

## Crystal data

C<sub>18</sub>H<sub>12</sub>N<sub>2</sub>O<sub>10</sub>S<sub>2</sub>*M<sub>r</sub>* = 480.43

Monoclinic

*P*2<sub>1</sub>/*c**a* = 10.510 (3) Å*b* = 10.288 (4) Å*c* = 10.227 (3) Å

β = 117.60 (2)°

*V* = 980.0 (6) Å<sup>3</sup>*Z* = 2*D<sub>x</sub>* = 1.63 Mg m<sup>-3</sup>*D<sub>m</sub>* not measured

## Data collection

Enraf–Nonius CAD-4  
diffractometer

ω scans

Absorption correction: none

1835 measured reflections

1728 independent reflections

1053 reflections with

*I* > 2σ(*I*)Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 25  
reflections

θ = 8.0–13.0°

μ = 0.335 mm<sup>-1</sup>*T* = 294 K

Prism

0.35 × 0.35 × 0.20 mm

White

*R*<sub>int</sub> = 0.063θ<sub>max</sub> = 25°*h* = -12 → 12*k* = 0 → 12*l* = 0 → 12

3 standard reflections

frequency: 60 min

intensity decay: 0.60%

## Refinement

Refinement on *F*<sup>2</sup>*R*(*F*) = 0.034*wR*(*F*<sup>2</sup>) = 0.077*S* = 1.066

1728 reflections

163 parameters

Only coordinates of H atoms  
refined $w = 1/[\sigma^2(F_o^2) + (0.0416P)^2 + 0.3497P]$ where  $P = (F_o^2 + 2F_c^2)/3$ (Δ/σ)<sub>max</sub> < 0.001Δρ<sub>max</sub> = 0.221 e Å<sup>-3</sup>Δρ<sub>min</sub> = -0.243 e Å<sup>-3</sup>

Extinction correction: none

Scattering factors from

*International Tables for  
Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °)

S1—O1	1.568 (3)	N1—C7	1.471 (6)
S1—C4	1.763 (6)	C1—C2	1.185 (5)
O1—C3	1.452 (4)	C1—C1'	1.387 (7)
O4—N1	1.216 (4)	C2—C3	1.450 (5)
O5—N1	1.218 (4)		
O1—S1—C4	103.55 (14)	O5—N1—C7	117.9 (3)
C3—O1—S1	118.0 (2)	C2—C1—C1'	179.5 (4)
O4—N1—O5	124.2 (3)	C1—C2—C3	178.8 (3)
O4—N1—C7	117.9 (3)	C2—C3—O1	110.7 (3)

Symmetry code: (i) 1 - *x*, -*y*, 1 - *z*.Backgrounds were obtained from analysis of the scan profile (Blessing *et al.*, 1974).Data collection: *CAD-4 Operations Manual* (Enraf–Nonius, 1977). Cell refinement: *CAD-4 Operations Manual*. Data reduction: *PROCESS* in *MolEN* (Fair, 1990). Program(s) used to solve structure: *SIR* (Burla *et al.*, 1989). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *BTABLE PTABLE CIF IN* in *MolEN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1048). Services for accessing these data are described at the back of the journal.

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*Acta Cryst.* (1998). **C54**, 1030–1033**(5*aR*,9*aR*)-2,4-Dimethyl-5*a*,6,7,8,9,9*a*-hexahydro-1*H*-1,5-benzodiazepine**

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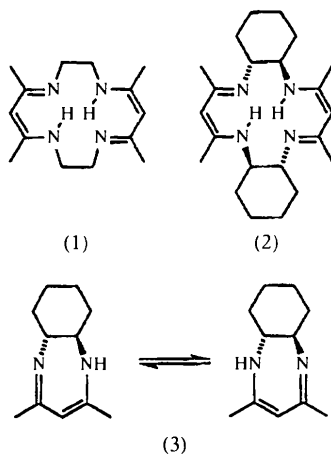
## Abstract

The title compound, C<sub>11</sub>H<sub>18</sub>N<sub>2</sub>, packs in the solid state with one molecule in the asymmetric unit, but with the chiral molecule disordered over two orientations related by twofold rotation. Thus, the molecule is the average of these two orientations, with the amine H

atom present with half occupancy at each N atom and 'pseudo-aromatic' character in the N—C—C—N moiety of the diazepine ring. The molecules are linked to form infinite chains parallel to the *c* axis via N—H...N hydrogen bonds across crystallographic twofold axes, with N...N 3.224 (3) and 3.110 (3) Å (the hydrogen-bonded H atom is disordered).

