0.008248 | 0.003405 | 0.185592 | 0.068* |
| C6   | 0.09733 (11) | 0.0253 (3) | 0.19161 (12) | 0.0538 (6) |
| H6A  | 0.106657 | −0.054243 | 0.227061 | 0.065* |
| H6B  | 0.131632 | 0.015195 | 0.159377 | 0.065* |
| C7   | 0.22610 (9) | 0.0114 (2) | 0.03095 (10) | 0.0389 (5) |
| C8   | 0.25500 (10) | 0.1070 (2) | 0.05725 (10) | 0.0431 (5) |
| H8   | 0.226597 | 0.164062 | 0.08315 | 0.052* |
| C9   | 0.32638 (10) | 0.1168 (2) | 0.07159 (10) | 0.0449 (5) |
| C10  | 0.37088 (10) | 0.0395 (2) | 0.03386 (11) | 0.0468 (5) |
| H10  | 0.418946 | 0.049122 | 0.043855 | 0.056* |
| C11  | 0.34091 (9) | −0.0527 (2) | −0.01928 (11) | 0.0442 (5) |
| C12  | 0.26950 (9) | −0.0699 (2) | −0.03464 (10) | 0.0428 (5) |
| H12  | 0.250959 | −0.135397 | −0.070496 | 0.051* |
| C13  | 0.14743 (10) | −0.0038 (3) | −0.01245 (10) | 0.0440 (5) |
| N1   | 0.10398 (8) | 0.1771 (2) | 0.22445 (8) | 0.0478 (5) |
| N2   | 0.00983 (8) | 0.1234 (2) | 0.09987 (9) | 0.0502 (5) |
| N3   | 0.35665 (12) | 0.2143 (3) | 0.13029 (11) | 0.0657 (6) |
### Atomic displacement parameters (Å²)

|     | $U^{11}$   | $U^{22}$   | $U^{33}$   | $U^{12}$   | $U^{13}$   | $U^{23}$   |
|-----|------------|------------|------------|------------|------------|------------|
| C1  | 0.084 (2)  | 0.088 (2)  | 0.085 (2)  | −0.0122 (16)| −0.0206 (15)| −0.0224 (17)|
| C2  | 0.0594 (14)| 0.0728 (18)| 0.0585 (14)| −0.0020 (12)| −0.0150 (11)| 0.0000 (13) |
| C3  | 0.0511 (12)| 0.0460 (13)| 0.0597 (13)| −0.0019 (10)| −0.0053 (10)| −0.0028 (11)|
| C4  | 0.0477 (12)| 0.0602 (15)| 0.0652 (14)| 0.0061 (11) | −0.0069 (11)| −0.0037 (13)|
| C5  | 0.0538 (13)| 0.0543 (14)| 0.0608 (14)| −0.0136 (11)| 0.0072 (11) | −0.0063 (12)|
| C6  | 0.0546 (13)| 0.0483 (14)| 0.0563 (13)| −0.0017 (10)| −0.0015 (10)| 0.0037 (12) |
| C7  | 0.0330 (9) | 0.0390 (11)| 0.0437 (11)| −0.0016 (8) | 0.0007 (8)  | 0.0063 (10)|
| C8  | 0.0431 (11)| 0.0413 (12)| 0.0448 (11)| −0.0019 (9) | 0.0053 (9)  | 0.0024 (10)|
| C9  | 0.0460 (11)| 0.0423 (12)| 0.0439 (11)| −0.0114 (10)| −0.0043 (9) | 0.0027 (10)|
| C10 | 0.0331 (10)| 0.0478 (12)| 0.0565 (13)| −0.0072 (9) | −0.0057 (9) | 0.0094 (11)|
| C11 | 0.0332 (10)| 0.0446 (12)| 0.0547 (12)| 0.0004 (9)  | 0.0049 (9)  | 0.0032 (11)|
| C12 | 0.0370 (10)| 0.0422 (12)| 0.0479 (11)| −0.0039 (9) | −0.0002 (9) | 0.0008 (10)|
| C13 | 0.0329 (10)| 0.0542 (14)| 0.0443 (11)| −0.0017 (10)| 0.0026 (9)  | 0.0081 (11)|
| N1  | 0.0446 (9) | 0.0524 (11)| 0.0437 (10)| −0.0038 (8) | −0.0048 (8) | −0.0025 (9)|
| N2  | 0.0331 (9) | 0.0683 (13)| 0.0477 (10)| −0.0049 (9) | −0.0013 (7) | −0.0090 (10)|
| N3  | 0.0674 (14)| 0.0690 (15)| 0.0579 (12)| −0.0222 (12)| −0.0030 (11)| −0.0041 (12)|
| N4  | 0.0428 (11)| 0.0591 (13)| 0.0833 (14)| 0.0009 (9)  | 0.0135 (10)| −0.0068 (12)|
| O1  | 0.0415 (8) | 0.0734 (11)| 0.0735 (11)| 0.0069 (8)  | 0.0153 (7)  | −0.0062 (9)|
| O2  | 0.0340 (8) | 0.0748 (11)| 0.0837 (11)| −0.0064 (8) | −0.0057 (7) | −0.0170 (10)|
| O3  | 0.1085 (17)| 0.0929 (16)| 0.0892 (15)| −0.0096 (13)| −0.0011 (12)| −0.0405 (13)|
| O4  | 0.0675 (12)| 0.1305 (19)| 0.0900 (14)| −0.0337 (12)| −0.0219 (10)| −0.0182 (13)|
| O5  | 0.0337 (9) | 0.0929 (14)| 0.1238 (16)| 0.0008 (9)  | 0.0167 (9)  | −0.0136 (12)|
| O6  | 0.0624 (11)| 0.1236 (18)| 0.1026 (14)| 0.0096 (11) | 0.0109 (10) | −0.0556 (14)|

