Crystal structure of ethidium heptafluorobutyrate

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In the title compound (systematic name: 3,8-diamino-5-ethyl-6-phenylphenanthridin-5-ium 2,2,3,3,4,4,4-heptafluorobutyrate), C_{21}H_{20}N_{3}^{+}/C_{1}C_{4}F_{7}O_{2}^{-}, two ethidium ions, C_{21}H_{20}N_{3}^{+} form a dimerized structure due to π–π interactions, even though they are positively charged. The heptafluorobutyrate anions are connected to neighbouring cation dimers via hydrogen-bonding interactions, the hydrogen-bonding donor sites of the –NH_{2} groups of the ethidium ions connecting to the hydrogen-bonding acceptor sites of the –COO^{-} groups of the heptafluorobutyrate anions.

Structure description

Ethidium salts are widely used in scientific research as a result of their important applications, including as intercalators for DNA (Chen et al., 2000) and as building units for covalent organic frameworks (Ma et al., 2016). In this study, the structure of an ethidium salt with a heptafluorobutyrate anion is reported (Fig. 1). Two ethidium cations form a dimerised structure (Fig. 2) via π–π stacking and four dimeric pairs are located in the unit cell. There are two ethidium cations and two heptafluorobutyrate anions as the crystallographically independent components. The ethidium cations do not exhibit a completely planar structure but instead show a slightly bent shape (C_{19}⋯C_{11}:C_{24} = 170.82°, C_{12}⋯C_{3}:C_{25} = 165.57°). The closest Cg⋯Cg separation between the ethidium cations is 3.7502 (3) Å, indicating the presence of a π–π interaction. Some hydrogen bonds with relatively short distances are observed between the ethidium cation and heptafluorobutyrate anion (e.g., N_{3}⋯H_{3}A⋯O_{1} = 2.899 Å, N_{3}⋯H_{3}⋯O_{4} = 2.909 Å, N_{5}⋯H_{5}A⋯O_{4} = 2.935 Å, N_{4}⋯H_{4}A⋯O_{2} = 2.990 Å, N_{6}⋯H_{6}A⋯O_{3} = 2.939 Å; Table 1), which would be related to the formation of this packing structure (Fig. 3).

Synthesis and crystallization

A methanol solution (1 ml) of silver(I) heptafluorobutyrate (64.2 mg, 0.20 mmol) was mixed with a methanol solution (30 ml) of ethidium bromide (78.9 mg, 0.20 mmol) and
then the mixture was stirred for 30 minutes at room temperature. The insoluble precipitate was removed by centrifugation. The remaining solution was evaporated to obtain a crude powder. The crude powder was dissolved in a mixed solvent (methanol:water = 1:1) and red crystals of the target compound were obtained by slow evaporation of the solution after 9 d at room temperature.
Refinement
Crystal data, data collection and structure refinement details are summarized in Table 2.

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References
Brandenburg, K. (2014). DIAMOND, Crystal Impact GbR, Bonn, Germany.

Brucker (2021). APEX4 and SAINT. Bruker AXS Inc., Madison, Wisconsin, USA.

Burla, M. C., Caliandro, R., Carrozzini, B., Cascarano, G. L., Cuoci, C., Giacovazzo, C., Mallamo, M., Mazzone, A. & Polidori, G. (2015). J. Appl. Cryst. 48, 306–309.

Chen, W., Turro, N. J. & Tomalia, D. A. (2000). Langmuir, 16, 15–19.

Kabuto, C., Akine, S., Nemoto, T. & Kwon, E. (2009). J. Crystallogr. Soc. Japan, 51, 218–224.

Krause, L., Herbst-Irmer, R., Sheldrick, G. M. & Stalke, D. (2015). J. Appl. Cryst. 48, 3–10.

Ma, H., Liu, B., Li, B., Zhang, L., Li, Y.-G., Tan, H.-Q., Zang, H.-Y. & Zhu, G. (2016). J. Am. Chem. Soc. 138, 5897–5903.

Sheldrick, G. M. (2015). Acta Cryst. C71, 3–8.
full crystallographic data

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Ethidium heptafluorobutyrate

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3,8-Diamino-5-ethyl-6-phenylphenanthridin-5-iium 2,2,3,3,4,4,4-heptafluorobutyrate

Crystal data

C21H20N3+·C4F7O2−  
Mr = 527.44  
Monoclinic, P21/n  
a = 12.1592 (8) Å  
b = 18.9260 (14) Å  
c = 20.3097 (17) Å  
β = 91.474 (3)°  
V = 4672.2 (6) Å³  
Z = 8

F(000) = 2160  
Dm = 1.500 Mg m⁻³  
Mo Kα radiation, λ = 0.71069 Å  
Cell parameters from 7105 reflections  
θ = 2.2–27.2°  
μ = 0.13 mm⁻¹  
T = 100 K  
Block, red  
0.25 × 0.20 × 0.15 mm

Data collection

Bruker PHOTON II CPAD  
diffractometer  
Radiation source: fine-focus sealed tube  
φ and θ scans  
Absorption correction: multi-scan  
(SADABS; Krause et al., 2015)  
Tmin = 0.605, Tmax = 0.711  
58553 measured reflections

Refinement

Refinement on F²  
Least-squares matrix: full  
R[F² > 2σ(F²)] = 0.089  
wR(F²) = 0.218  
S = 1.11  
12404 reflections  
669 parameters  
0 restraints

Hydrogen site location: inferred from  
neighbouring sites  
H-atom parameters constrained  
w = 1/[σ²(FO²) + (0.0532P)² + 9.0949P]  
where P = (FO² + 2FC²)/3  
(Δ/σ)max < 0.001  
Δρmax = 0.47 e Å⁻³  
Δρmin = −0.45 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.
**Refinement.** Refinement of F² against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F², conventional R-factors R are based on F, with F set to zero for negative F². The threshold expression of F² > 2σ(F²) is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F² are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

All of hydrogen atoms are geometrically fixed using a riding-model approximation with C–H = 0.95 (for phenyl), 0.98 (for methyl), 0.99 (for methylene), and N–H = 0.88 Å.

