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P2871-1

P R I N C E T O N U N I V E R S I T Y

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Report No. 94033

$C_{10}H_{18}N_6S_2$

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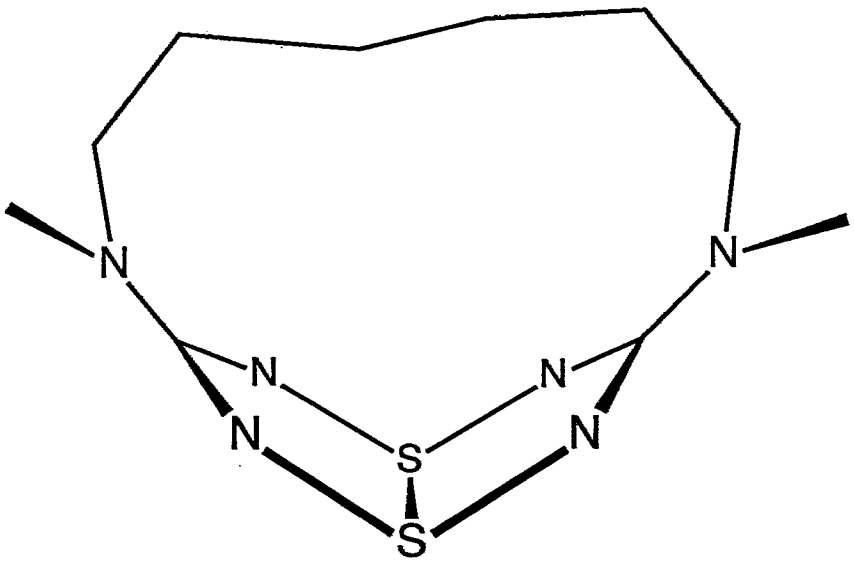


$C_{10}H_{18}N_6S_2$

S2

P2871-2

Experimental.

A yellow irregular chunk was cut to 0.42 x 0.50 x 0.50 mm in size, mounted on a glass fiber with epoxy cement, and then transferred to a Siemens P4 diffractometer for characterization and data collection at 296K [graphite-monochromated Mo Kα radiation, λ = 0.71073 Å]. Unit cell parameters were determined from the setting angles of 25 centered reflections having $30 \leq 2\theta \leq 40^{\circ}$ and were as follows: $\underline{a}$ = 8.356(1), $\underline{b}$ = 12.991(2), $\underline{c}$ = 13.298(2) Å, β = 111.705(9)$^{\circ}$ and V = 1341.2(3) Å^3. Axial photographs and preliminary peak scans through reciprocal space were consistent with the monoclinic space group $P2_1/c$.

One quadrant of data ($+h,+k,\pm\ell$) was collected in the ω scan mode with 2θ ranging from 4.0 to 50.0°, and scan speeds varying from 3.97 to 8.08°/min. Three standards (200, 161, 1010) were measured for every 97 reflections during the data collection period, and showed no significant deviations from their mean intensity values (0.9940, 1.0008, 1.0071 for min., mean, max., respectively, i.e., within ±0.7% of the mean). A total of 2669 reflections were measured, 2371 were unique (R_{int} = 1.21%), and 1952 had $F > 3.0\sigma(F)$ and were considered observed. Corrections were made for Lorentz and polarization effects but not for absorption or extinction.

The structure was successfully solved by direct methods (XS:TREF) in the monoclinic space group $P2_1/c$ (No. 14) and refined by full-matrix least-squares using the Siemens SHELXTL PLUS program package.[1] All of the non-H atoms were refined with anisotropic displacement coefficients, H atoms were included with a riding model [C-H = 0.96 Å, U(H) = 1.2U(C)], and the weighting scheme employed was $w^{-1} = \sigma^2(F) + 0.0008F^2$. The methyl H atoms were located in a difference-Fourier map and their positions idealized to give C-H = 0.96 Å and tetrahedral angles at the C atoms. The refinements converged to R = 3.88%, wR = 5.12% and S = 1.33 with 163 variables and 12.0 reflections per refined parameter.[2] The maximum Δ/σ in the final cycle of least-squares was 0.001, and the residual peaks on the final $\Delta\rho$ map ranged from −0.28 to 0.30 eÅ^{-3}. Scattering factors were taken from the *International Tables for Crystallography, Vol C.*[3]

P2871-3

Footnotes and references.

1. (a) Sheldrick, G. M. (1990). SHELXTL PLUS 4.21 for Siemens Crystallographic Research Systems. Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA. (b) All computations were performed on a MicroVAX computer. (c) All non-hydrogen scattering factors were corrected for both the real and imaginary components of anomalous dispersion.

2. (a) $R = \sum||F_o|-|F_c|| \,/\, \sum|F_o|$, (b) $wR = [\sum w(|F_o|-|F_c|)^2 \,/\, \sum w|F_o|^2]^{1/2}$, (c) $S = [\sum w(|F_o|-|F_c|)^2 \,/\, (M-N)]^{1/2}$ where M is the number of observed reflections, and N is the number of parameters refined.

3. (a) Maslen, E. N., Fox, A. G. & O'Keefe, M. A. (1992). International Tables for Crystallography: Mathematical, Physical and Chemical Tables, Vol C, Chapter 6, edited by A. J. C. Wilson, pp. 476-516, Dordrecht, The Netherlands: Kluwer. (b) Creagh, D. C. & McAuley, W. J. (1992). International Tables for Crystallography: Mathematical, Physical and Chemical Tables, Vol C, Chapter 4, edited by A. J. C. Wilson, pp. 206-222, Dordrecht, The Netherlands: Kluwer.

P2871-4

Miscellaneous.

1. The observed S-S distance of 2.443(1) Å is comparable to the value of 2.428 Å reported for PTZCNB (JACS, 1981, 103, 1540-1544) but is significantly longer than the value of 2.408 Å seen in the closely related cyclophane 92009 (Acta Cryst., 1994, C50, 108-110).

2. (a) The average N-S-N angles in PTZCNB, 92009 and 94033 are 113.8, 113.2 and 111.8°, respectively.

   (b) The average dihedral angles between the N_2S_2 planes in PTZCNB, 92009 and 94033 are 113.8, 113.1 and 111.7°, respectively.

   (c) The average dihedral angles between the CN_2 and N_2S_2 planes in PTZCNB, 92009 and 94033 are 165.6, 167.8 and 156.5°, respectively.

   (d) The average dihedral angles between the CN_2S_2 planes in PTZCNB, 92009 and 94033 are 108.9, 108.9 and 103.6°, respectively.

   (e) These observations 2a-d are consistent with additional folding of the dithiatetrazocine rings in these cyclophanes due in part to the shortening of the $(CH_2)_x$ bridge in the current study, i.e., x = 8 in 92009 versus x = 6 in 94033.

3. The exocyclic N atoms bend slightly outwards and away from each other. The N-C bond is bent out of the CN_2 plane by approximately 5.2° . The corresponding values in PTZCNB and 92009 are 6.0 and 5.0°, respectively.

4. In contrast to PTZCNB and 92009, there are no close intermolecular S•••S contacts in 94033. The shortest in the latter is S(1)•••S(1) (1-x,1-y,-z) = 4.559(1) Å.

5. The N-C-N-CH_2 twist angles are 11.3 and 20.9° in 94033, and 5.4 and 12.8° in 92009.

STRUCTURE DETERMINATION SUMMARY

Crystal Data

Formula	$C_{10}H_{18}N_6S_2$
Color; Habit	Yellow irregular chunk
Crystal Size (mm)	0.42 x 0.50 x 0.50
Crystal System	Monoclinic
Space Group	$P2_1/c$ (No. 14)
Unit Cell Dimensions	$\underline{a}$ = 8.356(1) Å
	$\underline{b}$ = 12.991(2) Å
	$\underline{c}$ = 13.298(2) Å
	β = 111.705(9)°
Volume	1341.2(3) $Å^3$
Z	4
Formula Weight	286.4
Density(calc.)	1.418 Mg/m^3
Absorption Coefficient	0.390 mm^{-1}
F(000)	608

P2871-6

Data Collection

Diffractometer Used	Siemens P4
Radiation	MoKα (λ = 0.71073 Å)
Temperature (K)	296
Monochromator	Highly oriented graphite crystal
2θ Range	4.0 to 50.0°
Scan Type	ω
Scan Speed	Variable; 3.97 to 8.08°/min. in ω
Scan Range (ω)	1.20°
Background Measurement	Stationary crystal and stationary counter at beginning and end of scan, each for 25.0% of total scan time
Standard Reflections	3 measured every 97 reflections
Index Ranges	$0 \leq h \leq 9$, $0 \leq k \leq 15$ $-15 \leq \ell \leq 14$
Reflections Collected	2669
Independent Reflections	2371 (R_{int} = 1.21%)
Observed Reflections	1952 ($F > 3.0\sigma(F)$)
Absorption Correction	N/A

P2871-7

Solution and Refinement

System Used	Siemens SHELXTL PLUS (VMS)
Solution	Direct Methods (XS:TREF)
Refinement Method	Full-Matrix Least-Squares (XLS)
Quantity Minimized	$\sum w(F_o - F_c)^2$
Absolute Structure	N/A
Extinction Correction	N/A
Hydrogen Atoms	Riding model, C–H = 0.96 Å, U(H) = 1.2U(C); methyl H atoms located in a difference-Fourier map and then idealized
Weighting Scheme	$w^{-1} = \sigma^2(F) + 0.0008F^2$
Number of Parameters Refined	163
Final R Indices (obs. data)	R = 3.88%, wR = 5.12%
R Indices (all data)	R = 4.64%, wR = 5.27%
Goodness-of-Fit	S = 1.33
Largest and Mean Δ/σ	0.001, 0.000
Data-to-Parameter Ratio	12.0:1
Largest Difference Peak	0.30 eÅ^{-3}
Largest Difference Hole	-0.28 eÅ^{-3}

P2871-8

Table S1. Atomic coordinates ($x10^4$) and equivalent isotropic displacement coefficients ($Å^2 x10^3$)

	x	y	z	U(eq)
S(1)	6100(1)	3472(1)	-289(1)	51(1)
S(2)	7390(1)	1979(1)	836(1)	43(1)
N(1)	5009(3)	2689(2)	-1235(2)	49(1)
N(2)	6169(3)	1249(2)	-94(2)	44(1)
N(3)	9148(3)	2236(2)	673(2)	43(1)
N(4)	7929(3)	3735(2)	-358(2)	50(1)
N(5)	4860(2)	1057(2)	-1952(2)	44(1)
N(6)	10398(3)	2976(2)	-440(2)	48(1)
C(1)	5393(3)	1678(2)	-1093(2)	39(1)
C(2)	9122(3)	2970(2)	-67(2)	41(1)
C(3)	3910(4)	1467(3)	-3026(2)	62(1)
C(4)	5369(3)	-31(2)	-1863(2)	52(1)
C(5)	6875(3)	-237(2)	-2199(2)	56(1)
C(6)	8606(3)	258(2)	-1502(2)	52(1)
C(7)	9060(4)	1180(2)	-2017(2)	55(1)
C(8)	10952(4)	1531(3)	-1476(2)	61(1)
C(9)	11445(3)	2062(2)	-378(2)	53(1)
C(10)	10548(4)	3829(2)	-1122(3)	68(1)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

P2871-9

Table S2. Bond lengths (Å)

S(1)-S(2)	2.443 (1)	S(1)-N(1)	1.613 (2)
S(1)-N(4)	1.601 (3)	S(2)-N(2)	1.592 (2)
S(2)-N(3)	1.598 (2)	N(1)-C(1)	1.348 (3)
N(2)-C(1)	1.363 (3)	N(3)-C(2)	1.364 (3)
N(4)-C(2)	1.358 (3)	N(5)-C(1)	1.333 (3)
N(5)-C(3)	1.454 (3)	N(5)-C(4)	1.468 (3)
N(6)-C(2)	1.332 (4)	N(6)-C(9)	1.459 (4)
N(6)-C(10)	1.466 (4)	C(4)-C(5)	1.507 (5)
C(5)-C(6)	1.541 (3)	C(6)-C(7)	1.496 (4)
C(7)-C(8)	1.544 (4)	C(8)-C(9)	1.527 (4)

Table S3. Bond angles (°)

S(2)-S(1)-N(1)	88.3(1)	S(2)-S(1)-N(4)	89.5(1)
N(1)-S(1)-N(4)	111.5(1)	S(1)-S(2)-N(2)	89.2(1)
S(1)-S(2)-N(3)	88.3(1)	N(2)-S(2)-N(3)	112.1(1)
S(1)-N(1)-C(1)	117.9(1)	S(2)-N(2)-C(1)	116.8(2)
S(2)-N(3)-C(2)	118.3(2)	S(1)-N(4)-C(2)	116.3(2)
C(1)-N(5)-C(3)	120.6(2)	C(1)-N(5)-C(4)	121.2(2)
C(3)-N(5)-C(4)	117.9(2)	C(2)-N(6)-C(9)	121.3(2)
C(2)-N(6)-C(10)	119.9(2)	C(9)-N(6)-C(10)	117.6(3)
N(1)-C(1)-N(2)	122.5(2)	N(1)-C(1)-N(5)	118.8(2)
N(2)-C(1)-N(5)	118.4(2)	N(3)-C(2)-N(4)	122.1(3)
N(3)-C(2)-N(6)	118.1(2)	N(4)-C(2)-N(6)	119.6(2)
N(5)-C(4)-C(5)	113.4(2)	C(4)-C(5)-C(6)	116.7(2)
C(5)-C(6)-C(7)	113.6(2)	C(6)-C(7)-C(8)	114.4(2)
C(7)-C(8)-C(9)	116.6(3)	N(6)-C(9)-C(8)	111.7(2)

