Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701
Editor: **George Ferguson**

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Acta Cryst. (2008). C**64**, o87–o90

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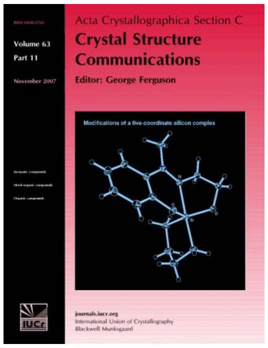

Volume 63
Part 11
November 2007
Acta Crystallographica Section C
Crystal Structure Communications
Editor: George Ferguson
Modifications of a five-coordinate silicon complex
journals.iucr.org
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Multipole refinement of 2-(indol-3-yl)-1,1,3,3-tetramethylthiouronium nitrate

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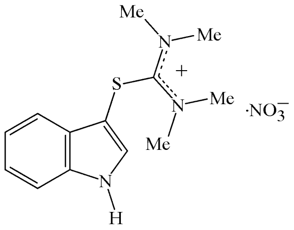
Received 10 December 2007
Accepted 8 January 2008
Online 22 January 2008

The cation of the title compound, $C_{13}H_{18}N_3S^+\cdot NO_3^-$, consists of two subunits, *viz.* a planar indole moiety and a nonplanar thiouronium moiety. An isolated intermolecular hydrogen bond connects the cation with the nitrate anion. The crystal packing is additionally characterized by short intermolecular contacts between parallel indole systems. A topological analysis of the electron density revealed C—S single bonds and partial double bonding in the N—C—N group.

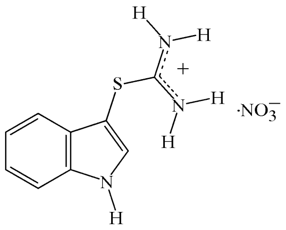
Comment

Urea and thiourea derivatives can be efficient metal-free organocatalysts (Takemoto, 2005). In this context, their hydrogen-bonding abilities play a central role in molecular recognition. We therefore performed crystal structure determinations of the title compound, (I), indole-3-thiouronium nitrate, (II) (Lutz *et al.*, 2008*a*), and indole-3-thiouronium iodide, (III) (Lutz *et al.*, 2008*b*). In order to investigate the bonding situation of the tetramethylthiouronium group, a multipole refinement and topological analysis of (I) were performed.

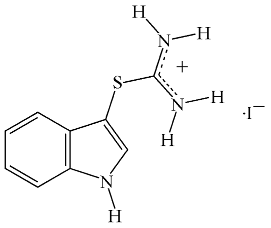
The molecular structure of (I) consist of two parts, *viz.* a planar indole moiety and a nonplanar thiouronium moiety (Fig. 1). The short C9—N bonds (Table 1) indicate a significant double-bond character, but they are slightly longer than those in the corresponding NH_2 compounds (II) and (III) [1.306 (2)–1.317 (2) Å]. The corresponding C—N bond lengths in urea (Zavodnik *et al.*, 1999) and *N*,*N*,*N*′,*N*′-tetramethylurea (Frampton & Parkes, 1996) are 1.343 and 1.3706 (13) Å, respectively. A comparison with the corresponding thiourea derivatives cannot be considered here, because free thiourea undergoes ferroelectric phase transitions (Takahashi *et al.*, 1990) and the crystal structure of *N*,*N*,*N*′,*N*′-tetramethylthiourea is not available in the literature.



(I)



(II)



(III)

As a result of the tetramethyl substitution of the thiouronium group, the molecule has only one NH hydrogen-bond donor. Atom O1 of the nitrate anion accepts this hydrogen bond (Table 2) to form an isolated cation–anion pair with graph-set descriptor *D* (Etter, 1990). The NH_2 derivatives (II) and (III) have five hydrogen-bond donors and form polymeric two- and three-dimensional networks, respectively. The density of 1.388 Mg m^{-3} in (I) is consequently lower than that of 1.513 Mg m^{-3} in (II).

The indole ring systems form centrosymmetric parallel dimers. The intermolecular distance between atom S1($1-x$, $1-y$, $1-z$) and the least-squares plane of the indole ring is 3.43323 (6) Å. Despite this relatively short distance we do not assume π-stacking interactions, because the indole systems are not on top of one another (Fig. 2). The intermolecular distance between the centers of gravity of the five-membered rings is consequently very long [4.5681 (2) Å].

