B5	0.5280 (1)	0.2302 (4)	0.5450 (1)	0.051 (3)
C1	0.4682 (2)	0.2837 (3)	0.5864 (4)	0.057 (3)
C2	0.4456 (3)	0.3707 (4)	0.5218 (5)	0.083 (4)
C3	0.3921 (3)	0.4212 (5)	0.5542 (6)	0.110 (5)
C4	0.3588 (3)	0.3867 (6)	0.6508 (7)	0.110 (5)
C5	0.3798 (3)	0.3015 (5)	0.7164 (5)	0.096 (5)
C6	0.4339 (2)	0.2495 (4)	0.6862 (4)	0.073 (3)
C7	0.6688 (2)	0.0401 (3)	0.5427 (3)	0.050 (3)
C8	0.7198 (2)	0.0626 (3)	0.6134 (4)	0.062 (3)
C9	0.7674 (2)	−0.0088 (4)	0.6287 (4)	0.071 (4)
C10	0.7649 (2)	−0.1048 (4)	0.5695 (4)	0.071 (4)
C11	0.7159 (2)	−0.1308 (4)	0.4991 (4)	0.082 (4)
C12	0.6682 (2)	−0.0582 (4)	0.4865 (4)	0.071 (3)
C13	0.6522 (3)	0.2197 (5)	0.3263 (5)	0.086 (4)
C14	0.5090 (3)	−0.0034 (4)	0.6776 (5)	0.069 (4)
H1	0.553 (2)	0.303 (3)	0.385 (3)	0.07 (2)
H7	0.585 (1)	0.071 (2)	0.734 (3)	0.04 (1)

Table 2. *Selected geometric parameters (Å, °)*

N1—N2	1.414 (5)	N3—C14	1.463 (7)
N1—B5	1.399 (6)	N3—H7	0.88 (3)
N1—H1	0.83 (3)	N4—B5	1.446 (6)
N2—B3	1.404 (6)	N4—B3	1.432 (6)
N2—C13	1.440 (7)	B5—C1	1.538 (6)
N3—N4	1.441 (4)	B3—C7	1.547 (6)
N2—N1—B5	110.3 (3)	N3—N4—B5	124.3 (3)
N2—N1—H1	117 (2)	N3—N4—B3	124.7 (3)
B5—N1—H1	132 (2)	B5—N4—B3	110.9 (3)
N1—N2—B3	109.6 (3)	N1—B5—N4	104.2 (4)
N1—N2—C13	116.4 (4)	N1—B5—C1	124.0 (4)
B3—N2—C13	133.8 (4)	N4—B5—C1	131.8 (4)
N4—N3—C14	110.4 (3)	N2—B3—N4	104.9 (4)
N4—N3—H7	101 (2)	N2—B3—C7	125.1 (4)
C14—N3—H7	115 (2)	N4—B3—C7	130.0 (4)
B5—N1—N2—B3	−0.7 (4)	B5—N1—N2—C13	−176.5 (4)
N1—N2—B3—N4	−0.4 (4)	N4—B3—N2—C13	174.4 (4)
N2—N1—B5—N4	1.4 (4)	C7—B3—N2—C13	−3.0 (7)
B3—N4—B5—N1	−1.7 (4)	C1—B5—N1—N2	−179.3 (4)
B5—N4—B3—N2	1.3 (4)	B5—N4—N3—C14	87.4 (4)
N3—N4—B5—N1	−178.6 (3)	B3—N4—N3—C14	−89.1 (4)
N3—N4—B3—N2	178.2 (3)	N4—B3—C7—C8	−83.7 (6)
N3—N4—B5—C1	2.3 (6)	N1—B5—C1—C2	−4.1 (6)
N3—N4—B3—C7	−4.6 (6)		

The structure was solved by direct methods using *MULTAN77* (Main, Lessinger, Woolfson, Germain & Declercq, 1977). Refinement was by full-matrix least-squares methods; heavy atoms were refined anisotropically and H atoms isotropically using *Xtal*3.0 (Hall & Stewart, 1990). Molecular graphics were drawn using *ORTEP*II (Johnson, 1976).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1263). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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3,7-Bis(2-thienyl)-1,5,2,4,6,8-dithiatetrazocine

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Abstract

The title molecule, 3,7-bis(2-thienyl)-1,5,2,4,6,8-dithiatetrazocine, $C_{10}H_6N_4S_4$, is planar within 0.069 (5) Å and crystallizes in the monoclinic space group $P2_1/c$. There are two centrosymmetric molecules in the cell; these are stacked such that each eight-membered $C_2N_4S_2$ ring has a thienyl ring above and below it. The mean interplanar separation is 3.55 (2) Å.