P2871-10

Table S4. Bond lengths involving H atoms (Å)

C(3)-H(3a)	0.960	C(3)-H(3b)	0.960
C(3)-H(3c)	0.960	C(4)-H(4a)	0.960
C(4)-H(4b)	0.960	C(5)-H(5a)	0.960
C(5)-H(5b)	0.960	C(6)-H(6a)	0.960
C(6)-H(6b)	0.960	C(7)-H(7a)	0.960
C(7)-H(7b)	0.960	C(8)-H(8a)	0.960
C(8)-H(8b)	0.960	C(9)-H(9a)	0.960
C(9)-H(9b)	0.960	C(10)-H(10a)	0.960
C(10)-H(10b)	0.960	C(10)-H(10c)	0.960

Table S5. Bond angles involving H atoms (°)

N(5)-C(3)-H(3a)	109.5(2)	N(5)-C(3)-H(3b)	109.5(2)
H(3a)-C(3)-H(3b)	109.5(1)	N(5)-C(3)-H(3c)	109.5(2)
H(3a)-C(3)-H(3c)	109.5(1)	H(3b)-C(3)-H(3c)	109.5(1)
N(5)-C(4)-H(4a)	108.5(1)	N(5)-C(4)-H(4b)	108.5(1)
H(4a)-C(4)-H(4b)	109.5(1)	H(4a)-C(4)-C(5)	108.5(1)
H(4b)-C(4)-C(5)	108.5(1)	C(4)-C(5)-H(5a)	107.6(1)
C(4)-C(5)-H(5b)	107.6(1)	H(5a)-C(5)-H(5b)	109.5(1)
H(5a)-C(5)-C(6)	107.6(1)	H(5b)-C(5)-C(6)	107.6(2)
C(5)-C(6)-H(6a)	108.4(1)	C(5)-C(6)-H(6b)	108.4(2)
H(6a)-C(6)-H(6b)	109.5(1)	H(6a)-C(6)-C(7)	108.4(2)
H(6b)-C(6)-C(7)	108.4(2)	C(6)-C(7)-H(7a)	108.2(1)
C(6)-C(7)-H(7b)	108.2(2)	H(7a)-C(7)-H(7b)	109.5(1)
H(7a)-C(7)-C(8)	108.2(2)	H(7b)-C(7)-C(8)	108.2(2)
C(7)-C(8)-H(8a)	107.7(2)	C(7)-C(8)-H(8b)	107.7(2)
H(8a)-C(8)-H(8b)	109.5(1)	H(8a)-C(8)-C(9)	107.7(2)
H(8b)-C(8)-C(9)	107.7(1)	N(6)-C(9)-H(9a)	108.9(1)
C(8)-C(9)-H(9a)	108.9(2)	N(6)-C(9)-H(9b)	108.9(2)
C(8)-C(9)-H(9b)	108.9(2)	H(9a)-C(9)-H(9b)	109.5(1)
N(6)-C(10)-H(10a)	109.5(2)	N(6)-C(10)-H(10b)	109.5(2)
H(10a)-C(10)-H(10b)	109.5(1)	N(6)-C(10)-H(10c)	109.5(1)
H(10a)-C(10)-H(10c)	109.5(1)	H(10b)-C(10)-H(10c)	109.5(1)

P2871-11

Table S6. Anisotropic displacement coefficients ($Å^2 x10^3$)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	58(1)	44(1)	54(1)	12(1)	26(1)	-2(1)
S(2)	51(1)	48(1)	32(1)	-2(1)	20(1)	-1(1)
N(1)	44(1)	53(1)	47(1)	11(1)	12(1)	4(1)
N(2)	50(1)	45(1)	39(1)	-7(1)	19(1)	3(1)
N(3)	46(1)	45(1)	36(1)	1(1)	14(1)	2(1)
N(4)	61(1)	34(1)	57(1)	-1(1)	24(1)	4(1)
N(5)	38(1)	56(1)	37(1)	-4(1)	13(1)	0(1)
N(6)	48(1)	52(1)	48(1)	-15(1)	22(1)	-2(1)
C(1)	31(1)	51(1)	39(1)	-2(1)	16(1)	3(1)
C(2)	46(1)	38(1)	36(1)	-12(1)	12(1)	-8(1)
C(3)	54(2)	88(2)	38(1)	7(2)	10(1)	1(1)
C(4)	61(2)	50(2)	42(1)	-20(1)	16(1)	-8(1)
C(5)	67(2)	44(1)	54(2)	-6(1)	21(1)	-12(1)
C(6)	59(2)	50(2)	46(1)	10(1)	18(1)	2(1)
C(7)	68(2)	52(2)	44(1)	2(1)	21(1)	0(1)
C(8)	57(2)	69(2)	68(2)	-9(1)	35(1)	-11(2)
C(9)	35(1)	71(2)	54(2)	-6(1)	17(1)	-6(1)
C(10)	77(2)	66(2)	70(2)	-27(2)	37(2)	1(2)

The anisotropic displacement factor exponent takes the form:

$$-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12})$$

Table S7. H-Atom coordinates ($x10^4$) and isotropic displacement coefficients ($Å^2 x10^3$)

	x	y	z	U
H(3a)	3355	913	-3506	74
H(3b)	4691	1812	-3291	74
H(3c)	3057	1945	-2990	74
H(4a)	5675	-242	-1124	62
H(4b)	4404	-429	-2317	62
H(5a)	7043	-969	-2185	67
H(5b)	6575	11	-2926	67
H(6a)	9498	-248	-1375	62
H(6b)	8544	464	-824	62
H(7a)	8847	1018	-2760	66
H(7b)	8331	1740	-1984	66
H(8a)	11187	2002	-1960	73
H(8b)	11668	933	-1379	73
H(9a)	12635	2262	-135	64
H(9b)	11284	1588	130	64
H(10a)	11642	3791	-1203	82
H(10b)	10463	4471	-789	82
H(10c)	9639	3783	-1821	82

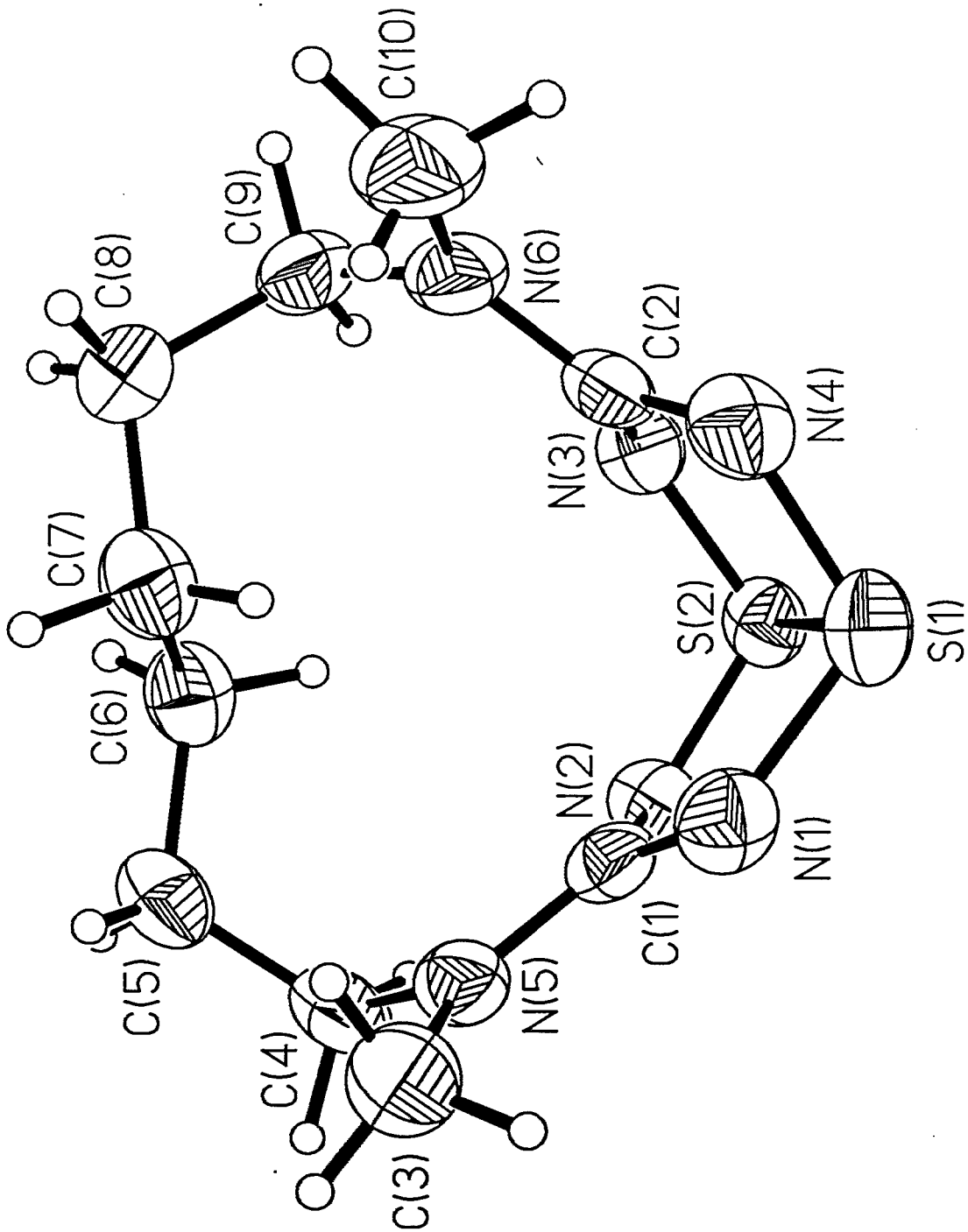
P2871-12

Table S8. Torsion angles (°)

N1	S1	S2	N2	-4.2(1)	N1	S1	S2	N3	108.0(1)
N4	S1	S2	N2	-115.7(1)	N4	S1	S2	N3	-3.5(1)
S2	S1	N1	C1	-8.4(2)	N4	S1	N1	C1	80.3(2)
S2	S1	N4	C2	16.0(2)	N1	S1	N4	C2	-72.0(2)
S1	S2	N2	C1	16.0(2)	N3	S2	N2	C1	-71.8(2)
S1	S2	N3	C2	-9.6(2)	N2	S2	N3	C2	78.8(2)
S1	N1	C1	N2	23.7(4)	S1	N1	C1	N5	-162.3(2)
S2	N2	C1	N1	-28.4(3)	S2	N2	C1	N5	157.7(2)
S2	N3	C2	N4	25.4(3)	S2	N3	C2	N6	-160.3(2)
S1	N4	C2	N3	-29.0(3)	S1	N4	C2	N6	156.8(2)
C3	N5	C1	N1	1.1(4)	C3	N5	C1	N2	175.3(2)
C4	N5	C1	N1	174.5(2)	C4	N5	C1	N2	-11.3(4)
C1	N5	C3	H3a	-163.9(2)	C1	N5	C3	H3b	76.1(2)
C1	N5	C3	H3c	-43.9(3)	C4	N5	C3	H3a	22.6(2)
C4	N5	C3	H3b	-97.4(2)	C4	N5	C3	H3c	142.6(2)
C1	N5	C4	H4a	22.9(3)	C1	N5	C4	H4b	141.7(2)
C1	N5	C4	C5	-97.7(3)	C3	N5	C4	H4a	-163.6(2)
C3	N5	C4	H4b	-44.8(2)	C3	N5	C4	C5	75.8(3)
C9	N6	C2	N3	20.9(3)	C9	N6	C2	N4	-164.6(2)
C10	N6	C2	N3	-171.8(2)	C10	N6	C2	N4	2.6(3)
C2	N6	C9	C8	103.9(3)	C2	N6	C9	H9a	-135.8(2)
C2	N6	C9	H9b	-16.4(2)	C10	N6	C9	C8	-63.6(3)
C10	N6	C9	H9a	56.7(2)	C10	N6	C9	H9b	176.0(2)
C2	N6	C10	H10a	168.7(2)	C2	N6	C10	H10b	48.7(2)
C2	N6	C10	H10c	-71.3(2)	C9	N6	C10	H10a	-23.6(2)
C9	N6	C10	H10b	-143.6(2)	C9	N6	C10	H10c	96.4(2)
N5	C4	C5	H5a	-174.4(1)	N5	C4	C5	H5b	-56.4(2)
N5	C4	C5	C6	64.6(3)	H4a	C4	C5	H5a	65.1(1)
H4a	C4	C5	H5b	-177.0(1)	H4a	C4	C5	C6	-56.0(2)
H4b	C4	C5	H5a	-53.8(1)	H4b	C4	C5	H5b	64.1(1)
H4b	C4	C5	C6	-174.8(2)	C4	C5	C6	H6a	135.7(2)
C4	C5	C6	H6b	16.9(2)	C4	C5	C6	C7	-103.7(3)
H5a	C5	C6	H6a	14.6(1)	H5a	C5	C6	H6b	-104.1(1)
H5a	C5	C6	C7	135.2(2)	H5b	C5	C6	H6a	-103.3(1)
H5b	C5	C6	H6b	137.9(1)	H5b	C5	C6	C7	17.3(3)
C5	C6	C7	H7a	-45.4(3)	C5	C6	C7	H7b	73.1(2)
C5	C6	C7	C8	-166.2(3)	H6a	C6	C7	H7a	75.2(1)
H6a	C6	C7	H7b	-166.3(1)	H6a	C6	C7	C8	-45.6(3)
H6b	C6	C7	H7a	-166.0(1)	H6b	C6	C7	H7b	-47.5(1)
H6b	C6	C7	C8	73.2(3)	C6	C7	C8	H8a	165.7(2)
C6	C7	C8	H8b	47.8(3)	C6	C7	C8	C9	-73.2(3)
H7a	C7	C8	H8a	45.0(1)	H7a	C7	C8	H8b	-72.9(1)
H7a	C7	C8	C9	166.0(2)	H7b	C7	C8	H8a	-73.6(1)
H7b	C7	C8	H8b	168.5(1)	H7b	C7	C8	C9	47.5(3)
C7	C8	C9	N6	-58.0(3)	C7	C8	C9	H9a	-178.3(2)
C7	C8	C9	H9b	62.4(2)	H8a	C8	C9	N6	63.1(2)
H8a	C8	C9	H9a	-57.3(1)	H8a	C8	C9	H9b	-176.6(1)
H8b	C8	C9	N6	-179.0(2)	H8b	C8	C9	H9a	60.7(1)
H8b	C8	C9	H9b	-58.7(1)					

