planar hexagons with C—C 1.39 Å and the exocyclic C and O atoms were restrained to lie in the aromatic ring planes by means of the FLAT instruction. Soft DFIX restraints were applied to the C—O and exocyclic C—C distances. The non-H atoms of the major (*A*,*B*) component were allowed anisotropic vibration parameters and the atoms of the minor component were held to a common isotropic displacement parameter. The (*A*,*B*)/(*C*,*D*) occupancy ratio refined to 0.869 (3)/0.131(3). The various O···O intermolecular contacts are consistent with only one hydrogen-bonding scheme for each of the *A*,*B* and *C*,*D* systems; the hydroxy-H atoms of the *A*,*B* system could be seen in difference map sections and were allowed for in the refinement by means of the appropriate *SHELXL* AFIX-147 instructions. No allowance was made for the hydroxy-H atoms of the minor component.

Compound (II) crystallized in the monoclinic system; space group $P2_1/n$ from the systematic absences. Difference maps calculated in planes normal to the relevant C—O bonds with the COFOUR option in *NRCVAX* showed clearly that the hydroxy-H atoms were equally disordered over two sites. These were allowed for in the *SHELXL*93 refinement by use of the AFIX-147 option.

For both compounds, data collection: *CAD*-4/*PC Software* (Enraf–Nonius, 1992); cell refinement: *SET*4 and *CELDIM* (Enraf–Nonius, 1992); data reduction: *DATRD*2 in *NRCVAX*94 (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1985) for (I); *SOLVER* in *NRCVAX*94 for (II). For both compounds, program(s) used to refine structures: *NRCVAX*94 and *SHELXL*93 (Sheldrick, 1993); molecular graphics: *NRCVAX*94, *ORTEP*II (Johnson, 1976), *PLATON* (Spek, 1995*a*), *PLUTON* (Spek, 1995*b*); software used to prepare material for publication: *NRCVAX*94, *SHELXL*93 and *WordPerfect* macro *PREPCIF*.

GF thanks NSERC (Canada) for Research Grants.

Lists of structure factors, least-squares-planes data, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1407). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). **C52**, 3062–3064

4,7-Bis(2-thiophenoyl)-1-thia-4,7-diazacyclononane

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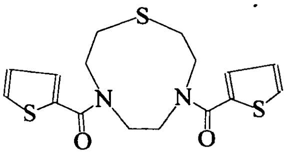
Abstract

The title compound, $C_{16}H_{18}N_2O_2S_3$, has two thiophenoyl arms linked to the N atoms of the central 1-thia-4,7-diazacyclononane ring. The resulting amide groups are close to planar. One of the thiophene rings shows disorder.

Comment

The structures of the Cu^{II} (Wasielewski & Mattes, 1990) and Pd^{II} (Chak, McAuley & Whitcome, 1994) complexes of 4,7-bis(pyridylmethyl)-1-thia-4,7-diazacyclononane have been determined. Here we report the structure of a closely related ligand, (1), where the pendant arms are thiophenoyl rather than pyridylmethyl.



(1)

The torsion angles C3—N4—C41—C42 and C8—N7—C71—C72 of 7.2 (4) and 9.8 (4)°, respectively, indicate that the amide units are almost planar: this is due to the partial double-bond character between C41/N4 and C71/N7. The N4—C41/N7—C71 and C41=O41/C71=O71 bond lengths of

1.348 (4)/1.344(4) and 1.236 (3)/1.236(3) Å are typical for tertiary amides (Allen *et al.*, 1987). There is some orientation disorder in one of the thiophene rings: the major conformation [83.0 (3)%] is related to the minor [17.0 (3)%] by a rotation of 180° about the C71—C72 bond.

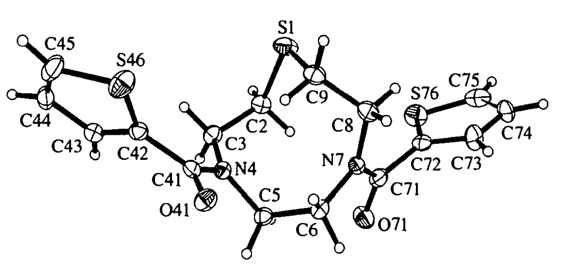


Fig. 1. A view of a molecule of (1) with the atom-numbering scheme. Displacement ellipsoids enclose 50% probability surfaces and H atoms are shown as spheres of arbitrary radii. Only the major orientation of the disordered thiophene ring (C72–S76) is shown.

Experimental

The title compound was prepared by reaction of 1-thia-4,7-diazacyclononane (Hart, Boeyens, Michael & Hancock, 1983) with 2-(chlorocarbonyl)thiophene and triethylamine (as base) in dichloromethane solution. The organic layer was washed sequentially with dilute HCl (50 ml), dilute NaOH (50 ml) and water (2 × 50 ml) and the product was isolated by evaporation and purified by recrystallization from hot ethanol. Crystals of (1) were obtained by slow evaporation of solvent from a solution in diethyl ether.