### Geometric parameters (Å, °)

|     | C1—C2  | C1—H1A | C1—H1B | C1—H1C | C2—N1  | C2—H2A | C2—H2B | C3—N1  | C3—C4  | C7—C8  | C7—C12 | C7—C13 | C8—C9  | C8—H8  | C9—C10 | C9—N3  | C10—C11 | C10—H10 | C11—H12 | sup-3 |
|-----|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| C1  | 1.484 (3)| 0.96   | 0.96   | 0.96   | 1.480 (3)| 0.97   | 0.97   | 1.453 (3)| 1.506 (3)| 1.381 (3)| 1.383 (3)| 1.522 (2)| 1.377 (3)| 0.93   | 1.368 (3)| 0.93   | 1.473 (3)|        |        |
| Bond       | Distance (Å) | Bond       | Distance (Å) |
|------------|--------------|------------|--------------|
| C3—H3A     | 0.97         | C11—C12    | 1.385 (2)    |
| C3—H3B     | 0.97         | C11—N4     | 1.467 (3)    |
| C4—N2      | 1.476 (3)    | C12—H12    | 0.93         |
| C4—H4A     | 0.97         | C13—O1     | 1.238 (2)    |
| C4—H4B     | 0.97         | C13—O2     | 1.250 (2)    |
| C5—N2      | 1.477 (3)    | N2—H21     | 0.907 (17)   |
| C5—C6      | 1.500 (3)    | N2—H22     | 0.922 (17)   |
| C5—H5A     | 0.97         | N3—O3      | 1.213 (3)    |
| C5—H5B     | 0.97         | N3—O4      | 1.216 (2)    |
| C6—N1      | 1.454 (3)    | N4—O6      | 1.212 (2)    |
| C6—H6A     | 0.97         | N4—O5      | 1.224 (2)    |
| C6—H6B     | 0.97         |            |              |
| C2—C1—H1A  | 109.5        | C8—C7—C12  | 119.22 (17)  |
| C2—C1—H1B  | 109.5        | C8—C7—C13  | 120.47 (18)  |
| H1A—C1—H1B | 109.5        | C12—C7—C13 | 120.31 (18)  |
| C2—C1—H1C  | 109.5        | C9—C8—C7   | 119.24 (19)  |
| H1A—C1—H1C | 109.5        | C9—C8—H8   | 120.4        |
| N1—C2—C1   | 113.6 (2)    | C10—C9—C8  | 123.05 (19)  |
| N1—C2—H2A  | 108.9        | C10—C9—N3  | 118.16 (18)  |
| C1—C2—H2A  | 108.9        | C8—C9—N3   | 118.8 (2)    |
| N1—C2—H2B  | 108.9        | C11—C10—C9 | 116.52 (17)  |
| C1—C2—H2B  | 108.9        | C11—C10—H10| 121.7        |
| H2A—C2—H2B | 107.7        | C9—C10—H10 | 121.7        |
| N1—C3—C4   | 111.11 (18)  | C10—C11—C12| 122.71 (19)  |
| N1—C3—H3A  | 109.4        | C10—C11—N4 | 118.60 (17)  |
| C4—C3—H3A  | 109.4        | C12—C11—N4 | 118.69 (18)  |
| N1—C3—H3B  | 109.4        | C7—C12—C11 | 119.23 (19)  |
| C4—C3—H3B  | 109.4        | C7—C12—H12 | 120.4        |
| H3A—C3—H3B | 108          | C11—C12—H12| 120.4        |
| N2—C4—C3   | 110.43 (17)  | O1—C13—O2  | 126.81 (18)  |
| N2—C4—H4A  | 109.6        | O1—C13—C7  | 117.20 (19)  |
| C3—C4—H4A  | 109.6        | O2—C13—C7  | 115.98 (18)  |
| N2—C4—H4B  | 109.6        | C3—N1—C6   | 109.69 (16)  |
| C3—C4—H4B  | 109.6        | C3—N1—C2   | 111.54 (17)  |
| H4A—C4—H4B | 108.1        | C6—N1—C2   | 108.66 (17)  |
| N2—C5—C6   | 110.30 (17)  | C4—N2—C5   | 110.20 (17)  |
| N2—C5—H5A  | 109.6        | C4—N2—H21  | 110 (2)      |
| C6—C5—H5A  | 109.6        | C5—N2—H21  | 111 (2)      |
| N2—C5—H5B  | 109.6        | C4—N2—H22  | 108 (2)      |
| C6—C5—H5B  | 109.6        | C5—N2—H22  | 110.3 (19)   |
| H5A—C5—H5B | 108.1        | H21—N2—H22 | 108 (3)      |
| N1—C6—C5   | 111.54 (18)  | O3—N3—O4   | 124.2 (2)    |
| N1—C6—H6A  | 109.3        | O3—N3—C9   | 117.8 (2)    |
| C5—C6—H6A  | 109.3        | O4—N3—C9   | 118.0 (2)    |
| N1—C6—H6B  | 109.3        | O6—N4—O5   | 123.5 (2)    |
| C5—C6—H6B  | 109.3        | O6—N4—C11  | 118.33 (18)  |
Hydrogen-bond geometry (Å, °)