### Comment

The 14-membered tetraaza macrocycle (Me<sub>4</sub>taen)H<sub>2</sub>, (1), was first reported by Truex & Holm (1972) and is made by stepwise condensations of 4-amino-3-penten-2-one and ethylenediamine. We reported the crystal structure of this compound and the use of the doubly-deprotonated (Me<sub>4</sub>taen)<sup>2-</sup> form as a ligand for zirconium(IV) complexes (Black *et al.*, 1995; Uhrhammer *et al.*, 1993). In an effort to prepare the chiral macrocycle (2), which is of interest for the construction of chiral organometallics, we investigated the reaction of (1*R*,2*R*)-1,2-diaminocyclohexane and 4-amino-3-penten-2-one. When conducted under the conditions used by Truex & Holm (1972) to prepare (1), this reaction yielded a white solid, (3), which was purified by recrystallization from ethanol.



The NMR and mass-spectral data for (3) suggested that this compound has the diazepine structure indicated in the scheme above rather than a macrocyclic structure. The NH resonance for (3) appears at  $\delta$  3.62 p.p.m. rather than at low field (8–12 p.p.m.), as observed for (1) and related compounds in which intramolecular hydrogen bonding is present (Truex & Holm, 1972). Additionally, the parent-ion peak at *m/e* = 178 is consistent with a diazepine structure. However, we could not be sure of the stability of (3) under the conditions of the ionization. To verify the structure, we determined the X-ray crystal structure of (3).

The structure of the molecule is shown in Fig. 1. The cyclohexane ring is in the usual chair conformation.

The seven-membered ring has a sofa conformation with the C8, C9, C10, N11 and C1 atoms coplanar (r.m.s. deviation 0.014 Å); the C6 and N7 atoms are 0.914 (2) and 0.371 (3) Å, respectively, above this plane.

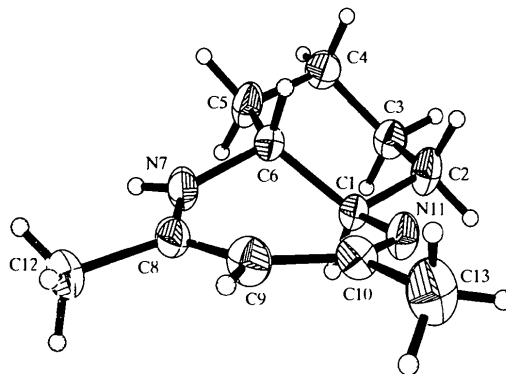


Fig. 1. View of the title molecule. Displacement ellipsoids are represented at the 35% probability level. The disordered H atom at N11 and one set of disordered H atoms at C12 and C13 are not shown.

Examination of the molecular packing (diagram archived as supplementary material) shows that the twofold symmetry operation  $1-x, y, 1-z$ , *i.e.* (i), generates N7<sup>i</sup> at a distance of 3.224 (3) Å from N7, and symmetry operation  $1-x, y, -z$ , *i.e.* (ii), generates N11<sup>ii</sup> 3.110 (3) Å from N11. By considering disorder in the molecular packing, these close contacts can be described as chemically reasonable amine–enamine hydrogen bonds instead of enamine–enamine and amine–amine close contacts. A twofold rotation about an axis passing through the C9 atom and the center of the cyclohexane ring generates an alternate molecular orientation (*i.e.* the enamine N atom is placed at the amine N atom position and *vice versa*) that, in combination with symmetry operation (i), places the enamine N atom in a position to accept a hydrogen bond from the amine group. A second hydrogen bond can be generated in a similar manner with symmetry operation (ii). The hydrogen-bond geometries are listed in Table 2. Thus, the asymmetric unit is an average of these two molecular orientations, with the amine H atom disordered at half occupancy between the H7 and H11 positions. This superposition of two orientations also effectively makes the N7—C8/N11—C1 and C8—C9/C9—C10 pairs of bonds equivalent (see Table 1).

Indications for two orientations of the C12 and C13 methyl H atoms were noted during checking of difference density maps generated near the end of the refinement. Two sets of methyl H-atom positions (H12A—C/H12D—F and H13A—C/H13D—F) were included at half occupancy for each in the final refinement.

The conformation of (3) is similar to that reported by theoretical approaches (Messinger & Buss, 1992).

Structures of medicinally important 1,4-benzodiazepines and related compounds have been reported (Kemmish & Hamor, 1988; Chananont *et al.*, 1981; Gilli *et al.*, 1978; Bandoli & Clemente, 1976; Petcher & Weber, 1976; Svensson & Timby, 1981). Structures of diazepinium salts (Ferguson *et al.*, 1980, 1984; Orioli & Lip, 1974) have also been reported.