Crystal data

$C_{16}H_{18}N_2O_2S_3$
$M_r = 366.50$
Monoclinic
$P2_1/c$
$a = 10.246\,(3)$ Å
$b = 16.104\,(5)$ Å
$c = 10.462\,(5)$ Å
$\beta = 106.94\,(2)°$
$V = 1651.3\,(11)$ Å^3
$Z = 4$
$D_x = 1.474$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 16 reflections
$\theta = 13–14°$
$\mu = 0.459$ mm^{-1}
$T = 150.0\,(2)$ K
Tablet
0.50 × 0.45 × 0.15 mm
Colourless

Data collection

Stoe Stadi-4 four-circle diffractometer
ω–2θ scans
Absorption correction: none
2140 measured reflections
2140 independent reflections
1819 observed reflections [$I > 2\sigma(I)$]

$\theta_{max} = 22.53°$
$h = -11 \rightarrow 10$
$k = 0 \rightarrow 16$
$l = 0 \rightarrow 11$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0317$
$wR(F^2) = 0.0895$
$S = 1.073$
2129 reflections
222 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.029P)^2 + 2.12P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = -0.025$
$\Delta\rho_{max} = 0.21$ e Å^{-3}
$\Delta\rho_{min} = -0.28$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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

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

	x	y	z	U_{eq}
S1	0.76124 (8)	0.01518 (4)	0.51276 (8)	0.0313 (2)
C2	0.7018 (3)	0.0512 (2)	0.6508 (3)	0.0215 (6)
C3	0.5830 (3)	0.1113 (2)	0.6143 (3)	0.0212 (6)
N4	0.6194 (2)	0.19319 (13)	0.5736 (2)	0.0181 (5)
C5	0.7249 (3)	0.2400 (2)	0.6723 (3)	0.0189 (6)
C6	0.8629 (3)	0.2493 (2)	0.6456 (3)	0.0214 (6)
N7	0.9503 (2)	0.17533 (13)	0.6650 (2)	0.0186 (5)
C8	0.9693 (3)	0.1359 (2)	0.5455 (3)	0.0232 (6)
C9	0.8366 (3)	0.1028 (2)	0.4521 (3)	0.0229 (6)
C41	0.5544 (3)	0.2324 (2)	0.4588 (3)	0.0187 (6)
O41	0.5977 (2)	0.29834 (11)	0.4263 (2)	0.0239 (5)
C42	0.4258 (2)	0.1962 (2)	0.3702 (2)	0.0197 (6)
C43	0.3079 (3)	0.1764 (2)	0.3983 (3)	0.0223 (6)
C44	0.1992 (3)	0.1577 (2)	0.2837 (3)	0.0260 (7)
C45	0.2357 (3)	0.1644 (2)	0.1701 (3)	0.0332 (8)
S46	0.40194 (8)	0.19313 (5)	0.20055 (7)	0.0330 (2)
C71	1.0117 (3)	0.1504 (2)	0.7908 (3)	0.0231 (6)
O71	0.9811 (2)	0.18023 (13)	0.8871 (2)	0.0321 (5)
C72†	1.1230 (3)	0.0872 (2)	0.8161 (2)	0.0193 (14)
C73†	1.2507 (5)	0.0955 (3)	0.8021 (6)	0.0284 (14)
C74†	1.3415 (4)	0.0311 (4)	0.8590 (6)	0.0303 (13)
C75†	1.2818 (6)	−0.0261 (3)	0.9177 (6)	0.0347 (14)
S76†	1.11656 (11)	−0.00184 (7)	0.90396 (13)	0.0316 (4)
C72′‡	1.1230 (3)	0.0872 (2)	0.8161 (2)	0.040 (8)
C73′‡	1.1255 (15)	0.0117 (8)	0.877 (2)	0.040 (8)
C74′‡	1.2529 (19)	−0.0289 (12)	0.903 (4)	0.040 (8)
C75′‡	1.3439 (14)	0.0168 (12)	0.861 (3)	0.040 (8)
S76′‡	1.2742 (8)	0.1086 (6)	0.7913 (10)	0.0316 (4)

† Occupancy = 0.830 (3). ‡ Occupancy = 0.170 (3).

