1,5,2,4,6,8-dithiatetrazocine. Synthesis, computation, crystallography and voltammetry of the parent heterocycle.

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Supplemental Information

1 Crystallographic details and the disorder model for the structure of **1**

2 Crystal packing in **1** compared to that in solid benzene

3 Crystallographic details for the structure of S_4N_4

4 Original NMR spectroscopic data for **1**

5 Original mass spectrum for **1**

5 Computed IR spectrum - graphical analysis for **1**

6 Comparative crystal structure distances and angles for **1** with **3**

7 Computational details for **1** and **2** at the B3LYP/6-311+G(2d,p) level of theory including the monocations and the monoanions

Table S1. Crystal data and structure refinement for 1

Identification code	rb06034	Theta range for data collection	3.32 to 27.54°.
Empirical formula	$C_2H_2N_4S_2$	Index ranges	-7<=h<=7, -9<=k<=9, -15<=l<=15
Formula weight	146.20	Reflections collected	5237
Temperature	173(2) K	Independent reflections	609 [R(int) = 0.0551]
Wavelength	0.71073 Å	Completeness to θ = 25.25°	100.0 %
Crystal system	Orthorhombic	Absorption correction	Semi-emp. from equiv.
Space group	*Pbca*	Max. and min. transmission	0.7456 and 0.5724
Unit cell dimensions	*a* = 5.979(3) Å α= 90°.	Refinement method	Full-matrix LS on F2
	b = 7.217(3) Å β= 90°.	Data / restraints / parameters	609 / 1 / 50
	c = 12.281(5) Å γ = 90°.	Goodness-of-fit on F2	1.109
Volume	530.0(4) Å3	Final R indices [I>2sigma(I)]	R1 = 0.0389,
Z	4		wR2 = 0.1042
Density (calculated)	1.832 Mg/m^3	R indices (all data)	R1 = 0.0481
Absorption coefficient	0.880 mm^{-1}		wR2 = 0.1117
F(000)	296	Largest diff. peak and hole	0.440 and -0.337 e.Å-3
Crystal size	0.20 x 0.18 x 0.08 mm^3		

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for 1. [U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.]

Atom	x	y	z	U(eq)	Atom	x	y	z	U(eq)
S(1)	1969(6)	3961(5)	-1058(3)	32(1)	N(3)	240(50)	4940(50)	-1410(30)	30(1)
N(1)	-137(14)	5047(16)	-1518(8)	30(1)	N(4)	2490(30)	3760(20)	-163(10)	30(1)
N(2)	2612(7)	3608(5)	165(2)	30(1)	C(2)	1800(80)	4040(70)	-1080(40)	32(1)
C(1)	1770(30)	4060(30)	1105(19)	32(1)	H(1)	2664	3547	1670	39
S(2)	2000(20)	3989(19)	1099(14)	32(1)	H(2)	2651	3450	-1635	38

Table S3. Bond lengths [Å] and angles [°] for 1

S(1)-N(2)	1.571(4)	N(2)-S(1)-N(1)	127.9(6)
S(1)-N(1)	1.588(6)	C(1)#1-N(1)-S(1)	135.7(13)
N(1)-C(1)#1	1.28(2)	C(1)-N(2)-S(1)	135.6(10)
N(2)-C(1)	1.30(2)	N(1)#1-C(1)-N(2)	141(2)
C(1)-H(1)	0.9500	N(1)#1-C(1)-H(1)	109.6
S(2)-N(4)	1.59(2)	N(2)-C(1)-H(1)	109.6
S(2)-N(3)#1	1.59(4)	N(4)-S(2)-N(3)#1	116.2(16)
N(3)-C(2)	1.21(3)	C(2)-N(3)-S(2)#1	146(4)
N(4)-C(2)	1.22(3)	C(2)-N(4)-S(2)	146(3)
C(2)-H(2)	0.9500	N(3)-C(2)-N(4)	131(6)
		N(3)-C(2)-H(2)	114.3
		N(4)-C(2)-H(2)	114.3

Symmetry transformations used to generate equivalent atoms: #1 -x,-y+1,-z

Table S4. Anisotropic displacement parameters ($Å^2$x 10^3) for 1.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S(1)	29(1)	33(1)	34(1)	-1(1)	8(1)	4(1)
N(1)	34(3)	33(2)	24(2)	2(1)	-6(2)	-2(2)
N(2)	24(1)	31(1)	37(2)	9(1)	-7(2)	3(1)
C(1)	27(3)	34(1)	36(1)	2(1)	-12(2)	4(1)
S(2)	27(3)	34(1)	36(1)	2(1)	-12(2)	4(1)
N(3)	34(3)	33(2)	24(2)	2(1)	-6(2)	-2(2)
N(4)	24(1)	31(1)	37(2)	9(1)	-7(2)	3(1)
C(2)	29(1)	33(1)	34(1)	-1(1)	8(1)	4(1)

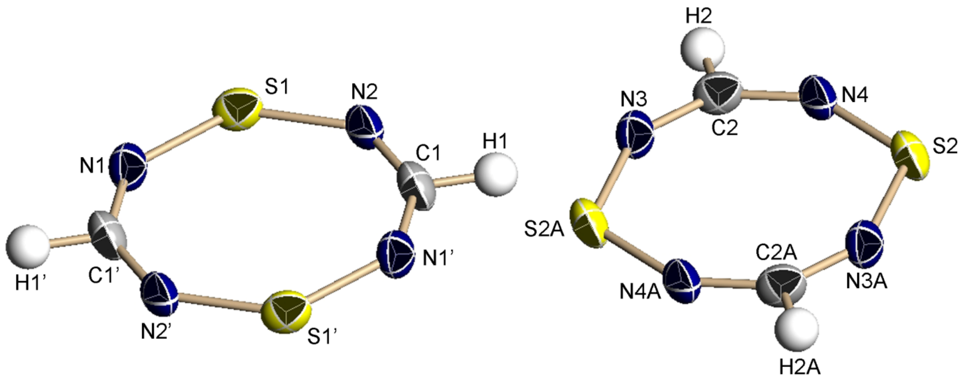
[The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2a^*2U_{11} + \ldots + 2\ h\ k\ a^*\ b^*\ U_{12}\ ]$

