C4a	0.1799 (6)	0.0688 (12)	0.4029 (6)	0.031 (3)
C4	0.2133 (7)	0.1846 (12)	0.3415 (6)	0.036 (3)
C5	0.1756 (6)	0.1858 (12)	0.2550 (6)	0.035 (3)
C6	0.0992 (6)	0.0701 (11)	0.2208 (5)	0.026 (2)
C7	0.0606 (6)	−0.0530 (11)	0.2801 (6)	0.029 (2)
C7a	0.1028 (7)	−0.0513 (12)	0.3721 (6)	0.031 (3)
C8	0.0810 (9)	−0.3182 (15)	0.6577 (7)	0.067 (4)
C9	0.2527 (7)	0.3571 (13)	0.5882 (7)	0.049 (3)
C10	0.1200 (8)	0.2245 (13)	0.0537 (6)	0.050 (3)
C11	0.0254 (8)	−0.3734 (13)	0.1896 (7)	0.049 (3)

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

S1—C2	1.757 (9)	S4—C6	1.763 (8)
S1—C7a	1.733 (8)	S4—C10	1.781 (10)
S2—C2	1.739 (8)	S5—C7	1.787 (9)
S2—C8	1.824 (12)	S5—C11	1.816 (10)
S3—C3	1.780 (9)	C2—C3	1.353 (12)
S3—C9	1.798 (9)	C3—C4a	1.440 (12)
C2—S1—C7a	90.7 (4)	C2—C3—C4a	114.7 (8)
C2—S2—C8	101.2 (5)	C3—C4a—C4	132.0 (9)
C3—S3—C9	101.2 (4)	C3—C4a—C7a	109.9 (8)
C6—S4—C10	102.6 (4)	S4—C6—C5	124.4 (7)
C7—S5—C11	100.8 (4)	S4—C6—C7	116.7 (7)
S1—C2—S2	124.0 (5)	S5—C7—C6	122.0 (6)
S1—C2—C3	111.5 (6)	S5—C7—C7a	120.4 (7)
S2—C2—C3	124.4 (7)	S1—C7a—C4a	113.2 (6)
S3—C3—C2	123.5 (7)	S1—C7a—C7	125.7 (7)
S3—C3—C4a	121.6 (7)		

The space group was uniquely determined to be $P2_1/n$ from the systematic absences: $h0l$, $h + l = 2n + 1$; $0k0$, $k = 2n + 1$.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1994). Program(s) used to solve structure: *SAPI91* (Fan, 1991). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, together with a stereoview of the unit-cell packing, have been deposited with the IUCr (Reference: FG1108). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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S-[(Dicyclohexylamino)(phenyl)(1-pyrrolidinyl)phosphinimino]cyclotrithiazene

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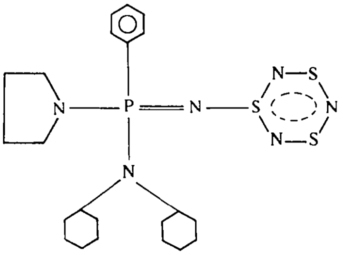
Abstract

In the title compound, $(C_6H_5)(NC_4H_8)[N(C_6H_{11})_2]PN(S_3N_3)$, the cyclotrithiazene ring adopts a distorted-chair conformation. The tricoordinated S atom has a maximum deviation of 0.658 (6) Å from the mean plane of the other five atoms of the S_3N_3 ring.

Comment

Very few crystal structure data on monosubstituted cyclotrithiazene derivatives are available (Chivers, Oakley, Cordes & Pennington, 1981; Elias, Sudheendra Rao & Varghese, 1990; Holt & Holt, 1974; Holt, Holt & Watson, 1977). Phosphiniminocyclotrithiazenes, which are examples of 8π-electron systems, provide an opportunity to study experimentally the effects of varying the substituents attached to phosphorus on the bonding pattern and the conformation of the heterocycle. A detailed and systematic investigation has been undertaken and the present work on the title compound, (I), forms a part of this study.



(I)

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The S—N bond distances in the S_3N_3 ring can be categorized into three groups: (i) 1.640 (5), 1.622 (4); (ii) 1.599 (5), 1.597 (5); (iii) 1.583 (6), 1.579 (6) Å. All these bonds are shorter than the S—N single-bond distance of 1.76 Å (Cruickshank, 1964) and longer than the double bond of 1.55 Å (Bata, Coppens & Koetzle, 1977). Similar types of S—N bond-length variations are also observed in $Ph_3PN\text{-}S_3N_3$ (Holt & Holt, 1974), $(C_5H_{10}N)_3PN\text{-}S_3N_3$ (Elias *et al.*, 1990) and $(C_6H_{12}N)Ph_2PN\text{-}S_3N_3$ (Mohan, 1990). In the S_3N_3 ring, the angle at S1, 106.1 (3)°, is the smallest, while the angle of 123.5 (3)° at N2 is the largest. The N1, S2, N2, S3 and N3 atoms are close to a plane; however, their deviations from the mean plane are significant. The tricoordinated S atom deviates from the mean plane of other skeletal atoms by 0.658 (6) Å. From the signs of the torsion angles, it can be concluded that the folding in the cyclotrithiazene ring tends towards a chair conformation. This pattern is noticeable in the three structures reported above.