| D—H···A       | D—H   | H···A   | D···A   | D—H···A |
|---------------|-------|--------|--------|---------|
| N2—H21···O1   | 0.91  (2) | 1.88  (2) | 2.768 (2) | 168 (3) |
| N2—H22···O2i  | 0.92  (2) | 1.77  (2) | 2.684 (2) | 171 (3) |

Symmetry code: (i) −x, −y, −z.

4-Methylpiperazin-1-ium 3,5-dinitrobenzoate (II)

Crystal data

C₅H₁₃N₄⁺·C₇H₃N₂O₆⁻

M_r = 312.29
Triclinic, P₁
Hall symbol: -P 1
a = 7.8023 (6) Å
b = 10.3920 (8) Å
c = 10.4770 (8) Å
α = 73.578 (8)°
β = 74.289 (8)°
γ = 71.828 (7)°
V = 758.49 (11) Å³

Z = 2
F(000) = 328
D_x = 1.367 Mg m⁻³
Mo Kα radiation, λ = 0.71073 Å

Cell parameters from 4819 reflections
θ = 2.6–25.4°
µ = 0.11 mm⁻¹
T = 293 K
Prism, orange

Data collection

Oxford Diffraction Xcalibur diffractometer
Graphite monochromator
ω scans
Absorption correction: multi-scan (CrysAlis RED; Oxford Diffraction, 2009)

2774 independent reflections
1935 reflections with I > 2σ(I)
R(int) = 0.010
θ_max = 25.4°, θ_min = 2.6°

h = −9→7
k = −12→8
l = −12→12

4819 measured reflections
Refinement

Refinement on $F^2$

Least-squares matrix: full

$R[F^2] > 2σ(F^2) = 0.044$

$wR(F) = 0.129$

$S = 1.03$

2774 reflections

206 parameters

2 restraints

0 constraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[σ^2(F_0^2) + (0.0593P)^2 + 0.1428P]$

where $P = (F_0^2 + 2F_c^2)/3$

$(Δ/σ)_{max} < 0.001$

$Δρ_{max} = 0.28$ e Å$^{-3}$

$Δρ_{min} = −0.15$ 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 ($A^2$)

|          | $x$     | $y$     | $z$     | $U_{iso}$/$U_{eq}$ |
|----------|---------|---------|---------|---------------------|
| O1       | 0.4259  | −0.2560 | 0.6053  | 0.1005 (6)          |
| O2       | 0.3187  | −0.2819 | 0.4415  | 0.0950 (5)          |
| O3       | 0.2206  | 0.1945  | 0.7260  | 0.1219 (7)          |
| O4       | 0.1284  | 0.3790  | 0.5805  | 0.1139 (7)          |
| O5       | 0.0144  | 0.3389  | 0.1645  | 0.1237 (7)          |
| O6       | 0.0455  | 0.1363  | 0.1329  | 0.1293 (8)          |
| N3       | 0.1771  | 0.2532  | 0.6173  | 0.0806 (5)          |
| N4       | 0.0540  | 0.2122  | 0.1988  | 0.0877 (6)          |
| C6       | 0.2667  | −0.0560 | 0.4726  | 0.0500 (4)          |
| C7       | 0.2608  | 0.0260  | 0.5580  | 0.0535 (4)          |
| H7       | 0.3075  | −0.0136 | 0.6370  | 0.064*              |
| C8       | 0.1847  | 0.1676  | 0.5250  | 0.0569 (4)          |
| C9       | 0.1152  | 0.2314  | 0.4090  | 0.0625 (5)          |
| H9       | 0.0641  | 0.3266  | 0.3881  | 0.075*              |
| C10      | 0.1249  | 0.1477  | 0.3253  | 0.0606 (5)          |
| C11      | 0.1974  | 0.0062  | 0.3551  | 0.0568 (5)          |
| H11      | 0.1997  | −0.0472 | 0.2966  | 0.068*              |
| C12      | 0.3453  | −0.2120 | 0.5093  | 0.0606 (5)          |
| N1       | 0.4346  | 0.7122  | 0.0237  | 0.0702 (5)          |
| N2       | 0.4591  | 0.5270  | 0.2826  | 0.0687 (5)          |
| C1       | 0.3857  | 0.8479  | −0.0671 | 0.1066 (9)          |
| H1A      | 0.4931  | 0.8650  | −0.1330 | 0.16*               |
| H1B      | 0.3384  | 0.9187  | −0.0151 | 0.16*               |
| H1C      | 0.2935  | 0.8490  | −0.1125 | 0.16*               |
| C2       | 0.2725  | 0.6783  | 0.1169  | 0.0697 (5)          |
| H2A      | 0.1840  | 0.6814  | 0.0658  | 0.084*              |
| H2B      | 0.2161  | 0.7468  | 0.1727  | 0.084*              |
| C3       | 0.3197  | 0.5366  | 0.2067  | 0.0739 (6)          |
### Atomic displacement parameters (Å²)

