

Supporting Information for

Breaking C-C ( $sp^3-sp^3$ )  $\sigma$  Bonds in 1,4-Diazabicyclo[2.2.2]octane (DABCO) by  
Oxidation with Antimony Pentchloride.

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## 1. Experimental Conditions

### *Instrument Information*

FTIR spectra were recorded on a Bruker Alpha FT-IR spectrometer using attenuated total reflectance (ATR). Nuclear magnetic resonance (NMR) spectra were obtained on Bruker Nanobay AVIIIHD 400 (400 MHz for  $^1\text{H}$ ) at room temperature. Chemical shifts were reported in parts per million ( $\delta$  scale).  $^1\text{H}$  NMR was measured at 400 MHz in  $\text{CD}_3\text{CN}$ .

### *Experimental Conditions*

Reaction solutions were all prepared in a dry glovebox. 1.37 mmol (154 mg) of DABCO was dissolved in 20 mL of dry acetonitrile in a 150 mL round-bottomed Schlenk flask and swirled to dissolve. 0.710 mmol (0.09 mL) of  $\text{SbCl}_5$  was added to the main reaction vessel, and swirled to encourage the reaction. Reaction went through the previously described color changes, until a yellow-tinged precipitate and bright yellow reaction solution were left. The flask was sealed with a glass stopper.

Reaction flask was removed from the glovebox, the stopper was removed, and the reaction solution was filtered through a glass frit filter to remove precipitate. The supernatant solution was dried *in vacuo* and was a bright yellow solid. Since it was likely the vivid yellow color was a result of antimony impurities, the solid was transferred to a scintillation vial, then added 20 mL of acetonitrile, and sonicated for 20 minutes. The resulting suspension was filtered through a glass frit filter, and the resulting colorless solid was washed three more times with acetonitrile. The colorless aqueous layer was collected and dried *in vacuo*, leaving off-white precipitate left over (78.6 mg, 0.425 mmol, 59.85% yield;  $\delta$ 3.06, s, 8H). Single crystals of the precipitate were grown after adding acetonitrile to a 10 mg sample of the solid, and filtering into a crystal tube. Multiple crystals were grown from the solid, all determined to be  $[\text{N}_2\text{C}_6\text{H}_{14}]\text{Cl}_2$ .

### *$[\text{N}_2\text{C}_6\text{H}_{14}]\text{Cl}_2$ Crystal Comparison and Information*

Colorless crystals were grown from dissolved  $[\text{N}_2\text{C}_6\text{H}_{14}]\text{Cl}_2$  solid in MeCN, and after 3 days were harvested for data collection. Crystals were then quickly mounted under 120 K (1) and 150 K (2) (respectively) liquid nitrogen cold streams provided by an Oxford Cryostream low

temperature apparatus on a Bruker Apex II diffractometer equipped with a fine-focus Mo sealed tube ( $\lambda = 0.71073\text{\AA}$ ). Preliminary solutions were found using Bruker APEX3 software.

Reference Code	$[\text{N}_2\text{C}_6\text{H}_{14}]\text{Cl}_2$	<b>EQUFIH<sup>1</sup></b>
Space Group	<i>Pna2</i> <sub>1</sub>	<i>Pna2</i> <sub>1</sub>
a	6.900	6.900
b	11.040	11.024
c	11.570	11.576
$\alpha$	90.000	90.000
$\beta$	90.000	90.000
$\gamma$	90.000	90.000
Volume	880	880.52
Color	Colorless	Colorless
Solvent	Acetonitrile	Ethanol

Table SII. Table showing comparison between preliminary crystal solutions and previously published results