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

| x         | y         | z         | Uiso*/Ueq |
|-----------|-----------|-----------|-----------|
| F1        | 1.10423 (16) | 0.34876 (11) | 0.57616 (10) | 0.0348 (5) |
| O1        | 0.81718 (17) | −0.14092 (12) | 0.72561 (11) | 0.0272 (5) |
| F2        | 0.69849 (17) | 0.00943 (11) | 0.65047 (11) | 0.0416 (5) |
| N1        | 0.64572 (19) | 0.32175 (13) | 0.36249 (12) | 0.0194 (5) |
| N2        | 0.60689 (19) | 0.18575 (12) | 0.61439 (12) | 0.0190 (5) |
| F3        | 0.96344 (17) | −0.02675 (11) | 0.71179 (12) | 0.0432 (6) |
| F4        | 1.27314 (17) | 0.37587 (12) | 0.55497 (10) | 0.0396 (5) |
| F5        | 0.91654 (18) | −0.09184 (11) | 0.59264 (11) | 0.0419 (5) |
| F6        | 1.25336 (18) | 0.50412 (11) | 0.60348 (12) | 0.0447 (6) |
| F7        | 0.8910 (2)   | 0.07025 (11) | 0.67357 (12) | 0.0483 (6) |
| C1        | 0.6334 (2)   | 0.35297 (14) | 0.47691 (14) | 0.0179 (5) |
| F8        | 0.7581 (2)   | −0.00011 (11) | 0.75221 (11) | 0.0463 (6) |
| N3        | 0.9615 (2)   | 0.19489 (14) | 0.28830 (13) | 0.0263 (5) |
| H3        | 0.923744     | 0.181066     | 0.253059     | 0.032*      |
| H3A       | 1.029377     | 0.179993     | 0.295114     | 0.032*      |
| O2        | 1.15659 (18) | 0.33758 (13) | 0.70389 (12) | 0.0324 (5) |
| F9        | 1.12268 (19) | 0.47801 (13) | 0.53262 (11) | 0.0480 (6) |
| O3        | 0.66684 (18) | −0.12731 (13) | 0.66078 (13) | 0.0346 (5) |
| C2        | 0.5845 (2)   | 0.34299 (14) | 0.41299 (14) | 0.0179 (5) |
| F10       | 0.8540 (2)   | 0.00707 (14) | 0.55507 (12) | 0.0572 (7) |
| F11       | 0.98781 (18) | 0.45093 (13) | 0.64091 (14) | 0.0536 (6) |
| C3        | 0.7493 (2)   | 0.34630 (14) | 0.48463 (14) | 0.0169 (5) |
| C4        | 0.8107 (2)   | 0.31722 (14) | 0.43182 (14) | 0.0176 (5) |
| C5        | 0.7883 (2)   | 0.13477 (14) | 0.44688 (15) | 0.0203 (6) |
| H5        | 0.866288     | 0.137570     | 0.447140     | 0.024*      |
| N4        | 0.9273 (2)   | 0.28652 (14) | 0.72447 (13) | 0.0272 (6) |
| H4        | 0.887391     | 0.301183     | 0.757333     | 0.033*      |
| H4A       | 0.997967     | 0.296386     | 0.723928     | 0.033*      |
| C6        | 0.5683 (2)   | 0.37085 (14) | 0.53133 (14) | 0.0183 (5) |
| H6        | 0.490632     | 0.374111     | 0.525647     | 0.022*      |
| C7        | 0.7207 (2)   | 0.19843 (14) | 0.61789 (14) | 0.0185 (5) |
| C8        | 0.7560 (2)   | 0.30125 (14) | 0.37144 (14) | 0.0179 (5) |
| C9        | 0.5560 (2)   | 0.16008 (14) | 0.56038 (14) | 0.0189 (5) |
| C10       | 0.6156 (2)   | 0.14439 (14) | 0.50267 (14) | 0.0188 (5) |
| C11       | 0.7837 (2)   | 0.17952 (14) | 0.56289 (14) | 0.0181 (5) |
| C12       | 0.6164 (2)   | 0.38361 (14) | 0.59262 (14) | 0.0192 (5) |
| C13       | 0.5596 (2)   | 0.12177 (15) | 0.44471 (14) | 0.0208 (6) |
| Atom | x     | y     | z     | Uiso  |
|------|-------|-------|-------|-------|
| H13  | 0.482034 | 0.115938 | 0.444544 | 0.025* |
| C14  | 0.7315 (2) | 0.15223 (14) | 0.50495 (14) | 0.0178 (5) |
| C15  | 0.7690 (2) | 0.23179 (15) | 0.67315 (14) | 0.0207 (6) |
| H15  | 0.725365 | 0.242914 | 0.709883 | 0.025* |
| F12  | 1.1169 (2) | 0.49419 (13) | 0.70211 (12) | 0.0530 (6) |
| C16  | 0.4646 (2) | 0.35300 (15) | 0.40168 (14) | 0.0194 (5) |
| C17  | 0.8079 (2) | 0.26311 (15) | 0.32207 (14) | 0.0207 (6) |
| H17  | 0.769895 | 0.253550 | 0.281587 | 0.025* |
| C18  | 0.8990 (2) | 0.19243 (15) | 0.56844 (15) | 0.0208 (6) |
| H18  | 0.944662 | 0.177669 | 0.533780 | 0.025* |
| C19  | 0.8796 (2) | 0.24854 (15) | 0.67443 (15) | 0.0215 (6) |
| C20  | 0.9232 (2) | 0.29873 (15) | 0.43770 (14) | 0.0200 (5) |
| H20  | 0.964477 | 0.312917 | 0.475781 | 0.024* |
| N5   | 0.5568 (2) | 0.39977 (14) | 0.64670 (12) | 0.0252 (5) |
| H5A  | 0.484588 | 0.402420 | 0.643371 | 0.030* |