|   | U₁₁  | U₂₂  | U₃₃  | U₁₂  | U₁₃  | U₂₃  |
|---|------|------|------|------|------|------|
| O1 | 0.1400 (15) | 0.0432 (8) | 0.1110 (13) | 0.0019 (8) | −0.0587 (12) | −0.0017 (8) |
| O2 | 0.1243 (14) | 0.0579 (9) | 0.0982 (12) | −0.0005 (8) | −0.0083 (12) | −0.0007 (8) |
| O3 | 0.188 (2) | 0.0895 (13) | 0.1115 (15) | −0.0329 (13) | −0.0574 (15) | −0.0344 (12) |
| O4 | 0.1277 (14) | 0.0523 (10) | 0.1664 (18) | −0.0016 (9) | −0.0407 (13) | −0.0441 (11) |
| O5 | 0.1127 (14) | 0.1017 (15) | 0.1015 (13) | 0.0206 (11) | −0.0330 (11) | 0.0208 (11) |
| O6 | 0.1450 (19) | 0.149 (2) | 0.0972 (14) | −0.0207 (14) | −0.0625 (13) | −0.0148 (14) |
| N3 | 0.0813 (12) | 0.0582 (11) | 0.1069 (16) | −0.0145 (9) | −0.0177 (11) | −0.0297 (11) |
| N4 | 0.0675 (12) | 0.0988 (16) | 0.0703 (13) | −0.0021 (10) | −0.0176 (9) | 0.0047 (12) |
| C6 | 0.0438 (9) | 0.0429 (9) | 0.0544 (10) | −0.0084 (7) | −0.0007 (7) | −0.0086 (8) |
| C7 | 0.0489 (9) | 0.0469 (10) | 0.0578 (10) | −0.0098 (7) | −0.0088 (8) | −0.0053 (8) |
| C8 | 0.0514 (10) | 0.0439 (10) | 0.0721 (12) | −0.0111 (7) | −0.0067 (9) | −0.0140 (9) |
| C9 | 0.0484 (10) | 0.0435 (10) | 0.0788 (13) | −0.0071 (7) | −0.0067 (9) | 0.0018 (9) |
| C10 | 0.0448 (10) | 0.0617 (12) | 0.0590 (11) | −0.0073 (8) | −0.0074 (8) | 0.0023 (9) |
| C11 | 0.0487 (10) | 0.0597 (11) | 0.0562 (10) | −0.0122 (8) | −0.0013 (8) | −0.0142 (9) |
| C12 | 0.0630 (11) | 0.0420 (10) | 0.0627 (12) | −0.0068 (8) | 0.0020 (9) | −0.0110 (9) |
| N1 | 0.0768 (11) | 0.0689 (11) | 0.0543 (9) | −0.0116 (8) | −0.0144 (8) | −0.0036 (8) |
| N2 | 0.0975 (13) | 0.0401 (8) | 0.0587 (10) | 0.0023 (8) | −0.0235 (9) | −0.0102 (7) |
| C1 | 0.123 (2) | 0.0942 (19) | 0.0786 (16) | −0.0234 (15) | −0.0293 (15) | 0.0223 (14) |
| C2 | 0.0695 (13) | 0.0647 (12) | 0.0737 (13) | −0.0130 (10) | −0.0253 (10) | −0.0075 (10) |
| C3 | 0.0870 (15) | 0.0604 (12) | 0.0751 (13) | −0.0214 (10) | −0.0180 (11) | −0.0115 (10) |
| C4 | 0.0717 (14) | 0.0743 (14) | 0.0922 (16) | 0.0063 (11) | −0.0325 (12) | −0.0237 (12) |
| C5 | 0.0638 (12) | 0.0790 (14) | 0.0780 (14) | −0.0189 (10) | −0.0099 (11) | −0.0061 (11) |

