

Fig. 1. Perspective view (ORTEP; Johnson, 1965) of the molecule giving the numbering scheme of the unique atoms. Thermal ellipsoids are drawn at the 50% probability level.

Table 1\* gives the atomic coordinates and the molecular dimensions are given in Table 2. The atom-numbering scheme for the molecule, which lies on a center of symmetry, is given in Fig. 1. A stereoview of the packing scheme dominated by edge-face interactions of the aromatic rings is seen in Fig. 2.

**Related literature.** The title compound was prepared in the course of our work on molecular tweezers (Harmata & Barnes, 1990).

\* Lists of H-atom parameters, anisotropic thermal parameters and structure-factor amplitudes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55416 (8 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: GR0203]

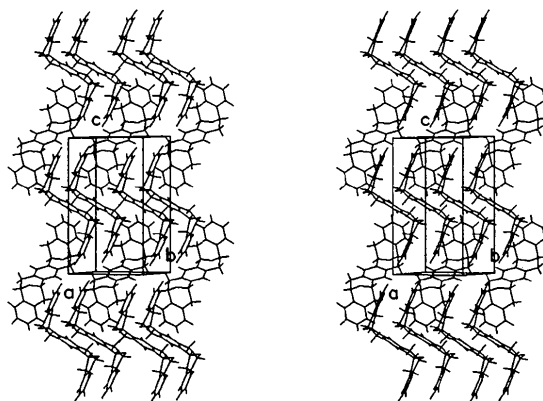


Fig. 2. Stereoview (PLUTO; Motherwell & Clegg, 1978) of the packing down the *a* axis.

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## Structure of a Substituted 2-(Ethyl glycinat- $\alpha$ -ylidene)-1,4-benzodiazepine

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**Abstract.**  $\alpha$ -(7-Chloro-1,3-dihydro-5-phenyl-2*H*-1,4-benzodiazepin-2-ylidene)-2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentane-1-acetic acid ethyl ester, C<sub>25</sub>H<sub>32</sub>ClN<sub>3</sub>O<sub>2</sub>Si<sub>2</sub>, *M*<sub>r</sub> = 498.17, triclinic, *P* $\bar{1}$ , *a* = 10.938 (2), *b* = 13.626 (2), *c* = 10.700 (2) Å,  $\alpha$  = 108.37 (1),  $\beta$  = 114.36 (1),  $\gamma$  = 73.79 (1)°, *V* = 1358.1 (4) Å<sup>3</sup>, *Z* = 2, *D*<sub>x</sub> = 1.218 g cm<sup>-3</sup>, m.p. 409–

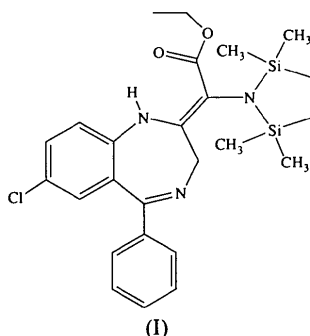
411 K,  $\lambda$ (Cu *K* $\alpha$ ) = 1.54178 Å,  $\mu$  = 23.16 cm<sup>-1</sup>, *F*(000) = 528, *T* = 296 K, *R* = 0.056, *wR* = 0.076 for 2495 unique reflections having *I* > 3.00 $\sigma$ (*I*). The compound has *E* geometry at the exocyclic double bond. A disordered C-atom position in the 2,5-disilazacyclopentane ring was identified. Internal hydrogen bonding of N(1)—H(1*N*) to the carbonyl

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atom O(24) forms a six-membered ring with a mean deviation of 0.012 Å from the plane. No intermolecular distances significantly shorter than normal values are found. High thermal motion is noted at the ethoxy moiety and at the methyl substituents on the disilazacyclopentane ring.

