Table S1. Bond lengths [Å] and angles [°] for compound **1** according to X-Ray diffraction data.

S(1)-C(1)	1.8142(4)	C(1)-S(1)-C(2)	90.413(15)
S(1)-C(2)	1.8605(4)	N(1A)-N(1)-C(2A)	104.81(3)
N(1)-N(1A)	1.4411(5)	N(1A)-N(1)-C(1)	108.538(19)
N(1)-C(2A)	1.4435(4)	C(2A)-N(1)-C(1)	113.59(2)
N(1)-C(1)	1.4891(4)	N(1)-C(1)-S(1)	105.061(19)
C(1)-H(1B)	0.988(8)	N(1)-C(1)-H(1B)	107.2(5)
C(1)-H(1A)	0.974(8)	S(1)-C(1)-H(1B)	109.3(5)
C(2)-N(1A)	1.4435(4)	N(1)-C(1)-H(1A)	112.6(5)
C(2)-H(2B)	0.968(9)	S(1)-C(1)-H(1A)	108.7(5)
C(2)-H(2A)	0.963(8)	H(1B)-C(1)-H(1A)	113.6(7)
		N(1A)-C(2)-S(1)	107.16(2)
		N(1A)-C(2)-H(2B)	110.3(5)
		S(1)-C(2)-H(2B)	110.6(5)
		N(1A)-C(2)-H(2A)	111.7(5)
		S(1)-C(2)-H(2A)	109.6(5)
		H(2B)-C(2)-H(2A)	107.4(7)

Table S2. Torsion and pseudo-torsion angles [°] for compound 1 according to X-Ray diffraction data.

C(1)-N(1)-N(1A)-C(2)	53.32
N(1)-C(1)-S(1)-C(2)	13.19
N(1A)-C(2)-S(1)-C(1)	15.5
C(1)-N(1)-N(1A)-C(1A)	-68.36
S(1)-C(1)-N(1)-N(1A)	-40.21
S(1)-C(2)-N(1A)-N(1)	-40.6
C(2A)-N(1)-N(1A)-C(2)	175.01
S(1)-C(1)-N(1)-C(2A)	-156.33
S(1)-C(2)-N(1A)-C(1A)	77.69
C(1)-N(1)-N(1A)-lp	171
lp-N(1)-N(1A)-lp	51
S(1)-C(1)-N(1)-lp	80
H(1A)-C(1)-N(1)-C(2A)	-38
H(1B)-C(1)-N(1)-C(2A)	88
S(1)-C(2)-N(1A)-lp	-159
H(2A)-C(2)-N(1A)-lp	-40
H(2B)-C(2)-N(1A)-lp	80
lp-N(1)-N(1A)-C(2)	-67
H(1A)-C(1)-S(1)-C(2)	-107
H(1A)-C(1)-N(1)-lp	-162
H(1B)-C(1)-N(1)-lp	-35
H(2A)-C(2)-S(1)-C(1)	-104
H(2A)-C(2)-N(1A)-N(1)	78
H(2B)-C(2)-N(1A)-N(1)	-162
lp-N(1)-N(1A)-C(1A)	171
H(1B)-C(1)-S(1)-C(2)	128
H(1A)-C(1)-N(1)-N(1A)	78
H(1B)-C(1)-N(1)-N(1A)	-155
H(2B)-C(2)-S(1)-C(1)	138

H(2A)-C(2)-N(1A)-C(1A)	-164
H(2B)-C(2)-N(1A)-C(1A)	-44

Table S3. Summary of symmetrically independent critical points (3,-1) for intermolecular contacts in the crystal of **1**.

	symmetry operation	ρ(r), eÅ^{-3}	$\nabla^2\rho$(r), eÅ^{-3}	v(r), a.u.	E, kcal/mol
S(1) - H(2A)	x, y-1, z	0.04	0.67	-0.00344	1.1
S(1) - H(1B)	1/2-x, -1/2+y, 1/2-z	0.05	0.56	-0.00343	1.1
S(1) - H(2B)	1/2-x, 1/2-y, -z	0.04	0.47	-0.00287	0.9
S(1) - S(1)	1/2-x, 1/2-y, -z	0.04	0.37	-0.00238	0.7
S(1) - S(1)	1/2-x, -1/2+y, 1/2-z	0.04	0.45	-0.0029	0.9
H(2B) - H(2B)	1-x, 1-y, -z	0.04	0.56	-0.00328	1.0
H(1A) - N(1)	x, y-1, z	0.03	0.56	-0.00258	0.8
H(2B) - H(1A)	x, -y, -1/2+z	0.04	0.56	-0.00288	0.9

Table S4. Summary of symmetrically independent $n\rightarrow\sigma^*$ NBO interactions in conformer **1** with energy > 1 kcal/mol according B3LYP/6-311G*