### Geometric parameters (Å, °)

|   | O1—C12 | N1—C5 | O2—C12 | N1—C1 | O3—N3 | N2—C3 | O4—N3 | N2—C4 | O5—N4 | N2—H21 | O6—N4 | N2—H22 | N3—C8 | C1—H1A | N4—C10 | C1—H1B | C6—C7 | C1—H1C |
|---|--------|-------|--------|-------|-------|-------|--------|-------|-------|--------|-------|--------|-------|--------|-------|-------|-------|-------|
|   | 1.233 (2) | 1.452 (3) | 1.241 (2) | 1.464 (3) | 1.213 (3) | 1.477 (3) | 1.219 (2) | 1.483 (3) | 1.224 (3) | 0.906 (16) | 1.212 (3) | 0.913 (16) | 1.467 (3) | 0.96  | 1.475 (3) | 0.96  | 1.384 (2) | 0.96  |
| Bond          | Length (Å) | Bond          | Length (Å) | Bond          | Length (Å) |
|--------------|------------|--------------|------------|--------------|------------|
| C6—C11       | 1.386 (2)  | C2—C3        | 1.502 (3)  |
| C6—C12       | 1.519 (2)  | C2—H2A       | 0.97       |
| C7—C8        | 1.384 (2)  | C2—H2B       | 0.97       |
| C7—H7        | 0.93       | C3—H3A       | 0.97       |
| C8—C9        | 1.374 (3)  | C3—H3B       | 0.97       |
| C9—C10       | 1.373 (3)  | C4—C5        | 1.506 (3)  |
| C9—H9        | 0.93       | C4—H4A       | 0.97       |
| C10—C11      | 1.377 (2)  | C4—H4B       | 0.97       |
| C11—H11      | 0.93       | C5—H5A       | 0.97       |
| N1—C2        | 1.446 (2)  | C5—H5B       | 0.97       |
| O3—N3—O4     | 123.6 (2)  | C3—N2—H22    | 108.4 (15) |
| O3—N3—C8     | 117.95 (18)| C4—N2—H22    | 109.2 (14) |
| O4—N3—C8     | 118.4 (2)  | H21—N2—H22   | 111 (2)    |
| O6—N4—O5     | 124.2 (2)  | N1—C1—H1A    | 109.5      |
| O6—N4—C10    | 117.9 (2)  | N1—C1—H1B    | 109.5      |
| O5—N4—C10    | 117.8 (2)  | H1A—C1—H1B   | 109.5      |
| C7—C6—C11    | 118.91 (16)| N1—C1—H1C    | 109.5      |
| C7—C6—C12    | 120.13 (16)| H1A—C1—H1C   | 109.5      |
| C11—C6—C12   | 120.95 (17)| H1B—C1—H1C   | 109.5      |
| C6—C7—C8     | 119.47 (17)| N1—C2—C3     | 111.25 (17)|
| C6—C7—H7     | 120.3      | N1—C2—H2A    | 109.4      |
| C8—C7—H7     | 120.3      | C3—C2—H2A    | 109.4      |
| C9—C8—C7     | 122.55 (18)| N1—C2—H2B    | 109.4      |
| C9—C8—N3     | 118.53 (17)| C3—C2—H2B    | 109.4      |
| C7—C8—N3     | 118.92 (18)| H2A—C2—H2B   | 108        |
| C10—C9—C8    | 116.73 (16)| N2—C3—C2     | 110.67 (16)|
| C10—C9—H9    | 121.6      | N2—C3—H3A    | 109.5      |
| C8—C9—H9     | 121.6      | C2—C3—H3A    | 109.5      |
| C9—C10—C11   | 122.66 (18)| N2—C3—H3B    | 109.5      |
| C9—C10—N4    | 118.52 (19)| C2—C3—H3B    | 109.5      |
| C11—C10—N4   | 118.8 (2)  | H3A—C3—H3B   | 108.1      |
| C10—C11—C6   | 119.67 (18)| N2—C4—C5     | 109.78 (16)|
| C10—C11—H11  | 120.2      | N2—C4—H4A    | 109.7      |
| C6—C11—H11   | 120.2      | C5—C4—H4A    | 109.7      |
| O1—C12—O2    | 126.92 (18)| N2—C4—H4B    | 109.7      |
| O1—C12—C6    | 116.25 (18)| C5—C4—H4B    | 109.7      |
| O2—C12—C6    | 116.81 (19)| H4A—C4—H4B   | 108.2      |
| C2—N1—C5     | 108.81 (15)| N1—C5—C4     | 110.61 (18)|
| C2—N1—C1     | 110.74 (18)| N1—C5—H5A    | 109.5      |
| C5—N1—C1     | 110.91 (18)| C4—C5—H5A    | 109.5      |
| C3—N2—C4     | 110.66 (16)| N1—C5—H5B    | 109.5      |
| C3—N2—H21    | 110.0 (15) | C4—C5—H5B    | 109.5      |
| C4—N2—H21    | 107.1 (14) | H5A—C5—H5B   | 108.1      |
| C11—C6—C7—C8 | 0.5 (2)    | C9—C10—C11—C6| −1.0 (3)   |
| C12—C6—C7—C8 | −178.42 (15)| N4—C10—C11—C6| 179.18 (15)|
| C6—C7—C8—C9  | −0.6 (3)   | C7—C6—C11—C10| 0.2 (2)    |
C6—C7—C8—N3 179.23 (15) C12—C6—C11—C10 179.17 (15)
O3—N3—C8—C9 172.3 (2) C7—C6—C12—O1 −10.5 (2)
O4—N3—C8—C9 −8.0 (3) C11—C6—C12—O1 170.56 (17)
O3—N3—C8—C7 −7.5 (3) C7—C6—C12—O2 168.17 (16)
O4—N3—C8—C7 172.18 (18) C11—C6—C12—O2 −10.8 (2)
C7—C8—C9—C10 −0.2 (3) C5—N1—C2—C3 −60.3 (2)
N3—C8—C9—C10 −179.99 (15) C1—N1—C2—C3 177.52 (19)
C8—C9—C10—C11 1.0 (3) C4—N2—C3—C2 −54.0 (2)
N3—C8—C9—C10 −7.5 (3) C1—N1—C2—C3 −57.2 (2)
C8—C9—C10—N4 179.21 (15) N1—C2—C3—N2 54.9 (2)
O6—N4—C10—C9 −172.5 (2) C2—N1—C5—C4 61.4 (2)
O5—N4—C10—C9 −179.99 (15) N1—C2—C3—N2 −176.53 (19)
O6—N4—C10—C11 7.3 (3) C1—N1—C5—C4 −59.1 (2)
O5—N4—C10—C11 −169.91 (18) N2—C4—C5—N1 57.2 (2)