Comment

The 1,5,2,4,6,8-dithiatetrazocine ring system is known for the structural dichotomy it displays as a function of the exocyclic 3,7-ligands (Ernst *et al.*, 1981): aryl substituents afford planar central rings, while amine groups induce a folding of the ring and the formation of a transannular S···S contact (Oakley, 1988). The thienyl group of the title compound, (I), results in a planar central ring with distances and angles [S—N = 1.556 (3),

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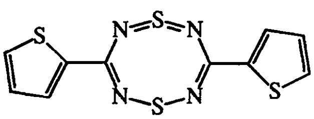
C—N = 1.326 (4) Å, N—S—N = 126.6 (2) and N—C—N = 130.1 (3)°] comparable with those reported for the phenyl, 4-methoxyphenyl (Ernst *et al.*, 1981) and 4-trifluoromethylphenyl (Boeré *et al.*, 1993) compounds.



(I)

These distances suggest the existence of a delocalized 10π electron system. The thienyl substituents of the title structure are disordered. The disorder involves a 180° rotation of the C4—C5 bond such that only S2, C3 and H3 are affected. The disorder was modeled by a 0.80 to 0.20 occupancy of the two positions; the 0.20 atoms were constrained to difference map positions with displacement parameters equal to their 0.80 counterparts. The most favored position was used for Fig. 1 and Table 2 of this report, and the disordered atoms of the minor component are S22, C32 and H32 in Table 1. Thienyl disorder of this type has been observed in a thienyl derivative of benzobis(1,2,5-dithiazole) (Kitamura, Tanaka & Yamashita, 1995, 1996).

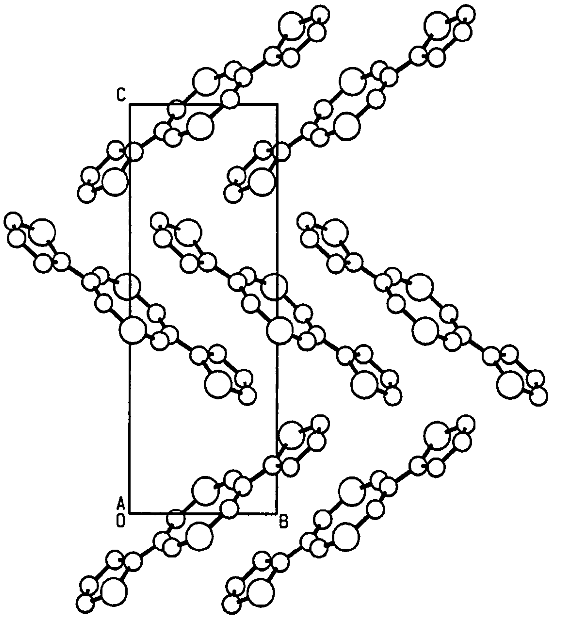


Fig. 1. *ORTEPII* (Johnsen, 1976) drawing of $C_{10}H_6N_4S_2$ with labeling scheme. The displacement ellipsoids are drawn at the 30% probability level. H atoms have artificially small temperature factors for clarity.

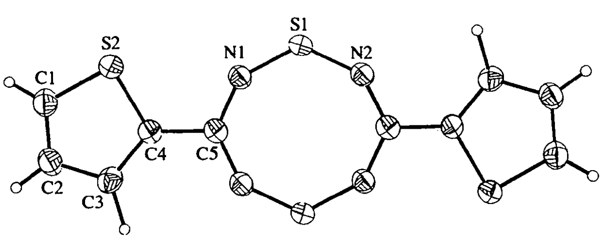


Fig. 2. The packing of the molecules as viewed in the *bc* projection.

Experimental

The title compound was first prepared in low yield (7%) from the reaction of 2-thienylamidine hydrochloride and sulfur dichloride (Amin & Rees, 1989). It is generated more efficiently (50% yield) by the reduction of 4-(2-thienyl)-1,2,3,5-dithiadiazolylium chloride with triphenylantimony in the presence of oxygen (Boeré *et al.*, 1993). Crystals suitable for X-ray analysis were grown by slow crystallization from chlorobenzene, and were mounted on a glass fiber with silicon glue.

Crystal data

$C_{10}H_6N_4S_4$
$M_r = 310.42$
Monoclinic
$P2_1/c$
$a = 6.9888\ (10)$ Å
$b = 5.6836\ (5)$ Å
$c = 16.019\ (2)$ Å
$\beta = 101.822\ (11)°$
$V = 622.80\ (13)$ Å^3
$Z = 2$
$D_x = 1.66$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 24 reflections
$\theta = 18$–$20°$
$\mu = 0.72$ mm^{-1}
$T = 293$ K
Block
0.42 × 0.32 × 0.12 mm
Yellow

Data collection

Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: analytical
$T_{\min} = 0.81$, $T_{\max} = 0.92$
2245 measured reflections
1094 independent reflections
805 observed reflections
$[I_{\rm net} > 3\sigma(I_{\rm net})]$

$R_{\rm int} = 0.016$
$\theta_{\max} = 24.91°$
$h = 0 \rightarrow 8$
$k = -6 \rightarrow 6$
$l = -19 \rightarrow 19$
3 standard reflections
frequency: 60 min
intensity decay: 1.6%