$[N_2C_6H_{14}]Cl_2$   $^1H$  NMR Spectrum

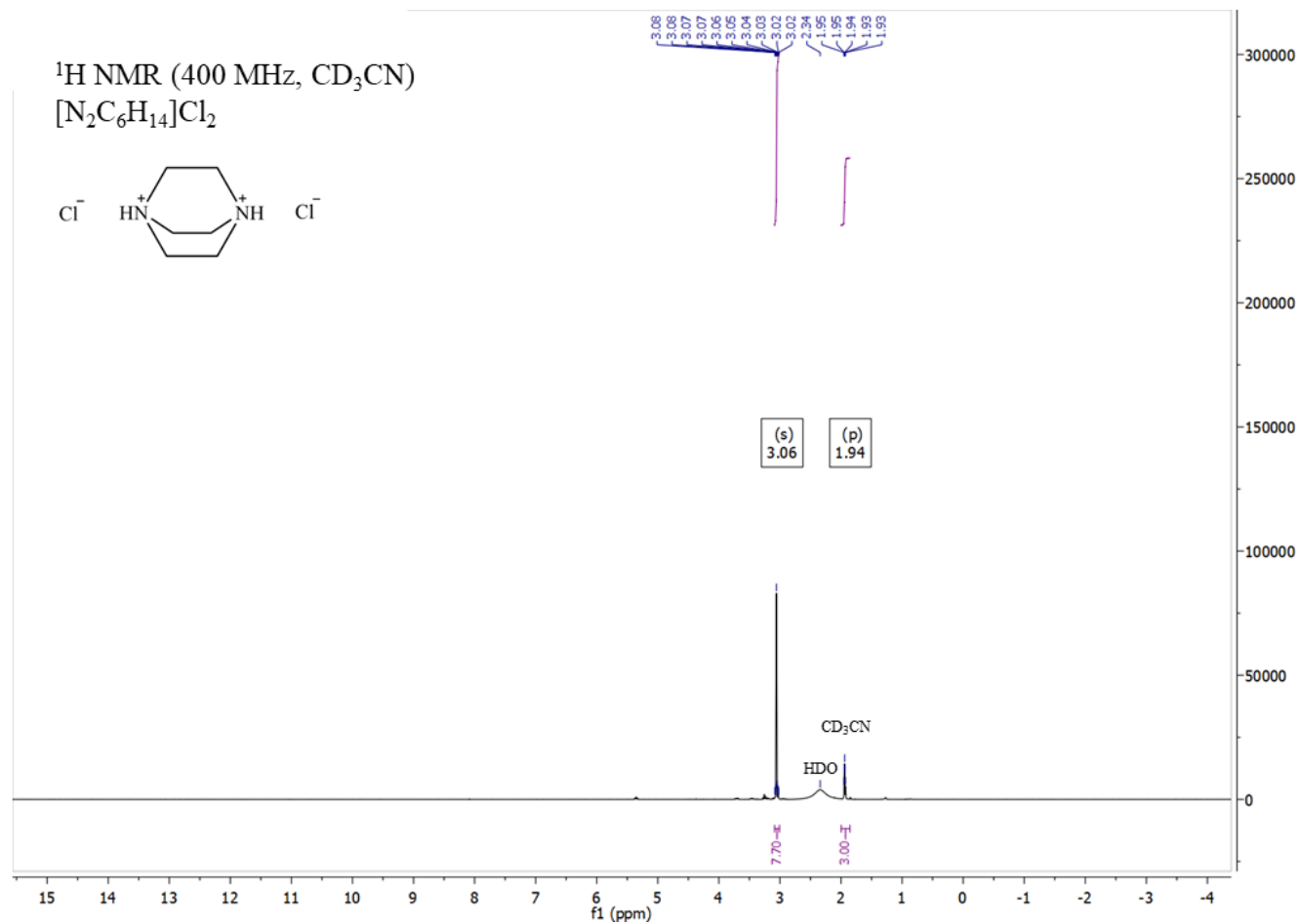


Figure S11.  $^1H$  NMR Spectrum of  $[N_2C_6H_{14}]Cl_2$  in  $CD_3CN$ .