Hydrogen-bond geometry (Å, °)

| D—H···A      | D—H | H···A | D···A | D—H···A |
|-------------|------|-------|-------|---------|
| N2—H21···O2i| 0.91 (2) | 1.82 (2) | 2.728 (2) | 175 (2) |
| N2—H22···O1ii| 0.91 (2) | 1.78 (2) | 2.691 (2) | 172 (2) |

Symmetry codes: (i) x, y+1, z; (ii) −x+1, −y, −z+1.

4-Methylpiperazin-1-ium 4-iodobenzoate (III)

Crystal data

C5H13N2+·C7H4IO2−
Mr = 348.17
Triclinic, P1
Hall symbol: -P 1
a = 6.2418 (4) Å
b = 9.5465 (8) Å
c = 12.5346 (9) Å
α = 110.708 (8)°
β = 90.235 (5)°
γ = 101.559 (6)°
V = 682.19 (9) Å³

Z = 2
F(000) = 344
Dc = 1.695 Mg m⁻³

Cell parameters from 4189 reflections
θ = 3.3–25.4°
µ = 2.34 mm⁻¹
T = 293 K

Rods, colourless
0.48 × 0.24 × 0.2 mm

Data collection

Oxford Diffraction Xcalibur
Graphite monochromator
ω scans
Absorption correction: multi-scan
(CrysAlis RED; Oxford Diffraction, 2009)

2492 independent reflections
2324 reflections with I > 2σ(I)

Refinement

Refinement on F²
Least-squares matrix: full
R[F² > 2σ(F²)] = 0.020
wR(F²) = 0.051
S = 1.11

2492 reflections
160 parameters
2 restraints
0 constraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed

**Supporting Information**

H atoms treated by a mixture of independent and constrained refinement

\[ w = \frac{1}{\sigma(F_o^2) + (0.0289P)^2 + 0.2845P} \]

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

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

\( \Delta \rho_{\text{max}} = 0.37 \ \text{e} \ \text{Å}^{-3} \)

\( \Delta \rho_{\text{min}} = -0.95 \ \text{e} \ \text{Å}^{-3} \)

**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)**

| Atom | x      | y      | z      | Uiso*/Ueq |
|------|--------|--------|--------|-----------|
| C1   | 1.2514 | 0.7762 | 0.1396 | 0.0712    |
| H1A  | 1.2424 | 0.6908 | 0.0689 | 0.107*    |
| H1B  | 1.2839 | 0.8700 | 0.1249 | 0.107*    |
| H1C  | 1.3655 | 0.7761 | 0.1911 | 0.107*    |
| C2   | 1.0513 | 0.8911 | 0.2981 | 0.0429    |
| H2A  | 1.0855 | 0.9866 | 0.2841 | 0.051*    |
| H2B  | 1.1672 | 0.8925 | 0.3505 | 0.051*    |
| C3   | 0.8371 | 0.8786 | 0.3512 | 0.0428    |
| H3A  | 0.8475 | 0.9637 | 0.4234 | 0.051*    |
| H3B  | 0.7224 | 0.8835 | 0.3010 | 0.051*    |
| C4   | 0.7745 | 0.6017 | 0.2629 | 0.0432    |
| H4A  | 0.6564 | 0.5968 | 0.2102 | 0.052*    |
| H4B  | 0.7456 | 0.5069 | 0.2779 | 0.052*    |
| C5   | 0.9887 | 0.6188 | 0.2099 | 0.0424    |
| H5A  | 1.1044 | 0.6147 | 0.2599 | 0.051*    |
| H5B  | 0.9800 | 0.5343 | 0.1375 | 0.051*    |
| C6   | 0.6076 | 0.2567 | 0.3636 | 0.0296    |
| C7   | 0.6850 | 0.1909 | 0.2577 | 0.0339    |
| H7   | 0.8121 | 0.1530 | 0.2539 | 0.041*    |
| C8   | 0.5770 | 0.1804 | 0.1574 | 0.0355    |
| H8   | 0.6295 | 0.1345 | 0.0869 | 0.043*    |
| C9   | 0.3881 | 0.2396 | 0.1635 | 0.0312    |
| C10  | 0.3100 | 0.3057 | 0.2684 | 0.0332    |
| H10  | 0.1842 | 0.3450 | 0.2725 | 0.04*     |
| C11  | 0.4189 | 0.3135 | 0.3679 | 0.0336    |
| H11  | 0.3645 | 0.3573 | 0.4381 | 0.04*     |
| C12  | 0.7285 | 0.2674 | 0.4722 | 0.0345    |
| I1   | 0.2266 | 0.2321 | 0.0133 | 0.0394    |
| N1   | 1.0417 | 0.7631 | 0.1909 | 0.0384    |
| N2   | 0.7815 | 0.7327 | 0.3708 | 0.0393    |
| O1   | 0.6295 | 0.2895 | 0.5608 | 0.0567    |
| O2   | 0.9237 | 0.2528 | 0.4656 | 0.0467    |
H21 0.876 (4) 0.728 (4) 0.420 (2) 0.056*
H22 0.653 (4) 0.728 (4) 0.400 (3) 0.056*