Atoms	**NBO energy (kcal/mol)**
lp-S(1)-C(1)-H(1A)	4.31
lp-S(1)-C(1)-H(1E)	3.82
lp-S(1)-C(2)-H(2E)	1.75
lp-S(1)-C(2)-H(2A)	4.18
lp-N(1)-C(1)-H(1A)	5.22
lp-N(1)-C(1)-H(1E)	2.95
lp-N(1A)-C(2)-S(1)	12.14
lp-N(1A)-N(1)-C(1)	7.43
lp-N(1A)-C(4)-H(2A)	2.96

Table S5. Summary of symmetrically independent $n\rightarrow\sigma^*$ NBO interactions in conformer **1B** with energy > 1 kcal/mol according B3LYP/6-311G*

Atoms	**NBO energy (kcal/mol)**
lp-S(1)-C(1)-N(1)	2.59
lp-S(1)-C(1)-H(1A)	4.74
lp-N(1)-C(1)-H(1E)	2.10
lp-N(1)-C(1)-H(1A)	5.89

Table S6. Summary of symmetrically independent $n \rightarrow \sigma^*$ NBO interactions in conformer **1C** with energy > 1 kcal/mol according B3LYP/6-311G*

Atoms	**NBO energy (kcal/mol)**
lp-S(1)-C(1)-N(1)	3.20
lp-S(1)-C(1)-H(1A)	5.07
lp-N(1)-C(1)-H(1A)	5.61
lp-N(1)-C(1)-H(1E)	3.52
lp-N(1)-N(1A)-C(1A)	1.83
lp-N(1)-C(2)-S(2)	10.41
lp-N(1)-N(1A)-C(2A)	1.74
lp-N(1)-C(2)-H(2A)	3.91

Table S7. Summary of symmetrically independent $n \rightarrow \sigma^*$ NBO interactions in conformer **1A** with energy > 1 kcal/mol according B3LYP/6-311G*

Atoms	**NBO energy (kcal/mol)**
lp-S(1)-C(1)-N(1)	2.95
lp-S(1)-C(1)-H(1A)	5.02
lp-N(1)-C(1)-H(1A)	6.52
lp-N(1)-C(1)-H(1E)	3.62
lp-N(1)-N(1A)-C(1A)	1.73

Table S8. Summary of symmetrically independent $n \rightarrow \sigma^*$ NBO interactions in conformer **1D** with energy > 1 kcal/mol according B3LYP/6-311G*

Atoms	**NBO energy (kcal/mol)**
lp-S(1)-C(1)-N(1)	3.07
lp-S(1)-C(1)-H(1A)	4.67
lp-N(1)-C(1)-S(1)	9.28
lp-N(1)-N(1A)-C(1A)	1.65
lp-N(1)-C(1)-H(1A)	4.16

Multipole refinement

Table S9. Monopole Populations, Radial Parameters and Net Atomic Charges.

Atom	Pval	Kappa	P00	Kappa'	Net charge
S(1)	6.007(19)	0.998	0.000	0.999	-0.006(19)
N(1)	5.079(13)	0.984	0.000	0.975	-0.079(13)
C(1)	4.171(21)	0.978	0.000	0.981	-0.171(21)
C(2)	4.155(20)	0.979	0.000	1.000	-0.155(20)
H(1B)	0.910(15)	1.200	0.000	1.200	+0.089(15)
H(2B)	0.876(14)	1.200	0.000	1.200	+0.123(14)
H(2A)	0.898(14)	1.200	0.000	1.200	+0.102(14)
H(1A)	0.903(13)	1.200	0.000	1.200	+0.096(13)

Table S10. Dipole Population Parameters.

Atom	D11+	D11-	D10	Kappa'
S(1)	0.012(11)	-0.030(12)	-0.038(10)	0.999
N(1)	-0.054(7)	0.107(6)	-0.025(7)	0.975
C(1)	0.017(9)	0.038(9)	0.030(9)	0.981
C(2)	-0.017(8)	0.053(10)	0.012(9)	1.000
H(1B)	0.000	0.000	0.105(10)	1.200
H(2B)	0.000	0.000	0.078(11)	1.200
H(2A)	0.000	0.000	0.130(11)	1.200
H(1A)	0.000	0.000	0.127(10)	1.200

Table S11. Quadrupole Population Parameters.