Table S5. Torsion angles [°] for 1

N(2)-S(1)-N(1)-C(1)#1	3(2)	N(3)#1-S(2)-N(4)-C(2)	-3(5)
N(1)-S(1)-N(2)-C(1)	-1.3(13)	S(2)#1-N(3)-C(2)-N(4)	-12(12)
S(1)-N(2)-C(1)-N(1)#1	-1(3)	S(2)-N(4)-C(2)-N(3)	9(9)

Symmetry transformations used to generate equivalent atoms: #1 -x,-y+1,-z

Positional disorder between CH and S was encountered. This was modelled using the SHELXTL "part" commands with refined occupancies of 75:25 later frozen. Anisotropic refinement of all the non-H atoms was possible using "eadp" restraints. The resulting model is presented in Figures S1 and S2.



Main Component (75%) Minor Component (25%)

Figure S1. Thermal ellipsoids plots (50%) showing the two components of the disorder model developed for **1**. The "CH" units are very similar in volume to S atoms, so that the observed disorder is fully intelligible for this class of molecule.

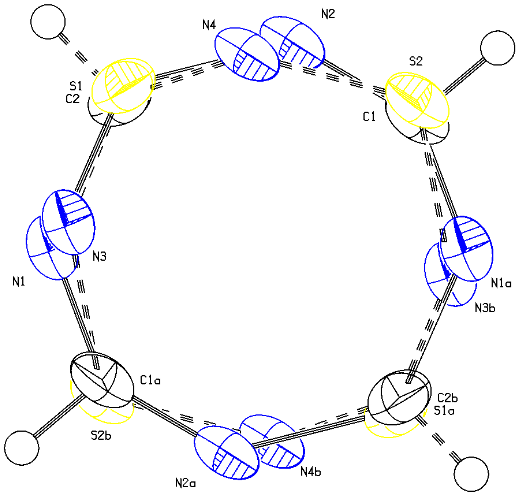


Figure S2 ORTEP-style plot produced by Platon which shows the superposition of the two components of the refined disorder model of **1**. The offset of the nitrogen positions is an essential requirement in view of the unequal lengths of the C-N and S-N bonds.

Crystallographic packing: the packing in **1** is strongly reminiscent of that in benzene. See the text for discussion. The interactions out to 0.2 > sum of the v.d. Waals' radii are depicted in Figure S3. A similar view of the crystal packing in benzene is shown in Figure S4.

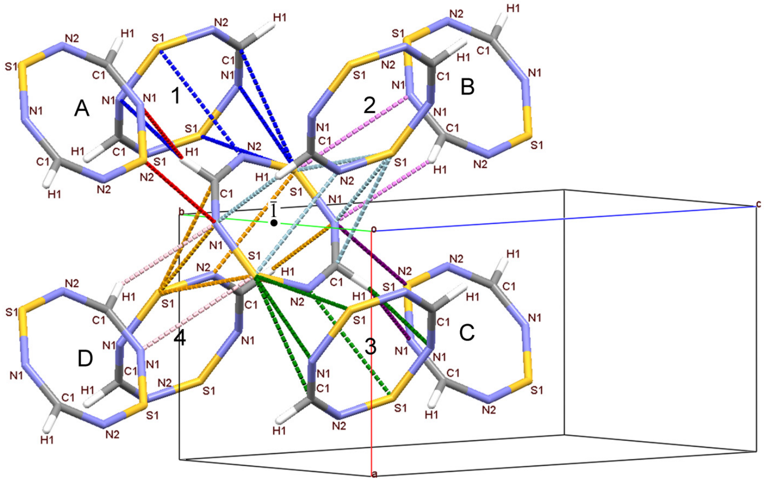


Figure S3 A packing diagram for the crystal structure determined for **1** that shows the shortest contacts to neighbouring sites. The generating molecule is centered on the (0, ½, 0) Wyckoff site and there are two kinds of neighbours. The shorter contacts, just as in benzene, are to the rings marked 1→ 4 which are related by *a* glides along the *b* direction. This set of interactions defines the (0 0 1) crystallographic plane. A second, somewhat longer, set of contacts occur to the rings marked A→ D which are located lower and higher in the *c* direction w.r.t. the generating ring; the relationship to these rings is the 2_1 screw axis parallel to *c* passing through (0, ¼. 0) and (0, ¾, 0). Rings A,D and B,C are components of identical layers above and below the generating layer related by the 2_1 screw.

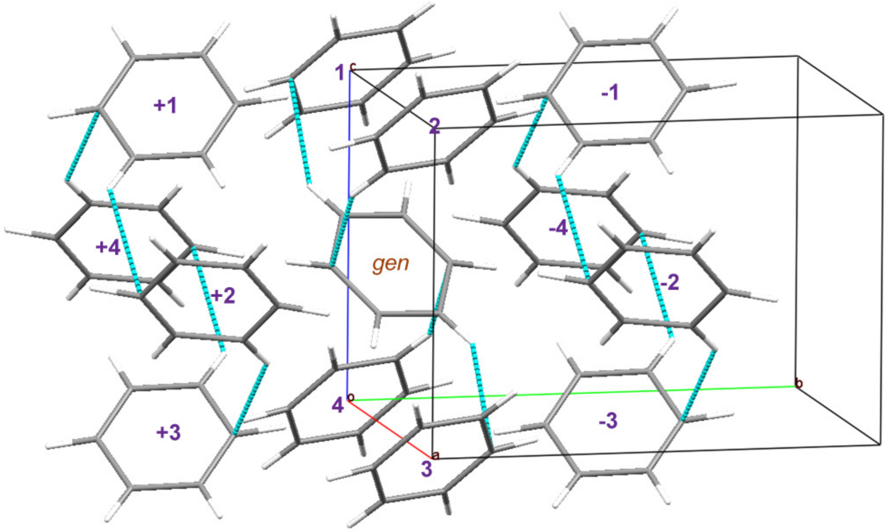


Figure S4 A packing diagram for the crystal structure (Refcode BENZEN11) determined for benzene in *P*bca with contacts less than the sums of the v.d. Waals' radiii. The generator ring is located at (½ 0 ½), surrounded by **1** - **4** related by glides with "T-shaped" interactions. Edge contacts to **-1** to **-4** and **+1** to **+4** in layers below and above, respectively are related by 2_1 screws.[1]

