Supplementary Material

Synthesis and structure of *N*-acetyliminosulfane-stabilized carbone $C(SPh_2NC(O)Me)_2$

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X-ray crystallography

Suitable single crystals for X-ray structural analysis were mounted at low temperature in inert oil. X-ray structure analyses were performed at a Rigaku HyPix-3000 area detector. The structures were solved by ShelXT method (Intrinsic Phasing) and a least-squares refinement on F^2 was carried out with SHELXL.[1] All non-hydrogen atoms were subjected to anisotropic refinement. All hydrogen atoms were generated geometrically and allowed to ride on their respective parent atoms. The crystal data collection and refinement parameters are given in Table S1. CCDC 2207010-2207011 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures/.

Table S1. Crystallographic date of **2** and **3**.

	2	**3**
Formula	$C_{29}H_{27}N_2O_6S_2Cl$	$C_{29}H_{26}N_2O_2S_2$
Formula weight [g·mol^{-1}]	599.09	498.64
Color	Colorless	Colorless
Crystal size [mm^3]	0.353×0.198×0.138	0.466×0.322×0.241
Temperature [K]	113	113
Wave lengths [Å]	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$
a [Å]	14.3460(3)	13.0393(3)
b [Å]	13.0987(2)	10.6284(3)
c [Å]	15.6455(3)	18.9410(6)
α [°]	90	90
β [°]	104.563(2)	99.478(3)
γ [°]	90	90
Volume [Å^3]	2845.55(10)	2589.14(13)
Z	4	4
Density (calculated) [M·gm^{-3}]	1.398	1.279
Absorption coefficient [mm^{-1}]	0.327	0.235
F (000) [e]	1248.0	1048.0
Max. and min. Transmission	1.00000 and 0.93052	1.00000 and 0.96534
ϑrange [°]	3.446 to 61.094	4.36 to 60.94
Reflection collected	33098	31443
Independent reflections	8399	7603
R_{int}	0.0274	0.0338
Data / restraints / parameters.	8399 / 0 / 366	7603 / 0 / 318
Final R indices (I > 2σ[I])	0.0539, 0.1488	0.0423, 0.1099
R_1, wR^2 (all data)	0.0633, 0.1556	0.0617, 0.1210
Goodness-of-fit on F^2	1.027	1.050
Date completeness	99.8	99.9
Largest diff. peak and hole [e·Å^{-3}]	1.43 and -0.98	0.420 and -0.450

Computational section

The geometries of **3** was optimized at the B3PW91/6-311G* level of theory. [2-4] The resulting structures were characterized as stationary points on the potential energy surface by evaluating vibrational frequencies at same level of theory. All calculation were performed using Gaussian09 suite of quantum chemical program. [5] The natural bond order and charge analysis were performed at the B3PW91/6-311G* level of theory using the NBO 3.1 program. [6]

Computational results

Table S2 presents the calculated NBO second-order perturbation analysis for **3**.

Table S2. NBO second-order perturbation analysis results for **3** at B3PW91/6-311G(d,p). Contribution for distribution of two LPs at C_{center}.

	3	
LP (donor)	σ^* (acceptor)	Energy (kcal mol^{-1})
$n\sigma_c$	S1–N1	8.77
	S1–C2	3.42
	S1–C3	3.76
	S2–N2	8.68
	S2–C4	3.86
	S2–C5	3.9
	Sum	**32.39**
$n\pi_c$	S1–N1	14.07
	S1–C2	19.86
	S2–N2	14.88
	S1–C4	19.86
	Sum	**68.67**

CARTESIAN COORDINATES OF OPTIMIZED GEOMETRIES
(B3PW91/6-311G(d,p))

3

S	1.3653960	-0.2847250	-0.0585100
S	-1.3161940	0.3060100	-0.0242610
O	-1.2170140	3.1214150	0.3170370
O	1.0644940	-3.0777660	0.1373400
N	1.4136580	-1.2891670	-1.2962690
N	-1.4277750	1.3777540	-1.1926170
C	2.0339160	1.2016860	-0.8064970
C	2.5274950	1.2128260	-2.1004530
C	-2.5516660	0.5911890	1.2302100
C	2.9895780	2.4208610	-2.6228450
C	2.3996570	-0.4370410	2.4811820
C	-3.7485310	1.1820250	0.8528990
C	1.1589660	-2.6046590	-0.9879610
C	2.6197710	-0.6920950	1.1403490
C	-2.3183270	0.2005010	2.5376030
C	-4.7126480	1.3940680	1.8202580
C	-4.4916550	1.0207700	3.1343380
C	2.9702710	3.5670800	-1.8469390
C	2.0166130	2.3435690	-0.0190010
C	0.0298120	-0.0075870	0.8300420
C	-1.9894350	-1.1332140	-0.8669760
C	-3.3046120	0.4159600	3.4919490
C	3.3975140	-0.7484230	3.3930300
C	-1.2819400	2.6926880	-0.8259930
C	3.8112180	-1.2394980	0.6945960
C	2.5012010	3.5329110	-0.5437170
C	4.5842700	-1.3029140	2.9683390
C	0.9807680	-3.4525850	-2.2228140
C	-1.9854180	-2.3259530	-0.1555770
C	-2.4918580	-1.0560420	-2.1524080
C	4.7939380	-1.5441880	1.6226910
C	-3.0349140	-3.4015390	-2.0487790
C	-3.0086470	-2.2112730	-2.7362610
C	-2.5279960	-3.4624230	-0.7625600
C	-1.2105370	3.6144850	-2.0176080
H	2.5507140	0.4175050	-2.6195140
H	3.3183960	2.4570690	-3.5133300
H	1.5798990	-0.0556030	2.7729520

H	-3.9020080	1.4352290	-0.0497760
H	-1.4956580	-0.2088820	2.7787020
H	-5.5368260	1.8009500	1.5802230
H	-5.1589070	1.1812610	3.7913470
H	3.2821750	4.3866530	-2.2123920
H	1.6775970	2.3115470	0.8677810
H	-3.1613860	0.1467410	4.3916570
H	3.2612550	-0.5778590	4.3175330
H	3.9520460	-1.4030880	-0.2304970
H	2.5112800	4.3200840	-0.0120360
H	5.2597510	-1.5199280	3.6001220
H	1.0376470	-4.4000520	-1.9795450
H	1.6845710	-3.2385640	-2.8703080
H	0.1040970	-3.2694640	-2.6210060
H	-1.6231010	-2.3685000	0.7215270
H	-2.4849440	-0.2333850	-2.6276960
H	5.6163830	-1.9211860	1.3327480
H	-3.3997170	-4.1791300	-2.4551970
H	-3.3480510	-2.1756130	-3.6228770
H	-2.5486710	-4.2845520	-0.2870700
H	-1.6454470	4.4649700	-1.7995660
H	-1.6677630	3.1998490	-2.7793150
H	-0.2724010	3.7770040	-2.2495180

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