| H5B  | 0.590542 | 0.407535 | 0.684857 | 0.030* |
| C21  | 0.7971 (2) | 0.36382 (15) | 0.54669 (14) | 0.0192 (5) |
| H21  | 0.874886 | 0.363064 | 0.552401 | 0.023* |
| C22  | 0.7334 (2) | 0.38185 (15) | 0.59871 (14) | 0.0202 (6) |
| H22  | 0.768009 | 0.393437 | 0.639774 | 0.024* |
| F13  | 1.0447 (2) | 0.55673 (12) | 0.62469 (15) | 0.0620 (8) |
| C23  | 0.7332 (2) | 0.11406 (15) | 0.39074 (15) | 0.0226 (6) |
| H23  | 0.773730 | 0.103458 | 0.352614 | 0.027* |
| C24  | 0.6170 (2) | 0.10799 (15) | 0.38796 (14) | 0.0212 (6) |
| C25  | 0.9149 (2) | 0.23925 (15) | 0.33223 (14) | 0.0205 (6) |
| C26  | 0.9456 (2) | 0.22516 (15) | 0.62169 (15) | 0.0223 (6) |
| H26  | 1.022906 | 0.232539 | 0.623817 | 0.027* |
| N6   | 0.5651 (2) | 0.08560 (15) | 0.33075 (13) | 0.0296 (6) |
| H6A  | 0.493293 | 0.079612 | 0.329379 | 0.035* |
| H6B  | 0.603644 | 0.077263 | 0.295503 | 0.035* |
| C27  | 0.9738 (2) | 0.26090 (16) | 0.38982 (15) | 0.0218 (6) |
| H27  | 1.049400 | 0.248987 | 0.395220 | 0.026* |
| C28  | 0.4343 (2) | 0.14853 (15) | 0.56064 (14) | 0.0205 (6) |
| O4   | 1.3299 (2) | 0.36498 (19) | 0.68042 (15) | 0.0545 (9) |
| C29  | 1.2309 (2) | 0.35991 (17) | 0.66902 (16) | 0.0260 (6) |
| C30  | 0.4161 (2) | 0.41967 (16) | 0.40651 (15) | 0.0239 (6) |
| H30  | 0.460104 | 0.460049 | 0.415984 | 0.029* |
| C31  | 0.3991 (2) | 0.29412 (16) | 0.38733 (15) | 0.0230 (6) |
| H31  | 0.431873 | 0.248751 | 0.383922 | 0.028* |
| C32  | 0.3920 (3) | 0.08359 (16) | 0.57879 (18) | 0.0290 (7) |
| H32  | 0.440069 | 0.046024 | 0.591124 | 0.035* |
| C33  | 0.5421 (2) | 0.19980 (16) | 0.67456 (14) | 0.0223 (6) |
| H33  | 0.463424 | 0.205209 | 0.661902 | 0.027* |
| H33A | 0.567472 | 0.244567 | 0.695105 | 0.027* |
| C34  | 0.2383 (2) | 0.36769 (18) | 0.38333 (16) | 0.0278 (7) |
| H34  | 0.160998 | 0.372794 | 0.377353 | 0.033* |
| C35  | 0.7493 (2) | −0.10657 (17) | 0.69107 (15) | 0.0244 (6) |
| C36  | 0.2866 (2) | 0.30157 (17) | 0.37806 (16) | 0.0266 (6) |
|      |        |        |        |        |        |        |
|------|--------|--------|--------|--------|--------|--------|
| H36  | 0.242373 | 0.261402 | 0.368075 | 0.032*  |
| C37  | 0.6013 (2) | 0.32601 (18) | 0.29317 (15) | 0.0259 (6)  |
| H37  | 0.520477 | 0.332442 | 0.293546 | 0.031*  |
| H37A | 0.616777 | 0.281270 | 0.269924 | 0.031*  |
| C38  | 0.8860 (3) | −0.00120 (17) | 0.66979 (17) | 0.0303 (7)  |
| C39  | 0.3034 (3) | 0.42642 (17) | 0.39738 (16) | 0.0284 (7)  |
| H39  | 0.270132 | 0.471666 | 0.400746 | 0.034*  |
| C40  | 0.2508 (3) | 0.19222 (18) | 0.54011 (17) | 0.0299 (7)  |
| H40  | 0.202339 | 0.229124 | 0.526610 | 0.036*  |
| C41  | 1.1930 (2) | 0.38599 (17) | 0.59907 (16) | 0.0262 (6)  |
| C42  | 0.5551 (3) | 0.14010 (18) | 0.72407 (16) | 0.0303 (7)  |
| H42  | 0.525777 | 0.096331 | 0.704727 | 0.046*  |
| H42A | 0.514629 | 0.151654 | 0.763772 | 0.046*  |
| H42B | 0.633197 | 0.133786 | 0.735664 | 0.046*  |
| C43  | 1.1618 (3) | 0.46488 (18) | 0.59370 (17) | 0.0303 (7)  |
| C44  | 0.3635 (2) | 0.20300 (17) | 0.54076 (16) | 0.0254 (6)  |
| H44  | 0.392532 | 0.247307 | 0.527260 | 0.030*  |
| C45  | 0.7712 (3) | −0.02542 (17) | 0.69042 (16) | 0.0270 (6)  |
| F14  | 1.0221 (2) | −0.00067 (16) | 0.59017 (17) | 0.0744 (9)  |
| C46  | 0.2090 (3) | 0.12757 (19) | 0.55915 (19) | 0.0349 (8)  |
| H46  | 0.131748 | 0.120142 | 0.558691 | 0.042*  |
| C47  | 0.2793 (3) | 0.07386 (18) | 0.5788 (2) | 0.0378 (8) |
| H47  | 0.249992 | 0.029861 | 0.592485 | 0.045*  |
| C48  | 0.6529 (3) | 0.3871 (2) | 0.25683 (17) | 0.0380 (8)  |
| H48  | 0.636602 | 0.431470 | 0.279466 | 0.057*  |
| C48A | 0.622816 | 0.38958 | 0.211641 | 0.057*  |
| H48B | 0.732801 | 0.380377 | 0.255904 | 0.057*  |
| C49  | 1.0752 (3) | 0.49156 (19) | 0.6410 (2) | 0.0380 (8)  |
| C50  | 0.9189 (3) | −0.0216 (2) | 0.6003 (2) | 0.0398 (9)  |