Table S6 Crystal data and structure refinement for S_4N_4

Empirical formula	N4 S4	Theta range for data collection	3.22 to 27.48°
Formula weight	184.28	Index ranges	-11<=h<=11, -9<=k<=9, -11<=l<=11
Temperature	173(2) K	Reflections collected	5966
Wavelength	0.71073 Å	Independent reflections	1228 [R(int) = 0.0561]
Crystal system	Monoclinic	Completeness to theta = 25.25°	99.9 %
Space group	P2(1)/n	Absorption correction	Semi-emp. from equiv.
Unit cell dimensions	a = 8.647(3) Å α= 90°	Max. and min. transmission	0.7455 and 0.610
	b = 7.101(3) Å β= 93.402(4)°	Refinement method	Full-matrix LS on F^2
	c = 8.732(3) Å γ = 90°	Data / restraints / parameters	1228 / 0 / 73
Volume	535.2(3) Å^3	Goodness-of-fit on F^2	0.941
Z	4	Final R indices [I>2sigma(I)]	R1 = 0.0299
Density (calculated)	2.287 Mg/m^3		wR2 = 0.0580
Absorption coefficient		R indices (all data) 1.649 mm^{-1}	R1 = 0.0450
F(000)	368		wR2 = 0.0611
Crystal size	0.287 x 0.095 x 0.030 mm^3	Largest diff. peak and hole	0.333 and -0.394 e.Å^{-3}

Table S7. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3)
[U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.]

	x	y	z	U(eq)		x	y	z	U(eq)
S(1)	5982(1)	2086(1)	11514(1)	21(1)	N(1)	7178(3)	3838(3)	11648(2)	25(1)
S(3)	5593(1)	2984(1)	8506(1)	22(1)	N(2)	8921(3)	2242(3)	9741(3)	31(1)
S(2)	7737(1)	470(1)	9598(1)	27(1)	N(3)	6494(3)	1043(3)	8190(2)	25(1)
S(4)	8036(1)	4219(1)	10061(1)	27(1)	N(4)	4759(3)	2631(3)	10097(2)	21(1)

Table S8. Bond lengths [Å] and angles [°] for S_4N_4

S(1)-N(1)	1.617(2)	N(1)-S(1)-N(4)	104.83(12)
S(1)-N(4)	1.626(2)	N(3)-S(3)-N(4)	104.91(12)
S(3)-N(3)	1.615(2)	N(2)-S(2)-N(3)	104.39(13)
S(3)-N(4)	1.623(2)	N(2)-S(4)-N(1)	104.18(12)
S(2)-N(2)	1.622(2)	S(1)-N(1)-S(4)	112.76(13)
S(2)-N(3)	1.636(2)	S(2)-N(2)-S(4)	112.31(14)
S(4)-N(2)	1.631(3)	S(3)-N(3)-S(2)	112.71(13)
S(4)-N(1)	1.632(2)	S(3)-N(4)-S(1)	112.72(14)

Table S9. Anisotropic displacement parameters ($Å^2$x 10^3) for 1.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	25(1)	23(1)	16(1)	3(1)	1(1)	-1(1)
S(3)	27(1)	23(1)	17(1)	3(1)	-1(1)	0(1)
S(2)	25(1)	28(1)	28(1)	-1(1)	2(1)	6(1)
S(4)	28(1)	30(1)	25(1)	0(1)	1(1)	-12(1)
N(1)	32(1)	26(1)	17(1)	-2(1)	-1(1)	-8(1)
N(2)	18(1)	41(2)	33(2)	1(1)	4(1)	-2(1)
N(3)	31(1)	23(1)	20(1)	-6(1)	0(1)	1(1)
N(4)	20(1)	22(1)	22(1)	3(1)	2(1)	0(1)

[The anisotropic displacement factor exponent takes the form: $-2p^{2}[\ h^{2}a{*}2U_{11} + \dots + 2\ h\ k\ a{*}\ b{*}\ U_{12}\ ]$]

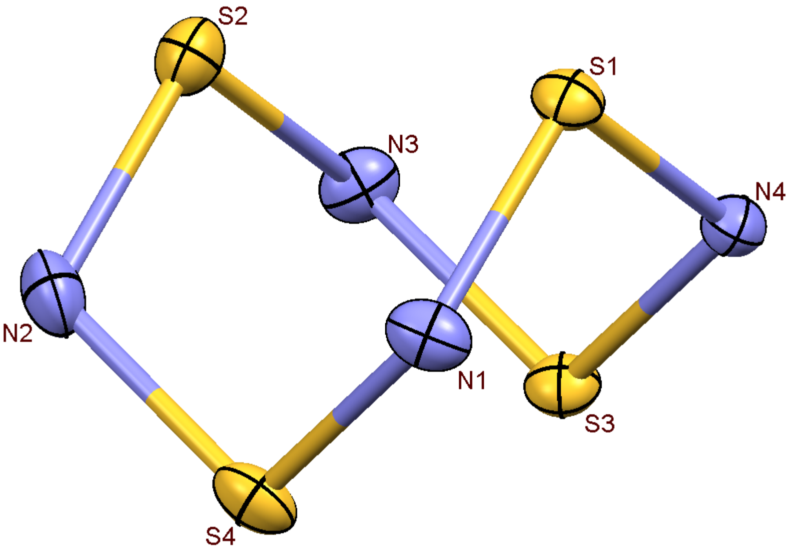


Figure S5 Molecular structure of S_4N_4 as found in the crystal lattice at 173 K (30% displacement ellipsoids).