**Experimental.** The title compound  $C_{25}H_{32}ClN_3O_2Si_2$  (I) was synthesized by reaction of the enolate of a *N,N*-bis(silyl)glycinate with a suitably substituted 1,4-benzodiazepine imino phosphate (Fryer, Kudzma, Gu, Lin & Rafalko, 1991). Crystals were



obtained from a methylene chloride–hexane solution by slow evaporation. An orange hexagonal-shaped crystal approximately  $0.20 \times 0.15 \times 0.25$  mm was selected and mounted on a glass fiber. Intensity data were collected on a Rigaku AFC-5 sealed-tube diffractometer with  $\omega/2\theta$  scans, scan speed  $8\text{--}32^\circ \text{ min}^{-1}$  in  $\omega$ , and a scan width of  $(1.57 + 0.30 \tan \theta)^\circ$  using graphite-monochromated  $Cu K\alpha$  radiation. Lattice parameters were determined by least squares using 25 reflections with  $40.2 < 2\theta < 59.2^\circ$ . Three standards ( $2\bar{1}0$ ,  $\bar{1}30$  and  $2\bar{3}1$ ) were measured every 150 reflections. No significant decay was observed (1.3% in 52 h). Data were corrected for Lorentz-polarization effects. An empirical  $\psi$ -scan absorption correction (maximum/minimum transmission factors 1.00/0.87) and a secondary-extinction correction,  $0.1123 \times 10^{-5}$  (Zachariasen, 1967), were applied. A total of 4284 reflections was measured ( $\sin \theta_{\max}/\lambda = 0.56 \text{ \AA}^{-1}$ ;  $0 \leq h \leq 12$ ,  $-15 \leq k \leq 15$ ,  $-12 \leq l \leq 12$ ), 4104 of which were unique ( $R_{\text{int}} = 0.039$ ). The structure was solved by direct methods using *MITHRIL* (Gilmore, 1984) and *DIRDIF* (Beurskens, 1984). 2495 reflections with  $I > 3.00\sigma(I)$  were used for structure solution and refinement. Non-H atoms were refined anisotropically. An occupancy factor of 0.50 was assigned to C(19A) and C(19B) to model the disorder found in the 2,5-disilazacyclopentane ring. All H atoms, except H(1N), were assigned idealized positions and temperature factors [ $H\text{—}C = 0.95 \text{ \AA}$ ;  $B_{\text{eq}}(\text{H}) = 1.2B_{\text{eq}}(\text{C})$ ]. The H atom H(1N), bonded to N(1), was located from a difference map

Table 1. Fractional atomic coordinates and equivalent isotropic temperature factors ( $\text{\AA}^2$ ) with e.s.d.'s in parentheses

$$B_{\text{eq}} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	$B_{\text{eq}}$
N(1)	0.0659 (4)	0.1573 (3)	0.8849 (4)	4.4 (2)
C(2)	0.1582 (4)	0.1854 (3)	0.8523 (5)	3.7 (2)
C(3)	0.1730 (5)	0.2993 (3)	0.9150 (5)	4.4 (2)
N(4)	0.0470 (4)	0.3667 (3)	0.8460 (4)	4.4 (2)
C(5)	−0.0568 (4)	0.3783 (3)	0.8792 (5)	3.9 (2)
C(6)	−0.0573 (4)	0.3246 (3)	0.9820 (5)	4.0 (2)
C(7)	−0.1184 (5)	0.3789 (3)	1.0817 (5)	4.6 (2)
C(8)	−0.1281 (5)	0.3287 (4)	1.1686 (6)	5.1 (2)
C(9)	−0.0801 (5)	0.2228 (4)	1.1586 (6)	5.3 (2)
C(10)	−0.0158 (5)	0.1687 (4)	1.0644 (6)	5.0 (2)
C(11)	−0.0005 (4)	0.2182 (3)	0.9772 (5)	4.1 (2)
Cl(12)	−0.2012 (2)	0.3992 (1)	1.2952 (2)	6.89 (8)
C(13)	0.2306 (4)	0.1172 (3)	0.7732 (5)	4.0 (2)
N(14)	0.3273 (4)	0.1493 (3)	0.7419 (4)	4.4 (2)
Si(15)	0.4983 (1)	0.1392 (1)	0.8461 (2)	5.66 (7)
C(16)	0.5866 (6)	0.0035 (5)	0.8567 (8)	8.3 (4)
C(17)	0.5266 (7)	0.2154 (6)	1.0320 (8)	9.9 (4)
C(18)	0.5569 (7)	0.1941 (6)	0.748 (1)	9.3 (4)
C(19A)†	0.441 (2)	0.252 (2)	0.646 (3)	10 (1)
C(19B)†	0.465 (2)	0.177 (1)	0.596 (2)	7.1 (8)
Si(20)	0.2843 (2)	0.1905 (1)	0.5882 (2)	6.23 (8)
C(21)	0.2203 (9)	0.0899 (6)	0.4248 (8)	10.6 (5)
C(22)	0.1510 (9)	0.3067 (5)	0.5704 (8)	9.5 (4)
C(23)	0.2116 (5)	0.0073 (4)	0.7203 (5)	4.7 (2)
O(24)	0.1372 (4)	−0.0303 (2)	0.7451 (4)	5.8 (2)
O(25)	0.2888 (4)	−0.0507 (3)	0.6443 (4)	6.8 (2)
C(26)	0.2824 (7)	−0.1642 (5)	0.5927 (8)	8.1 (4)
C(27)	0.179 (1)	−0.1799 (7)	0.460 (1)	12.3 (6)
C(28)	−0.1825 (5)	0.4458 (3)	0.8079 (5)	4.4 (2)
C(29)	−0.3090 (5)	0.4457 (4)	0.8070 (6)	6.2 (3)
C(30)	−0.4238 (6)	0.5085 (5)	0.7372 (8)	7.7 (3)
C(31)	−0.4146 (7)	0.5721 (5)	0.6657 (7)	8.1 (3)
C(32)	−0.2903 (7)	0.5720 (5)	0.6647 (7)	7.6 (3)
C(33)	−0.1757 (5)	0.5089 (4)	0.7327 (6)	5.6 (2)
H(1N)	0.061 (5)	0.088 (4)	0.848 (5)	5.1