Atomic displacement parameters (Å²)

|      |  \( U_1^{11} \) |  \( U_2^{22} \) |  \( U_3^{33} \) |  \( U_1^{12} \) |  \( U_1^{13} \) |  \( U_2^{23} \) |
|------|----------------|----------------|----------------|----------------|----------------|----------------|
| F1   | 0.0375 (11)    | 0.0321 (10)    | 0.0343 (11)    | −0.0072 (8)    | −0.0076 (8)    | −0.0019 (8)    |
| O1   | 0.0229 (10)    | 0.0265 (11)    | 0.0321 (12)    | −0.0015 (8)    | 0.0014 (9)     | 0.0064 (9)     |
| F2   | 0.0363 (11)    | 0.0372 (12)    | 0.0511 (13)    | 0.0142 (9)     | −0.0055 (9)    | 0.0075 (10)    |
| N1   | 0.0186 (11)    | 0.0224 (12)    | 0.0172 (12)    | −0.0015 (9)    | 0.0004 (9)     | −0.0017 (9)    |
| N2   | 0.0182 (11)    | 0.0184 (11)    | 0.0208 (12)    | 0.0014 (9)     | 0.0052 (9)     | −0.0012 (9)    |
| F3   | 0.0340 (11)    | 0.0366 (12)    | 0.0578 (14)    | −0.0118 (9)    | −0.0205 (10)   | 0.0162 (10)    |
| F4   | 0.0418 (11)    | 0.0466 (12)    | 0.0312 (11)    | 0.0077 (9)     | 0.0151 (9)     | 0.0037 (9)     |
| F5   | 0.0514 (13)    | 0.0348 (11)    | 0.0401 (12)    | 0.0074 (9)     | 0.0159 (10)    | 0.0062 (9)     |
| F6   | 0.0497 (12)    | 0.0328 (11)    | 0.0590 (15)    | −0.0151 (9)    | 0.0084 (10)    | 0.0105 (10)    |
| F7   | 0.0676 (15)    | 0.0212 (10)    | 0.0555 (15)    | −0.0098 (10)   | −0.0093 (12)   | 0.0071 (9)     |
| C1   | 0.0197 (13)    | 0.0133 (12)    | 0.0207 (14)    | −0.0029 (9)    | 0.0005 (10)    | 0.0000 (10)    |
| F8   | 0.0762 (16)    | 0.0325 (11)    | 0.0308 (11)    | 0.0037 (10)    | 0.0115 (10)    | −0.0092 (9)    |
| N3   | 0.0231 (12)    | 0.0319 (14)    | 0.0239 (13)    | 0.0063 (10)    | 0.0040 (10)    | −0.0028 (11)   |
| O2   | 0.0248 (11)    | 0.0415 (14)    | 0.0310 (12)    | −0.0027 (10)   | 0.0021 (9)     | 0.0082 (10)    |
| F9   | 0.0575 (14)    | 0.0498 (14)    | 0.0365 (12)    | 0.0109 (11)    | −0.0017 (10)   | 0.0192 (10)    |