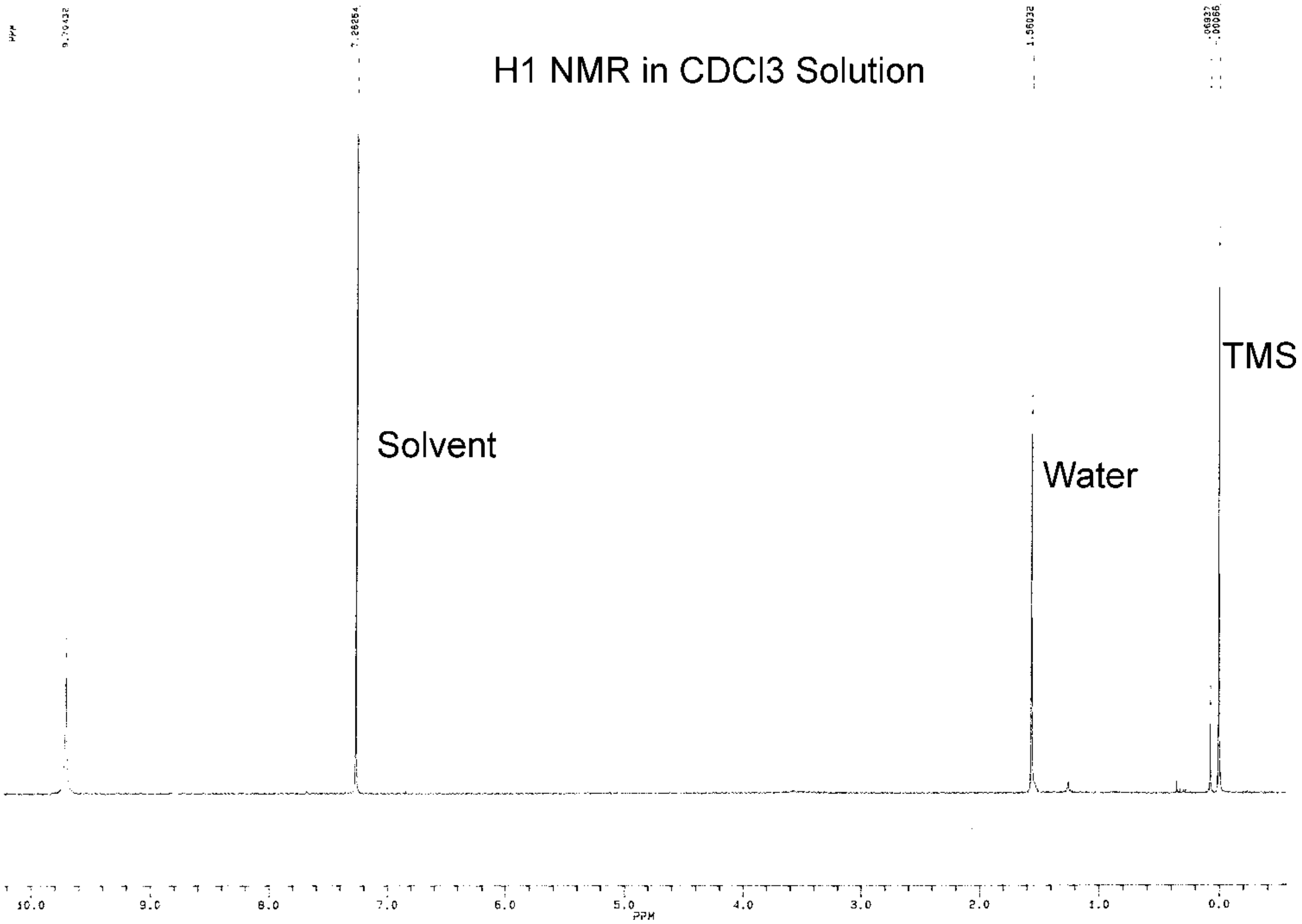


Figure S6 Solution ^{1}H NMR spectrum of **1** in $CDCl_3$ solution. The single peak is found at +9.70 ppm w.r.t TMS.