## Experimental

See the work of Truex & Holm (1972) for details of sample preparation. (1*R*,2*R*)-1,2-Diaminocyclohexane was used in place of ethylenediamine for the stepwise condensations with 4-amino-3-penten-2-one to produce (3). Crystals of (3) suitable for X-ray analysis were grown from a CHCl<sub>3</sub> solution at room temperature as colorless plates. The configuration of (3) was deduced from the known configuration of the starting materials that is retained during synthesis. NMR and mass-spectral data for (3): <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 4.52 (*s*, 1H), 3.62 (broad singlet, 1H), 2.93 (*d*, *J* = 9.2 Hz, 2H), 2.21 (*d*, *J* = 11.5 Hz, 2H), 1.90 (*s*, 6H), 1.71 (*m*, 2H), 1.26 p.p.m. (*m*, 4H); <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 156.8, 93.1, 61.7, 35.0, 26.2, 24.1 p.p.m.; MS: *m/e* 178 (*M*<sup>+</sup>).

### Crystal data

C<sub>11</sub>H<sub>18</sub>N<sub>2</sub>  
*M<sub>r</sub>* = 178.27  
 Monoclinic  
 C2  
*a* = 16.603 (5) Å  
*b* = 6.743 (1) Å  
*c* = 12.136 (5) Å  
 β = 130.77 (2)°  
*V* = 1029 (1) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 1.151 Mg m<sup>-3</sup>  
*D<sub>m</sub>* not measured

Mo *K*α radiation  
 λ = 0.7107 Å  
 Cell parameters from 25 reflections  
 θ = 12–18°  
 μ = 0.069 mm<sup>-1</sup>  
*T* = 291 (2) K  
 Plate  
 0.49 × 0.44 × 0.24 mm  
 Colorless

### Data collection

Enraf–Nonius CAD-4 diffractometer  
 θ–2θ scans  
 Absorption correction: none  
 4006 measured reflections  
 2571 independent reflections  
 2135 reflections with *I* > 2σ(*I*)

*R*<sub>int</sub> = 0.022  
 θ<sub>max</sub> = 30.0°  
*h* = –23 → 17  
*k* = –9 → 9  
*l* = –11 → 17  
 4 standard reflections  
 frequency: 240 min  
 intensity decay: none

### Refinement

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.044  
*wR* (*F*<sup>2</sup>) = 0.109  
*S* = 1.041  
 2571 reflections  
 120 parameters  
 H atoms riding  
*w* = 1/[σ<sup>2</sup>(*F*<sub>o</sub><sup>2</sup>) + (0.0514*P*)<sup>2</sup> + 0.2726*P*]  
 where *P* = (*F*<sub>o</sub><sup>2</sup> + 2*F*<sub>c</sub><sup>2</sup>)/3

(Δ/σ)<sub>max</sub> = –0.026  
 Δρ<sub>max</sub> = 0.185 e Å<sup>-3</sup>  
 Δρ<sub>min</sub> = –0.148 e Å<sup>-3</sup>  
 Extinction correction: none  
 Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °)

C1–N11	1.461 (2)	C6–N7	1.458 (2)
C1–C2	1.533 (2)	N7–C8	1.314 (2)
C1–C6	1.550 (2)	C8–C9	1.396 (3)
C2–C3	1.512 (2)	C8–C12	1.517 (3)
C3–C4	1.506 (2)	C9–C10	1.402 (3)
C4–C5	1.513 (3)	C10–N11	1.311 (2)
C5–C6	1.528 (2)	C10–C13	1.516 (3)
N11–C1–C2	105.98 (12)	C8–N7–C6	122.94 (14)
N11–C1–C6	113.89 (13)	N7–C8–C9	127.5 (2)
C2–C1–C6	111.47 (13)	N7–C8–C12	115.2 (2)
C3–C2–C1	114.73 (14)	C9–C8–C12	117.3 (2)
C4–C3–C2	109.6 (2)	C8–C9–C10	130.2 (2)
C3–C4–C5	109.9 (2)	N11–C10–C9	129.1 (2)
C4–C5–C6	115.24 (15)	N11–C10–C13	114.8 (2)
N7–C6–C5	106.27 (13)	C9–C10–C13	116.0 (2)
N7–C6–C1	113.54 (13)	C10–N11–C1	124.78 (14)
C5–C6–C1	112.04 (13)		

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

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
N7–H7...N7 <sup>i</sup>	0.86	2.40	3.224 (3)	156
N11–H11...N11 <sup>ii</sup>	0.86	2.25	3.110 (3)	175

Symmetry codes: (i) 1 – *x*, *y*, 1 – *z*; (ii) 1 – *x*, *y*, –*z*.