Atomic displacement parameters (Å²)

|     | U₁¹  | U₂²  | U₃³  | U₁₂  | U₁₃  | U₂₃  |
|-----|------|------|------|------|------|------|
| C1  | 0.0331 (15) | 0.135 (3) | 0.056 (2) | 0.0112 (18) | 0.0100 (14) | 0.051 (2) |
| C2  | 0.0390 (14) | 0.0381 (14) | 0.0506 (16) | −0.0024 (11) | −0.0094 (12) | 0.0208 (12) |
| C3  | 0.0459 (14) | 0.0405 (14) | 0.0395 (14) | 0.0171 (12) | −0.0055 (11) | 0.0075 (12) |
| C4  | 0.0434 (14) | 0.0365 (14) | 0.0484 (16) | −0.0033 (11) | −0.0035 (12) | 0.0204 (12) |
| C5  | 0.0455 (15) | 0.0428 (14) | 0.0373 (14) | 0.0159 (12) | 0.0009 (11) | 0.0092 (12) |
| C6  | 0.0241 (10) | 0.0347 (12) | 0.0346 (12) | 0.0059 (9) | 0.0019 (9) | 0.0183 (10) |
| C7  | 0.0272 (11) | 0.0423 (13) | 0.0378 (13) | 0.0142 (10) | 0.0040 (9) | 0.0174 (11) |
| C8  | 0.0362 (13) | 0.0404 (13) | 0.0311 (12) | 0.0142 (10) | 0.0056 (10) | 0.0110 (11) |
| C9  | 0.0291 (11) | 0.0343 (12) | 0.0326 (12) | 0.0050 (9) | −0.0031 (9) | 0.0162 (10) |
| C10 | 0.0239 (11) | 0.0430 (13) | 0.0380 (13) | 0.0108 (10) | 0.0029 (9) | 0.0193 (11) |
| C11 | 0.0299 (11) | 0.0446 (14) | 0.0321 (12) | 0.0117 (10) | 0.0066 (9) | 0.0186 (11) |
| C12 | 0.0258 (11) | 0.0471 (14) | 0.0354 (13) | 0.0087 (10) | 0.0017 (9) | 0.0203 (11) |
| I1  | 0.03737 (10) | 0.05212 (12) | 0.03188 (10) | 0.01315 (7) | −0.00148 (7) | 0.01691 (8) |
| N1  | 0.0269 (10) | 0.0595 (14) | 0.0346 (11) | 0.0059 (9) | 0.0023 (8) | 0.0260 (10) |
| N2  | 0.0279 (10) | 0.0639 (14) | 0.0327 (11) | 0.0124 (10) | 0.0036 (8) | 0.0241 (11) |
| O1  | 0.0371 (10) | 0.1100 (18) | 0.0370 (11) | 0.0261 (11) | 0.0097 (8) | 0.0379 (12) |
| O2  | 0.0319 (9) | 0.0780 (14) | 0.0400 (10) | 0.0216 (9) | 0.0035 (8) | 0.0278 (10) |

Geometric parameters (Å, °)