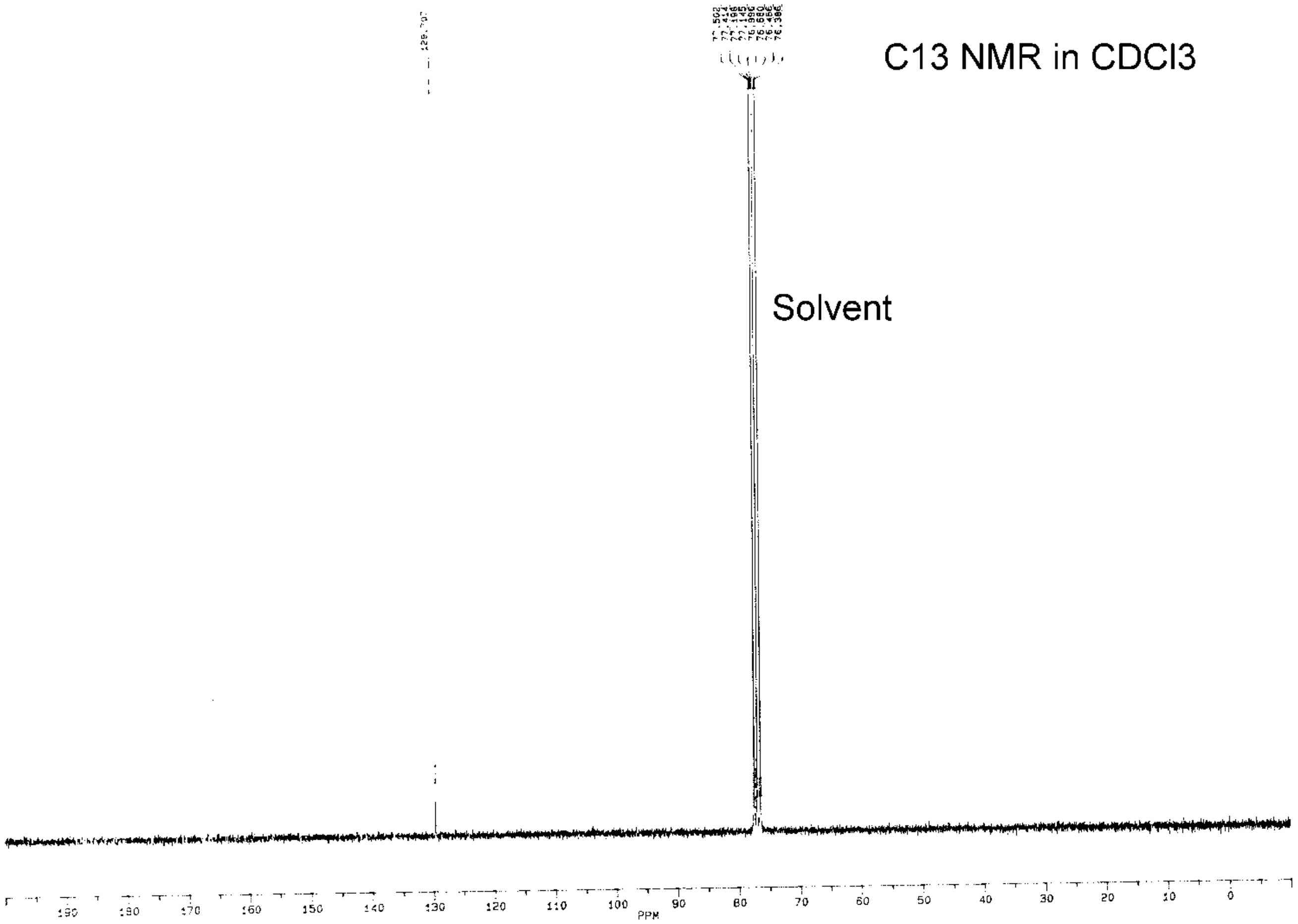


Figure S7 Solution {^{1}H}–^{13}C NMR spectrum of **1** in CDCl$_3$ solution. The single carbon resonance is found at +129.7 ppm w.r.t. TMS.

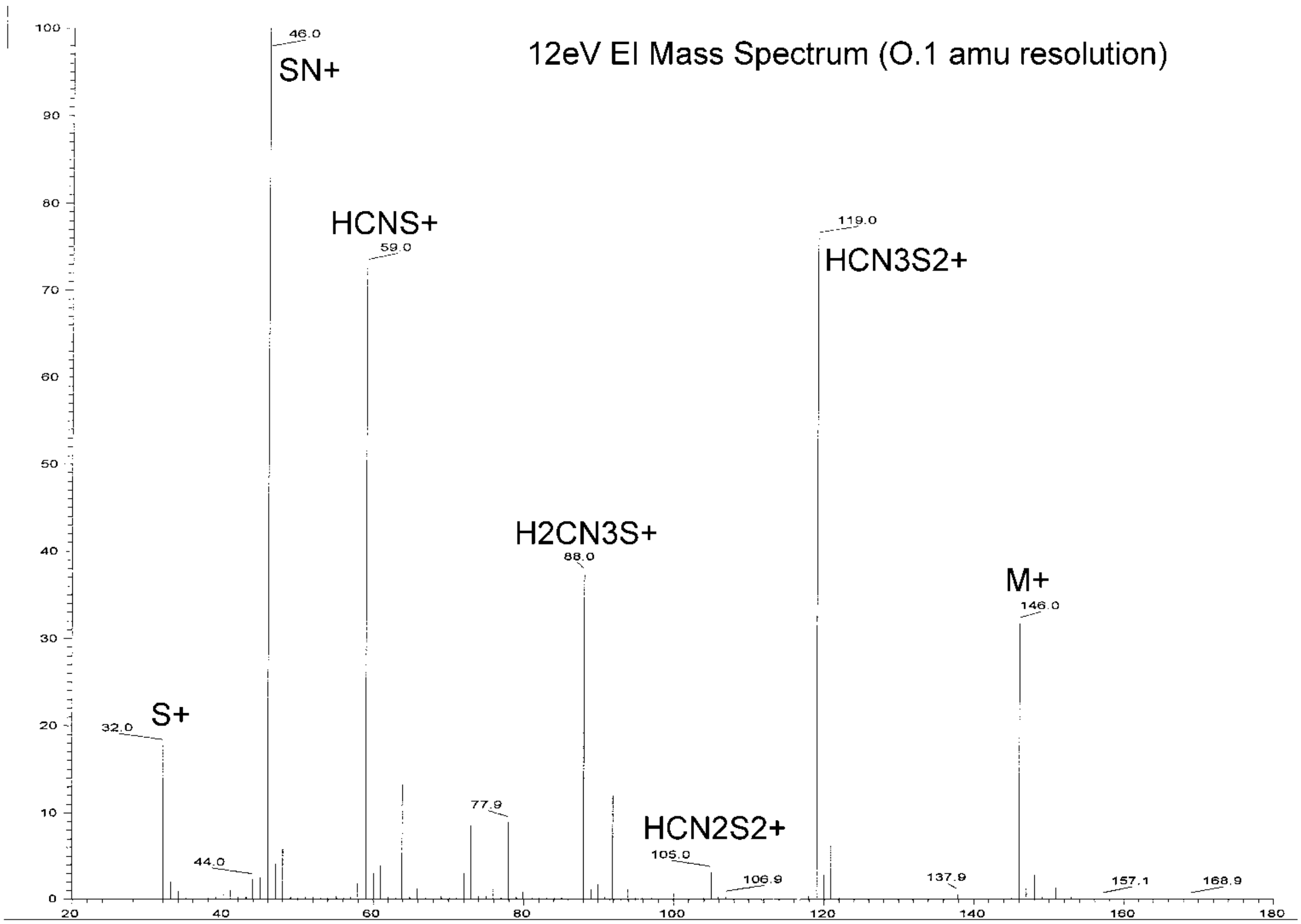


Figure S8 An 11 eV EI mass spectrum to 0.1 amu resolution obtained on **1**.