A search of the Cambridge Structural Database (update of August 2007; Allen, 2002) revealed 38 entries containing thiouronium and four entries for *N*,*N*,*N*′,*N*′-tetramethylthiouronium compounds, of which 12 are drawn with an S=C9

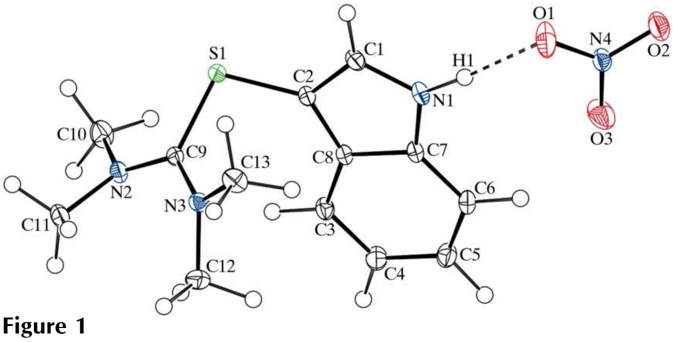


Figure 1
The molecular structure of (I) after multipole refinement. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. The N—H···O hydrogen bond is drawn with a dashed line.

DOI: 10.1107/S0108270108000668

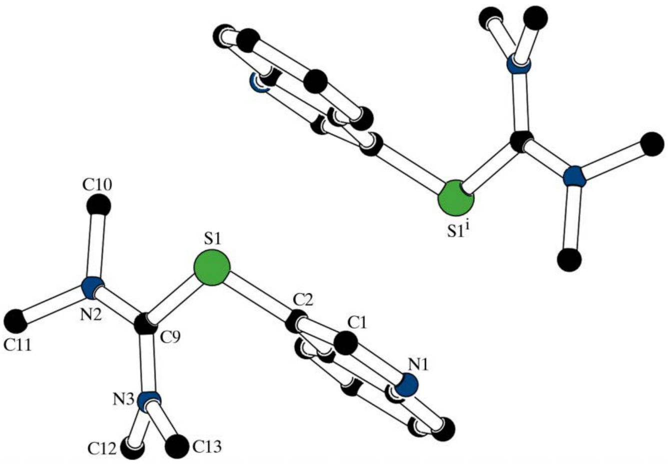


Figure 2
The centrosymmetric dimer of the indole systems, viewed along the crystallographic [110] direction. H atoms and nitrate anions have been omitted for clarity. [Symmetry code: (i) $1 - x, 1 - y, 1 - z$.]

double bond (*e.g.* Abashev *et al.*, 1987). 20 entries have a C9=N double bond and consequently a positive charge on an N atom (*e.g.* Garner *et al.*, 1998). Nine entries have the positive charge delocalized over the N—C—N group (*e.g.* Ishii *et al.*, 2000) and one entry has no indication about the bond order. To investigate the bonding situation of the thiouronium group, we performed a high-resolution diffraction experiment on (I), followed by a multipole refinement of the structure. Deformation densities of the indole system and the environment of atom C9 are shown in Fig. 3.

A topological analysis of the cation shows that the Laplacians at the bond critical points of the C9—N bonds have the highest magnitudes, of −26.33 (7) and −26.02 (7) e Å^{-5} (Table 3). Because the Laplacian at the bond critical point is a measure of the bond strength (Bader, 1990), this analysis clearly shows that these are the strongest bonds in the cations. The negative sign of the values indicates covalent bonding. A quantum-chemical study of urea (Gatti *et al.*, 1994) gives a value of −1.15 a.u. (corresponding to −27.71 e Å^{-5}) for the

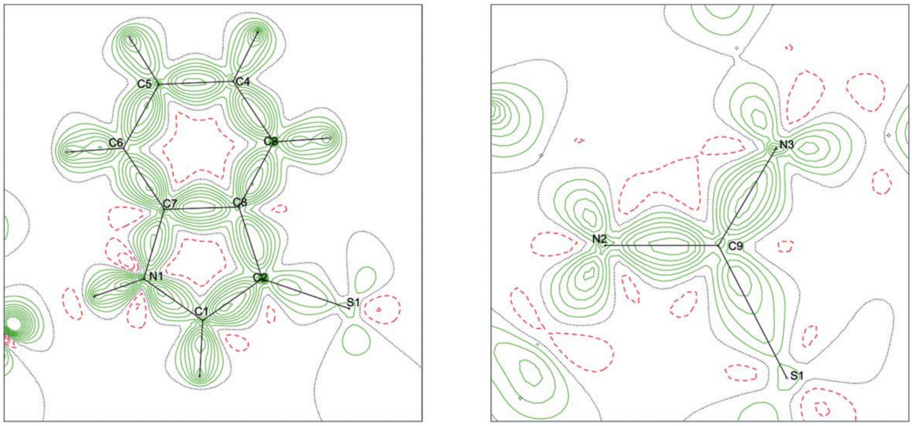


Figure 3
Deformation density in the plane of the indole system (left) and the planar environment of atom C9 (right). Contour lines correspond to 0.1 e Å^{-3}. Positive values are drawn as solid lines (green in the electronic version of the paper), negative values as dashed lines (red) and the zero level as dotted lines (black).

