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# (*E*)-5-(2-Chlorophenyl)-7-ethyl-2-oxo-2,3-dihydro-1*H*-thieno[2,3-e][1,4]-diazepin-4-ium 2,4,6-trinitrophenolate

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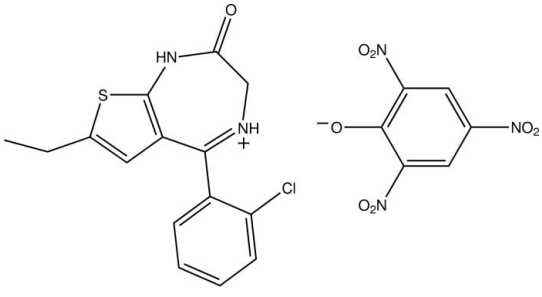
Key indicators: single-crystal X-ray study; $T$ = 200 K; mean $\sigma$(C–C) = 0.002 Å; disorder in main residue; $R$ factor = 0.031; $wR$ factor = 0.081; data-to-parameter ratio = 16.3.

In the title molecular salt, $C_{15}H_{14}ClN_2OS^+\cdot C_6H_2N_3O_7^-$, protonation occurred on the double-bonded N atom. One of the nitro groups shows slight disorder over two orientations, with an occupancy ratio of 0.91:0.09. In the crystal, classical N—H···O hydrogen bonds, as well as C—H···O contacts connect the components into a three-dimensional network. The seven-membered ring adopts a boat-like conformation. The least-squares plane defined by its non-H atoms encloses an angle of 38.99 (6)° with the benzene ring bonded to it.

## Related literature

For pharmaceutical background to benzodiazepines, see: Robol *et al.* (1996); Evans *et al.* (2001). For related structures, see: Scammells *et al.* (2001); Jasinski *et al.* (2010). For graph-set analysis of hydrogen bonds, see: Etter *et al.* (1990); Bernstein *et al.* (1995). For puckering analysis, see: Cremer & Pople (1975).




## Experimental

### Crystal data

$C_{15}H_{14}ClN_2OS^+\cdot C_6H_2N_3O_7^-$
$M_r$ = 533.90
Monoclinic, $P2_1/c$
$a$ = 10.5704 (2) Å
$b$ = 20.0667 (5) Å
$c$ = 11.3741 (2) Å
$\beta$ = 110.666 (1)°
$V$ = 2257.35 (8) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 0.32 mm$^{-1}$
$T$ = 200 K
0.59 × 0.49 × 0.36 mm

### Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2008).
$T_{min}$ = 0.807, $T_{max}$ = 0.892
21254 measured reflections
5607 independent reflections
5073 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.013

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.081
$S$ = 1.05
5607 reflections
343 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.38 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.24 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N1—H71···O31 | 0.870 (19) | 1.865 (19) | 2.6847 (13) | 156.3 (17) |
| N2—H72···O31$^{i}$ | 0.836 (18) | 2.047 (18) | 2.8331 (13) | 156.4 (16) |
| N2—H72···O362$^{i}$ | 0.836 (18) | 2.400 (17) | 2.9495 (16) | 123.9 (14) |
| C2—H2*A*···O321 | 0.99 | 2.49 | 3.2465 (16) | 133 |
| C2—H2*B*···O342$^{ii}$ | 0.99 | 2.48 | 3.2505 (17) | 134 |
| C23—H23···O321$^{iii}$ | 0.95 | 2.51 | 3.4193 (18) | 161 |

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

Data collection: *APEX2* (Bruker, 2010); cell refinement: *SAINT* (Bruker, 2010); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2009).

ASD thanks the University of Mysore for research facilities. HSY thanks R. L. Fine Chem., Bengaluru, for the gift sample.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: PK2384).

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# supplementary materials

*Acta Cryst.* (2012). E**68**, o516-o517 [ **doi:10.1107/S1600536812002607** ]

# (*E*)-5-(2-Chlorophenyl)-7-ethyl-2-oxo-2,3-dihydro-1*H*-thieno[2,3-*e*][1,4]diazepin-4-ium 2,4,6-trinitrophenolate

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## Comment

Five-atom heterocyclic fused benzodiazepine ring systems occupy a prominent place among drugs for treatment of central nervous system (*CNS*) disorders (Robol *et al.*, 1996; Evans *et al.*, 2001). The crystal structures of 6,7-dimethyl-5-phenyl-1*H*-thieno[2,3-*e*][1,4]diazepin-2(3*H*) -one (Scammells *et al.*, 2001) and 5,7-dimethyl-2,3-dihydro-1*H*-1,4- diazepin-4-ium picrate (Jasinski *et al.*, 2010) have been reported. In view of the importance of heterocyclic fused diazepine ring systems, the paper reports the crystal structure of the title compound.