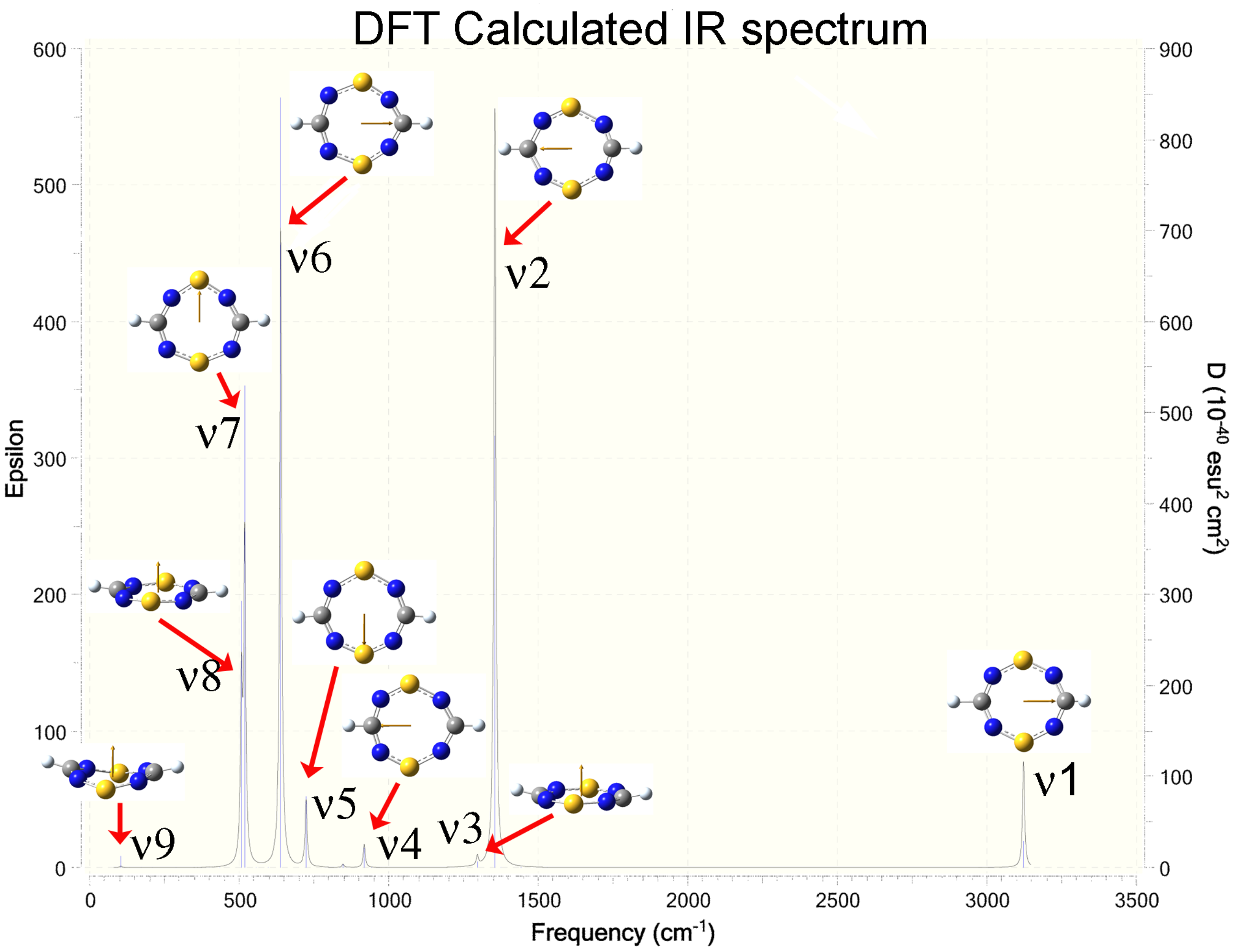


Figure S9. Calculated infra-red spectrum from B3LYP/6-311G+(2d,p) frequency calculations. Experimental values for ν1 = 2931 cm^{-1}; ν2 = 1321 cm^{-1}; ν5 = 728 cm^{-1}; ν6 = 633 cm^{-1}; ν7 = 513 cm^{-1}; ν8 = 492 cm^{-1}. (GaussView 4.1).

Table S10 Comparison of Inter-atomic Distances and Angles to Experimental X-ray data for known planar dithiatetrazocines and the DFT calculations

Compound	C—N (Å)	s.u.	N—S (Å)	s.u.	S···S (Å)	s.u.	N-C-N (°)	s.u.	C-N-S (°)	s.u.	N-S-N (°)	s.u.
p-NO2C6H4	1.333	0.002	1.5628	0.018	3.806	0.001	128.8	0.2	141.60	0.16	126.47	0.09
	1.327	0.002	1.5593	0.018					143.09	0.16		
p-Br	1.323	0.005	1.569	0.003	3.796	0.002	129.9	0.4	140.9	0.3	127.0	0.2
	1.326	0.006	1.558	0.004	3.788	0.002	128.6	0.4	142.1	0.4	127.2	0.2
	1.329	0.006	1.56						142.1	0.3		
	1.338	0.005	1.555						142.0	0.4		
p-Br/NO2-C6H4	1.339	0.01	1.561	0.007	3.815	0.004	129.5	0.7	140.6	0.6	126.5	0.4
	1.322	0.01	1.568	0.006					143.5	0.6		
Ph	1.319		1.569		3.79		129.2		140.9		127.0	
	1.327		1.559						142.9			
pCF3C6H4	1.322	0.003	1.563	0.002	3.788		129.2	0.2	142.4	0.2	126.8	0.1
	1.323	0.003	1.561	0.002					141.6	0.2		
pMeOC6H4	1.33	0.003	1.559	0.002	3.781		128.5	0.2	142.2	0.2	127.2	0.1
	1.328	0.003	1.564	0.002					142.2	0.2		
tBu	1.323	0.003	1.567	0.002	3.784		128.6	0.2	142.2	0.2	127.2	0.12
	1.328	0.003	1.57	0.002					140.0	0.2		
2-thienyl	1.324	0.004	1.557	0.003	3.803		130.1	0.3	141.8	0.2	126.00	0.16
	1.329	0.004	1.554	0.003					141.5	0.3		
Averages	1.3272		1.5620		3.7946		129.16		141.87		126.82	
s.u. (std dev)	0.0054		0.0049		0.0113		0.5855		0.8817		0.4177	
H xray	1.3000	0.02	1.5880	0.006	3.8150	0.005	141	0.2	135.7	1.3	127.9	0.6
			1.5710	0.004					135.6	1.0		
H xray average	**1.30**		**1.5795**		**3.815**		**141**		**135.65**		**127.9**	
H DFT calc	**1.3179**		**1.5845**		**3.8554**		**140.42**		**133.1**		**126.06**	
diff to calc	0.0179		0.005		0.0404		0.58		2.55		1.84	
diff to xray	0.0272		0.0175		0.0204		11.8444		6.2161		1.0811	
	calc		calc		other		calc		calc		other	