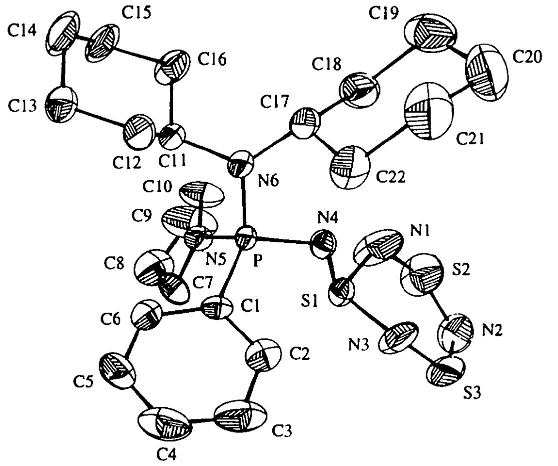

Fig. 1. View of $(C_6H_5)(NC_4H_8)[N(C_6H_{11})_2]PN\text{-}(S_3N_3)$ showing the labelling of the non-H atoms. Displacement ellipsoids are shown at the 50% probability level.

The exocyclic P—N4 bond distance, 1.590 (4) Å, is shorter than the P—N single-bond distance, while the adjoining S1—N4 bond length, 1.581 (4) Å, is longer than the S—N double-bond distance. This feature is also apparent in the three reported structures. This could be due to the electron delocalization at N4. The angle at N4 is 120.8 (2)°, compared with 120.0 (2), 121.0 (6) and 126.5 (3)° in the three reported cyclotrithiazene structures. It may be suggested that the observed sp^2-hybridized state of N4 offers a favourable situation for π bonding between the heterocycle and the exocyclic part of the compound. However, contribution of the π-manifold of the heterocycle to the S—N bond shortening cannot be discounted.

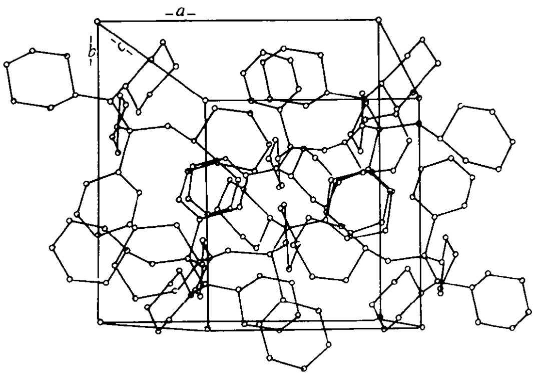

Fig. 2. Packing of the molecules in the unit cell of $(C_6H_5)(NC_4H_8)[N(C_6H_{11})_2]PN\text{-}(S_3N_3)$.

Experimental

Synthesis was carried out by the reaction of $(C_6H_5)(NC_4H_8)[N(C_6H_{11})_2]P$ with S_4N_4. Crystals of the title compound were obtained by evaporation of a CH_2Cl_2/CH_3CN (1:1) solution.

Crystal data

$C_{22}H_{35}N_6PS_3$
$M_r = 510.71$
Monoclinic
$P2_1/n$
$a = 10.1856\,(1)$ Å
$b = 10.8535\,(1)$ Å
$c = 23.1658\,(2)$ Å
$\beta = 94.77\,(1)°$
$V = 2552.10\,(4)$ Å^3
$Z = 4$
$D_x = 1.329$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 4–19°$
$\mu = 0.376$ mm^{-1}
$T = 300\,(1)$ K
Cuboid
0.3 × 0.1 × 0.1 mm
Red

Data collection

Enraf- Nonius CAD-4 diffractometer
$\omega–2\theta$ scans
Absorption correction: none
5038 measured reflections
2905 independent reflections
2752 observed reflections [$I > 3\sigma(I)$]
$R_{\rm int} = 0.0365$

$\theta_{\rm max} = 24.98°$
$h = -12 \rightarrow 12$
$k = 0 \rightarrow 12$
$l = 0 \rightarrow 27$
2 standard reflections monitored every 100 reflections
frequency: 60 min
intensity decay: 3%

Refinement

Refinement on F^2
$R(F) = 0.0551$
$wR(F^2) = 0.1470$
$S = 1.093$
2752 reflections
429 parameters
H atoms refined isotropically
$w = 1/[\sigma^2(F_o^2) + (0.1057P)^2 + 2.5452P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = 0.938$
$\Delta\rho_{\rm max} = 0.496$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.446$ 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 (Å²)*