|     |     |  |     |     |  |  |
|-----|-----|-----|-----|-----|-----|-----|
| C1—N1 | 1.464 (3) | C5—H5B | 0.97 |
| C1—H1A | 0.96 | C6—C11 | 1.386 (3) |
| C1—H1B | 0.96 | C6—C7 | 1.388 (3) |
| C1—H1C | 0.96 | C6—C12 | 1.514 (3) |
| C2—N1 | 1.453 (4) | C7—C8 | 1.386 (4) |
| C2—C3 | 1.498 (4) | C7—H7 | 0.93 |
| C2—H2A | 0.97 | C8—C9 | 1.398 (3) |
| C2—H2B | 0.97 | C8—H8 | 0.93 |
| C3—N2 | 1.474 (4) | C9—C10 | 1.381 (3) |
| C3—H3A | 0.97 | C9—HII | 2.103 (2) |
| C3—H3B | 0.97 | C10—C11 | 1.389 (3) |
| C4—N2 | 1.475 (4) | C10—H10 | 0.93 |
| C4—C5 | 1.501 (4) | C11—H11 | 0.93 |
| C4—H4A | 0.97 | C12—O1 | 1.246 (3) |
| C4—H4B | 0.97 | C12—O2 | 1.254 (3) |
| C5—N1 | 1.454 (4) | N2—H21 | 0.874 (18) |
| C5—H5A | 0.97 | N2—H22 | 0.881 (18) |
| N1—C1—H1A | 109.5 | C11—C6—C7 | 118.6 (2) |
| N1—C1—H1B | 109.5 | C11—C6—C12 | 120.8 (2) |
| H1A—C1—H1B | 109.5 | C7—C6—C12 | 120.6 (2) |
| N1—C1—H1C | 109.5 | C8—C7—C6 | 121.5 (2) |
H1A—C1—H1C 109.5  C8—C7—H7  119.3
H1B—C1—H1C 109.5  C6—C7—H7  119.3
N1—C2—C3  110.8 (2)  C7—C8—C9  119.1 (2)
N1—C2—H2A  109.5  C7—C8—H8  120.4
C3—C2—H2A  109.5  C9—C8—H8  120.4
N1—C2—H2B  109.5  C10—C9—C8  119.9 (2)
C3—C2—H2B  109.5  C10—C9—I1  120.07 (17)
H2A—C2—H2B  108.1  C8—C9—I1  120.00 (18)
N2—C3—C2  110.0 (2)  C9—C10—C11  120.1 (2)
N2—C3—H3A  109.7  C9—C10—H10  119.9
C2—C3—H3A  109.7  C11—C10—H10  120.8 (2)
N2—C3—H3B  109.7  C6—C11—C10  119.6
C2—C3—H3B  109.7  C6—C11—H11  119.6
H3A—C3—H3B  108.2  C10—C11—H11  119.6
N2—C4—C5  110.2 (2)  O1—C12—O2  124.5 (2)
N2—C4—H4A  109.6  O1—C12—C6  118.7 (2)
C5—C4—H4A  109.6  O2—C12—C6  116.7 (2)
N2—C4—H4B  109.6  C2—N1—C5  110.3 (2)
C5—C4—H4B  109.6  C2—N1—C1  110.5 (2)
H4A—C4—H4B  108.1  C5—N1—C1  109.6 (2)
N1—C5—C4  111.1 (2)  C3—N2—C4  110.6 (2)
N1—C5—H5A  109.4  C3—N2—H21  112 (2)
C4—C5—H5A  109.4  C4—N2—H21  108 (2)
N1—C5—H5B  109.4  C3—N2—H22  108 (2)
C4—C5—H5B  109.4  C4—N2—H22  111 (2)
H5A—C5—H5B  108  H21—N2—H22  108 (3)
N1—C2—C3—N2  58.1 (3)  C9—C10—C11—C6  0.6 (4)
N2—C4—C5—N1  −56.7 (3)  C11—C6—C12—O1  18.7 (4)
C11—C6—C7—C8  −0.4 (4)  C7—C6—C12—O1  −161.8 (2)
C12—C6—C7—C8  −179.8 (2)  C11—C6—C12—O2  −161.4 (2)
C6—C7—C8—C9  1.0 (4)  C7—C6—C12—O2  18.0 (4)
C7—C8—C9—C10  −0.8 (4)  C3—C2—N1—C5  −58.7 (3)
C7—C8—C9—I1  177.94 (18)  C3—C2—N1—C1  180.0 (2)
C8—C9—C10—C11  0.0 (4)  C4—C5—N1—C2  58.0 (3)
I1—C9—C10—C11  −178.72 (18)  C4—C5—N1—C1  179.9 (2)
C7—C6—C11—C10  −0.4 (4)  C2—C3—N2—C4  −56.8 (3)
C12—C6—C11—C10  179.0 (2)  C5—C4—N2—C3  56.1 (3)

Hydrogen-bond geometry (Å, °)

$Cg2$ is the centroid of the C6–C11 ring.

| D—H······A          | D—H | H······A   | D······A  | D—H······A |
|---------------------|-----|-----------|-----------|-----------|
| C3—H3.4······O2i    | 0.97| 2.56      | 3.272 (3) | 130       |
| C5—H5.4······O1ii   | 0.97| 2.56      | 3.469 (3) | 156       |
| N2—H21······O2iii   | 0.87(2)| 1.83(2)  | 2.696 (3) | 172 (3)   |

Acta Cryst. (2021). E77, 1135-1139
| Bond                  | d (Å)     | e (Å)     | d (Å)     | ϕ (°)     |
|----------------------|-----------|-----------|-----------|-----------|
| N2—H22···O1\textsuperscript{iii} | 0.88 (2)  | 1.83 (2)  | 2.700 (3) | 172 (3)   |
| C4—H4B···Cg2\textsuperscript{iv} | 0.97      | 2.59      | 3.473 (3) | 152       |

Symmetry codes: (i) x, y+1, z; (ii) −x+2, −y+1, −z+1; (iii) −x+1, −y+1, −z+1; (iv) −x, −y, −z.