The title compound is the picrate salt of (*E*)-5-(2-chlorophenyl)-7- ethyl-1*H*-thieno[2,3-*e*][1,4]diazepin-2(3*H*)-one. Due to involvement of the free electron pair on the – formally – $sp^3$ hybridized nitrogen atom in amide-type resonance, protonation occurred on the double-bonded nitrogen atom. According to a puckering analysis (Cremer & Pople, 1975), the seven-membered heterocycle adopts a boat-like conformation ($Q_2$: 0.7754 (12) Å, $Q_3$: 0.2281 (12) Å, $\varphi_2$: 262.69 (9)°, $\varphi_3$: 207.4 (3)°) (Fig. 1).

In the crystal structure, classical hydrogen bonds of the N–H···O type as well as C–H···O contacts whose range falls by more than 0.2 Å below the sum of van-der-Waals radii of the corresponding atoms are apparent. While the classical hydrogen bonds are supported by both nitrogen-bound H atoms and have the phenolic as well as nitrogen-bound oxygen atoms as acceptor, the C–H···O contacts exclusively apply the latter type of oxygen atoms as acceptors. The C–H···O contacts stem from both hydrogen atoms of the intracyclic methylene group as well as the hydrogen atom in *ortho* position to the chlorine atom. In terms of graph-set analysis (Etter *et al.*, 1990; Bernstein *et al.*, 1995), the descriptor for the classical hydrogen bonds is *DDD* on the unitary level (due to bifurcation of one of the classical hydrogen bonds). The same descriptor is necessary to describe the C–H···O contacts on the identical level. Metrical information about the contacts is summarized in Table 1. In total, the entities of the title compound are connected to a three-dimensional network. The shortest intercentroid distance between two aromatic systems was measured at 4.8063 (7) Å and is apparent between the thiophene moieties of two neighbouring molecules. (Fig. 2).

## Experimental

(*E*)-5-(2-Chlorophenyl)-7-ethyl-1*H*-thieno[2,3-*e*] [1,4]diazepin-2(3*H*)-one was obtained as a gift sample from *R. L*. Fine Chem., Bengaluru, India. (*E*)-5-(2-Chlorophenyl)-7-ethyl-1*H*-thieno [2,3-*e*][1,4]diazepin-2(3*H*)-one (3.04 g, 0.01 mol) was dissolved in 10 ml of methanol and picric acid (2.29 g, 0.01 mol) was also dissolved in 10 ml of methanol. Both solutions were mixed and stirred in a beaker at 333 K for 30 minutes. The mixture was kept aside for a day at room temperature. The salt formed was filtered and dried in a vaccum desiccator over phosphorous pentoxide. The compound was recrystallized from a mixture (*v*:*v* = 1:1) of DMSO and ethanol by slow evaporation (m.p: 518 K).

### Refinement

Carbon-bound H atoms were placed in calculated positions (C—H 0.95 Å for aromatic carbon atoms, C—H 0.99 Å for methylene groups) and were included in the refinement in the riding model approximation, with $U$(H) set to 1.2$U_{eq}$(C). The H atoms of the methyl group were allowed to rotate with a fixed angle around the C—C bond (C—H 0.98 Å) to best fit the experimental electron density (HFIX 137 in the *SHELX* program suite (Sheldrick, 2008), with $U$(H) set to 1.5$U_{eq}$(C). Both nitrogen-bound H atoms were located on a difference Fourier map and refined freely.

### Figures

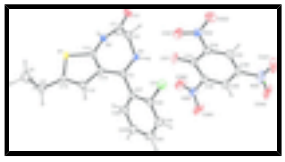

Fig. 1. The molecular structure of the title compound, with anisotropic displacement ellipsoids (drawn at 50% probability level). For clarity, only the major component of the disordered nitro group is depicted.

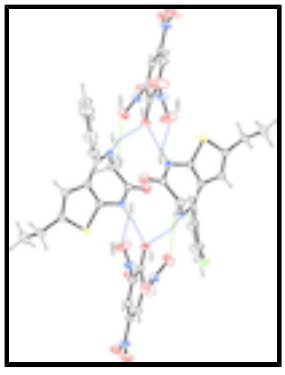

Fig. 2. Intermolecular contacts, viewed approximately along [-1 -1 -1]. For clarity, only selected intermolecular contacts are depicted. Blue dashed lines show classical hydrogen bonds of the N–H···O type, green dashed lines C–H···O contacts. Symmetry operator: $^{i}$ -$x$ + 1, -$y$, -$z$. Only the major component of the disordered nitro group is depicted.