The two sets of C12 (H12*A*–*C* and H12*D*–*F*) and C13 (H13*A*–*C* and H13*D*–*F*) methyl H atoms were included as riding groups [tetrahedral angles, C–H = 0.96 Å, *U*<sub>iso</sub>(H) = 1.5*U*<sub>iso</sub>(C), occupancy = 0.5], with rotation about the C–CH<sub>3</sub> bond allowed. All other H atoms were included as riding atoms. The occupancies of H7 and H11 were set to 0.5. The H-atom positions (partial and full occupancy) were verified by examination of difference density maps calculated with the H-atom parameters omitted.

Data collection: *CAD-4 Operations Manual* (Enraf–Nonius, 1977). Cell refinement: *CAD-4 Operations Manual* (Enraf–Nonius, 1977). Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *MULTAN80* (Main *et al.*, 1980). Program(s) used to refine structure: *SHELXTL* (Sheldrick, 1995). Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1368). Services for accessing these data are described at the back of the journal.

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## Comment

It has been shown recently (Peseke *et al.*, 1994) that the reaction of certain secondary amines with 3-aryl-2-cyano-5,5-bis(methylthio)penta-2,4-dienitriles, (1), could lead to the 5-monoamino- or 5,5-diamino-substitution product or a pyridine derivative, depending upon the reaction conditions. As part of an ongoing research programme on the design and synthesis of donor-acceptor push-pull polyenes capable of second harmonic generation, we have synthesized compounds (3a) and (3b) from the reaction of (1) and L-(–)-2-hydroxymethylpyrrolidine, (2) (George *et al.*, 1997). It was observed that (1a) and (1b) undergo an intramolecular rearrangement to give the pyridine derivatives (4a) and (4b), respectively, when refluxed in dry methanol in the presence of any base, such as pyridine or secondary amines, or even potassium carbonate, as catalyst.

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## 2-Phenyl-3-(5,6,7,7a-tetrahydro-1H,3H-pyrrolo[1,2-c]oxazol-3-ylidene)-1-propene-1,1-dicarbonitrile and 4-(4-Methoxyphenyl)-2,6-bis(methylthio)pyridine-3-carbonitrile

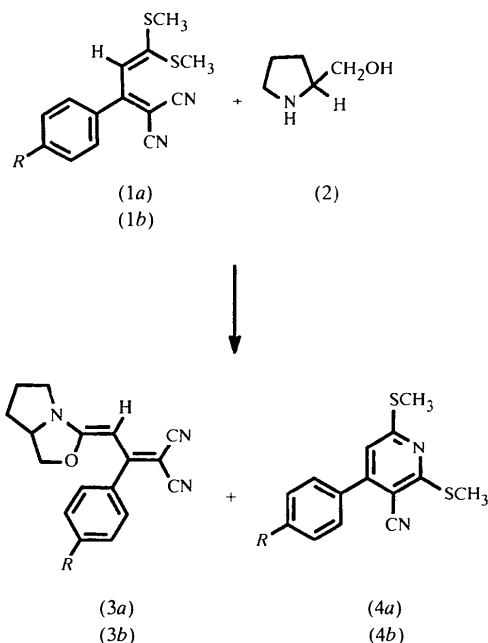
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## Abstract

The reaction of 3-aryl-2-cyano-5,5-bis(methylthio)penta-2,4-dienitrile, (1), with L-(–)-2-hydroxymethylpyrrolidine, (2), gave two types of product, the normal substitution product, (3), and a pyridine derivative, (4). The structures of two representative examples, 2-phenyl-3-(5,6,7,7a-tetrahydro-1H,3H-pyrrolo[1,2-c]oxazol-3-ylidene)-1-propene-1,1-dicarbonitrile, (3a), as its hemibenzene solvate, C<sub>17</sub>H<sub>15</sub>N<sub>3</sub>O.0.5C<sub>6</sub>H<sub>6</sub>, and 4-(4-methoxyphenyl)-2,6-bis(methylthio)pyridine-3-carbonitrile, (4b), C<sub>15</sub>H<sub>14</sub>N<sub>2</sub>OS<sub>2</sub>, have been unambiguously established by X-ray crystallographic analysis. The molecular packing of (4b) involves loosely held dimers, with S1···S1' distances of 3.424(1) Å.



For (a) R=H,  
and (b) R=OCH<sub>3</sub>

We report herein the X-ray structures of compounds (3a) and (4b) (Figs. 1 and 2). Molecule (3a) crystallizes with half a molecule of benzene located on a twofold rotation axis. The absolute configuration of this compound could not be determined reliably [Flack (1983) parameter = –0.4(20)]. The molecular structure of (3a) incorporates a diene-dicarbonitrile skeleton attached to a pyrrolo-oxazole unit at one end and a phenyl substituent at the C2 position. The mean planes containing the phenyl ring (C6–C11, mean deviation 0.005 Å) and the diene-dicarbonitrile moiety (C1, C2, C4, N1, C5 and N2, mean deviation 0.005 Å) make an angle of 84.5(2)° with each other.