P2871-13

Figure S1.



P2871-14

Figure S2.

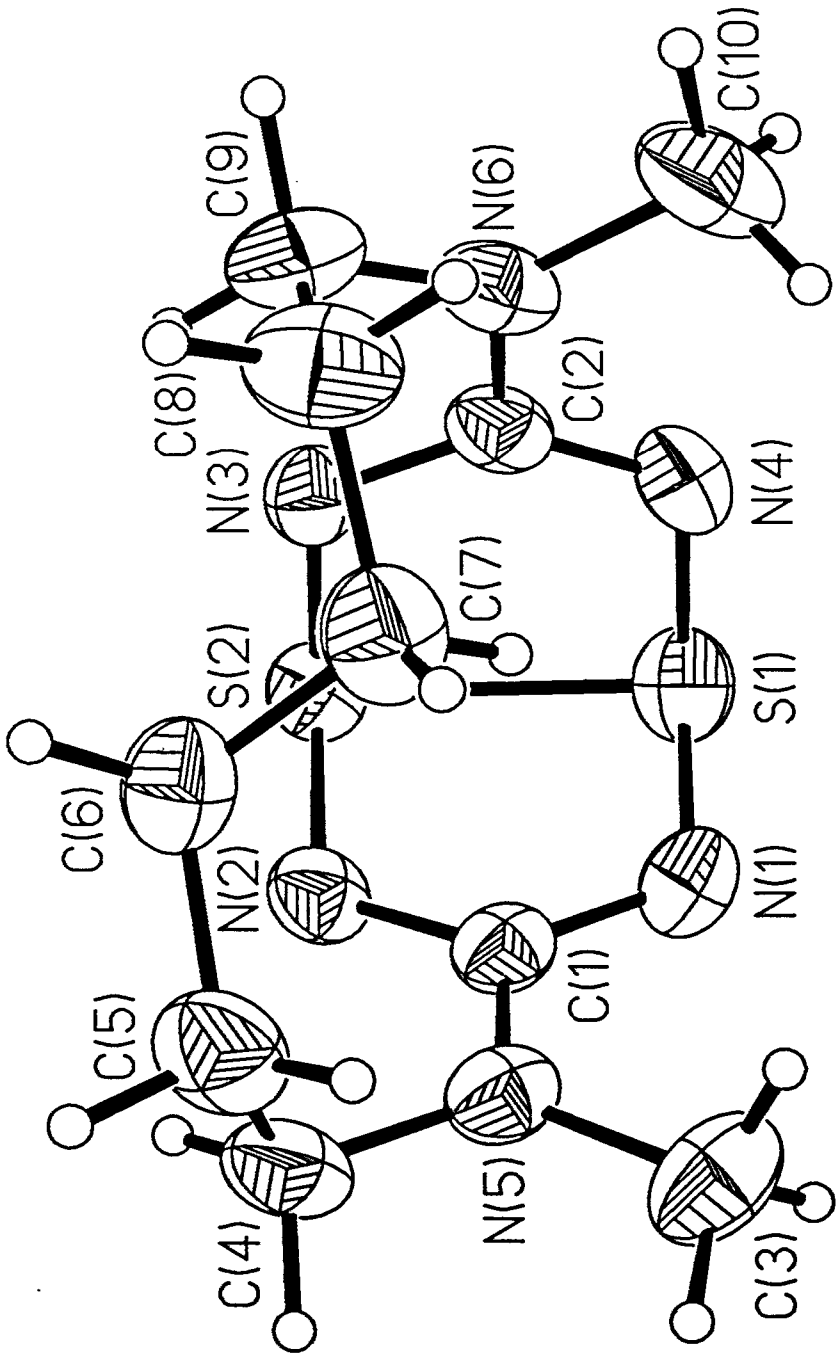
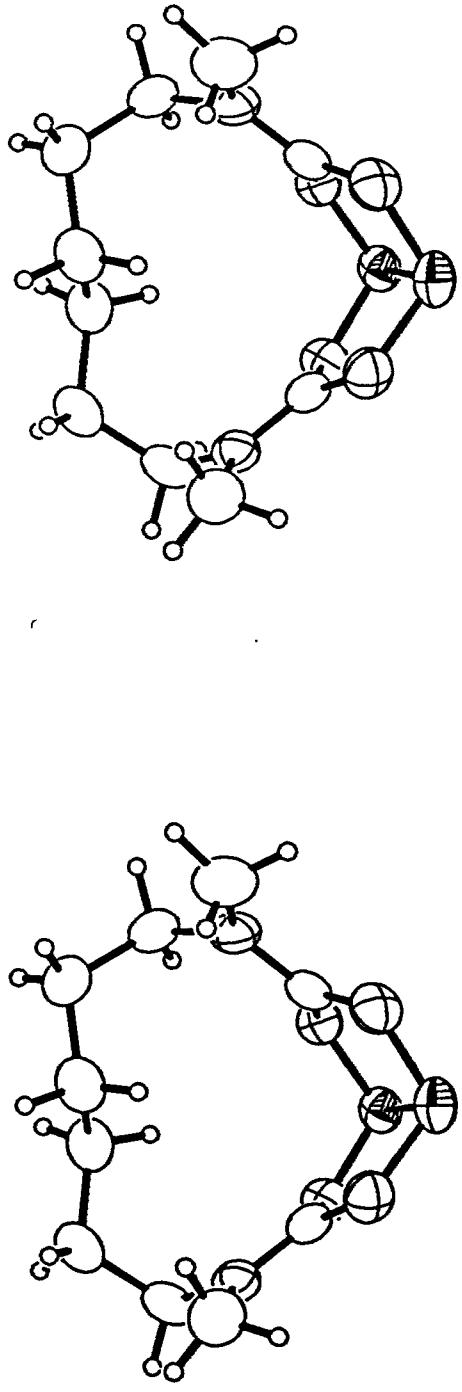
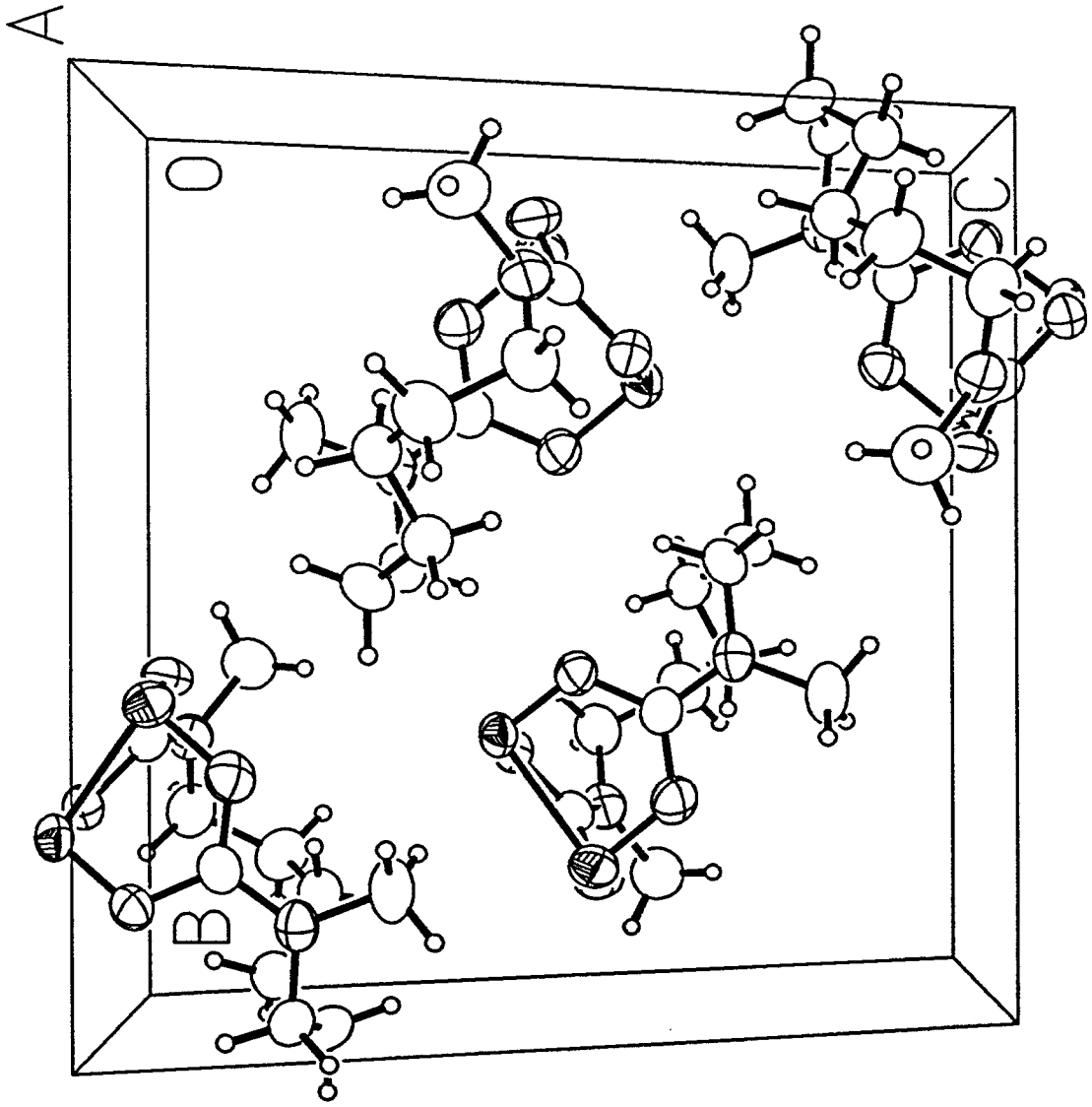


Figure S3.



P2871-16

Figure S4.



P2871-17

Figure S5.