### (*E*)-5-(2-Chlorophenyl)-7-ethyl-2-oxo-2,3-dihydro-1*H*- thieno[2,3-*e*][1,4]diazepin-4-ium 2,4,6-trinitrophenolate

*Crystal data*

| | |
|---|---|
| $C_{15}H_{14}ClN_2OS^+·C_6H_2N_3O_7^-$ | $F$(000) = 1096 |
| $M_r$ = 533.90 | $D_x$ = 1.571 Mg m$^{-3}$ |
| Monoclinic, $P2_1/c$ | Melting point: 518 K |
| Hall symbol: -P 2ybc | Mo $K\alpha$ radiation, λ = 0.71073 Å |
| $a$ = 10.5704 (2) Å | Cell parameters from 9909 reflections |
| $b$ = 20.0667 (5) Å | θ = 2.9–28.3° |
| $c$ = 11.3741 (2) Å | μ = 0.32 mm$^{-1}$ |
| β = 110.666 (1)° | $T$ = 200 K |
| $V$ = 2257.35 (8) Å$^3$ | Block, brown |
| $Z$ = 4 | 0.59 × 0.49 × 0.36 mm |

*Data collection*

| | |
|---|---|
| Bruker APEXII CCD diffractometer | 5607 independent reflections |

| | |
|---|---|
| Radiation source: fine-focus sealed tube | 5073 reflections with $I > 2\sigma(I)$ |
| graphite | $R_{int} = 0.013$ |
| φ and ω scans | $\theta_{max} = 28.3°$, $\theta_{min} = 2.0°$ |
| Absorption correction: multi-scan (*SADABS*; Bruker, 2008). | $h = -13\rightarrow14$ |
| $T_{min} = 0.807$, $T_{max} = 0.892$ | $k = -26\rightarrow26$ |
| 21254 measured reflections | $l = -15\rightarrow15$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Primary atom site location: structure-invariant direct methods |
| Least-squares matrix: full | Secondary atom site location: difference Fourier map |
| $R[F^2 > 2\sigma(F^2)] = 0.031$ | Hydrogen site location: inferred from neighbouring sites |
| $wR(F^2) = 0.081$ | H atoms treated by a mixture of independent and constrained refinement |
| $S = 1.05$ | $w = 1/[\sigma^2(F_o^2) + (0.0349P)^2 + 1.1718P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| 5607 reflections | $(\Delta/\sigma)_{max} < 0.001$ |
| 343 parameters | $\Delta\rho_{max} = 0.38$ e Å$^{-3}$ |
| 0 restraints | $\Delta\rho_{min} = -0.24$ e Å$^{-3}$ |

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

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ | Occ. (<1) |
|---|---|---|---|---|---|
| Cl1 | 0.57956 (3) | 0.230591 (16) | 0.27567 (3) | 0.03062 (8) | |
| S1 | 0.08122 (3) | 0.038903 (15) | −0.15866 (3) | 0.02327 (8) | |
| O1 | 0.53537 (10) | 0.04170 (5) | −0.16774 (10) | 0.0361 (2) | |
| O31 | 0.75141 (9) | 0.09665 (4) | 0.21426 (8) | 0.02763 (19) | |
| O321 | 0.75835 (10) | 0.21026 (6) | 0.09075 (9) | 0.0377 (2) | |
| O322 | 0.96274 (13) | 0.23796 (7) | 0.11380 (11) | 0.0495 (3) | |
| O341 | 1.27262 (12) | 0.24856 (6) | 0.54001 (12) | 0.0505 (3) | |
| O342 | 1.25204 (13) | 0.17919 (7) | 0.67751 (12) | 0.0607 (4) | |
| N36 | 0.84539 (12) | 0.04459 (6) | 0.46335 (11) | 0.0328 (3) | |
| O361 | 0.8483 (2) | 0.04566 (12) | 0.57264 (12) | 0.0591 (7) | 0.913 (5) |
| O362 | 0.79227 (19) | −0.00036 (7) | 0.39045 (12) | 0.0432 (5) | 0.913 (5) |
| O363 | 0.8925 (12) | 0.0218 (6) | 0.5586 (12) | 0.023 (3)* | 0.087 (5) |
| O364 | 0.7289 (16) | 0.0258 (8) | 0.3784 (12) | 0.037 (4)* | 0.087 (5) |
| N1 | 0.49406 (10) | 0.12534 (5) | 0.07439 (9) | 0.01965 (19) | |
| H71 | 0.5767 (19) | 0.1274 (9) | 0.1273 (17) | 0.040 (5)* | |
| N2 | 0.34466 (10) | 0.03182 (5) | −0.12197 (9) | 0.0216 (2) | |
| H72 | 0.3224 (17) | −0.0023 (9) | −0.1669 (16) | 0.033 (4)* | |
| N32 | 0.87981 (11) | 0.21070 (6) | 0.15093 (10) | 0.0277 (2) | |
| N34 | 1.21470 (12) | 0.20290 (6) | 0.57125 (12) | 0.0375 (3) | |
| C1 | 0.45809 (12) | 0.06515 (6) | −0.12171 (11) | 0.0229 (2) | |
| C2 | 0.47774 (12) | 0.13264 (6) | −0.05765 (11) | 0.0228 (2) | |
| H2A | 0.5588 | 0.1545 | −0.0645 | 0.027* | |