† Assigned occupancy factor of 0.50.

Table 2. Selected bond distances ( $\text{\AA}$ ) and bond angles ( $^\circ$ ) with e.s.d.'s in parentheses

N(1)—C(2)	1.371 (5)	Si(15)—C(16)	1.846 (6)
N(1)—C(11)	1.389 (6)	Si(15)—C(17)	1.871 (7)
C(2)—C(3)	1.510 (6)	Si(15)—C(18)	1.844 (7)
C(2)—C(13)	1.361 (6)	C(18)—C(19A)	1.51 (2)
C(3)—N(4)	1.473 (6)	C(18)—C(19B)	1.50 (2)
N(4)—C(5)	1.279 (5)	C(19A)—Si(20)	1.90 (2)
C(5)—C(6)	1.502 (6)	C(19B)—Si(20)	1.90 (2)
C(6)—C(11)	1.403 (6)	Si(20)—C(21)	1.856 (8)
C(8)—Cl(12)	1.744 (5)	Si(20)—C(22)	1.827 (7)
C(13)—N(14)	1.438 (5)	C(23)—O(24)	1.222 (5)
C(13)—C(23)	1.465 (6)	C(23)—O(25)	1.338 (5)
N(14)—Si(15)	1.730 (4)	N(1)—H(1N)	0.91 (4)
N(14)—Si(20)	1.742 (4)		
C(2)—N(1)—C(11)	127.1 (4)	C(13)—N(14)—Si(20)	122.5 (3)
N(1)—C(2)—C(3)	113.1 (4)	Si(15)—N(14)—Si(20)	114.8 (2)
N(1)—C(2)—Cl(13)	123.4 (4)	N(14)—Si(15)—C(18)	98.9 (3)
C(3)—C(2)—Cl(13)	123.5 (4)	Si(15)—C(18)—C(19A)	112.5 (7)
C(2)—C(3)—N(4)	109.7 (4)	Si(15)—C(18)—C(19B)	109.6 (7)
C(3)—N(4)—C(5)	118.0 (4)	C(18)—C(19A)—Si(20)	107.6 (9)
N(4)—C(5)—C(6)	123.4 (4)	C(18)—C(19B)—Si(20)	108.2 (9)
C(5)—C(6)—C(11)	120.9 (4)	N(14)—Si(20)—C(19A)	97.3 (6)
N(1)—C(11)—C(6)	123.3 (4)	N(14)—Si(20)—C(19B)	97.0 (6)
C(2)—C(13)—N(14)	121.9 (4)	C(13)—C(23)—O(24)	124.9 (4)
C(2)—C(13)—C(23)	119.3 (4)	C(13)—C(23)—O(25)	113.0 (4)
N(14)—C(13)—C(23)	118.8 (4)	O(24)—C(23)—O(25)	122.1 (4)
C(13)—N(14)—Si(15)	122.5 (3)		

and refined isotropically. Full-matrix least-squares refinement minimizing  $\sum w(|F_o| - |F_c|)^2$ , where  $w = 1/\sigma^2(F)$ , resulted in values of  $R = 0.056$ ,  $wR = 0.076$  and  $S = 1.72$ .  $|\Delta/\sigma|_{\max} < 0.1$  in the final refinement cycle and the minimum and maximum peaks in the

final difference Fourier map were  $-0.25$  and  $0.39 \text{ e } \text{Å}^{-3}$ , respectively. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2A). Calculations were performed on a VAX II computer using the *TEXSAN* software package (Molecular Structure Corporation, 1985). Atomic parameters are given in Table 1, selected bond distances and angles in Table 2.\* Fig. 1 shows the atom-labeling scheme.