### *[N<sub>2</sub>C<sub>6</sub>H<sub>14</sub>]Cl<sub>2</sub> FTIR Spectrum*

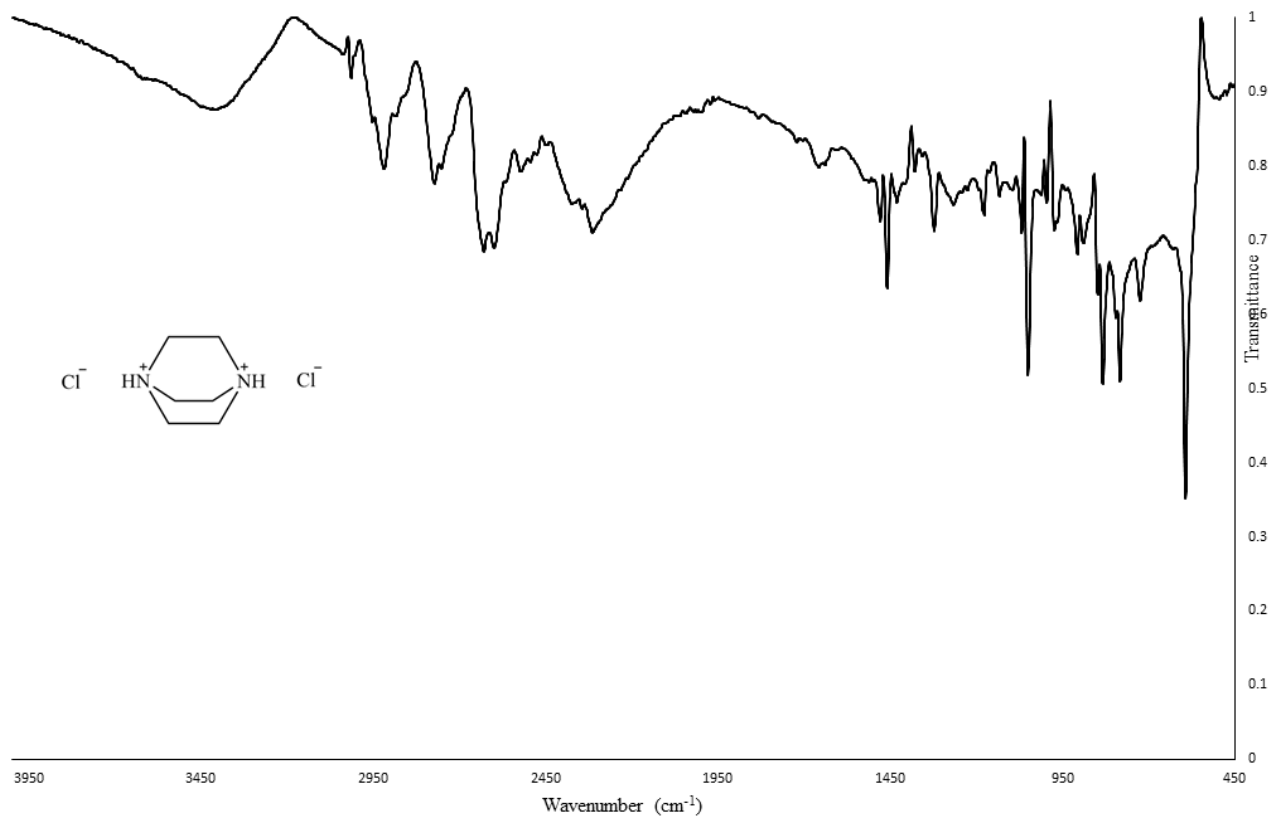


Figure SI2. FTIR Spectrum of [N<sub>2</sub>C<sub>6</sub>H<sub>14</sub>]Cl<sub>2</sub> (solid), showing similar peaks seen in previous literature.<sup>2</sup>

## **2. *In Situ* Infrared Spectrum**

### *Instrument Information*

*In Situ* FTIR Analysis was performed using a Mettler Toledo ReactIR 700 (serial number B929971514) with a liquid N<sub>2</sub> MCT detector fitted with a DiComp probe (serial number B939349478). The system was filled with liquid N<sub>2</sub> and allowed to cool for 1 h before kinetic experiments began. Initial trends were found using iC IR 7.1 and further analyzed using Microsoft Excel.