| | | | | |
|---|---|---|---|---|
| H2B | 0.3985 | 0.1613 | −0.1002 | 0.027* |
| C3 | 0.39456 (11) | 0.11469 (5) | 0.11481 (10) | 0.0186 (2) |
| C4 | −0.11953 (12) | 0.08838 (7) | −0.07592 (13) | 0.0272 (3) |
| H4A | −0.1330 | 0.1015 | 0.0028 | 0.033* |
| H4B | −0.1627 | 0.0444 | −0.1017 | 0.033* |
| C5 | −0.18803 (14) | 0.13922 (8) | −0.17752 (15) | 0.0399 (3) |
| H5A | −0.1502 | 0.1835 | −0.1498 | 0.060* |
| H5B | −0.2854 | 0.1397 | −0.1933 | 0.060* |
| H5C | −0.1727 | 0.1273 | −0.2549 | 0.060* |
| C11 | 0.24806 (11) | 0.05778 (6) | −0.07911 (10) | 0.0194 (2) |
| C12 | 0.26416 (11) | 0.09611 (6) | 0.02726 (10) | 0.0198 (2) |
| C13 | 0.13619 (12) | 0.10916 (6) | 0.04104 (11) | 0.0230 (2) |
| H13 | 0.1277 | 0.1342 | 0.1088 | 0.028* |
| C14 | 0.02920 (12) | 0.08249 (6) | −0.05130 (11) | 0.0232 (2) |
| C21 | 0.42065 (11) | 0.11893 (6) | 0.25106 (11) | 0.0210 (2) |
| C22 | 0.50465 (12) | 0.16687 (6) | 0.33080 (11) | 0.0243 (2) |
| C23 | 0.52897 (15) | 0.16634 (8) | 0.45900 (13) | 0.0368 (3) |
| H23 | 0.5859 | 0.1992 | 0.5119 | 0.044* |
| C24 | 0.47029 (17) | 0.11802 (9) | 0.50923 (13) | 0.0428 (4) |
| H24 | 0.4878 | 0.1174 | 0.5971 | 0.051* |
| C25 | 0.38611 (16) | 0.07037 (8) | 0.43273 (14) | 0.0377 (3) |
| H25 | 0.3456 | 0.0373 | 0.4678 | 0.045* |
| C26 | 0.36134 (13) | 0.07120 (7) | 0.30489 (12) | 0.0283 (3) |
| H26 | 0.3028 | 0.0387 | 0.2526 | 0.034* |
| C31 | 0.85448 (11) | 0.12197 (6) | 0.29523 (11) | 0.0208 (2) |
| C32 | 0.92952 (12) | 0.17741 (6) | 0.27217 (11) | 0.0225 (2) |
| C33 | 1.04736 (12) | 0.20209 (6) | 0.35838 (12) | 0.0256 (2) |
| H33 | 1.0953 | 0.2371 | 0.3363 | 0.031* |
| C34 | 1.09452 (12) | 0.17498 (6) | 0.47757 (12) | 0.0267 (3) |
| C35 | 1.02603 (13) | 0.12448 (6) | 0.51186 (12) | 0.0280 (3) |
| H35 | 1.0569 | 0.1080 | 0.5955 | 0.034* |
| C36 | 0.91220 (12) | 0.09847 (6) | 0.42255 (11) | 0.0244 (2) |

*Atomic displacement parameters (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Cl1 | 0.03397 (16) | 0.02676 (15) | 0.03248 (16) | −0.01114 (12) | 0.01341 (13) | −0.00916 (11) |
| S1 | 0.01661 (13) | 0.02786 (15) | 0.02118 (14) | −0.00278 (10) | 0.00153 (10) | −0.00509 (10) |
| O1 | 0.0307 (5) | 0.0438 (6) | 0.0402 (5) | −0.0040 (4) | 0.0204 (4) | −0.0127 (4) |
| O31 | 0.0212 (4) | 0.0225 (4) | 0.0289 (4) | −0.0008 (3) | −0.0038 (3) | −0.0028 (3) |
| O321 | 0.0293 (5) | 0.0464 (6) | 0.0305 (5) | 0.0064 (4) | 0.0020 (4) | 0.0102 (4) |
| O322 | 0.0465 (6) | 0.0593 (7) | 0.0426 (6) | −0.0143 (6) | 0.0155 (5) | 0.0147 (5) |
| O341 | 0.0336 (6) | 0.0361 (6) | 0.0629 (8) | −0.0136 (5) | −0.0065 (5) | −0.0026 (5) |
| O342 | 0.0493 (7) | 0.0693 (9) | 0.0367 (6) | −0.0165 (6) | −0.0183 (5) | 0.0039 (6) |
| N36 | 0.0317 (6) | 0.0376 (6) | 0.0242 (5) | −0.0089 (5) | 0.0037 (4) | 0.0028 (5) |
| O361 | 0.0699 (12) | 0.0805 (14) | 0.0235 (6) | −0.0390 (11) | 0.0124 (6) | −0.0028 (7) |
| O362 | 0.0621 (11) | 0.0307 (7) | 0.0354 (6) | −0.0185 (7) | 0.0154 (6) | −0.0032 (5) |
| N1 | 0.0162 (4) | 0.0225 (5) | 0.0180 (4) | −0.0010 (4) | 0.0032 (4) | −0.0027 (3) |