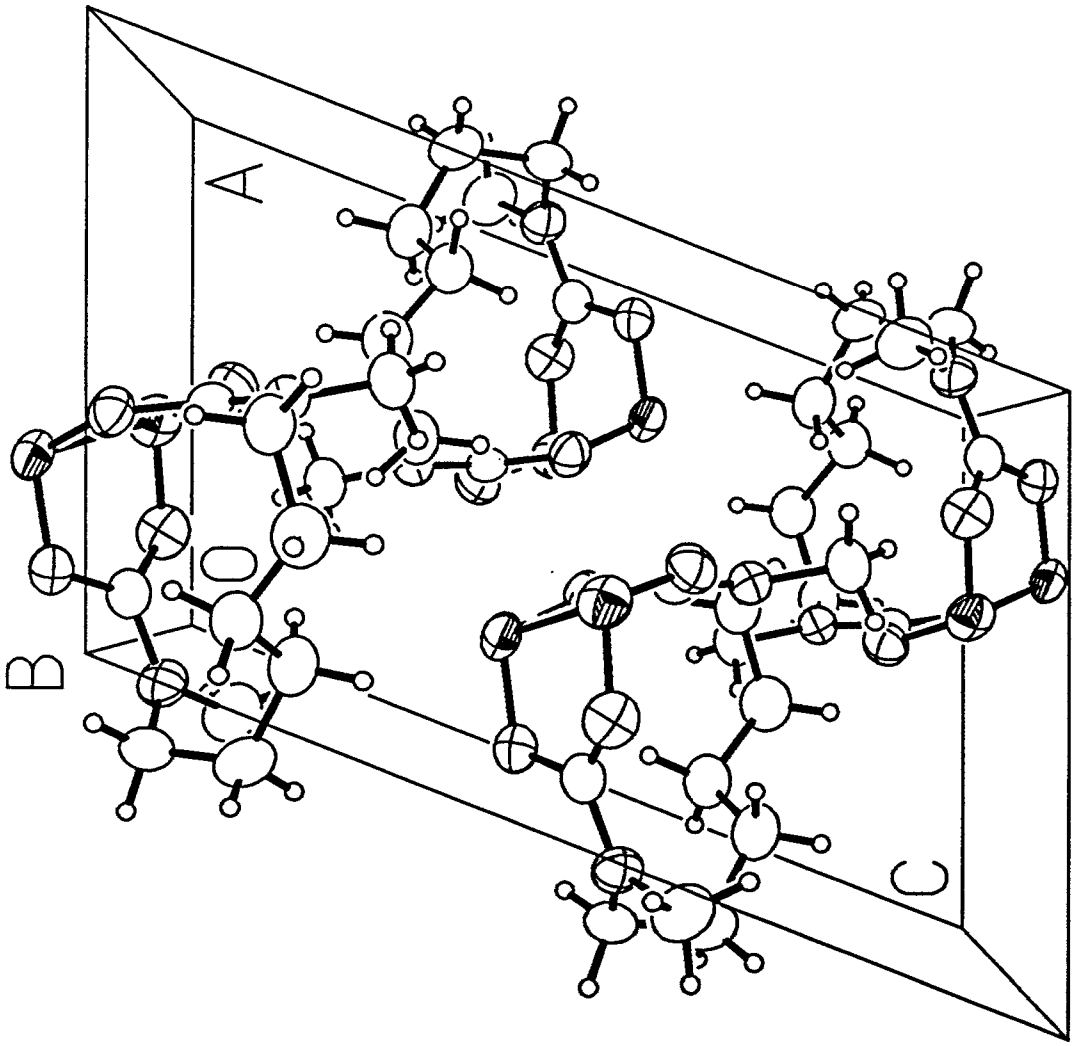
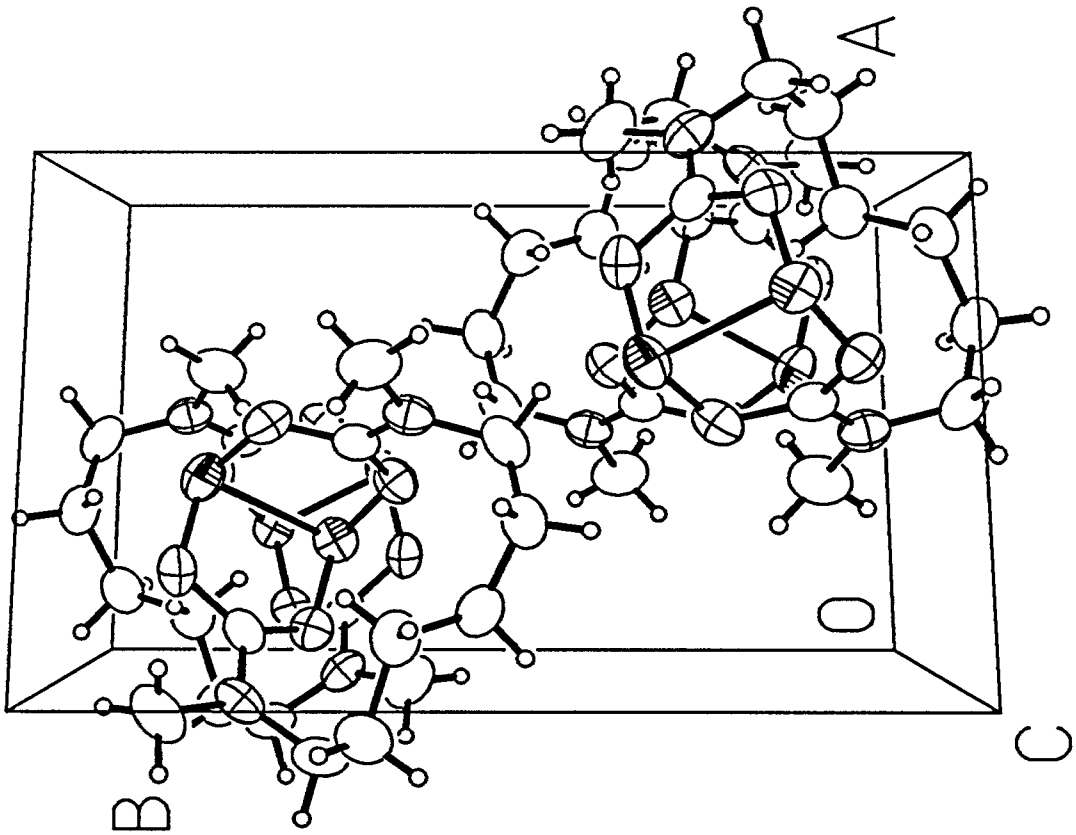


Figure S6.



P2871-19

P R I N C E T O N U N I V E R S I T Y

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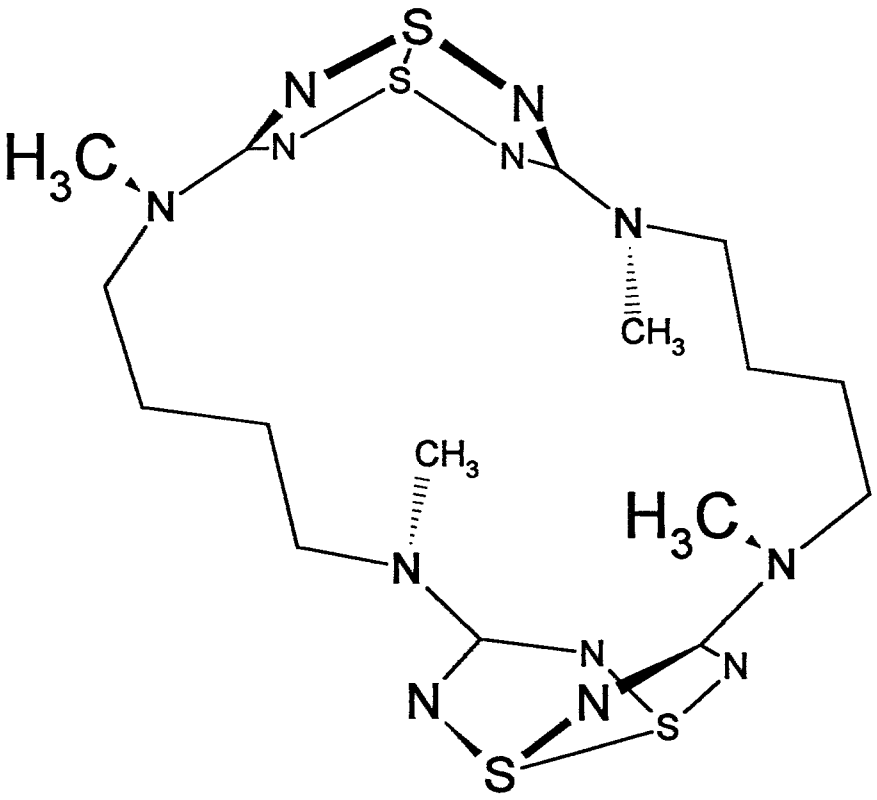
Report No. 95018

$C_{16}H_{28}N_{12}S_4 \cdot 0.69CH_2Cl_2$

Submitted July 14, 1995

Steven J. Dell, Robert A. Pascal, Jr. and Douglas M. Ho



$C_{16}H_{28}N_{12}S_4 \cdot 0.69CH_2Cl_2$

P2871-20

Experimental.

A yellow plate cut to approximately 0.10 x 0.20 x 0.38 mm in size was mounted on a glass fiber with epoxy cement and then transferred to a Siemens P4 diffractometer equipped with an LT-2 low-temperature device and graphite-monochromated Mo Kα radiation (λ = 0.71073 Å).[1] Lattice parameters at 230 K were determined from the setting angles of 50 centered reflections having $10.98^\circ \leq \theta \leq 12.49^\circ$ and were as follows: a = 9.6095(8) Å, b = 11.7085(11) Å, c = 13.2683(10) Å, α = 66.243(7)°, β = 82.340(6)°, γ = 73.989(7)° and V = 1312.9(2) Å^3. Preliminary peak scans through reciprocal space revealed no systematic absences indicating that the compound had crystallized in the triclinic space group P1 or P$\bar{1}$. The latter space group P$\bar{1}$ was selected based on the observed mean $|E^2 - 1|$ value of 0.983 (versus the expected value of 0.968 for centrosymmetric and 0.736 for non-centrosymmetric).

One hemisphere of data ($+h,\pm k,\pm \ell$) was collected in the ω scan mode with θ ranging from 1.68 to 25.00° and with scan speeds varying from 4.00 to 8.00°/min. Three standards (02$\bar{1}$, 425, 853) were measured for every 97 reflections during the data collection period and showed no significant deviations from their mean intensity values (0.9905, 1.0013 and 1.0141 for min., mean, max., respectively, i.e., within ±1.3% of the mean). A total of 4799 reflections were collected of which 4501 were unique (R_{int} = 1.32%). Corrections were made for Lorentz and polarization effects, but not for absorption or extinction.

The structure was solved in the triclinic space group P$\bar{1}$ (No. 2) by direct methods (SHELXTL-PLUS),[2] and refined by full-matrix least-squares on F^2 (SHELXL-93).[3] Except where noted below, all of the non-H atoms were refined with anisotropic displacement coefficients, H atoms were included with a riding model and isotropic displacement coefficents U(H) = 1.2U(C), and the weighting scheme employed was $w = 1/[\sigma^2(F_o^2) + (0.0430P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$. Two of the four methyl groups exhibited rotational disorder and were modelled with 6 half hydrogens apiece yielding H(13A,13B,13C), H(13D,13E,13F), H(15A,15B,15C) and H(15D,15E,15F) with occupancy factors of 0.57(3), 0.43(3), 0.54(3) and 0.46(3), respectively. A severely disordered methylene chloride molecule was also present in the lattice and was treated with a 3-site model with one common isotropic displacement coefficient for the carbons, anisotropic displacement coefficients with similarity restraints for the chlorines, common C-Cl and Cl•••Cl variables, and three group occupancy parameters. The refined model gave C-Cl = 1.703(6) Å, Cl-C-Cl = 113.1(7)°, and occupancy factors of 0.22(1), 0.24(1) and 0.23(1) for sites A, B and C, respectively, i.e., $0.69CH_2Cl_2$. The refinements converged to

P2871-21

R(F) = 3.63%, $wR(F^2)$ = 8.10% and S = 1.06 for 3149 reflections with $I > 2\sigma(I)$, and R(F) = 5.81%, $wR(F^2)$ = 9.44% and S = 0.92 for 4500 unique reflections, 364 variables and 39 restraints.[4] One reflection (001 with a $\Delta F^2/\sigma$ of 30.40) was considered aberrant and was suppressed. All of the remaining reflections had $\Delta F^2/\sigma$ values of 5.19 or less. The maximum Δ/σ in the final cycle of least-squares was 0.001, and the residual peaks on the final $\Delta\rho$ map ranged from -0.236 to 0.209 $eÅ^{-3}$. Scattering factors were taken from the *International Tables for Crystallography, Vol C.*[5]

Footnotes and references.

1. Siemens (1994). XSCANS, Release 2.10b. Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA.

2. Sheldrick, G. M. (1990). SHELXTL-PLUS, Release 4.21. Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA.

3. Sheldrick, G. M. (1993). SHELXL-93. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

4. (a) $R(F) = R1 = \sum||F_o|-|F_c|| \; / \; \sum|F_o|$

(b) $wR(F^2) = wR2 = [\sum w(F_o^2 - F_c^2)^2 \; / \; \sum w(F_o^2)^2]^{1/2}$

(c) S = Goodness-of-fit on $F^2 = [\sum w(F_o^2 - F_c^2)^2 \; / \; (n-p)]^{1/2}$ where n is the number of reflections and p is the number of parameters refined.

5. (a) Maslen, E. N., Fox, A. G. & O'Keefe, M. A. (1992). International Tables for Crystallography: Mathematical, Physical and Chemical Tables, Vol C, Chapter 6, edited by A. J. C. Wilson, pp. 476-516, Dordrecht, The Netherlands: Kluwer. (b) Creagh, D. C. & McAuley, W. J. (1992). International Tables for Crystallography: Mathematical, Physical and Chemical Tables, Vol C, Chapter 4, edited by A. J. C. Wilson, pp. 206-222, Dordrecht, The Netherlands: Kluwer.

P2871-22

Miscellaneous.