### *Experimental Conditions*

Reagent solutions were all prepared in a dry glovebox. 5.34 mmol of DABCO was dissolved in 25 mL of dry acetonitrile in a 200 mL round-bottomed Schlenk flask (main reaction vessel), and sealed with a glass stopper and stopcock to maintain an inert environment. A solution of 5.34 mmol  $\text{SbCl}_5$  in 7 mL dry acetonitrile was prepared in a separate 250 mL round-bottomed Schlenk flask, and was sealed with a rubber septa and rubber band. Both flasks were removed from the glovebox. Another 100 mL round-bottomed flask was dried, purged, and left under 100% dinitrogen atmosphere for needle purges. A 25 mL plastic syringe and metal needle were purged using this flask. The instrument was first blanked with dry acetonitrile using a 25 mL round-bottomed flask with 20 mL of the solvent.

In order to have the IR detector in the reaction solution but still have the reaction under dry, inert conditions, a rubber septa was prepared as the sealer by cutting a hole in it, pressing the probe through the septa, and then letting it reseal over the probe (also further used parafilm to ensure seal). Using a balloon filled with inert Argon gas, quickly purged the headspace of the main reaction vessel using the gas and swapped the glass stopper with the septa/probe, then further purging the headspace with a balloon and needle. An initial spectra of the DABCO • acetonitrile solution was taken.

The analysis was started at 10 second intervals for the first 5 minutes of the reaction, and then 1 minute intervals for the remaining time. The air-free needle in the 100 mL round-bottomed flask was then used to qualitatively transfer the  $\text{SbCl}_5$  • acetonitrile solution to the main reaction vessel. The reaction proceeded as normal, and underwent a significant heat release as the reaction solution rose from 20°C to 45°C, then slowly decreased back to the starting temperature. The reaction was monitored via FTIR for approximately 90 min and was deemed to be fully reacted.

Polyvinylpiperazine (PVP) was synthesized according to literature for comparison.<sup>3</sup>