Comparative data compiled from ref. 2.

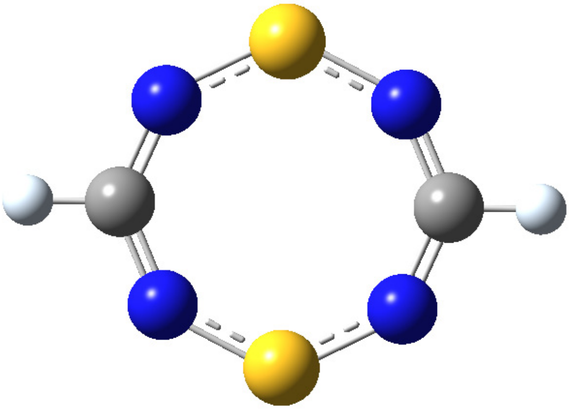
Gaussion 03 Results

Calculations were undertaken at the B3LYP/6311G+(2d,p) level of theory. Full geometry optimization under the appropriate symmetry point group were undertaken for all species. Frequency calculations were used to identify possible non-planar deviation from the flat molecules in **1** and **2**. When imaginary frequencies were identified (cation of **1** and anions of **2-**), the structure was deformed in the direction of the most intense imaginary vibrational modes. **1** is found to be most stable in the planar form both neutral and anionic, but the energy difference is much smaller for **1-**.[3] However, **1+** is lower in energy in the gentle 'bowl-shaped' deformation shown below. **2** is only stable as flat, with no folded or puckered alternative in the neutral form. However, **2-** is not a minimum as a flat molecule, but instead deforms to the well-known puckered "chair" conformation.[4] However, the planar form is stable for **2+**.

Calculations undertaken with Gaussian 03 release 2.6; results visualized with GaussView 4.1.2).[5]

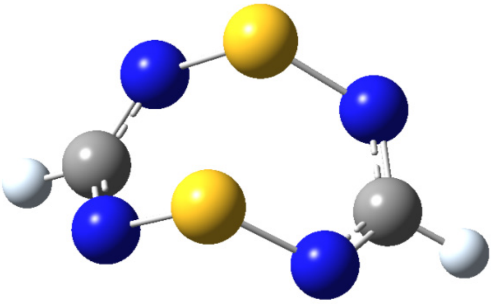
Coordinates for **1** in neutral flat ground state geometry

Tag	Symbol	X	Y	Z
1	N	0.0000000	1.2090960	1.4121910
2	C	0.0000000	0.0000000	1.9366510
3	N	0.0000000	-1.2090960	1.4121910
4	S	0.0000000	-1.9276920	0.0000000
5	S	0.0000000	1.9276920	0.0000000
6	N	0.0000000	1.2090960	-1.4121910
7	N	0.0000000	-1.2090960	-1.4121910
8	C	0.0000000	0.0000000	-1.9366510
9	H	0.0000000	0.0000000	-3.0248630
10	H	0.0000000	0.0000000	3.0248630



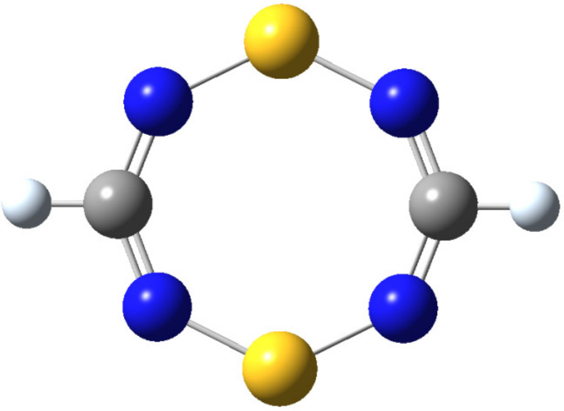
Coordinates for **1** in folded excited state

Tag	Symbol	X	Y	Z
1	C	0.0000000	1.8092630	0.6759130
2	N	-1.1907730	1.3610170	0.3082050
3	S	-1.2713590	0.0000000	-0.6026870
4	S	1.2713590	0.0000000	-0.6026870
5	N	1.1907730	1.3610170	0.3082050
6	N	1.1907730	-1.3610170	0.3082050
7	N	-1.1907730	-1.3610170	0.3082050
8	C	0.0000000	-1.8092630	0.6759130
9	H	0.0000000	2.7181700	1.2726460
10	H	0.0000000	-2.7181700	1.2726460



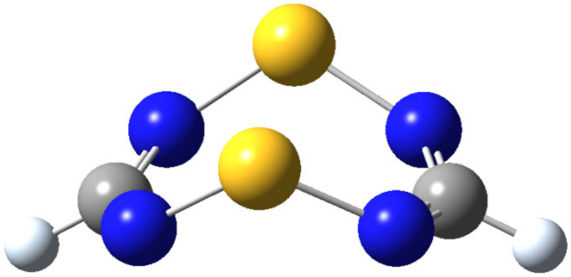
Coordinates for **1-** flat ground state