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

	x	*y*	*z*	U_{eq}
P	0.42453 (10)	0.22992 (10)	0.09698 (5)	0.0305 (3)
S1	0.66415 (10)	0.20102 (11)	0.05134 (6)	0.0418 (3)
S2	0.8777 (2)	0.3133 (2)	0.00550 (9)	0.0792 (6)
S3	0.90502 (13)	0.08152 (14)	0.05659 (9)	0.0745 (6)
N1	0.7449 (5)	0.3267 (5)	0.0372 (3)	0.081 (2)
N2	0.9576 (4)	0.1903 (5)	0.0196 (2)	0.072 (2)
N3	0.7708 (4)	0.1098 (4)	0.0851 (2)	0.0650 (14)
N4	0.5803 (3)	0.2455 (4)	0.1018 (2)	0.0433 (10)
N5	0.3436 (3)	0.2602 (3)	0.0353 (2)	0.0378 (9)
N6	0.3723 (3)	0.3273 (3)	0.1443 (2)	0.0328 (8)
C1	0.3808 (4)	0.0733 (4)	0.1121 (2)	0.0361 (10)
C2	0.2505 (5)	0.0343 (5)	0.1041 (3)	0.0519 (14)
C3	0.2176 (6)	−0.0844 (5)	0.1173 (3)	0.064 (2)
C4	0.3134 (7)	−0.1643 (6)	0.1382 (3)	0.069 (2)
C5	0.4417 (7)	−0.1276 (5)	0.1480 (3)	0.069 (2)
C6	0.4758 (5)	−0.0090 (4)	0.1340 (2)	0.0469 (13)
C7	0.3196 (7)	0.1712 (6)	−0.0126 (3)	0.058 (2)
C8	0.2708 (10)	0.2431 (8)	−0.0631 (3)	0.087 (2)
C9	0.3419 (13)	0.3649 (9)	−0.0522 (4)	0.113 (4)
C10	0.3425 (10)	0.3843 (6)	0.0101 (3)	0.067 (2)
C11	0.4542 (4)	0.3687 (4)	0.1965 (2)	0.0379 (11)
C12	0.5517 (6)	0.4693 (5)	0.1852 (3)	0.0493 (13)
C13	0.6220 (7)	0.5134 (7)	0.2421 (4)	0.069 (2)
C14	0.6848 (6)	0.4126 (7)	0.2776 (3)	0.068 (2)
C15	0.5879 (6)	0.3125 (7)	0.2889 (3)	0.062 (2)
C16	0.5194 (6)	0.2647 (5)	0.2327 (3)	0.0479 (12)
C17	0.2285 (4)	0.3538 (4)	0.1429 (2)	0.0320 (10)
C18	0.1600 (5)	0.2933 (5)	0.1916 (3)	0.0429 (12)
C19	0.0126 (5)	0.3207 (5)	0.1842 (3)	0.0538 (15)
C20	−0.0149 (6)	0.4568 (6)	0.1818 (3)	0.065 (2)
C21	0.0558 (5)	0.5186 (6)	0.1350 (3)	0.058 (2)
C22	0.2039 (4)	0.4932 (4)	0.1427 (3)	0.0423 (12)

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

P—N4	1.590 (4)	S2—N2	1.583 (6)
P—N5	1.622 (4)	S2—N1	1.599 (5)
P—N6	1.643 (4)	S3—N2	1.579 (6)
P—C1	1.799 (4)	S3—N3	1.597 (5)
S1—N4	1.581 (4)	N6—C11	1.480 (6)
S1—N3	1.622 (4)	N6—C17	1.490 (5)
S1—N1	1.640 (5)		
N4—P—N5	118.1 (2)	S2—N1—S1	118.2 (3)
N4—P—N6	105.1 (2)	S3—N2—S2	123.5 (3)
N5—P—N6	106.8 (2)	S3—N3—S1	118.7 (3)
N4—P—C1	110.4 (2)	S1—N4—P	120.8 (2)
N5—P—C1	104.3 (2)	C10—N5—P	121.5 (4)
N6—P—C1	112.2 (2)	C7—N5—P	124.7 (4)
N4—S1—N3	102.2 (2)	C11—N6—C17	116.4 (3)
N4—S1—N1	101.8 (3)	C11—N6—P	123.3 (3)
N3—S1—N1	106.1 (3)	C17—N6—P	118.8 (3)
N2—S2—N1	114.9 (3)	C6—C1—P	120.3 (3)
N2—S3—N3	114.9 (2)	C2—C1—P	120.7 (3)

All H atoms were located from difference electron density maps.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *CAD*-4 *Software*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *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: DE1019). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Conformationally Restricted Aspartic Acid Analogue

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Abstract

In the title compound, (1*R*,2*R*,3*S*,4*S*)-3-benzamido-3-methoxycarbonylbicyclo[2.2.1]heptane-2-carboxylic acid, $C_{17}H_{19}NO_5$, the norbornyl group shows distortion from $C_{2v}(mm2)$ symmetry of the parent hydrocarbon. The values determined for the torsion angles about the N—C$^{\alpha}$ (φ) and C$^{\alpha}$—CO (ψ) bonds correspond to a semi-extended conformation for the amino acid residue. The structure is stabilized by an intermolecular O—H···O hydrogen bond between the carboxy and amide groups and an intramolecular N—H···O hydrogen bond involving the benzamido and the carboxylic acid groups.