## FTIR Spectra

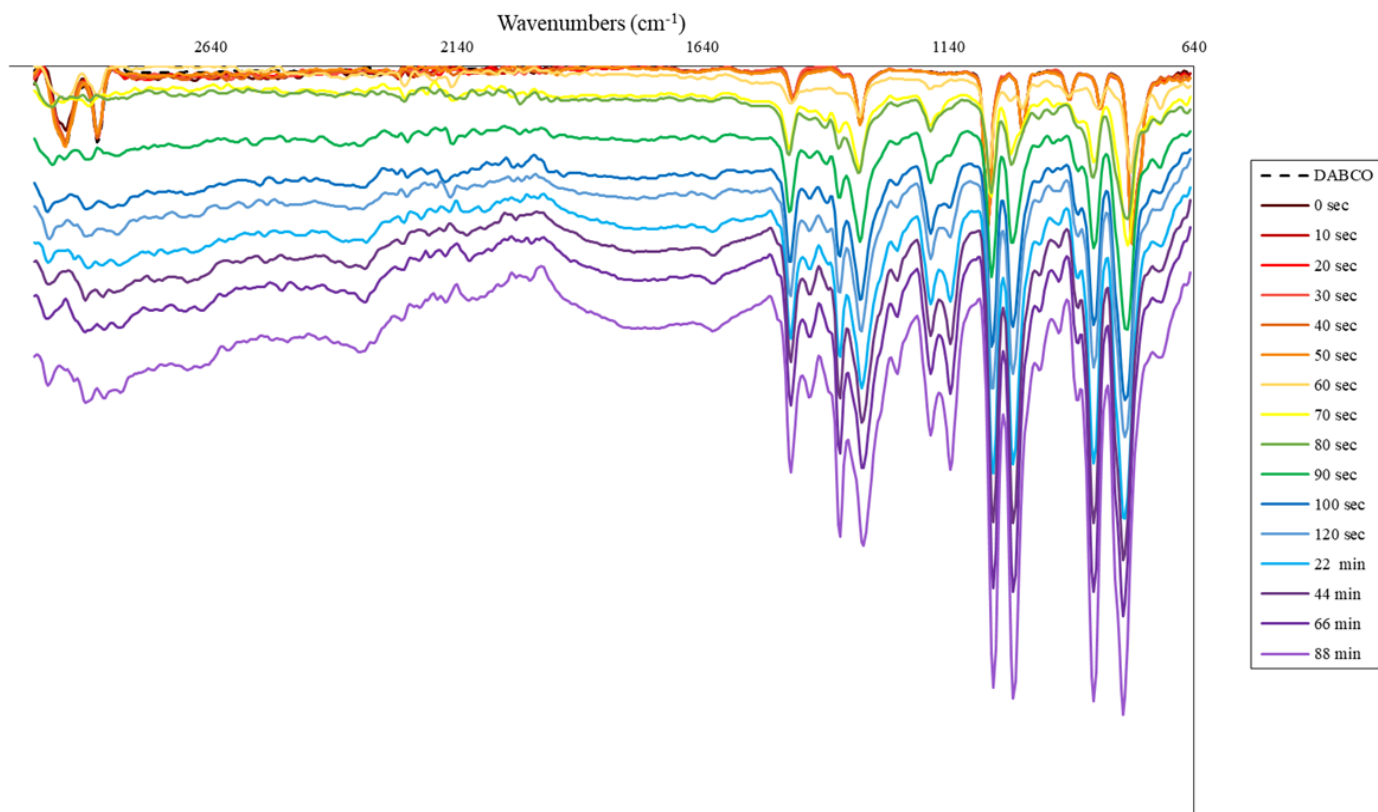


Figure S13. Stacked FTIR spectra of *in-situ* reaction monitoring over the course of 88 minutes. The black dashed line represents DABCO in MeCN. All other colored lines refer to time after the addition of SbCl<sub>5</sub>. Solvent normalization was done by measuring 20 mL of dry MeCN, and done using iC IR 7.1.