| | | | | | | |
|---|---|---|---|---|---|---|
| N2 | 0.0201 (5) | 0.0224 (5) | 0.0212 (5) | −0.0016 (4) | 0.0061 (4) | −0.0056 (4) |
| N32 | 0.0303 (5) | 0.0265 (5) | 0.0250 (5) | 0.0003 (4) | 0.0082 (4) | 0.0009 (4) |
| N34 | 0.0264 (6) | 0.0322 (6) | 0.0397 (7) | −0.0035 (5) | −0.0060 (5) | −0.0066 (5) |
| C1 | 0.0205 (5) | 0.0290 (6) | 0.0179 (5) | −0.0004 (4) | 0.0052 (4) | −0.0012 (4) |
| C2 | 0.0228 (5) | 0.0253 (5) | 0.0201 (5) | −0.0040 (4) | 0.0074 (4) | −0.0002 (4) |
| C3 | 0.0166 (5) | 0.0174 (5) | 0.0194 (5) | 0.0000 (4) | 0.0035 (4) | −0.0028 (4) |
| C4 | 0.0158 (5) | 0.0295 (6) | 0.0344 (6) | −0.0011 (4) | 0.0065 (5) | −0.0028 (5) |
| C5 | 0.0244 (6) | 0.0466 (8) | 0.0456 (8) | 0.0098 (6) | 0.0083 (6) | 0.0099 (7) |
| C11 | 0.0168 (5) | 0.0203 (5) | 0.0185 (5) | −0.0011 (4) | 0.0030 (4) | −0.0006 (4) |
| C12 | 0.0163 (5) | 0.0213 (5) | 0.0199 (5) | −0.0009 (4) | 0.0041 (4) | −0.0025 (4) |
| C13 | 0.0186 (5) | 0.0248 (5) | 0.0247 (5) | 0.0001 (4) | 0.0066 (4) | −0.0043 (4) |
| C14 | 0.0177 (5) | 0.0242 (5) | 0.0263 (6) | 0.0001 (4) | 0.0059 (4) | −0.0011 (4) |
| C21 | 0.0184 (5) | 0.0240 (5) | 0.0195 (5) | −0.0013 (4) | 0.0052 (4) | −0.0040 (4) |
| C22 | 0.0218 (5) | 0.0271 (6) | 0.0237 (6) | −0.0050 (4) | 0.0077 (4) | −0.0051 (4) |
| C23 | 0.0376 (7) | 0.0466 (8) | 0.0237 (6) | −0.0133 (6) | 0.0077 (5) | −0.0128 (6) |
| C24 | 0.0486 (9) | 0.0593 (10) | 0.0206 (6) | −0.0123 (8) | 0.0125 (6) | −0.0044 (6) |
| C25 | 0.0406 (8) | 0.0459 (8) | 0.0302 (7) | −0.0110 (6) | 0.0168 (6) | 0.0014 (6) |
| C26 | 0.0278 (6) | 0.0305 (6) | 0.0267 (6) | −0.0073 (5) | 0.0099 (5) | −0.0036 (5) |
| C31 | 0.0171 (5) | 0.0210 (5) | 0.0218 (5) | 0.0022 (4) | 0.0037 (4) | −0.0029 (4) |
| C32 | 0.0212 (5) | 0.0226 (5) | 0.0215 (5) | 0.0022 (4) | 0.0049 (4) | −0.0002 (4) |
| C33 | 0.0204 (5) | 0.0226 (5) | 0.0317 (6) | −0.0009 (4) | 0.0065 (5) | −0.0029 (5) |
| C34 | 0.0185 (5) | 0.0257 (6) | 0.0283 (6) | −0.0011 (4) | −0.0014 (5) | −0.0056 (5) |
| C35 | 0.0260 (6) | 0.0291 (6) | 0.0223 (5) | −0.0002 (5) | 0.0005 (5) | −0.0009 (5) |
| C36 | 0.0227 (5) | 0.0246 (6) | 0.0231 (5) | −0.0023 (4) | 0.0044 (5) | −0.0004 (4) |

*Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| Cl1—C22 | 1.7337 (13) | C4—C5 | 1.5199 (19) |
| S1—C11 | 1.7164 (11) | C4—H4A | 0.9900 |
| S1—C14 | 1.7415 (12) | C4—H4B | 0.9900 |
| O1—C1 | 1.2102 (15) | C5—H5A | 0.9800 |
| O31—C31 | 1.2590 (14) | C5—H5B | 0.9800 |
| O321—N32 | 1.2234 (15) | C5—H5C | 0.9800 |
| O322—N32 | 1.2277 (15) | C11—C12 | 1.3925 (15) |
| O341—N34 | 1.2222 (18) | C12—C13 | 1.4396 (15) |
| O342—N34 | 1.2273 (18) | C13—C14 | 1.3528 (16) |
| N36—O363 | 1.118 (12) | C13—H13 | 0.9500 |
| N36—O362 | 1.2196 (16) | C21—C26 | 1.3985 (17) |
| N36—O361 | 1.2330 (19) | C21—C22 | 1.4029 (16) |
| N36—O364 | 1.323 (14) | C22—C23 | 1.3885 (18) |
| N36—C36 | 1.4542 (16) | C23—C24 | 1.379 (2) |
| N1—C3 | 1.3056 (15) | C23—H23 | 0.9500 |
| N1—C2 | 1.4574 (15) | C24—C25 | 1.384 (2) |
| N1—H71 | 0.870 (19) | C24—H24 | 0.9500 |
| N2—C1 | 1.3720 (15) | C25—C26 | 1.3836 (18) |
| N2—C11 | 1.3795 (15) | C25—H25 | 0.9500 |
| N2—H72 | 0.836 (18) | C26—H26 | 0.9500 |
| N32—C32 | 1.4534 (15) | C31—C36 | 1.4380 (16) |
| N34—C34 | 1.4519 (15) | C31—C32 | 1.4431 (16) |

| | | | |
|---|---|---|---|
| C1—C2 | 1.5170 (17) | C32—C33 | 1.3771 (16) |
| C2—H2A | 0.9900 | C33—C34 | 1.3803 (18) |
| C2—H2B | 0.9900 | C33—H33 | 0.9500 |
| C3—C12 | 1.4358 (15) | C34—C35 | 1.3793 (18) |
| C3—C21 | 1.4776 (15) | C35—C36 | 1.3745 (17) |
| C4—C14 | 1.5011 (16) | C35—H35 | 0.9500 |
| C11—S1—C14 | 92.26 (5) | C12—C11—S1 | 111.57 (8) |
| O363—N36—O362 | 107.3 (6) | C11—C12—C3 | 122.62 (10) |
| O362—N36—O361 | 122.68 (13) | C11—C12—C13 | 111.32 (10) |
| O363—N36—O364 | 124.9 (9) | C3—C12—C13 | 125.89 (10) |
| O361—N36—O364 | 115.2 (6) | C14—C13—C12 | 113.81 (10) |
| O363—N36—C36 | 120.9 (6) | C14—C13—H13 | 123.1 |
| O362—N36—C36 | 119.46 (11) | C12—C13—H13 | 123.1 |
| O361—N36—C36 | 117.83 (12) | C13—C14—C4 | 130.33 (11) |
| O364—N36—C36 | 114.2 (6) | C13—C14—S1 | 111.02 (9) |
| C3—N1—C2 | 124.21 (10) | C4—C14—S1 | 118.55 (9) |
| C3—N1—H71 | 120.1 (12) | C26—C21—C22 | 117.76 (11) |
| C2—N1—H71 | 115.7 (12) | C26—C21—C3 | 118.24 (10) |
| C1—N2—C11 | 124.78 (10) | C22—C21—C3 | 123.97 (11) |
| C1—N2—H72 | 117.2 (11) | C23—C22—C21 | 120.93 (12) |
| C11—N2—H72 | 116.2 (11) | C23—C22—Cl1 | 116.52 (10) |
| O321—N32—O322 | 123.13 (12) | C21—C22—Cl1 | 122.52 (9) |
| O321—N32—C32 | 118.95 (11) | C24—C23—C22 | 119.79 (13) |
| O322—N32—C32 | 117.92 (11) | C24—C23—H23 | 120.1 |
| O341—N34—O342 | 123.85 (12) | C22—C23—H23 | 120.1 |
| O341—N34—C34 | 118.31 (12) | C23—C24—C25 | 120.57 (13) |
| O342—N34—C34 | 117.84 (13) | C23—C24—H24 | 119.7 |
| O1—C1—N2 | 122.16 (12) | C25—C24—H24 | 119.7 |
| O1—C1—C2 | 123.78 (11) | C26—C25—C24 | 119.56 (13) |
| N2—C1—C2 | 114.05 (10) | C26—C25—H25 | 120.2 |
| N1—C2—C1 | 110.59 (10) | C24—C25—H25 | 120.2 |
| N1—C2—H2A | 109.5 | C25—C26—C21 | 121.37 (12) |
| C1—C2—H2A | 109.5 | C25—C26—H26 | 119.3 |
| N1—C2—H2B | 109.5 | C21—C26—H26 | 119.3 |
| C1—C2—H2B | 109.5 | O31—C31—C36 | 123.67 (11) |
| H2A—C2—H2B | 108.1 | O31—C31—C32 | 124.57 (11) |
| N1—C3—C12 | 119.59 (10) | C36—C31—C32 | 111.76 (10) |
| N1—C3—C21 | 118.98 (10) | C33—C32—C31 | 124.39 (11) |
| C12—C3—C21 | 121.36 (10) | C33—C32—N32 | 116.33 (11) |
| C14—C4—C5 | 112.41 (11) | C31—C32—N32 | 119.27 (10) |
| C14—C4—H4A | 109.1 | C32—C33—C34 | 118.69 (12) |
| C5—C4—H4A | 109.1 | C32—C33—H33 | 120.7 |
| C14—C4—H4B | 109.1 | C34—C33—H33 | 120.7 |
| C5—C4—H4B | 109.1 | C35—C34—C33 | 121.57 (11) |
| H4A—C4—H4B | 107.9 | C35—C34—N34 | 119.12 (12) |
| C4—C5—H5A | 109.5 | C33—C34—N34 | 119.21 (12) |
| C4—C5—H5B | 109.5 | C36—C35—C34 | 118.68 (12) |
| H5A—C5—H5B | 109.5 | C36—C35—H35 | 120.7 |
| C4—C5—H5C | 109.5 | C34—C35—H35 | 120.7 |