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| Atoms | U^21 (Å^2) | U^22 (Å^2) | U^23 (Å^2) | U^31 (Å^2) | U^32 (Å^2) | U^33 (Å^2) |
|-------|------------|------------|------------|------------|------------|------------|
| O3    | 0.0241     | 0.0366     | 0.0427     | -0.0017    | -0.0050    | -0.0055    |
| C2    | 0.0181     | 0.0151     | 0.0204     | -0.0012    | 0.0007     | 0.0008     |
| F10   | 0.0867     | 0.0517     | 0.0334     | 0.0229     | 0.0070     | 0.0139     |
| F11   | 0.0338     | 0.0446     | 0.0832     | -0.0017    | 0.0185     | 0.0066     |
| C3    | 0.0190     | 0.0128     | 0.0189     | -0.0022    | 0.0002     | 0.0020     |
| C4    | 0.0179     | 0.0145     | 0.0205     | -0.0038    | -0.0004    | 0.0021     |
| C5    | 0.0194     | 0.0152     | 0.0265     | -0.0003    | 0.0046     | 0.0019     |
| C6    | 0.0213     | 0.0302     | 0.0297     | 0.0004     | -0.0042    | -0.0048    |
| C7    | 0.0216     | 0.0176     | 0.0203     | -0.0014    | 0.0001     | 0.0003     |
| C8    | 0.0213     | 0.0150     | 0.0196     | 0.0014     | 0.0033     | 0.0028     |
| C9    | 0.0190     | 0.0150     | 0.0192     | 0.0021     | 0.0040     | 0.0039     |
| C10   | 0.0204     | 0.0150     | 0.0192     | 0.0021     | 0.0040     | 0.0039     |
| C11   | 0.0217     | 0.0150     | 0.0211     | -0.0017    | 0.0025     | 0.0013     |
| C12   | 0.0193     | 0.0205     | 0.0229     | 0.0020     | 0.0011     | 0.0026     |
| C13   | 0.0189     | 0.0145     | 0.0202     | 0.0016     | 0.0046     | 0.0041     |
| C14   | 0.0215     | 0.0199     | 0.0208     | 0.0033     | 0.0029     | 0.0016     |
| C15   | 0.0209     | 0.0210     | 0.0223     | -0.0028    | 0.0008     | 0.0022     |
| N5    | 0.0215     | 0.0357     | 0.0184     | 0.0031     | 0.0100     | 0.0024     |
| C17   | 0.0202     | 0.0186     | 0.0199     | 0.0002     | 0.0029     | 0.0020     |
| C18   | 0.0177     | 0.0196     | 0.0254     | 0.0031     | 0.0051     | 0.0037     |
| C19   | 0.0243     | 0.0172     | 0.0230     | 0.0008     | -0.0021    | 0.0023     |
| C20   | 0.0217     | 0.0210     | 0.0223     | -0.0028    | 0.0008     | 0.0022     |
| N6    | 0.0261     | 0.0400     | 0.0225     | 0.0026     | 0.0012     | -0.0031    |
| C27   | 0.0162     | 0.0235     | 0.0259     | -0.0008    | 0.0021     | 0.0051     |
| C28   | 0.0218     | 0.0202     | 0.0199     | -0.0012    | 0.0047     | -0.0007    |
| C4    | 0.0221     | 0.093      | 0.0479     | -0.0125    | -0.0055    | 0.0342     |
| C29   | 0.0220     | 0.0268     | 0.0293     | -0.0008    | -0.0066    | 0.0077     |
| C30   | 0.0271     | 0.0204     | 0.0240     | 0.0000     | -0.0030    | 0.0018     |
| C31   | 0.0214     | 0.0216     | 0.0259     | -0.0011    | 0.0003     | -0.0020    |
| C32   | 0.0234     | 0.0194     | 0.045      | 0.0017     | 0.0037     | 0.0027     |
| C33   | 0.0196     | 0.0270     | 0.0207     | 0.0022     | 0.0077     | -0.0030    |
| C34   | 0.0168     | 0.0363     | 0.0302     | 0.0034     | -0.0005    | 0.0008     |
| C35   | 0.0202     | 0.0287     | 0.0244     | 0.0024     | 0.0045     | 0.0002     |
| C36   | 0.0193     | 0.0304     | 0.0300     | -0.0032    | 0.0007     | -0.0028    |
| C37   | 0.0199     | 0.0395     | 0.0182     | 0.0009     | -0.0030    | -0.0041    |
| C38   | 0.0333     | 0.0211     | 0.0361     | -0.0038    | -0.0069    | 0.0067     |
| C39   | 0.0305     | 0.0220     | 0.0324     | 0.0082     | -0.0027    | 0.0024     |
| C40   | 0.0223     | 0.0293     | 0.0381     | 0.0070     | 0.0024     | 0.0008     |
| Atom  | U1  | U2  | U3  | U12 | U13 | U23 |
|-------|-----|-----|-----|-----|-----|-----|
| C41   | 0.0236 (14) | 0.0300 (16) | 0.0252 (16) | -0.0015 (12) | 0.0030 (12) | 0.0020 (12) |
| C42   | 0.0347 (17) | 0.0319 (17) | 0.0249 (16) | 0.0002 (13) | 0.0108 (13) | -0.0008 (13) |
| C43   | 0.0310 (16) | 0.0307 (17) | 0.0292 (17) | -0.0023 (13) | 0.0011 (13) | 0.0073 (13) |
| C44   | 0.0230 (14) | 0.0221 (14) | 0.0312 (16) | 0.0007 (11) | 0.0031 (12) | 0.0042 (12) |
| C45   | 0.0307 (16) | 0.0248 (15) | 0.0254 (16) | 0.0078 (12) | -0.0009 (12) | -0.0005 (12) |
| F14   | 0.0552 (16) | 0.0700 (19) | 0.100 (2) | -0.0157 (14) | 0.0377 (16) | 0.0174 (17) |
| C46   | 0.0200 (14) | 0.0347 (18) | 0.050 (2) | -0.0007 (13) | 0.0045 (14) | -0.0023 (16) |
| C47   | 0.0261 (16) | 0.0257 (17) | 0.062 (2) | -0.0063 (13) | 0.0062 (16) | 0.0044 (16) |
| C48   | 0.0379 (19) | 0.051 (2) | 0.0247 (17) | 0.0022 (16) | -0.0039 (14) | 0.0114 (15) |
| C49   | 0.043 (2) | 0.0252 (17) | 0.047 (2) | 0.0019 (14) | 0.0104 (16) | 0.0055 (15) |
| C50   | 0.0394 (19) | 0.036 (2) | 0.045 (2) | 0.0013 (15) | 0.0103 (16) | 0.0153 (16) |

**Geometric parameters (Å, °)**

| Bond/Angle | Length/Distance | Angle |
|------------|----------------|-------|
| F1—C41    | 1.361 (4)      |       |
| O1—C35    | 1.252 (4)      |       |
| F2—C45    | 1.356 (4)      |       |
| N1—C2     | 1.344 (4)      |       |
| N1—C8     | 1.403 (3)      |       |
| N1—C37    | 1.497 (4)      |       |
| N2—C7     | 1.405 (3)      |       |
| N2—C32    | 1.494 (3)      |       |
| F3—C38    | 1.344 (4)      |       |
| F4—C41    | 1.354 (4)      |       |
| F5—C50    | 1.338 (4)      |       |
| F6—C43    | 1.349 (4)      |       |
| F7—C38    | 1.356 (4)      |       |
| C1—C6     | 1.417 (4)      |       |
| C1—C3     | 1.419 (4)      |       |
| C1—C2     | 1.427 (4)      |       |
| F8—C45    | 1.356 (4)      |       |
| N3—C25    | 1.359 (4)      |       |
| N3—H3     | 0.8800         |       |
| O2—C29    | 1.237 (4)      |       |
| F9—C43    | 1.340 (4)      |       |
| O3—C35    | 1.227 (4)      |       |
| C2—C16    | 1.482 (4)      |       |
| F10—C50   | 1.313 (4)      |       |
| F11—C49   | 1.312 (4)      |       |
| C3—C21    | 1.414 (4)      |       |
| C3—C4     | 1.432 (4)      |       |
| C4—C8     | 1.413 (4)      |       |
| C4—C20    | 1.414 (4)      |       |
| C5—C23    | 1.365 (4)      |       |
| C5—C14    | 1.421 (4)      |       |
| C5—H5     | 0.9500         |       |