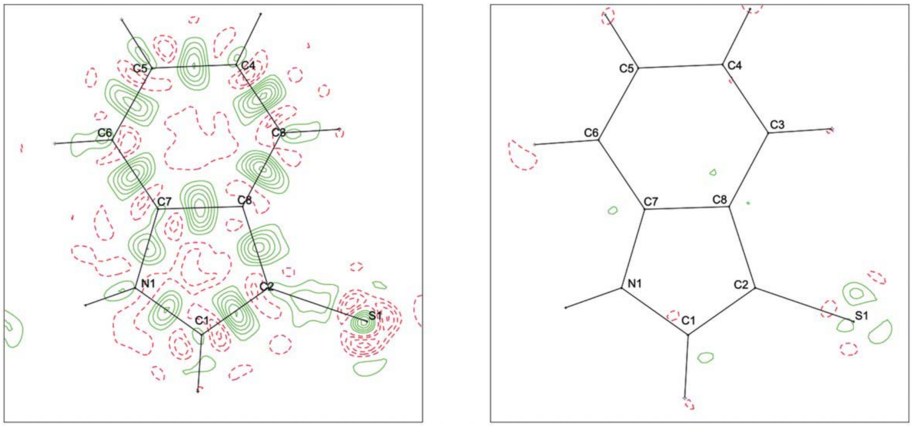


Figure 4
Residual density in the plane of the indole system after spherical atom refinement (left) and after multipole refinement (right). Contour lines correspond to 0.1 e Å^{-3}. Positive values are drawn as solid lines (green in the electronic version of the paper) and negative values as dashed lines (red). The zero level has been omitted for clarity.

Laplacian at the bond critical point of the C—N single bond. In an experimental study of urea (Zavodnik *et al.*, 1999), a value of -27.34 e Å^{-5} was determined. We can therefore conclude that the bond strengths of the C—N bonds in (I) and in urea are very similar.

The Laplacians at the bond critical points of the C—S bonds of -4.918 (19) and -5.008 (19) e Å^{-5} are very similar to the C—S single bonds of the dipeptide DL-alanylmethionine, with values of -4.9 and -4.7 e Å^{-5} (Guillot *et al.*, 2001). The bond order of the C—S bonds in (I) is thus best described as a single bond.

The net charges of the atoms (Table 4) derived from the monopole populations indicate a negative charge concentration on the C atoms of the four methyl groups. As expected, the positive charges are distributed over the H atoms. Adding these charges gives a negative charge of -0.51 for the nitrate anion and, because of the applied electroneutrality constraint, +0.51 for the cation.

A thermal motion analysis using the program *THMA11* (Schomaker & Trueblood, 1998) results in a low weighted R value $\{R = [\Sigma(w\Delta U)^2/\Sigma(wU_{\rm obs})^2]^{1/2}\}$ of 0.093, indicating that the molecule behaves as a rigid body in the solid state at 110 K. This value can be decreased if the thiouronium moiety is treated as an independent rigid body with the S1—C9 bond as rotation axis, resulting in $R = 0.065$. This analysis additionally supports the description of S1—C9 as a single bond allowing free rotation.

Experimental

For the preparation of 2-(indol-3-yl)-1,1,3,3-tetramethylthiouronium iodide, I_2 (1.30 g, 5.12 mmol) and KI (0.850 g, 5.12 mmol) were added to a solution of indole (0.600 g, 5.12 mmol) and *N*,*N*,*N*′,*N*′-tetramethylthiourea (0.677 g, 5.12 mmol) in a 4:1 (*v*/*v*) mixture of methanol and water (20 ml). The mixture was stirred overnight and then evaporated to dryness. The residue was washed with water and ether, yielding a dark-yellow powder (yield: 1.67 g, 4.45 mmol, 87%). Analysis calculated for $C_{13}H_{18}IN_3S$: C 41.61, H 4.83, N 11.20, S 8.54%; found: C 41.53, H 4.78, N 11.15, S 8.65%. ^{1}H NMR (DMSO-d_6): δ 12.00 (*s*, *br*, 1H, NH), 7.99 (*d*, $^3J_{\rm H-H}$ = 2.7 Hz, 1H, indolyl 2-H), 7.53 (*d*, $^3J_{\rm H-H}$ = 7.9 Hz, 1H, indolyl H), 7.43 (*d*, $^3J_{\rm H-H}$ = 7.9 Hz, 1H, indolyl H), 7.26 (*td*, $^3J_{\rm H-H}$ = 7.6 Hz, $^4J_{\rm H-H}$ = 1.2 Hz, 1H, indolyl H), 7.18 (*t*, $^3J_{\rm H-H}$ = 7.4 Hz, 1H, indolyl H), 3.14 (*s*, 12H, CH$_3$). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 174.76 [C(NMe$_2$)$_2$], 136.25, 132.65, 126.97, 122.77, 121.02, 117.28, 112.75, 94.54 (8 × indolyl C), 43.58 (CH$_3$). FT–IR (ATR, ν, cm^{-1}): 3136, 3099, 1600, 1498, 1455, 1413, 1380, 1340, 1256, 1235, 1166, 1100, 1006, 874, 758, 751, 691.