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

S1—C2	1.818 (3)	C8—C9	1.521 (4)
C2—C3	1.515 (4)	C9—S1	1.810 (3)
C3—N4	1.467 (3)	N4—C41	1.348 (3)
N4—C5	1.467 (3)	C41—O41	1.236 (3)
C5—C6	1.527 (4)	N7—C71	1.344 (4)
C6—N7	1.468 (3)	C71—O71	1.236 (3)
N7—C8	1.465 (3)		
C9—S1—C2	107.80 (13)	C8—N7—C6	117.4 (2)
C3—C2—S1	115.8 (2)	N7—C8—C9	112.6 (2)
N4—C3—C2	113.2 (2)	C8—C9—S1	116.2 (2)
C41—N4—C3	125.4 (2)	O41—C41—N4	121.6 (2)
C41—N4—C5	117.3 (2)	O41—C41—C42	119.2 (2)
C3—N4—C5	117.0 (2)	N4—C41—C42	119.2 (2)
N4—C5—C6	116.9 (2)	O71—C71—N7	121.6 (2)
N7—C6—C5	117.0 (2)	O71—C71—C72	118.8 (2)
C71—N7—C8	124.4 (2)	N7—C71—C72	119.5 (2)
C71—N7—C6	118.1 (2)		
C9—S1—C2—C3	67.7 (2)	C6—N7—C8—C9	−62.7 (3)
S1—C2—C3—N4	−69.6 (3)	N7—C8—C9—S1	−68.2 (3)
C2—C3—N4—C5	−60.7 (3)	C2—S1—C9—C8	68.5 (2)
C3—N4—C5—C6	109.4 (3)	C3—N4—C41—C42	7.2 (4)
N4—C5—C6—N7	−73.1 (3)	C8—N7—C71—C72	9.8 (4)
C5—C6—N7—C8	109.6 (3)		

As part of the modelling of the disorder in one thiophene ring, both components were restrained to have bond lengths and valence angles similar to those in the ordered ring. A common isotropic thermal displacement parameter for the C atoms of the minor component refined to 0.040 (8) Å^2.

Data collection: *DIF*4 (Stoe & Cie, 1992). Cell refinement: *DIF*4. Data reduction: *X-RED* (Stoe & Cie, 1995). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1994). Software used to prepare material for publication: *SHELXL*93.

We thank EPSRC for provision of a four-circle diffractometer and for postdoctoral support (to JPD).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HA1177). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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An Unusual 3*H*-Pyrrole at 150 K

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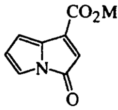
Abstract

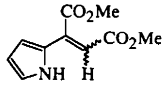
Most pyrroles are observed to form the 1*H*-tautomer; here we report the structure of a rare example of a 3*H*-pyrrole, trimethyl 6-oxo-5,5a,10b,10c-tetrahydro-3*H*-pyrrolizino[1,2-*e*]indole-4,5,10b-tricarboxylate, $C_{19}H_{18}N_2O_7$. The molecules pack as dimers linked *via* bifurcated hydrogen bonds.

Comment

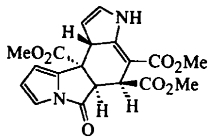
As part of our studies of the unusual properties of 1-methoxycarbonylpyrrolizin-3-one, (1), obtained by flash vacuum pyrolysis of the vinylpyrroles, (2) (Comer, Despinoy, Gould, McNab & Parsons, 1996), we adventitiously obtained a single crystal of (3), which is formally a [4 + 2] cycloadduct of (1) and (2). Here we report details of the structure of (3) which is of interest in view of the unusual tautomeric form of the pyrrole unit, and because of the boat conformation of the central cyclohexene ring.



(1)



(2*a*) *E* isomer
(2*b*) *Z* isomer



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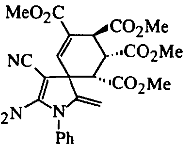
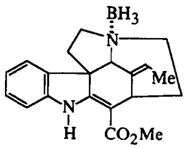


(4)



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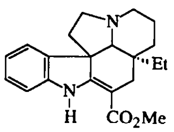

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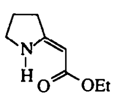

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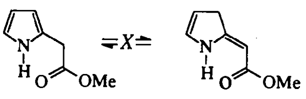

(8)

Compound (3) is composed of a 3*H*-pyrrole unit and a dihydropyrrolizinone unit linked *via* a cyclohexene ring in the boat conformation (Cremer–Pople puckering parameters θ = 88.3°, φ = 305.5°; Spek, 1995); ester substituents are located on C1, C13 and C14 (Fig. 1). The formulation of the 3*H*-pyrrole substructure was based on H-atom positions derived from electron density difference maps and supported by examination of the bond lengths. Thus the bond length C8—C12 [1.515 (7) Å] is much longer than anticipated for a typical pyrrole α–β double bond [1.375 (18) Å; Allen *et al.*, 1987], and the sum of the angles at C8 (331.0°) is clearly inconsistent with the normal 1*H*-pyrrole tautomer. There is little structural precedent for a pyrrole of this type in the literature; the spiro compound (4) is 3,3-disubstituted and encumbered by polar substituents (Kildea, Hiller, Frey & Eger, 1990). Other 3*H*-pyrrole structures have endocyclic N1═C2 double bonds (van Meersche, Gilson, Germain & Declercq, 1981; Chiu, Lai & Sammes, 1990). A range of indole alkaloid skeletons,