*IUCrData (2022). 7, x220884*
N4—C19 1.362 (4)  C34—H34 0.9500
N4—H4  0.8800    C35—C45 1.559 (4)
N4—H4A 0.8800    C36—H36 0.9500
C6—C12 1.383 (4)  C37—C48 1.517 (5)
C6—H6  0.9500    C37—H37 0.9900
C7—C15 1.403 (4)  C37—H37A 0.9900
C7—C11 1.416 (4)  C38—C50 1.526 (5)
C8—C17 1.399 (4)  C38—C45 1.538 (5)
C9—C10 1.425 (4)  C39—H39 0.9500
C9—C28 1.496 (4)  C40—C46 1.384 (5)
C10—C13 1.411 (4)  C40—C44 1.385 (4)
C10—C14 1.416 (4)  C40—H40 0.9500
C11—C14 1.420 (4)  C41—C43 1.544 (5)
C11—C18 1.424 (4)  C42—H42 0.9800
C12—N5  1.366 (4)  C42—H42A 0.9800
C12—C22 1.425 (4)  C42—H42B 0.9800
C13—C24 1.387 (4)  C43—C49 1.529 (5)
C13—H13 0.9500    C44—H44 0.9500
C15—C19 1.381 (4)  F14—C50 1.337 (4)
C15—H15 0.9500    O4—C29—O2 115.2 (3)
F12—C49 1.330 (5)  O4—C29—C41 114.4 (3)
C16—C31 1.397 (4)  O2—C29—C41 115.2 (3)
C16—C30 1.397 (4)  C32—C28—C9 119.6 (3)
C17—C25 1.387 (4)  C32—C28—C14 120.1 (3)
C17—H17 0.9500    C32—C28—C4 120.3 (3)
C2—N1—C8 122.0 (2) C32—C28—C37 119.9 (3)
C2—N1—C37 120.5 (2) C32—C28—C30 119.2 (3)
C8—N1—C37 117.2 (2) C44—C29—O2 133.4 (3)
C9—N2—C7 122.5 (2)  O4—C29—C41 114.4 (3)
C9—N2—C33 119.6 (2)  O2—C29—C41 115.2 (3)
C7—N2—C33 117.9 (2)  C39—C30—C16 119.5 (3)
C6—C1—C3 120.5 (3)  C39—C30—H30 120.2
C6—C1—C2 120.9 (2)  C39—C30—H30 120.2
C3—C1—C2 118.6 (2)  C16—C31—C14 120.3 (3)
C25—N3—H3 120.0    C36—C31—C14 119.9
C25—N3—H3A 120.0    C16—C31—H31 119.9
H3—N3—H3A 120.0    C16—C31—H31 119.9
N1—C2—C1 120.5 (2)  C47—C32—C28 119.5 (3)
N1—C2—C16 118.8 (2)  C47—C32—H32 120.2
C1—C2—C16 120.6 (2)  C28—C32—H32 120.2
C21—C3—C1 117.5 (2)  C28—C32—C21 120.2
C21—C3—C4 123.2 (2)  N2—C33—H33 111.2 (2)
C1—C3—C4 119.1 (2)  N2—C33—H33A 109.4
C8—C4—C20 117.0 (3)  C42—C33—H33A 109.4
C8—C4—C3 119.3 (2)  H33—C33—H33A 108.0
C20—C4—C3 123.6 (3)  H33—C33—H33A 108.0
C23—C5—C14 121.4 (3)  C36—C34—C39 119.9 (3)
| Bond                  | Angle (°) | Bond                  | Angle (°) |
|-----------------------|-----------|-----------------------|-----------|
| C23—C5—H5            | 119.3     | C36—C34—H34          | 120.1     |
| C14—C5—H5            | 119.3     | C39—C34—H34          | 120.1     |
| C19—N4—H4            | 120.0     | O3—C35—O1            | 129.3 (3) |
| C19—N4—H4A           | 120.0     | O3—C35—C45           | 116.7 (3) |
| C12—C6—C1            | 120.8 (2) | O1—C35—C45           | 113.9 (3) |
| C12—C6—H6            | 119.6     | C31—C36—C34          | 120.0 (3) |
| C1—C6—H6             | 119.6     | C31—C36—H36          | 120.0     |
| C15—C7—N2            | 120.6 (2) | N1—C37—C48           | 110.8 (3) |
| C15—C7—C11           | 121.4 (2) | N1—C37—H37           | 109.5     |
| N2—C7—C11            | 118.0 (3) | C48—C37—H37          | 109.5     |
| C17—C8—N1            | 119.8 (2) | N1—C37—H37A          | 109.5     |
| C17—C8—C4            | 121.4 (2) | C48—C37—H37A         | 109.5     |
| N1—C8—C4             | 118.7 (2) | H37—C37—H37A         | 108.1     |
| N2—C9—C10            | 121.1 (2) | F3—C38—F7            | 107.0 (3) |
| N2—C9—C28            | 119.1 (2) | F3—C38—C50           | 107.4 (3) |
| C10—C9—C28           | 119.7 (3) | F7—C38—C50           | 107.0 (3) |
| C13—C10—C14          | 121.1 (2) | F3—C38—C45           | 110.2 (3) |
| C13—C10—C9           | 120.3 (2) | F7—C38—C45           | 108.8 (3) |
| C14—C10—C9           | 118.5 (3) | C50—C38—C45          | 116.0 (3) |
| C7—C11—C14           | 120.4 (2) | C30—C39—C34          | 120.7 (3) |
| C7—C11—C18           | 116.4 (3) | C30—C39—H39          | 119.7     |
| C14—C11—C18          | 123.1 (3) | C34—C39—H39          | 119.7     |
| N5—C12—C6            | 122.8 (3) | C46—C40—C44          | 119.9 (3) |
| N5—C12—C22           | 119.0 (3) | C46—C40—H40          | 120.1     |
| C6—C12—C22           | 118.2 (3) | C44—C40—H40          | 120.1     |
| C24—C13—C10          | 120.5 (3) | F4—C41—F1            | 106.2 (3) |
| C24—C13—H13          | 119.7     | F4—C41—C43           | 105.7 (3) |
| C10—C13—H13          | 119.7     | F1—C41—C43           | 106.5 (2) |
| C10—C14—C11          | 119.2 (2) | F4—C41—C29           | 110.9 (2) |
| C10—C14—C5           | 116.9 (3) | F1—C41—C29           | 111.1 (2) |
| C11—C14—C5           | 123.8 (2) | C43—C41—C29          | 115.9 (3) |
| C19—C15—C7           | 120.3 (3) | C33—C42—H42          | 109.5     |
| C19—C15—H15          | 119.8     | C33—C42—H42A         | 109.5     |
| C7—C15—H15           | 119.8     | H42—C42—H42A         | 109.5     |
| C31—C16—C30          | 119.7 (3) | C33—C42—H42B         | 109.5     |
| C31—C16—C2           | 119.0 (3) | H42—C42—H42B         | 109.5     |
| C30—C16—C2           | 121.3 (3) | H42A—C42—H42B        | 109.5     |
| C25—C17—C8           | 120.0 (3) | F9—C43—F6            | 107.8 (3) |
| C25—C17—H17          | 120.0     | F9—C43—C49           | 106.7 (3) |
| C8—C17—H17           | 120.0     | F6—C43—C49           | 107.7 (3) |