For the preparation of 2-(indol-3-yl)-1,1,3,3-tetramethylthiouronium nitrate, 2-(indol-3-yl)-1,1,3,3-tetramethylthiouronium iodide (0.100 g, 0.266 mmol) was added to a solution of AgNO$_3$ (0.0453 g, 0.266 mmol) in EtOH (10 ml). The mixture was refluxed for 1 h and then filtered to remove AgCl. The resulting cream-colored solution was concentrated *in vacuo*. Ether was added overnight by vapor diffusion. Colorless crystals formed, which proved to be suitable for X-ray diffraction studies. The crystals remaining after X-ray analysis were filtered off, washed with ether and dried *in vacuo* (yield: 0.0667 g, 2.15 mmol, 81%). Analysis calculated for $C_{13}H_{18}N_4O_3S$: C 50.31, H 5.85, N 18.05, S 10.33%; found: C 50.46, H 5.80, N 18.15, S 10.25%. The ^{1}H NMR spectrum was identical to that of the starting compound. FT–IR (ATR, ν, cm^{-1}): 3100, 2927, 1599, 1502, 1456, 1362, 1324, 1256, 1238, 1208, 1166, 1112, 1101, 1059, 1042, 1009, 876, 830, 784, 760, 748.

Crystal data

$C_{13}H_{18}N_3S^+\cdot NO_3^-$
M_r = 310.37
Orthorhombic, *Pbca*
a = 12.46443 (1) Å
b = 11.02991 (7) Å
c = 21.60929 (4) Å
V = 2970.88 (2) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.23 mm^{-1}
T = 110 (2) K
0.36 × 0.24 × 0.24 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2006)
$T_{\rm min}$ = 0.744, $T_{\rm max}$ = 0.943
247693 measured reflections
12242 independent reflections
9926 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.034

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.019
$wR(F^2)$ = 0.011
S = 2.03
9926 reflections
570 parameters
H-atom parameters constrained
$\Delta\rho_{\rm max}$ = 0.34 e Å^{-3}
$\Delta\rho_{\rm min}$ = -0.29 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—C2	1.7452 (3)	N2—C9	1.3291 (4)
S1—C9	1.7614 (3)	N3—C9	1.3355 (4)
C2—S1—C9	101.142 (14)	S1—C9—N3	122.03 (2)
S1—C9—N2	117.25 (3)	N2—C9—N3	120.72 (3)
C2—S1—C9—N2	−142.61 (3)	C11—N2—C9—S1	−148.75 (3)
C2—S1—C9—N3	36.25 (3)	C12—N3—C9—S1	−142.67 (3)
C10—N2—C9—S1	16.08 (5)	C13—N3—C9—S1	30.69 (5)

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$\cdots$O1	0.99	1.87	2.8642 (7)	176

Table 3
Topological characteristics of the electron density at the bond critical points in the cation of (I).