1. Averages from PTZCNB (JACS, 1981, 103, 1540-1544), 92009 (Acta Cryst., 1994, C50, 108-110), 94024 (previous unpublished) and 95018 (this work):

	PTZCNB	92009	94024	95018
S-S	2.428	2.408	2.434	2.375
S-N	1.605	1.603	1.602	1.602
C-N	1.348	1.342	1.350	1.348
N-S-N	113.8	113.2	112.4	113.4
N2S2-N2S2	113.8	113.1	112.4	113.4
CN2-N2S2	165.6	167.8	161.3	167.8
CN2S2-CN2S2	108.9	108.9	106.0	109.1

2. The closest intermolecular S•••S distances in 95018 are S(2)•••S(3) (x, 1+y, z) = 3.536(1) Å, S(2)•••S(4) (x, 1+y, z) = 3.690(1) Å and S(4)•••S(4) (-x, -y, 1-z) = 3.757(1) Å. The first of these is less than the sum of the van der Waals' radii for two S atoms, i.e., 3.6 Å.

3. As indicated in the unit cell diagram, the compound crystallizes with a layered structure perforated with channels running parallel to the *a-axis*.

P2871-23

Table S9. Crystal data and structure refinement for $C_{16}H_{28}N_{12}S_4 \cdot 0.69CH_2Cl_2$.

Formula	$C_{16}H_{28}N_{12}S_4 \cdot 0.69CH_2Cl_2$
Formula weight	575.23
Temperature	230(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P\bar{1}$ (No. 2)
Unit cell dimensions	a = 9.6095(8) Å α = 66.243(7)° b = 11.7085(11) Å β = 82.340(6)° c = 13.2683(10) Å γ = 73.989(7)°
Volume	1312.9(2) $Å^3$
Z	2
Density (calculated)	1.455 Mg/m^3
Absorption coefficient	0.534 mm^{-1}
F(000)	602
Crystal size	0.10 x 0.20 x 0.38 mm
θ range for data collection	1.68 to 25.00°
Index ranges	$0 \le h \le 11$, $-12 \le k \le 12$, $-15 \le \ell \le 15$
Reflections collected	4799
Independent reflections	4501 (R_{int} = 0.0132)
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4500 / 39 / 364
Goodness-of-fit on F^2	0.925
Final R indices [I>2σ(I)]	R1 = 0.0363, wR2 = 0.0810
R indices (all data)	R1 = 0.0581, wR2 = 0.0944
Largest diff. peak and hole	0.209 and -0.236 $eÅ^{-3}$

Table S10. Atomic coordinates [x 10^4] and equivalent isotropic displacement parameters [$Å^2$ x 10^3] for $C_{16}H_{28}N_{12}S_4 \cdot 0.69CH_2Cl_2$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
S(1)	4136(1)	4485(1)	8193(1)	45(1)
S(2)	2540(1)	5847(1)	6713(1)	40(1)
S(3)	595(1)	-1354(1)	7166(1)	34(1)
S(4)	1912(1)	-617(1)	5491(1)	33(1)
N(1)	2782(2)	4121(2)	8980(2)	43(1)
N(2)	4817(2)	3549(2)	7548(2)	45(1)
N(3)	1192(2)	5469(2)	7500(2)	35(1)
N(4)	3215(2)	4912(2)	6070(2)	41(1)
N(5)	365(2)	4099(2)	9131(2)	41(1)
N(6)	4622(2)	2938(2)	6127(2)	40(1)
N(7)	2076(2)	-1971(2)	7833(2)	36(1)
N(8)	-127(2)	105(2)	7041(2)	36(1)
N(9)	3396(2)	-1200(2)	6146(2)	31(1)
N(10)	1168(2)	846(2)	5341(2)	36(1)
N(11)	4522(2)	-2104(2)	7817(2)	39(1)
N(12)	-155(2)	2263(2)	6116(2)	39(1)
C(1)	1473(3)	4537(2)	8517(2)	33(1)
C(2)	4180(3)	3793(3)	6605(2)	38(1)
C(3)	5680(3)	1714(2)	6634(2)	43(1)
C(4)	5168(3)	559(2)	6713(2)	40(1)
C(5)	6241(3)	-698(2)	7322(2)	43(1)
C(6)	5893(3)	-1866(3)	7266(2)	44(1)
C(7)	3305(3)	-1712(2)	7258(2)	31(1)
C(8)	334(3)	1050(2)	6192(2)	32(1)
C(9)	-1124(3)	2596(3)	6963(3)	50(1)
C(10)	-548(3)	3365(3)	7423(2)	48(1)
C(11)	-1524(3)	3626(3)	8348(3)	60(1)
C(12)	-1101(3)	4563(3)	8710(3)	53(1)
C(13)	585(4)	3113(3)	10245(2)	62(1)
C(14)	4169(3)	3244(3)	5025(2)	50(1)
C(15)	4513(4)	-2767(3)	9018(2)	60(1)
C(16)	210(3)	3330(2)	5175(2)	55(1)
Cl(1A)	533(17)	0(14)	9936(19)	193(8)
Cl(2A)	3066(17)	928(15)	9140(15)	213(8)
C(1A)	2233(22)	-59(27)	10221(15)	120(4)
Cl(1B)	1484(15)	-99(10)	9352(10)	129(5)
Cl(2B)	3850(17)	796(15)	9563(9)	154(6)
C(1B)	2714(35)	-187(39)	10209(11)	120(4)
Cl(1C)	2157(14)	328(13)	9107(11)	164(5)
Cl(2C)	4789(18)	-394(15)	10212(16)	207(8)
C(1C)	2979(21)	-306(37)	10341(12)	120(4)

P2871-25

Table S11. Bond lengths [Å] for $C_{16}H_{28}N_{12}S_4 \cdot 0.69CH_2Cl_2$.

S(1)-S(2)	2.384(1)	S(1)-N(1)	1.597(2)
S(1)-N(2)	1.605(2)	S(2)-N(3)	1.595(2)
S(2)-N(4)	1.600(2)	S(3)-S(4)	2.366(1)
S(3)-N(7)	1.607(2)	S(3)-N(8)	1.605(2)
S(4)-N(9)	1.603(2)	S(4)-N(10)	1.604(2)
N(1)-C(1)	1.350(3)	N(2)-C(2)	1.356(3)
N(3)-C(1)	1.355(3)	N(4)-C(2)	1.355(3)
N(5)-C(1)	1.339(3)	N(5)-C(12)	1.462(4)
N(5)-C(13)	1.461(3)	N(6)-C(2)	1.339(3)
N(6)-C(3)	1.463(3)	N(6)-C(14)	1.455(3)
N(7)-C(7)	1.356(3)	N(8)-C(8)	1.350(3)
N(9)-C(7)	1.351(3)	N(10)-C(8)	1.358(3)
N(11)-C(6)	1.459(3)	N(11)-C(7)	1.338(3)
N(11)-C(15)	1.465(3)	N(12)-C(8)	1.333(3)
N(12)-C(9)	1.468(3)	N(12)-C(16)	1.453(3)
C(3)-C(4)	1.524(3)	C(4)-C(5)	1.519(3)
C(5)-C(6)	1.525(3)	C(9)-C(10)	1.517(3)
C(10)-C(11)	1.522(4)	C(11)-C(12)	1.524(4)
Cl(1A)-C(1A)	1.703(6)	Cl(2A)-C(1A)	1.703(6)
Cl(1B)-C(1B)	1.703(6)	Cl(2B)-C(1B)	1.703(6)
Cl(1C)-C(1C)	1.703(6)	Cl(2C)-C(1C)	1.703(6)

P2871-26

Table S12. Bond angles [°] for $C_{16}H_{28}N_{12}S_4 \cdot 0.69CH_2Cl_2$.

S(2)-S(1)-N(1)	89.9(1)	S(2)-S(1)-N(2)	90.0(1)
N(1)-S(1)-N(2)	113.8(1)	S(1)-S(2)-N(3)	89.9(1)
S(1)-S(2)-N(4)	90.1(1)	N(3)-S(2)-N(4)	113.2(1)
S(4)-S(3)-N(7)	90.3(1)	S(4)-S(3)-N(8)	90.2(1)
N(7)-S(3)-N(8)	113.2(1)	S(3)-S(4)-N(9)	90.3(1)
S(3)-S(4)-N(10)	90.3(1)	N(9)-S(4)-N(10)	113.4(1)
S(1)-N(1)-C(1)	117.7(2)	S(1)-N(2)-C(2)	117.6(2)
S(2)-N(3)-C(1)	117.7(2)	S(2)-N(4)-C(2)	117.7(2)
C(1)-N(5)-C(12)	121.6(2)	C(1)-N(5)-C(13)	121.1(2)
C(12)-N(5)-C(13)	117.3(2)	C(2)-N(6)-C(3)	122.0(2)
C(2)-N(6)-C(14)	120.9(2)	C(3)-N(6)-C(14)	116.9(2)
S(3)-N(7)-C(7)	117.1(2)	S(3)-N(8)-C(8)	117.8(2)
S(4)-N(9)-C(7)	117.5(2)	S(4)-N(10)-C(8)	117.5(2)
C(6)-N(11)-C(7)	121.8(2)	C(6)-N(11)-C(15)	117.5(2)
C(7)-N(11)-C(15)	120.7(2)	C(8)-N(12)-C(9)	121.8(2)
C(8)-N(12)-C(16)	121.8(2)	C(9)-N(12)-C(16)	116.4(2)
N(1)-C(1)-N(5)	118.4(2)	N(1)-C(1)-N(3)	123.2(2)
N(3)-C(1)-N(5)	118.1(2)	N(2)-C(2)-N(4)	123.2(2)
N(2)-C(2)-N(6)	118.4(2)	N(4)-C(2)-N(6)	118.1(2)
C(4)-C(3)-N(6)	112.8(2)	C(3)-C(4)-C(5)	111.3(2)
C(4)-C(5)-C(6)	113.1(2)	C(5)-C(6)-N(11)	113.2(2)
N(7)-C(7)-N(9)	123.4(2)	N(7)-C(7)-N(11)	118.1(2)
N(9)-C(7)-N(11)	118.2(2)	N(8)-C(8)-N(10)	122.9(2)
N(8)-C(8)-N(12)	119.4(2)	N(10)-C(8)-N(12)	117.4(2)
C(10)-C(9)-N(12)	112.7(2)	C(9)-C(10)-C(11)	111.7(2)
C(10)-C(11)-C(12)	112.8(2)	N(5)-C(12)-C(11)	113.1(2)
Cl(1A)-C(1A)-Cl(2A)	113.1(7)	Cl(1B)-C(1B)-Cl(2B)	113.1(7)
Cl(1C)-C(1C)-Cl(2C)	113.1(7)		

P2871-27

Table S13. Bond lengths [Å] involving H atoms for $C_{16}H_{28}N_{12}S_4 \cdot 0.69CH_2Cl_2$.

C(3)-H(3A)	0.98	C(3)-H(3B)	0.98
C(4)-H(4A)	0.98	C(4)-H(4B)	0.98
C(5)-H(5A)	0.98	C(5)-H(5B)	0.98
C(6)-H(6A)	0.98	C(6)-H(6B)	0.98
C(9)-H(9A)	0.98	C(9)-H(9B)	0.98
C(10)-H(10A)	0.98	C(10)-H(10B)	0.98
C(11)-H(11A)	0.98	C(11)-H(11B)	0.98
C(12)-H(12A)	0.98	C(12)-H(12B)	0.98
C(13)-H(13A)	0.97	C(13)-H(13B)	0.97
C(13)-H(13C)	0.97	C(13)-H(13D)	0.97
C(13)-H(13E)	0.97	C(13)-H(13F)	0.97
C(14)-H(14A)	0.97	C(14)-H(14B)	0.97
C(14)-H(14C)	0.97	C(15)-H(15A)	0.97
C(15)-H(15B)	0.97	C(15)-H(15C)	0.97
C(15)-H(15D)	0.97	C(15)-H(15E)	0.97
C(15)-H(15F)	0.97	C(16)-H(16A)	0.97
C(16)-H(16B)	0.97	C(16)-H(16C)	0.97

P2871-28

Table S14. Bond angles [°] involving H atoms for $C_{16}H_{28}N_{12}S_4 \cdot 0.69CH_2Cl_2$.