| | | | |
|---|---|---|---|
| H5A—C5—H5C | 109.5 | C35—C36—C31 | 124.71 (11) |
| H5B—C5—H5C | 109.5 | C35—C36—N36 | 116.33 (11) |
| N2—C11—C12 | 129.56 (10) | C31—C36—N36 | 118.94 (10) |
| N2—C11—S1 | 118.77 (8) | | |
| C11—N2—C1—O1 | −175.18 (12) | C22—C23—C24—C25 | −0.7 (3) |
| C11—N2—C1—C2 | 5.61 (16) | C23—C24—C25—C26 | 0.3 (3) |
| C3—N1—C2—C1 | −77.66 (14) | C24—C25—C26—C21 | 0.6 (2) |
| O1—C1—C2—N1 | −117.45 (13) | C22—C21—C26—C25 | −1.1 (2) |
| N2—C1—C2—N1 | 61.75 (13) | C3—C21—C26—C25 | 177.14 (13) |
| C2—N1—C3—C12 | 12.62 (17) | O31—C31—C32—C33 | −175.40 (12) |
| C2—N1—C3—C21 | −170.29 (10) | C36—C31—C32—C33 | 4.22 (17) |
| C1—N2—C11—C12 | −41.65 (19) | O31—C31—C32—N32 | 4.86 (18) |
| C1—N2—C11—S1 | 142.17 (10) | C36—C31—C32—N32 | −175.52 (10) |
| C14—S1—C11—N2 | 177.15 (10) | O321—N32—C32—C33 | −152.12 (12) |
| C14—S1—C11—C12 | 0.32 (9) | O322—N32—C32—C33 | 28.00 (17) |
| N2—C11—C12—C3 | −0.8 (2) | O321—N32—C32—C31 | 27.64 (17) |
| S1—C11—C12—C3 | 175.59 (9) | O322—N32—C32—C31 | −152.24 (12) |
| N2—C11—C12—C13 | −176.29 (12) | C31—C32—C33—C34 | −3.70 (19) |
| S1—C11—C12—C13 | 0.10 (13) | N32—C32—C33—C34 | 176.05 (11) |
| N1—C3—C12—C11 | 32.88 (17) | C32—C33—C34—C35 | −0.45 (19) |
| C21—C3—C12—C11 | −144.13 (12) | C32—C33—C34—N34 | −176.78 (12) |
| N1—C3—C12—C13 | −152.30 (12) | O341—N34—C34—C35 | −178.51 (13) |
| C21—C3—C12—C13 | 30.68 (18) | O342—N34—C34—C35 | 1.4 (2) |
| C11—C12—C13—C14 | −0.65 (15) | O341—N34—C34—C33 | −2.1 (2) |
| C3—C12—C13—C14 | −175.96 (11) | O342—N34—C34—C33 | 177.82 (14) |
| C12—C13—C14—C4 | −175.42 (12) | C33—C34—C35—C36 | 3.5 (2) |
| C12—C13—C14—S1 | 0.88 (14) | N34—C34—C35—C36 | 179.86 (12) |
| C5—C4—C14—C13 | 99.93 (17) | C34—C35—C36—C31 | −2.8 (2) |
| C5—C4—C14—S1 | −76.14 (14) | C34—C35—C36—N36 | 178.98 (12) |
| C11—S1—C14—C13 | −0.69 (10) | O31—C31—C36—C35 | 178.71 (12) |
| C11—S1—C14—C4 | 176.10 (10) | C32—C31—C36—C35 | −0.92 (17) |
| N1—C3—C21—C26 | −138.62 (12) | O31—C31—C36—N36 | −3.08 (18) |
| C12—C3—C21—C26 | 38.41 (16) | C32—C31—C36—N36 | 177.29 (11) |
| N1—C3—C21—C22 | 39.47 (17) | O363—N36—C36—C35 | −7.5 (9) |
| C12—C3—C21—C22 | −143.50 (12) | O362—N36—C36—C35 | −144.83 (16) |
| C26—C21—C22—C23 | 0.68 (19) | O361—N36—C36—C35 | 33.3 (2) |
| C3—C21—C22—C23 | −177.42 (12) | O364—N36—C36—C35 | 173.3 (8) |
| C26—C21—C22—Cl1 | −177.61 (10) | O363—N36—C36—C31 | 174.1 (8) |
| C3—C21—C22—Cl1 | 4.29 (17) | O362—N36—C36—C31 | 36.8 (2) |
| C21—C22—C23—C24 | 0.2 (2) | O361—N36—C36—C31 | −145.06 (19) |
| Cl1—C22—C23—C24 | 178.56 (13) | O364—N36—C36—C31 | −5.1 (9) |