Bond	d (Å)	d_1 (Å)	d_2 (Å)	ρ (e Å^{-3})	Ellipticity	$\nabla^2\rho$ (e Å^{-5})
S1—C2	1.7455	0.8861	0.8593	1.334 (8)	0.13	−4.202 (14)
S1—C9	1.7618	0.8748	0.8870	1.320 (8)	0.24	−3.818 (14)
N1—C1	1.3708	0.8162	0.5547	2.17 (2)	0.16	−21.15 (9)
N1—C7	1.3789	0.7892	0.5897	2.193 (18)	0.20	−19.76 (7)
N2—C9	1.3291	0.7685	0.5606	2.490 (18)	0.25	−26.93 (8)
N2—C10	1.4609	0.8630	0.5979	1.738 (19)	0.07	−11.60 (6)
N2—C11	1.4684	0.8551	0.6133	1.662 (16)	0.03	−8.87 (5)
N3—C9	1.3355	0.7738	0.5617	2.442 (18)	0.22	−26.12 (8)
N3—C12	1.4646	0.8524	0.6122	1.694 (18)	0.10	−9.74 (6)
N3—C13	1.4587	0.8690	0.5897	1.693 (18)	0.04	−10.84 (6)
C1—C2	1.3799	0.7189	0.6610	2.214 (14)	0.31	−19.60 (4)
C2—C8	1.4372	0.7176	0.7196	1.966 (13)	0.18	−14.80 (3)
C3—C4	1.3862	0.7034	0.6829	2.198 (15)	0.22	−19.98 (4)
C3—C8	1.4042	0.6769	0.7273	2.109 (14)	0.21	−18.67 (4)
C4—C5	1.4111	0.7036	0.7075	2.078 (14)	0.21	−17.75 (4)
C5—C6	1.3867	0.7230	0.6636	2.171 (16)	0.21	−19.25 (4)
C6—C7	1.4025	0.6665	0.7360	2.114 (15)	0.23	−18.74 (4)
C7—C8	1.4158	0.7206	0.6952	2.106 (13)	0.21	−18.32 (3)

Table 4
Net atomic charges derived from the monopole populations.

S1	−0.123	C13	−0.244
O1	−0.214	H1	+0.241
O2	−0.142	H2	+0.224
O3	−0.174	H3	+0.177
N1	−0.097	H4	+0.161
N2	−0.128	H5	+0.147
N3	−0.136	H6	+0.192
N4	+0.025	H7	+0.181
C1	−0.149	H8	+0.153
C2	−0.173	H9	+0.166
C3	−0.143	H10	+0.169
C4	−0.127	H11	+0.171
C5	−0.160	H12	+0.189
C6	−0.112	H13	+0.206
C7	−0.109	H14	+0.203
C8	−0.102	H15	+0.214
C9	−0.112	H16	+0.238
C10	−0.300	H17	+0.167
C11	−0.389	H18	+0.162
C12	−0.251		

The initial refinement was performed with a spherical atom model using the program *SHELXL97* (Sheldrick, 2008) on F^2 of all reflections. H atoms were refined freely with isotropic displacement parameters.

The results of the *SHELXL97* refinement were then transferred to the program *XD* (Koritsanszky *et al.*, 2003). After a spherical atom refinement, the H atoms were fixed and a spherical atom refinement of the non-H atoms was performed on data with $\sin\theta/\lambda$ larger than 0.7 $Å^{-1}$. In the following step, the non-H atoms were fixed and the positions and isotropic displacement parameters of the H atoms were refined on data with $\sin\theta/\lambda$ smaller than 0.7 $Å^{-1}$. A polarized density function with a bond-directed dipole was used here for the H atoms. The polarized H atom was introduced by Stewart *et al.* (1975) and adapted to the *XD* package by Macchi (2000).

In a final refinement, the positions and displacement parameters of the H atoms were fixed and non-H atoms were refined anisotropically. Multipole parameters were also refined in this step, for S atoms up to the hexadecapole level, and for C, N and O atoms up to the octopole level. For H atoms, a monopole and a dipole in bond direction was refined. The refinement was performed on F of reflections with $F > 2\sigma(F)$. The weights in the least-squares refinement were $1/\sigma^2$. 93.7% of the reflections were measured six or more times for useful merged σ values. Residual electron densities of the spherical atom refinement and the multipole refinement are given in Fig. 4.

The largest differences of mean-squares displacement amplitudes in the direction of the bonds (Hirshfeld, 1976) are 0.0014 (2) $Å^2$ for N4—O2 in the anion and 0.0012 (2) $Å^2$ for N2—C10 in the cation. The largest peaks and holes of the difference electron-density map are close to atom O3 of the nitrate anion, at distances of 0.52 and 0.50 Å, respectively.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *PEAKREF* (Schreurs, 2005); data reduction: *EVAL15* (Xian *et al.*, 2006) and *SADABS* (Sheldrick, 2006); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *XD* (Koritsanszky *et al.*, 2003); molecular graphics: *XD* and *PLATON* (Spek, 2003); software used to prepare material for publication: *XD*.

This work was supported by the Council for Chemical Sciences of the Netherlands Organization for Scientific Research (CW–NWO). A. M. M. Schreurs is kindly acknowledged for his help with the data integration.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TR3035). Services for accessing these data are described at the back of the journal.

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