C(4)-C(3)-H(3A)	109.0(2)	N(6)-C(3)-H(3A)	109.0(2)
C(4)-C(3)-H(3B)	109.0(2)	N(6)-C(3)-H(3B)	109.0(2)
H(3A)-C(3)-H(3B)	107.8	C(3)-C(4)-H(4A)	109.4(2)
C(5)-C(4)-H(4A)	109.4(2)	C(3)-C(4)-H(4B)	109.4(2)
C(5)-C(4)-H(4B)	109.4(2)	H(4A)-C(4)-H(4B)	108.0
C(4)-C(5)-H(5A)	109.0(2)	C(6)-C(5)-H(5A)	109.0(2)
C(4)-C(5)-H(5B)	109.0(2)	C(6)-C(5)-H(5B)	109.0(2)
H(5A)-C(5)-H(5B)	107.8	C(5)-C(6)-H(6A)	108.9(2)
N(11)-C(6)-H(6A)	108.9(2)	C(5)-C(6)-H(6B)	108.9(2)
N(11)-C(6)-H(6B)	108.9(2)	H(6A)-C(6)-H(6B)	107.8
C(10)-C(9)-H(9A)	109.0(2)	N(12)-C(9)-H(9A)	109.0(2)
C(10)-C(9)-H(9B)	109.0(2)	N(12)-C(9)-H(9B)	109.0(2)
H(9A)-C(9)-H(9B)	107.8	C(9)-C(10)-H(10A)	109.3(2)
C(11)-C(10)-H(10A)	109.3(2)	C(9)-C(10)-H(10B)	109.3(2)
C(11)-C(10)-H(10B)	109.3(2)	H(10A)-C(10)-H(10B)	107.9
C(10)-C(11)-H(11A)	109.0(2)	C(12)-C(11)-H(11A)	109.0(2)
C(10)-C(11)-H(11B)	109.0(2)	C(12)-C(11)-H(11B)	109.0(2)
H(11A)-C(11)-H(11B)	107.8	N(5)-C(12)-H(12A)	109.0(2)
C(11)-C(12)-H(12A)	109.0(2)	N(5)-C(12)-H(12B)	109.0(2)
C(11)-C(12)-H(12B)	109.0(2)	H(12A)-C(12)-H(12B)	107.8
N(5)-C(13)-H(13A)	109.5(2)	N(5)-C(13)-H(13B)	109.5(2)
N(5)-C(13)-H(13C)	109.5(2)	H(13A)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13C)	109.5	H(13B)-C(13)-H(13C)	109.5
N(5)-C(13)-H(13D)	109.5(2)	N(5)-C(13)-H(13E)	109.5(2)
N(5)-C(13)-H(13F)	109.5(2)	H(13D)-C(13)-H(13E)	109.5
H(13D)-C(13)-H(13F)	109.5	H(13E)-C(13)-H(13F)	109.5
N(6)-C(14)-H(14A)	109.5(2)	N(6)-C(14)-H(14B)	109.5(2)
N(6)-C(14)-H(14C)	109.5(2)	H(14A)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14C)	109.5	H(14B)-C(14)-H(14C)	109.5
N(11)-C(15)-H(15A)	109.5(2)	N(11)-C(15)-H(15B)	109.5(2)
N(11)-C(15)-H(15C)	109.5(2)	H(15A)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15C)	109.5	H(15B)-C(15)-H(15C)	109.5
N(11)-C(15)-H(15D)	109.5(2)	N(11)-C(15)-H(15E)	109.5(2)
N(11)-C(15)-H(15F)	109.5(2)	H(15D)-C(15)-H(15E)	109.5
H(15D)-C(15)-H(15F)	109.5	H(15E)-C(15)-H(15F)	109.5
N(12)-C(16)-H(16A)	109.5(2)	N(12)-C(16)-H(16B)	109.5(2)
N(12)-C(16)-H(16C)	109.5(2)	H(16A)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16C)	109.5	H(16B)-C(16)-H(16C)	109.5

P2871-29

Table S15. Anisotropic displacement parameters [$Å^2$ x 10^3] for $C_{16}H_{28}N_{12}S_4 \cdot 0.69CH_2Cl_2$. The anisotropic displacement factor exponent takes the form:

$$-2\pi^2 [(ha^*)^2U_{11} + ... + 2hka^*b^*U_{12}]$$

	U11	U22	U33	U23	U13	U12
S(1)	34(1)	59(1)	59(1)	-41(1)	-1(1)	-12(1)
S(2)	50(1)	31(1)	44(1)	-19(1)	8(1)	-16(1)
S(3)	33(1)	30(1)	41(1)	-13(1)	1(1)	-12(1)
S(4)	35(1)	34(1)	31(1)	-16(1)	-4(1)	-6(1)
N(1)	39(1)	50(1)	42(1)	-23(1)	-6(1)	-4(1)
N(2)	34(1)	54(1)	61(2)	-39(1)	-4(1)	-5(1)
N(3)	35(1)	29(1)	40(1)	-14(1)	-1(1)	-6(1)
N(4)	51(2)	36(1)	41(1)	-21(1)	7(1)	-13(1)
N(5)	42(1)	44(1)	43(1)	-21(1)	10(1)	-17(1)
N(6)	40(1)	41(1)	48(1)	-27(1)	5(1)	-12(1)
N(7)	39(1)	34(1)	32(1)	-6(1)	-3(1)	-13(1)
N(8)	35(1)	34(1)	43(1)	-18(1)	7(1)	-10(1)
N(9)	29(1)	34(1)	30(1)	-13(1)	2(1)	-8(1)
N(10)	41(1)	27(1)	32(1)	-6(1)	-7(1)	-4(1)
N(11)	36(1)	35(1)	42(1)	-9(1)	-13(1)	-7(1)
N(12)	38(1)	29(1)	51(1)	-18(1)	-6(1)	-4(1)
C(1)	38(2)	32(2)	38(2)	-23(2)	1(2)	-7(2)
C(2)	33(2)	47(2)	46(2)	-26(2)	14(2)	-23(2)
C(3)	33(2)	48(2)	61(2)	-34(2)	2(2)	-11(2)
C(4)	28(2)	45(2)	57(2)	-28(2)	3(2)	-12(2)
C(5)	30(2)	53(2)	55(2)	-28(2)	-2(2)	-11(2)
C(6)	29(2)	41(2)	62(2)	-25(2)	-11(2)	5(2)
C(7)	36(2)	21(2)	38(2)	-12(2)	-4(2)	-6(2)
C(8)	27(2)	34(2)	39(2)	-16(2)	-8(2)	-6(2)
C(9)	32(2)	48(2)	84(2)	-43(2)	4(2)	-10(2)
C(10)	37(2)	54(2)	67(2)	-36(2)	6(2)	-17(2)
C(11)	40(2)	71(2)	95(3)	-56(2)	20(2)	-27(2)
C(12)	39(2)	61(2)	76(2)	-49(2)	19(2)	-17(2)
C(13)	87(3)	57(2)	43(2)	-19(2)	21(2)	-29(2)
C(14)	56(2)	54(2)	49(2)	-31(2)	10(2)	-16(2)
C(15)	70(2)	56(2)	45(2)	-6(2)	-24(2)	-12(2)
C(16)	70(2)	28(2)	58(2)	-7(2)	-16(2)	-4(2)
Cl(1A)	231(21)	69(4)	246(12)	-32(5)	34(20)	-49(12)
Cl(2A)	188(16)	192(12)	247(15)	-117(11)	76(13)	-15(10)
Cl(1B)	167(14)	102(6)	122(8)	-39(5)	-49(8)	-26(6)
Cl(2B)	212(14)	180(11)	131(8)	-96(8)	73(8)	-124(11)
Cl(1C)	158(13)	143(11)	189(10)	-77(8)	28(9)	-29(7)
Cl(2C)	287(15)	205(16)	139(13)	-127(12)	-16(12)	23(14)

P2871-30

Table S16. Hydrogen coordinates [x 10^4] and isotropic displacement parameters [$Å^2$ x 10^3] for $C_{16}H_{28}N_{12}S_4 \cdot 0.69CH_2Cl_2$.

	x	y	z	U(eq)
H(3A)	5878(3)	1613(2)	7375(2)	51
H(3B)	6589(3)	1734(2)	6200(2)	51
H(4A)	4225(3)	569(2)	7101(2)	48
H(4B)	5046(3)	619(2)	5970(2)	48
H(5A)	6247(3)	-816(2)	8095(2)	52
H(5B)	7214(3)	-645(2)	7005(2)	52
H(6A)	5859(3)	-1736(3)	6492(2)	53
H(6B)	6675(3)	-2628(3)	7606(2)	53
H(9A)	-1261(3)	1802(3)	7566(3)	59
H(9B)	-2073(3)	3097(3)	6645(3)	59
H(10A)	-472(3)	4186(3)	6831(2)	58
H(10B)	425(3)	2890(3)	7702(2)	58
H(11A)	-1482(3)	2811(3)	8981(3)	72
H(11B)	-2526(3)	3978(3)	8101(3)	72
H(12A)	-1173(3)	5387(3)	8082(3)	63
H(12B)	-1788(3)	4717(3)	9284(3)	63
H(13A)	1613(6)	2736(67)	10363(28)	93
H(13B)	105(91)	2449(49)	10335(27)	93
H(13C)	182(96)	3500(19)	10777(3)	93
H(13D)	-346(6)	3054(67)	10620(28)	93
H(13E)	1162(91)	3341(49)	10648(26)	93
H(13F)	1084(96)	2290(18)	10206(3)	93
H(14A)	3767(19)	4164(4)	4673(6)	75
H(14B)	3439(15)	2792(14)	5073(2)	75
H(14C)	4997(5)	2980(16)	4595(5)	75
H(15A)	5405(53)	-2789(95)	9300(9)	90
H(15B)	4432(122)	-3639(34)	9214(3)	90
H(15C)	3695(69)	-2311(61)	9335(7)	90
H(15D)	3616(53)	-3037(95)	9266(9)	90
H(15E)	4589(122)	-2187(34)	9352(3)	90
H(15F)	5327(69)	-3515(61)	9231(7)	90
H(16A)	580(20)	3051(6)	4573(6)	83
H(16B)	944(16)	3620(12)	5379(5)	83
H(16C)	-649(6)	4032(8)	4944(10)	83

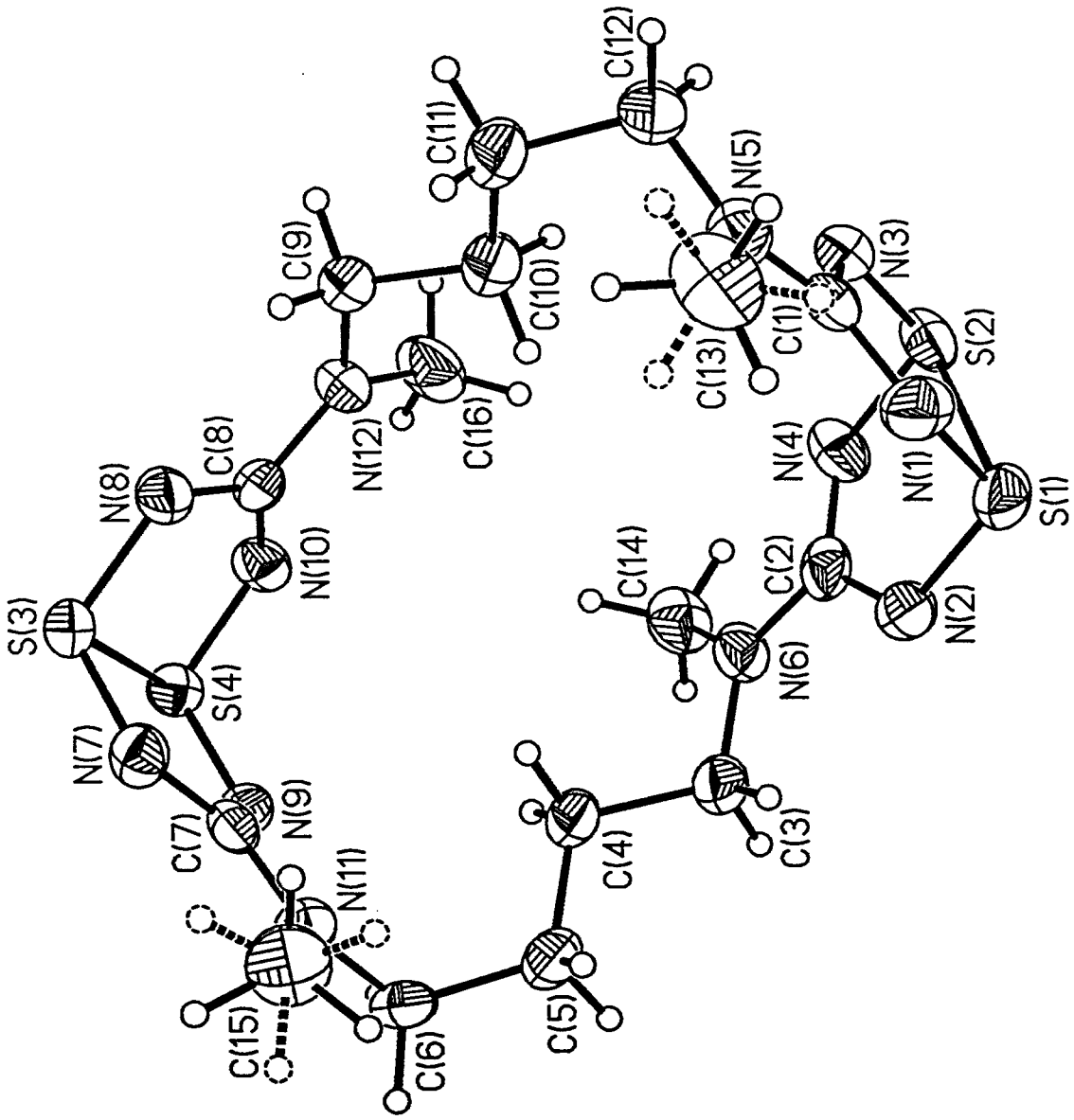
P2871-31

Table S17. Torsion angles [°] for $C_{16}H_{28}N_{12}S_4 \cdot 0.69CH_2Cl_2$.