| C26—C18—C11          | 122.1 (3) | F9—C43—C41           | 109.0 (3) |
| C26—C18—H18          | 118.9     | F6—C43—C41           | 108.7 (3) |
| C11—C18—H18          | 118.9     | C49—C43—C41          | 116.6 (3) |
| N4—C19—C15           | 122.1 (3) | C40—C44—C28          | 119.8 (3) |
| N4—C19—C26           | 119.2 (3) | C40—C44—H44          | 120.1     |
| C15—C19—C26          | 118.8 (3) | C28—C44—H44          | 120.1     |
| C27—C20—C4           | 121.5 (3) | F2—C45—F8            | 107.0 (3) |
C27—C20—H20 119.3  F2—C45—C38 105.9 (3)
C4—C20—H20 119.3  F8—C45—C38 106.0 (3)
C12—N5—H5A 120.0  F2—C45—C35 112.1 (3)
C12—N5—H5B 120.0  F8—C45—C35 108.4 (3)
H5A—N5—H5B 120.0  C38—C45—C35 116.9 (2)
C22—C21—C3 121.2 (3)  C47—C46—C40 120.2 (3)
C22—C21—H21 119.4  C47—C46—H46 119.9
C3—C21—H21 119.4  C40—C46—H46 119.9
C21—C22—C12 121.5 (3)  C46—C47—C32 120.5 (3)
C21—C22—H22 119.3  C46—C47—H47 119.7
C12—C22—H22 119.3  C32—C47—H47 119.7
C5—C23—C24 121.6 (3)  C37—C48—H48 109.5
C5—C23—H23 119.2  C37—C48—H48A 109.5
C24—C23—H23 119.2  H48—C48—H48A 109.5
N6—C24—C13 122.0 (3)  C37—C48—H48B 109.5
N6—C24—C23 119.6 (3)  H48—C48—H48B 109.5
C13—C24—C23 118.3 (3)  H48A—C48—H48B 109.5
N3—C25—C17 120.6 (3)  F11—C49—F13 108.8 (3)
N3—C25—C27 120.7 (3)  F11—C49—F12 108.2 (3)
C17—C25—C27 118.8 (3)  F13—C49—F12 107.2 (3)
C18—C26—C19 120.5 (3)  F11—C49—C43 112.1 (3)
C18—C26—H26 119.7  F13—C49—C43 110.1 (3)
C19—C26—H26 119.7  F12—C49—C43 110.3 (3)
C24—N6—H6A 120.0  F10—C50—F14 108.6 (3)
C24—N6—H6B 120.0  F10—C50—F5 108.6 (3)
H6A—N6—H6B 120.0  F14—C50—F5 107.1 (3)
C20—C27—C25 120.8 (3)  F10—C50—C38 112.0 (3)
C20—C27—H27 119.6  F14—C50—C38 109.7 (3)
C25—C27—H27 119.6  F5—C50—C38 110.7 (3)
C8—N1—C2—C1 7.0 (4)  C8—C17—C25—N3 171.8 (3)
C37—N1—C2—C1 −166.9 (3)  C8—C17—C25—C27 −7.0 (4)
C8—N1—C2—C16 −170.5 (2)  C11—C18—C26—C19 −0.5 (4)
C37—N1—C2—C16 15.6 (4)  N4—C19—C26—C18 −174.4 (3)
C6—C1—C2—N1 −175.8 (3)  C15—C19—C26—C18 5.7 (4)
C3—C1—C2—N1 5.7 (4)  C4—C20—C27—C25 0.4 (4)
C6—C1—C2—C16 1.7 (4)  N3—C25—C27—C20 −172.4 (3)
C3—C1—C2—C16 −176.8 (2)  C17—C25—C27—C20 6.4 (4)
C6—C1—C3—C21 −5.1 (4)  N2—C9—C28—C32 −9.1 (4)
C2—C1—C3—C21 173.4 (2)  C10—C9—C28—C32 88.8 (4)
C6—C1—C3—C4 170.0 (2)  N2—C9—C28—C44 89.8 (3)
C2—C1—C3—C4 −11.5 (4)  C10—C9—C28—C44 −89.5 (3)
C21—C3—C4—C8 180.0 (3)  C31—C16—C30—C39 0.4 (4)
C1—C3—C4—C8 5.1 (4)  C2—C16—C30—C39 −178.2 (3)
C21—C3—C4—C20 4.4 (4)  C30—C16—C31—C36 −0.1 (4)
C1—C3—C4—C20 −170.4 (3)  C2—C16—C31—C36 178.5 (3)
C3—C1—C6—C12 1.4 (4)  C44—C28—C32—C47 −1.8 (5)
C2—C1—C6—C12 −177.1 (3)  C9—C28—C32—C47 179.9 (3)
C9—N2—C7—C15 173.7 (3) C9—N2—C33—C42 99.4 (3)
C33—N2—C7—C15 −8.1 (4) C7—N2—C33—C42 −78.8 (3)
C9—N2—C7—C11 −3.4 (4) C16—C31—C36—C34 −0.3 (5)
C33—N2—C7—C11 174.7 (2) C39—C34—C36—C31 0.6 (5)
C7—N2—C33—C42 −13.5 (4) C2—N1—C37—C48 105.0 (3)
C33—N2—C33—C42 99.4 (3) C8—N1—C37—C48 −69.2 (3)
C9—N2—C33—C42 −8.1 (4) C16—C30—C39—C34 −0.2 (5)
C7—N2—C33—C42 −178.4 (2) C36—C34—C39—C30 −0.3 (5)
C20—C4—C8—C17 5.7 (4) C36—C34—C39—F9 61.8 (3)
C3—C4—C8—C17 −170.1 (3) C39—C34—C39—F9 −50.9 (3)
C20—C4—C8—N1 −177.0 (2) C46—C40—C44—C28 0.0 (5)
C3—C4—C8—N1 7.1 (4) C1—C6—C12—N5 −178.8 (3)
C9—C2—C16—C31 66.4 (4) C1—C6—C12—C22 3.2 (4)
C9—C2—C16—C31 −111.1 (3) N1—C2—C16—C31 66.4 (4)
C1—C2—C16—C31 −115.0 (3) C1—C2—C16—C30 67.5 (4)
C1—C2—C16—C30 66.4 (4) N1—C2—C16—C30 −115.0 (3)
C1—C2—C16—C30 −111.1 (3) C1—C2—C16—C30 67.5 (4)
C1—C2—C16—C30 −175.5 (3) N2—C7—C15—C19 −175.5 (3)
C9—C2—C16—C30 −175.5 (3) C16—C31—C36—C34 −0.3 (5)
C7—C15—C19 −175.5 (3) C15—C19—C35—C36 −1.0 (6)
C11—C7—C15—C19 1.5 (4) N1—C2—C16—C30 −115.0 (3)
C11—C7—C15—C19 −175.5 (3) C1—C2—C16—C30 67.5 (4)
C11—C7—C15—C19 1.5 (4) N1—C2—C16—C30 −176.3 (3)
C9—C2—C16—C30 −176.3 (3) N1—C2—C16—C30 67.5 (4)
C1—C2—C16—C30 −176.3 (3) C1—C2—C16—C30 −111.1 (3)
C2—C1—C6—C12 7.1 (4) C1—C2—C16—C31 66.4 (4)
C2—C1—C6—C12 −111.1 (3) C1—C2—C16—C31 −111.1 (3)
C1—C2—C16—C31 66.4 (4) C1—C2—C16—C31 −111.1 (3)
C1—C2—C16—C31 −115.0 (3) C1—C2—C16—C31 67.5 (4)
C1—C2—C16—C31 67.5 (4) C1—C2—C16—C30 −115.0 (3)
C1—C2—C16—C30 67.5 (4) C1—C2—C16—C30 −176.3 (3)
C1—C2—C16—C30 −176.3 (3) C1—C2—C16—C30 67.5 (4)
C1—C2—C16—C30 67.5 (4) C1—C2—C16—C30 −111.1 (3)
C1—C2—C16—C30 −111.1 (3) C1—C2—C16—C30 67.5 (4)
C7—C15—C19—N4 174.0 (3) F6—C43—C49—F13 66.7 (4)
C7—C15—C19—C26 −6.1 (4) C41—C43—C49—F13 −170.9 (3)
C8—C4—C20—C27 −6.3 (4) F9—C43—C49—F12 −166.9 (3)
C3—C4—C20—C27 169.3 (3) F6—C43—C49—F12 −51.4 (4)
C1—C3—C21—C22 4.4 (4) C41—C43—C49—F12 71.1 (4)
C4—C3—C21—C22 −170.5 (3) C4—C38—C50—F10 −173.6 (3)
C3—C21—C22—C12 0.1 (4) F7—C38—C50—F10 −59.0 (4)
N5—C12—C22—C21 177.9 (3) C45—C38—C50—F10 62.6 (4)
C6—C12—C22—C21 −4.0 (4) F3—C38—C50—F10 −52.9 (4)
C14—C5—C23—C24 −0.9 (4) F7—C38—C50—F10 61.7 (4)
C10—C13—C24—N6 179.7 (3) C45—C38—C50—F14 −176.7 (3)
C10—C13—C24—C23 2.9 (4) F3—C38—C50—F5 65.1 (4)
C5—C23—C24—N6 −178.7 (3) F7—C38—C50—F5 179.7 (3)
C5—C23—C24—C23 −1.8 (4) C45—C38—C50—F5 −58.8 (4)