Tag	Symbol	X	Y	Z
1	N	0.0000000	1.2267660	1.4772490
2	C	0.0000000	0.0000000	1.9553710
3	N	0.0000000	-1.2267660	1.4772490
4	S	0.0000000	-1.9571940	0.0000000
5	S	0.0000000	1.9571940	0.0000000
6	N	0.0000000	1.2267660	-1.4772490
7	N	0.0000000	-1.2267660	-1.4772490
8	C	0.0000000	0.0000000	-1.9553710
9	H	0.0000000	0.0000000	-3.0511270
10	H	0.0000000	0.0000000	3.0511270



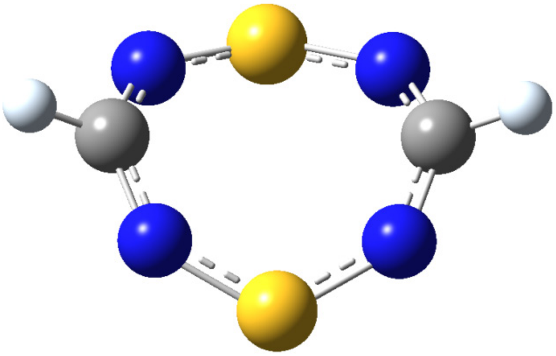
Coordinates for **1-** folded excited state

Tag	Symbol	X	Y	Z
1	C	0.0000000	1.8281590	0.5754900
2	N	-1.2265000	1.4092850	0.3129490
3	S	-1.5403820	0.0000000	-0.5590230
4	S	1.5403820	0.0000000	-0.5590230
5	N	1.2265000	1.4092850	0.3129490
6	N	1.2265000	-1.4092850	0.3129490
7	N	-1.2265000	-1.4092850	0.3129490
8	C	0.0000000	-1.8281590	0.5754900
9	H	0.0000000	2.7836860	1.1101380
10	H	0.0000000	-2.7836860	1.1101380



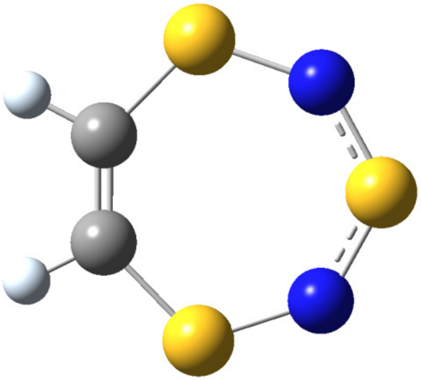
Coordinates for **1+** in puckered ground state

Tag	Symbol	X	Y	Z
1	N	1.1968150	1.3590770	0.1026970
2	C	0.0000000	1.8130940	0.4443670
3	N	-1.1968150	1.3590770	0.1026970
4	S	-1.8536140	0.0000000	-0.3183150
5	S	1.8536140	0.0000000	-0.3183150
6	N	1.1968150	-1.3590770	0.1026970
7	N	-1.1968150	-1.3590770	0.1026970
8	C	0.0000000	-1.8130940	0.4443670
9	H	0.0000000	-2.7559200	0.9890700
10	H	0.0000000	2.7559200	0.9890700



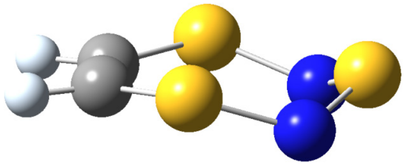
Coordinates for neutral **2** in flat ground state

Tag	Symbol	X	Y	Z
1	C	0.0000000	0.6776280	-1.7125980
2	S	0.0000000	-1.9053830	-0.5194390
3	S	0.0000000	1.9053830	-0.5194390
4	N	0.0000000	1.3821100	1.0155240
5	N	0.0000000	-1.3821100	1.0155240
6	H	0.0000000	1.1765640	-2.6792790
7	S	0.0000000	0.0000000	1.7696520
8	C	0.0000000	-0.6776280	-1.7125980
9	H	0.0000000	-1.1765640	-2.6792790



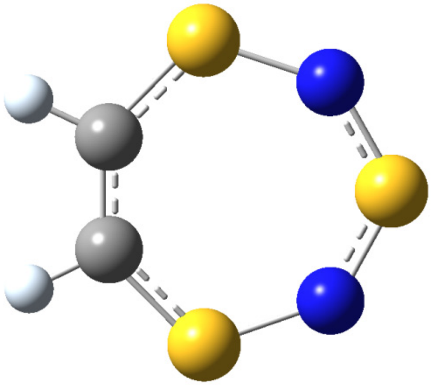
Coordinates for **2-** in lowest-energy chair conformation

Tag	Symbol	X	Y	Z
1	C	-0.5561110	1.6546940	0.6758920
2	S	-0.0399590	0.5164720	-1.8932940
3	S	-0.0399590	0.5164720	1.8932940
4	N	-0.0399590	-1.0863350	1.3937450
5	N	-0.0399590	-1.0863350	-1.3937450
6	H	-0.8982140	2.5648680	1.1687530
7	S	0.6442420	-1.6440300	0.0000000
8	C	-0.5561110	1.6546940	-0.6758920
9	H	-0.8982140	2.5648680	-1.1687530



Coordinates for **2+** in flat ground state

Tag	Symbol	X	Y	Z
1	C	0.0000040	-1.6891950	0.7023000
2	S	0.0000040	-0.5294510	-1.8994660
3	S	0.0000040	-0.5294510	1.8994660
4	N	0.0000330	1.0196070	1.3631670
5	N	0.0000330	1.0196070	-1.3631670
6	H	-0.0000640	-2.6670330	1.1834220
7	S	-0.0000320	1.7670200	0.0000000
8	C	0.0000040	-1.6891950	-0.7023000
9	H	-0.0000640	-2.6670330	-1.1834220



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