N(1)-S(1)-S(2)-N(3)	-0.5(1)	N(2)-S(1)-S(2)-N(3)	113.3(1)
N(1)-S(1)-S(2)-N(4)	-113.7(1)	N(2)-S(1)-S(2)-N(4)	0.1(1)
N(8)-S(3)-S(4)-N(9)	112.1(1)	N(7)-S(3)-S(4)-N(9)	-1.1(1)
N(8)-S(3)-S(4)-N(10)	-1.3(1)	N(7)-S(3)-S(4)-N(10)	-114.5(1)
N(2)-S(1)-N(1)-C(1)	-82.3(2)	S(2)-S(1)-N(1)-C(1)	7.6(2)
N(1)-S(1)-N(2)-C(2)	83.2(2)	S(2)-S(1)-N(2)-C(2)	-6.7(2)
N(4)-S(2)-N(3)-C(1)	83.4(2)	S(1)-S(2)-N(3)-C(1)	-6.7(2)
N(3)-S(2)-N(4)-C(2)	-83.5(2)	S(1)-S(2)-N(4)-C(2)	6.5(2)
N(8)-S(3)-N(7)-C(7)	-83.1(2)	S(4)-S(3)-N(7)-C(7)	7.3(2)
N(7)-S(3)-N(8)-C(8)	85.4(2)	S(4)-S(3)-N(8)-C(8)	-5.0(2)
N(10)-S(4)-N(9)-C(7)	85.3(2)	S(3)-S(4)-N(9)-C(7)	-5.2(2)
N(9)-S(4)-N(10)-C(8)	-83.1(2)	S(3)-S(4)-N(10)-C(8)	7.4(2)
C(13)-N(5)-C(1)-N(1)	-5.0(3)	C(12)-N(5)-C(1)-N(1)	176.3(2)
C(13)-N(5)-C(1)-N(3)	-178.8(2)	C(12)-N(5)-C(1)-N(3)	2.6(3)
S(1)-N(1)-C(1)-N(5)	171.1(2)	S(1)-N(1)-C(1)-N(3)	-15.5(3)
S(2)-N(3)-C(1)-N(5)	-171.7(2)	S(2)-N(3)-C(1)-N(1)	14.9(3)
C(14)-N(6)-C(2)-N(4)	4.9(4)	C(3)-N(6)-C(2)-N(4)	178.9(2)
C(14)-N(6)-C(2)-N(2)	-169.3(2)	C(3)-N(6)-C(2)-N(2)	4.8(3)
S(2)-N(4)-C(2)-N(6)	172.3(2)	S(2)-N(4)-C(2)-N(2)	-13.8(3)
S(1)-N(2)-C(2)-N(6)	-172.2(2)	S(1)-N(2)-C(2)-N(4)	14.0(3)
C(2)-N(6)-C(3)-C(4)	128.3(2)	C(14)-N(6)-C(3)-C(4)	-57.4(3)
N(6)-C(3)-C(4)-C(5)	-175.6(2)	C(3)-C(4)-C(5)-C(6)	-171.0(2)
C(7)-N(11)-C(6)-C(5)	98.4(3)	C(15)-N(11)-C(6)-C(5)	-80.2(3)
C(4)-C(5)-C(6)-N(11)	-64.4(3)	C(6)-N(11)-C(7)-N(9)	6.8(3)
C(15)-N(11)-C(7)-N(9)	-174.7(2)	C(6)-N(11)-C(7)-N(7)	-179.9(2)
C(15)-N(11)-C(7)-N(7)	-1.4(3)	S(4)-N(9)-C(7)-N(11)	-174.5(2)
S(4)-N(9)-C(7)-N(7)	12.6(3)	S(3)-N(7)-C(7)-N(11)	173.2(2)
S(3)-N(7)-C(7)-N(9)	-13.8(3)	C(16)-N(12)-C(8)-N(8)	-174.9(2)
C(9)-N(12)-C(8)-N(8)	3.4(3)	C(16)-N(12)-C(8)-N(10)	-1.4(3)
C(9)-N(12)-C(8)-N(10)	176.9(2)	S(3)-N(8)-C(8)-N(12)	-174.5(2)
S(3)-N(8)-C(8)-N(10)	12.3(3)	S(4)-N(10)-C(8)-N(12)	173.0(2)
S(4)-N(10)-C(8)-N(8)	-13.8(3)	C(8)-N(12)-C(9)-C(10)	125.2(3)
C(16)-N(12)-C(9)-C(10)	-56.5(3)	N(12)-C(9)-C(10)-C(11)	-176.4(3)
C(9)-C(10)-C(11)-C(12)	-171.4(3)	C(1)-N(5)-C(12)-C(11)	101.9(3)
C(13)-N(5)-C(12)-C(11)	-76.8(3)	C(10)-C(11)-C(12)-N(5)	-60.8(4)

P2871-32

Figure S7.



P2871-33

Figure S8.

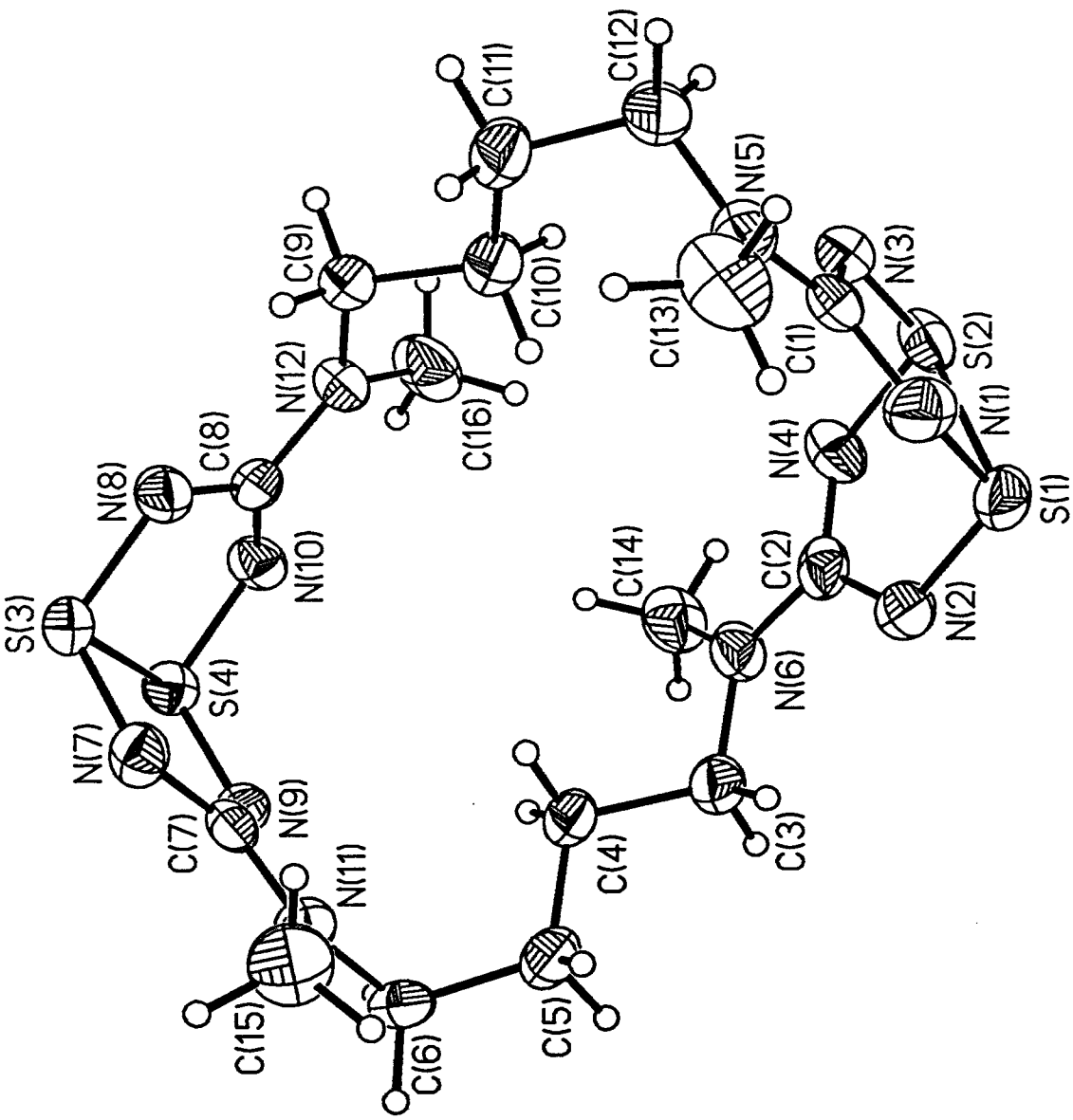


Figure S9.

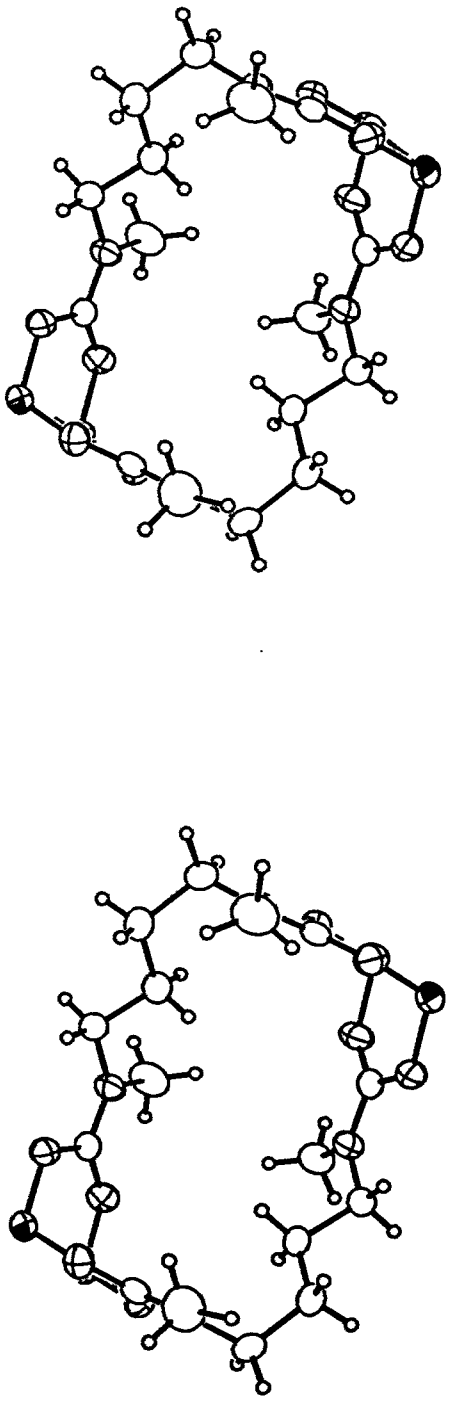
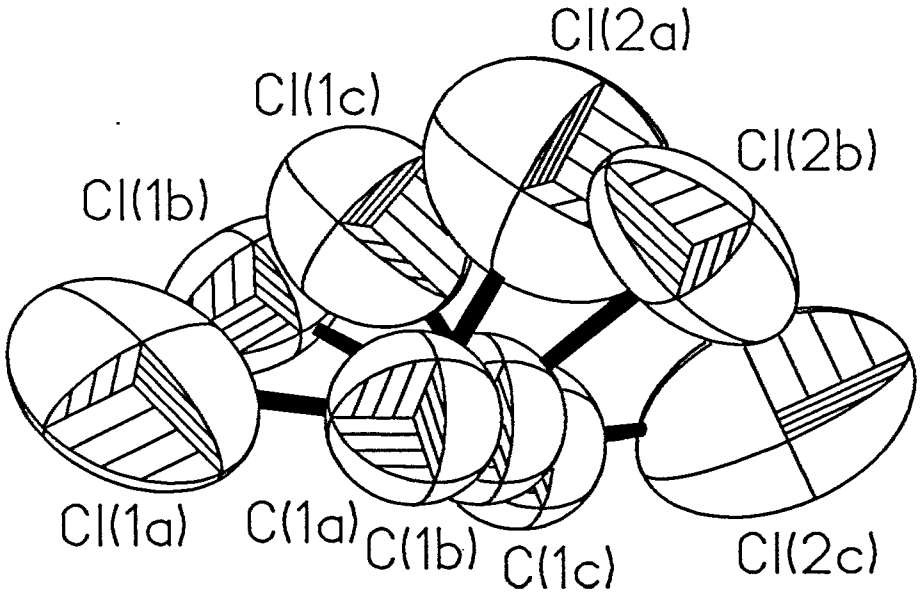
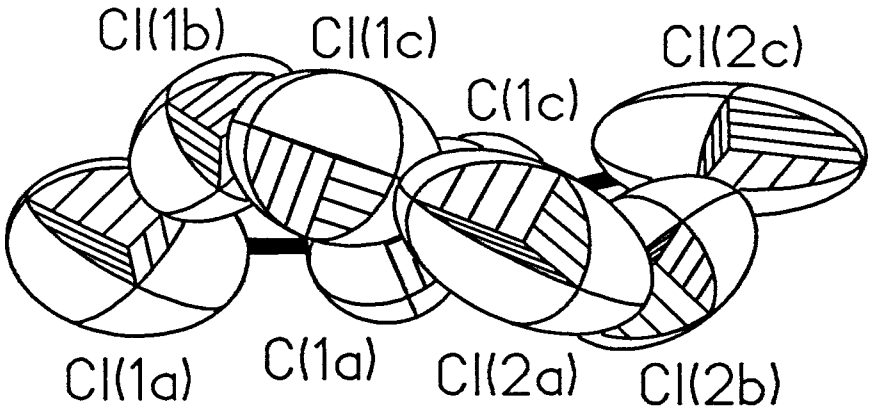