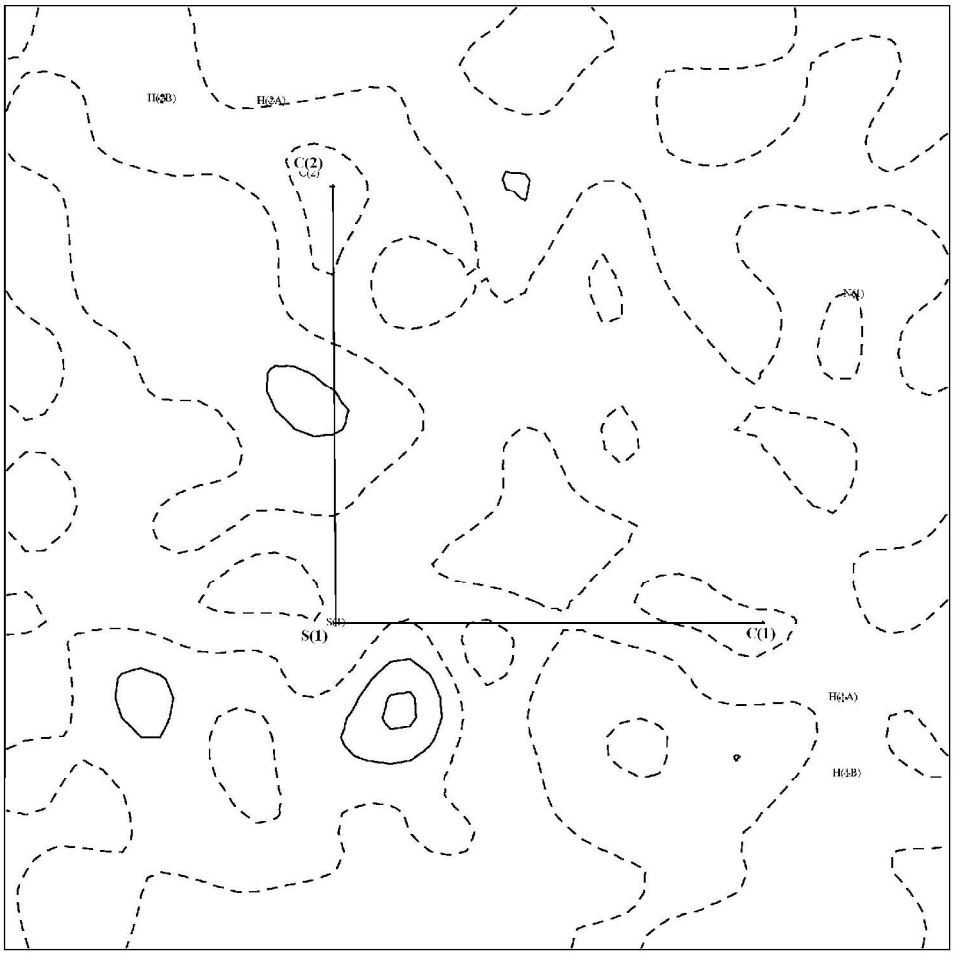
Atom	Q20	Q21+	Q21-	Q22+	Q22-	Kappa'
S(1)	-0.174(13)	-0.060(10)	0.054(11)	0.126(9)	0.020(12)	0.999
N(1)	-0.018(7)	0.016(7)	-0.033(7)	-0.001(7)	-0.088(7)	0.975
C(1)	0.051(9)	0.011(9)	-0.010(8)	-0.064(9)	-0.002(9)	0.981
C(2)	0.055(9)	0.009(8)	-0.032(8)	-0.076(8)	0.000(9)	1.000
H(1B)	0.000	0.000	0.000	0.000	0.000	1.200
H(2B)	0.000	0.000	0.000	0.000	0.000	1.200
H(2A)	0.000	0.000	0.000	0.000	0.000	1.200
H(1A)	0.000	0.000	0.000	0.000	0.000	1.200

Table S12. Octupole Population Parameters.

Atom	O30	O31+	O31-	O32+	O32-	O33+	O33-	Kappa'
S(1)	0.127(12)	0.017(11)	-0.051(11)	0.032(11)	-0.019(10)	0.007(10)	-0.055(11)	0.999
N(1)	0.150(10)	-0.006(10)	0.007(10)	-0.023(9)	-0.058(9)	0.114(9)	0.037(9)	0.975
C(1)	0.234(12)	0.029(11)	0.033(11)	0.008(11)	-0.022(12)	0.015(12)	-0.182(11)	0.981
C(2)	0.222(12)	0.007(11)	-0.042(11)	-0.001(11)	0.005(12)	0.007(11)	-0.204(12)	1.000

Differences of Mean-Squares Displacement Amplitudes (DMSDA)
(1.E4 A**2) along interatomic vectors (*bonds)

ATOM-->	ATOM	/ DIST	DMSDA	ATOM	/ DIST	DMSDA	ATOM	/ DIST	DMSDA
S(1)	N(1)	2.6289	9	C(1)	1.8145	12	C(2)	1.8602	14
N(1)	C(1)	1.4882	3	C(2)	2.2852	4			
C(1)	C(2)	2.6077	2						



The residual electron density map in the S(1)C(1)C(2) plane. Contours are drawn with 0.1 eÅ^{-3} step, the negative and zero contours are dashed.