Refinement

Refinement on F
$R = 0.035$
$wR = 0.059$
$S = 1.05$
805 reflections
82 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F) + 0.0025F^2]$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.26$ e Å^{-3}
$\Delta\rho_{\min} = -0.30$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
S1	0.78292 (14)	0.52035 (16)	0.05439 (6)	0.0573 (5)
S2	1.09462 (17)	1.1027 (2)	0.18792 (7)	0.0564 (7)
S22†	1.4280	1.0570	0.1046	0.0568
N1	0.9481 (4)	0.7058 (5)	0.08085 (16)	0.0495 (15)
N2	0.7776 (4)	0.3194 (5)	−0.01186 (16)	0.0510 (15)

C1	1.2773 (6)	1.2986 (7)	0.2152 (2)	0.062 (2)
C2	1.4218 (6)	1.2746 (7)	0.1729 (2)	0.060 (2)
C3	1.3795 (7)	1.0956 (7)	0.1114 (3)	0.055 (2)
C32†	1.1750	1.0800	0.1850	0.0552
C4	1.2100 (5)	0.9720 (6)	0.11546 (19)	0.0443 (16)
C5	1.1199 (5)	0.7700 (5)	0.06559 (18)	0.0445 (16)

† 0.20 occupancy components of the disorder described in the *Comment*.

Table 2. *Selected geometric parameters (Å, °)*

S1—N1	1.557 (3)	N2—C5^{i}	1.329 (4)
S1—N2	1.554 (3)	C1—C2	1.334 (6)
S2—C1	1.683 (4)	C2—C3	1.406 (6)
S2—C4	1.712 (3)	C3—C4	1.390 (6)
N1—C5	1.324 (4)	C4—C5	1.466 (4)
N1—S1—N2	126.60 (16)	S2—C4—C3	109.7 (3)
C1—S2—C4	91.48 (18)	S2—C4—C5	120.0 (2)
S1—N1—C5	141.8 (2)	C3—C4—C5	130.2 (3)
S1—N2—C5^{i}	141.5 (3)	N1—C5—N2^{i}	130.1 (3)
S2—C1—C2	114.4 (3)	N1—C5—C4	114.8 (3)
C1—C2—C3	111.0 (4)	N2^{i}—C5—C4	115.1 (3)
C2—C3—C4	113.0 (4)		

Symmetry code: (i) $2 - x, 1 - y, -z$.

The structure was solved using direct methods, with the H atoms placed in idealized positions (C—H = 0.95 Å).

Data collection: *CAD-4/PC* (Enraf–Nonius, 1994). Cell refinement: *CAD-4/PC*. Data reduction: *DATRD*2 in *NRCVAX* (Gabe, LePage, Charland, Lee & White, 1989). Program(s) used to solve structure: *NRCVAX*. Program(s) used to refine structure: *NRCVAX*. Molecular graphics: *NRCVAX*. Software used to prepare material for publication: *NRCVAX*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1274). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Crystalline Complexes Involving Amino Acids. I. L-Argininium Hydrogen Squarate

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Abstract

The title compound, $C_6H_{15}N_4O_2^+.C_4HO_4^-$, crystallizes in the triclinic space group $P1$ with two independent formula units in the unit cell. The arginine molecules are protonated zwitterions with the amino and guanidyl moieties each accepting a proton from the acid group and the squaric acid. The torsion angles along the central N—C—$(CH_2)_3$—N chains are −166.8 (2), 165.7 (2), 168.9 (2), 178.2 (2)° in molecule I and −170.0 (1), 148.9 (2), 164.1 (2), 163.7 (2)° in molecule II, respectively. The C—C bond lengths within the squarate anions are consistent with a delocalized double bond around the hydroxyl-bearing C atom, 1.426 (3) and 1.433 (3) Å *versus* 1.496 (3) and 1.491 (3) Å for the adjacent and opposite bonds, respectively. The crystal structure consists of alternate layers of squarate and argininium moieties stacked along the *c* axis. The adjacent layers are connected to each other through specific ion-pair interactions (salt bridges) between the guanidyl group of the argininium and the squarate moieties.

Comment

The search for new classes of organic compounds with large non-linear optical coefficients and enough photochemical resistance against laser light is directed towards compounds with high dipole moments, asymmetric conjugated π-electron systems and those which produce non-centrosymmetric crystals. This article is a part of a project investigating the non-linear optical properties of crystalline materials involving salts of optically active amino acids, amines and guanidine derivatives with oxocarbons – deltic, squaric, croconic and rhodisonic acids as well as their sulfur derivatives [see West (1980)].

The structures of the free arginine and its molecular complexes including arginine dihydrate (Karle & Karle, 1964), hydrochloride (Mazumdar, Venkatesan, Mez & Donohue, 1969), hydrochloride monohydrate (Dow, Jensen, Mazumdar, Srinivasan & Ramachandran, 1970), phosphate monohydrate (Aoki, Nagano & Iitaka,