*Hydrogen-bond geometry (Å, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N1—H71···O31 | 0.870 (19) | 1.865 (19) | 2.6847 (13) | 156.3 (17) |
| N2—H72···O31$^{i}$ | 0.836 (18) | 2.047 (18) | 2.8331 (13) | 156.4 (16) |
| N2—H72···O362$^{i}$ | 0.836 (18) | 2.400 (17) | 2.9495 (16) | 123.9 (14) |

| | | | | |
|---|---|---|---|---|
| C2—H2A···O321 | 0.99 | 2.49 | 3.2465 (16) | 133. |
| C2—H2B···O342$^{ii}$ | 0.99 | 2.48 | 3.2505 (17) | 134. |
| C23—H23···O321$^{iii}$ | 0.95 | 2.51 | 3.4193 (18) | 161. |

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

**Fig. 1**

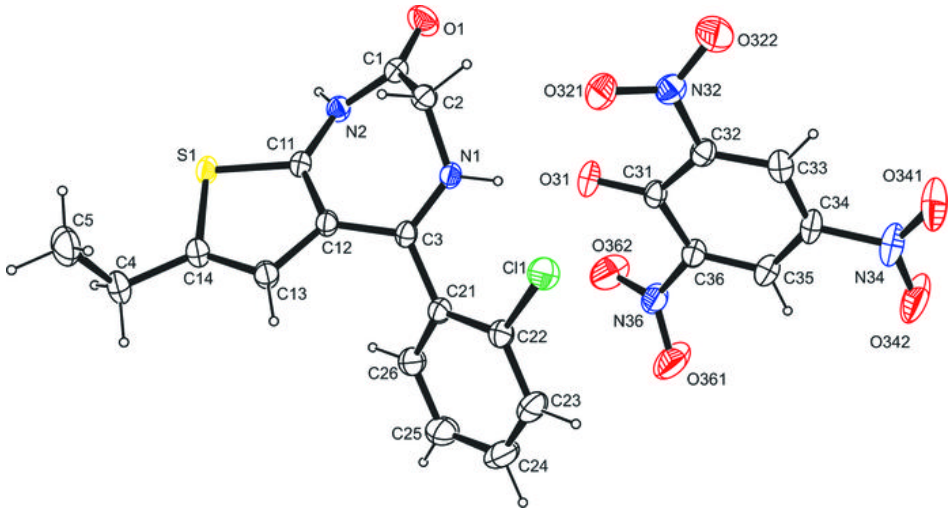
O1
C1
C2
N2
N1
S1
C11
C5
C4
C14
C12
C3
C13
C21
Cl1
C22
C26
C23
C25
C24
O322
O321
N32
C32
O31
C31
C33
O341
C34
O362
C36
C35
N34
N36
O342
O361

**Fig. 2**