Hydrogen-bond geometry (Å, °)

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|-----|------|-------|--------|
| N3—H3···O4 | 0.88 | 2.04 | 2.909 (4) | 171 |
| N3—H3···O1 | 0.88 | 2.06 | 2.899 (3) | 159 |
| N4—H4···O3 | 0.88 | 2.26 | 3.088 (4) | 158 |
| N4—H4···O2 | 0.88 | 2.13 | 2.991 (3) | 166 |
| C15—H15···O1 | 0.95 | 2.62 | 3.353 (4) | 135 |
| N5—H5···O4 | 0.88 | 2.16 | 2.934 (3) | 146 |
| N5—H5···O1 | 0.88 | 2.30 | 3.076 (3) | 147 |
| N5—H5···F3 | 0.88 | 2.54 | 3.208 (3) | 133 |
| C26—H26···F1 | 0.95 | 2.61 | 3.184 (3) | 119 |
| N6—H6···O3 | 0.88 | 2.16 | 2.938 (3) | 147 |
| N6—H6···O2 | 0.88 | 2.56 | 3.184 (4) | 129 |
| N6—H6···F1 | 0.88 | 2.34 | 3.097 (4) | 144 |
| C33—H33···N3 | 0.99 | 2.59 | 3.223 (4) | 122 |

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