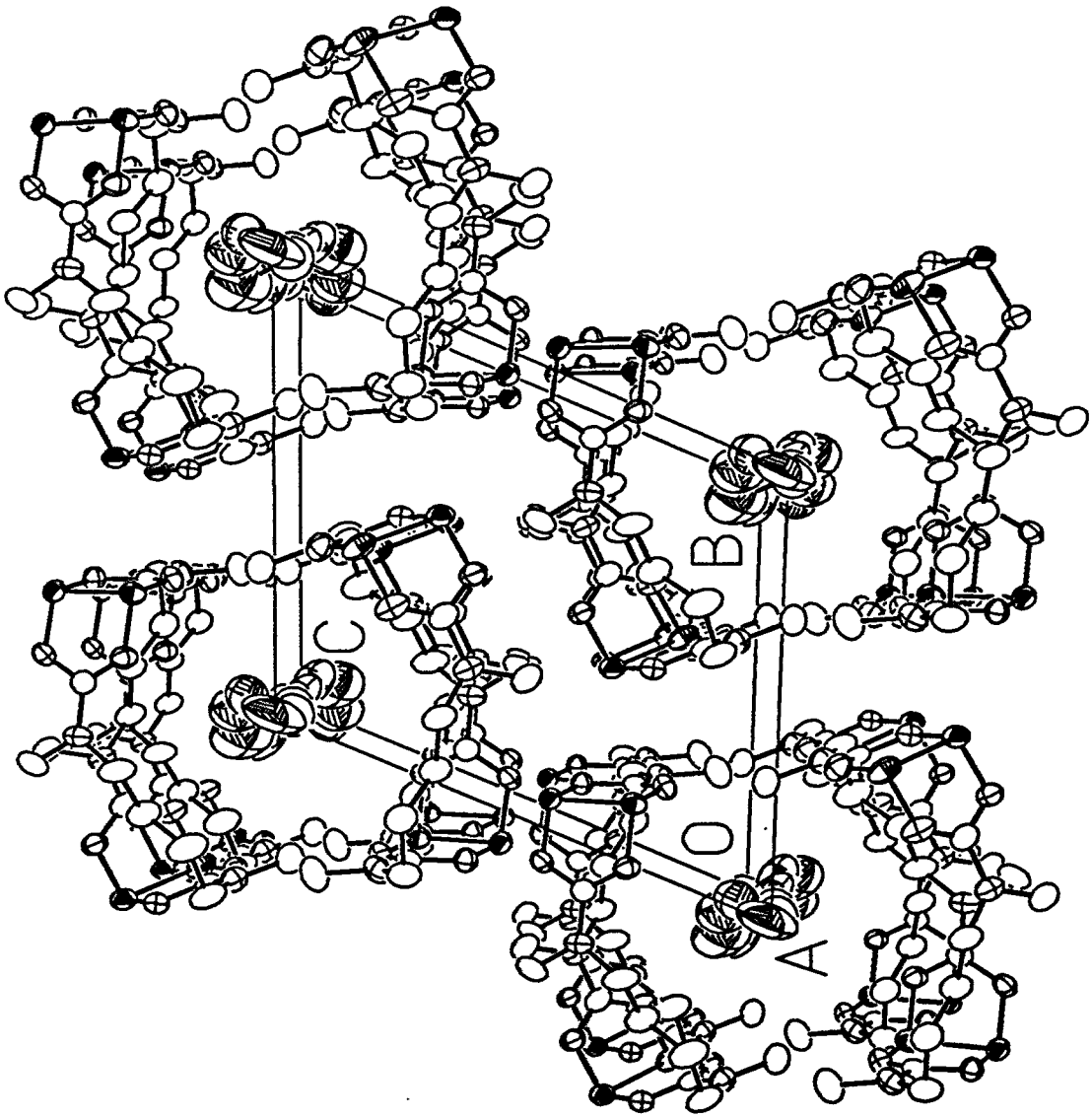
Figure S10.


Cl(2a)
Cl(1c)
Cl(2b)
Cl(1b)
Cl(1a)
C(1a)
C(1b)
C(1c)
Cl(2c)


Cl(1b)
Cl(1c)
Cl(2c)
C(1c)
Cl(1a)
C(1a)
Cl(2a)
Cl(2b)

P2871-36

Figure S11.



P2871-37

P R I N C E T O N U N I V E R S I T Y

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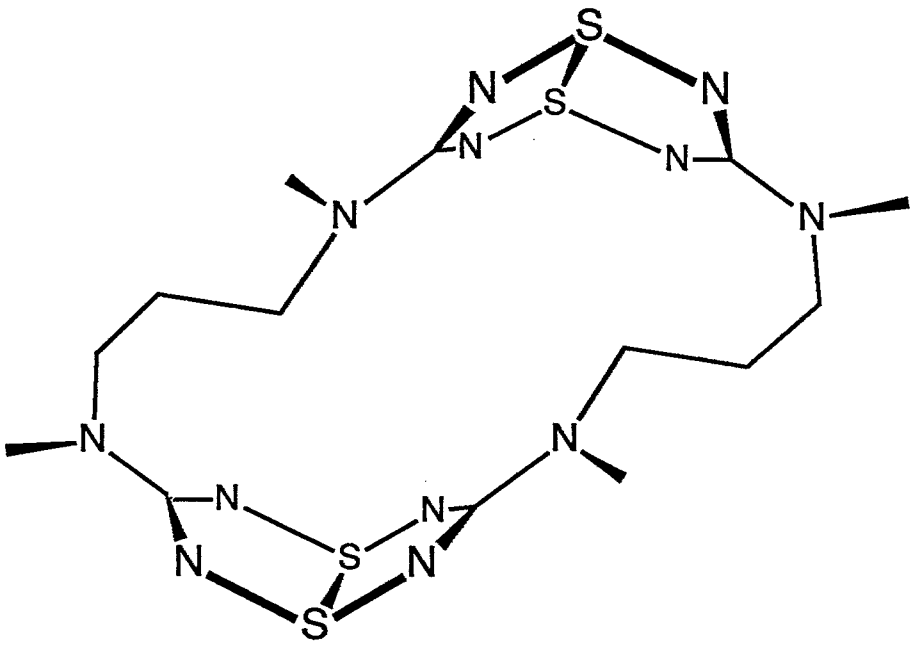
Report No. 94025

$C_{14}H_{24}N_{12}S_4$

Submitted August 24, 1994

Steven J. Dell, Robert A. Pascal, Jr. and Douglas M. Ho



$C_{14}H_{24}N_{12}S_4$

Experimental.

A thin yellow needle cut to 0.02 x 0.08 x 0.40 mm in size was mounted on a glass fiber with epoxy cement, and then transferred to a Siemens P4 diffractometer for characterization and data collection at 296K [graphite-monochromated Mo Kα radiation, λ = 0.71073 Å]. Unit cell parameters were determined from the setting angles of 25 centered reflections having $13 \leq 2\theta \leq 33^{\circ}$ and were as follows: $\underline{a}$ = 6.304(1), $\underline{b}$ = 8.366(1), $\underline{c}$ = 21.357(3) Å, α = 91.03(1), β = 92.26(1), γ = 110.56(1)$^{\circ}$ and V = 1053.2(3) Å^3. Axial photographs and preliminary peak scans through reciprocal space were consistent with the triclinic space groups P1 and P$\bar{1}$. The latter centrosymmetric space group P$\bar{1}$ was selected based on E-statistics.

One hemisphere of data ($+h,\pm k,\pm \ell$) was collected in the ω scan mode with 2θ ranging from 4.0 to 50.0°, and scan speeds varying from 2.00 to 8.08°/min. Three standards (100, 1$\bar{2}$0, 107) were measured for every 97 reflections during the data collection period, and showed no significant deviations from their mean intensity values (0.9859, 0.9978, 1.0130 for min., mean, max., respectively, i.e., within ±1.6% of the mean). A total of 4106 reflections were measured, 3734 were unique (R_{int} = 1.91%), and 1906 had $F > 3.0\sigma(F)$ and were considered observed. Corrections were made for Lorentz and polarization effects but not for absorption or extinction.

The structure was successfully solved by direct methods (XS:TREF) in the triclinic space group P$\bar{1}$ (No. 2) and refined by full-matrix least-squares using the Siemens SHELXTL PLUS program package.[1] All of the non-H atoms were refined with anisotropic displacement coefficients, H atoms were included with a riding model [C-H = 0.96 Å, U(H) = 1.2U(C)], and the weighting scheme employed was $w^{-1} = \sigma^2(F) + 0.0008F^2$. The methyl H atoms were located in a difference-Fourier map and their positions idealized to give C-H = 0.96 Å and tetrahedral angles at the C atoms. The refinements converged to R = 4.50%, wR = 4.36% and S = 0.78 with 271 variables and 7.0 reflections per refined parameter.[2] The maximum Δ/σ in the final cycle of least-squares was 0.001, and the residual peaks on the final $\Delta\rho$ map ranged from -0.26 to 0.28 eÅ^{-3}. Scattering factors were taken from the *International Tables for Crystallography, Vol C.*[3]

Footnotes and references.

1. (a) Sheldrick, G. M. (1990). SHELXTL PLUS 4.21 for Siemens Crystallographic Research Systems. Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA. (b) All computations were performed on a MicroVAX computer. (c) All non-hydrogen scattering factors were corrected for both the real and imaginary components of anomalous dispersion.

2. (a) $R = \sum||F_o|-|F_c|| \,/\, \sum|F_o|$, (b) $wR = [\sum w(|F_o|-|F_c|)^2 \,/\, \sum w|F_o|^2]^{1/2}$, (c) $S = [\sum w(|F_o|-|F_c|)^2 \,/\, (M-N)]^{1/2}$ where M is the number of observed reflections, and N is the number of parameters refined.

3. (a) Maslen, E. N., Fox, A. G. & O'Keefe, M. A. (1992). International Tables for Crystallography: Mathematical, Physical and Chemical Tables, Vol C, Chapter 6, edited by A. J. C. Wilson, pp. 476–516, Dordrecht, The Netherlands: Kluwer. (b) Creagh, D. C. & McAuley, W. J. (1992). International Tables for Crystallography: Mathematical, Physical and Chemical Tables, Vol C, Chapter 4, edited by A. J. C. Wilson, pp. 206–222, Dordrecht, The Netherlands: Kluwer.

Miscellaneous.

1. Structure 94025 may be compared to PTZCNB (JACS, 1981, 103, 1540-1544) and 92009 (Acta Cryst., 1994, C50, 108-110).
   (a) The average S-S distances for PTZCNB, 92009 and 94025 are 2.428, 2.408 2.434 Å, respectively.
   (b) The average S-N distances for PTZCNB, 92009 and 94025 are 1.605, 1.603 1.602 Å, respectively.
   (c) The average C-N distances for PTZCNB, 92009 and 94025 are 1.348, 1.342 1.350 Å, respectively.
   The S-S distance in 92009 is the one anomaly. It is significantly shorter than in PTZCNB and 94025, but unfortunately, the other distances (S-N and C-N) do not hint as to why this is so.

2. The average N-S-N angles in PTZCNB, 92009 and 94025 are 113.8, 113.2 and 112.4°, respectively. These values suggest that the dithiatetrazocine rings in the latter two compounds may possess a bit of tension as a result of cyclophane formation.

3. The average dihedral angles between the N_2S_2 planes in PTZCNB, 92009 and 94025 are 113.8, 113.1 and 112.4°, respectively, and exhibit the same trend as seen with the N-S-N angles.

4. The average dihedral angles between the CN_2 and N_2S_2 planes in PTZCNB, 92009 and 94025 are 165.6, 167.8 and 161.3°, respectively, indicating a slight folding along the N•••N vectors. The endocyclic C atoms bend slightly inwards and towards each other.

5. The average dihedral angles between the CN_2S_2 planes in PTZCNB, 92009 and 94025 are 108.9, 108.9 and 106.0°, respectively. These values exhibit the same trend as in item 3. Actually, these values give an approximate measure of the combined effects of items 3 and 4 on the dithiatetrazocine rings.

6. The exocyclic N atoms exhibit the opposite behavior to that seen with the endocyclic C atoms. The effect is less pronounced, but the N atoms bend slightly outwards and away from each other. The N-C bond is bent out of the CN_2 plane by 6.0, 5.0, and 5.8° for PTZCNB, 92009 and 94025, respectively.