**Related literature.** The title compound is a useful intermediate in the synthesis of highly functionalized 1,4-benzodiazepines. Although X-ray crystal structures of numerous 1,4-benzodiazepines are known, structures of 1,4-benzodiazepines with an exocyclic double bond with possible *E* or *Z* isomers have not been reported in the literature. *E* configuration at the exocyclic double bond of the title compound was suggested by <sup>1</sup>H-<sup>1</sup>H 2D-NOSEY NMR spectra (Fryer *et al.*, 1991) and is now confirmed by X-ray crystal-structure analysis. The apparently erroneous *Z* configuration previously assigned at the exocyclic double bond of related compounds was based solely

\* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, least-squares-planes data, bond distances and angles involving H atoms, additional bond distances and angles involving non-H atoms, and intermolecular distances less than 3.6 Å have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55402 (40 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

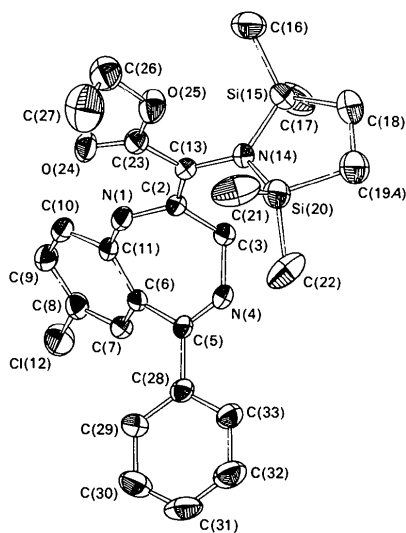


Fig. 1. ORTEP plot (Johnson, 1976) of the title compound with atom numbering and 30% probability ellipsoids. Atom C(19B) and H atoms are omitted.

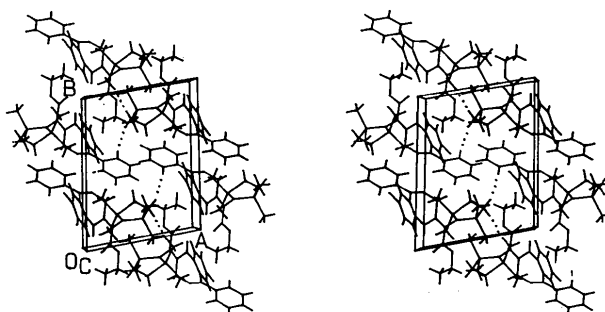


Fig. 2. Stereoview of the molecular packing projected along *c*. Close approaches to C(18) are marked with broken lines. Atom C(19B) and associated H atoms are removed for clarity.

on facile cyclizations to imidazo[1,5-*a*][1,4]benzodiazepines (Walser, Flynn & Fryer, 1978).

To avoid an unfavorable eclipsed conformation of C atoms C(18) and C(19) in the disilazacyclopentane ring, C(19) is disordered. Positions C(19A) and C(19B) are found above and below the disilazacyclopentane ring plane, defined by Si(15)—N(14)—Si(20), by 0.643 and 0.369 Å, respectively. Multiple occupancy by C(18) may be restricted owing to intermolecular close approaches of 2.34–2.49 Å by the aromatic H(29) and the silane methyl-C(21)-group H atoms (Dunitz, 1979). Fig. 2 shows a stereoview in which close approaches to H atoms associated with C(18) are indicated by broken lines. Some disorder or high thermal motion is noted for C(18) above and below the disilazacyclopentane ring which yields an averaged, and therefore shorter than expected, bond length for C(18)—Si(15) of 1.844 Å (Allen *et al.*, 1987). Pronounced thermal motion is noted, particularly for those atoms comprising the ethoxy tail and the disilazacyclopentane ring.

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