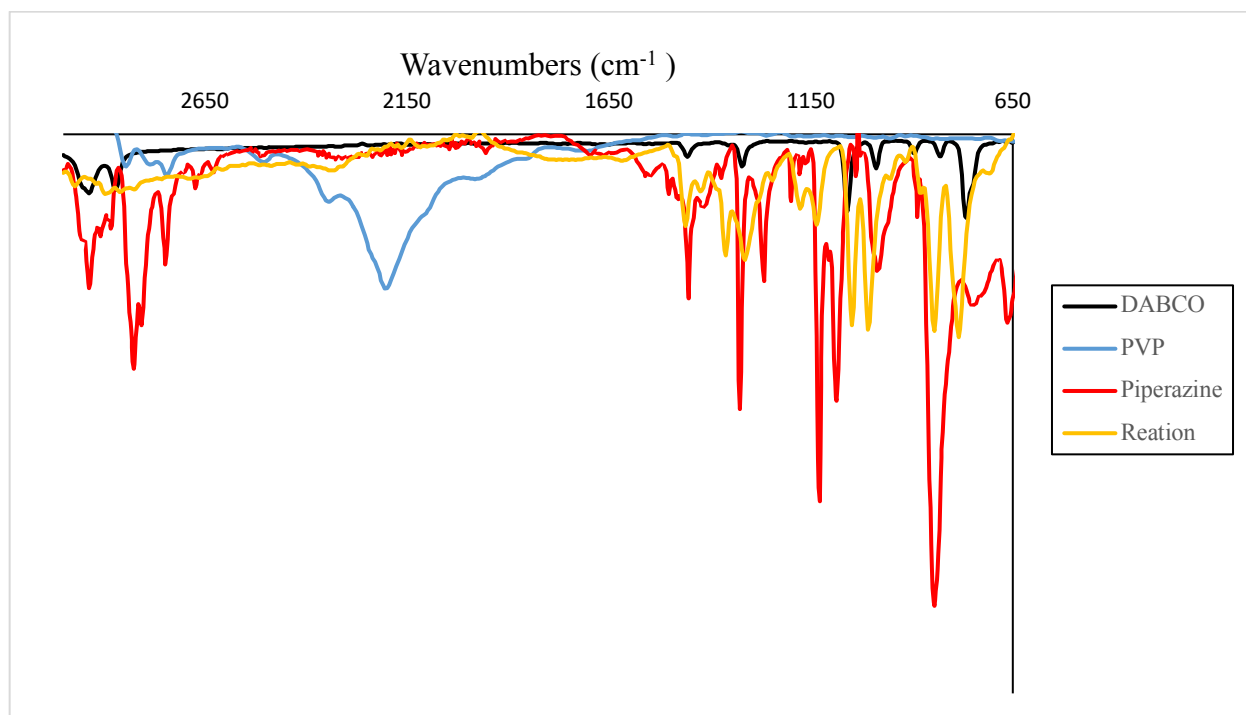


Figure SI4. Overlaid FTIR Spectra of DABCO, polyvinylpiperazine (PVP), piperazine, and the reaction solution (from *in-situ* FTIR).

### 3. Crystallographic Details

Table SI2. Crystal data and information for (1)

Crystal data and structure refinement for  $[\text{C}_{18}\text{H}_{36}\text{N}_6][\text{Cl}_6\text{OSb}_2]_2$  (1)

Identification code	LB112TW4C1	(LB112)
Empirical formula	$\text{C}_{18} \text{H}_{36} \text{Cl}_{12} \text{N}_6 \text{O}_2 \text{Sb}_4$	
Formula weight	1280.93	
Temperature	129(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	$a = 13.5244(13)$ Å	$\alpha = 90^\circ$ .
	$b = 12.1427(11)$ Å	$\beta = 96.829(2)^\circ$ .
	$c = 23.120(2)$ Å	$\gamma = 90^\circ$ .

Volume	3770.0(6) Å <sup>3</sup>
Z	4
Density (calculated)	2.257 Mg/m <sup>3</sup>
Absorption coefficient	3.717 mm <sup>-1</sup>
F(000)	2440
Crystal size	0.242 x 0.100 x 0.037 mm <sup>3</sup>
Crystal color and habit	Colorless Plate
Diffractometer	Bruker Photon2 CMOS
Theta range for data collection	2.261 to 27.514°.
Index ranges	-17<=h<=17, -15<=k<=15, -29<=l<=30
Reflections collected	8246
Independent reflections	4334 [R(int) = 0.0274]
Observed reflections (I > 2sigma(I))	3518
Completeness to theta = 25.242°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.6738 and 0.3968
Solution method	SHELXT (Sheldrick, 2015) Acta Cryst., A71, 3-8
Refinement method	SHELXL-2018/3 (Sheldrick, 2018) Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	4334 / 0 / 214
Goodness-of-fit on F <sup>2</sup>	1.171
Final R indices [I>2sigma(I)]	R1 = 0.0457, wR2 = 0.1214
R indices (all data)	R1 = 0.0560, wR2 = 0.1252
Largest diff. peak and hole	1.777 and -1.402 e.Å <sup>-3</sup>

Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ )  
for LB112TW4C1.  $U(\text{eq})$  is defined as one third of the trace of the orthogonalized  $U^{ij}$  tensor.

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	x	y	z	$U(\text{eq})$
Sb(1)	6107(1)	5782(1)	3222(1)	29(1)
Sb(2)	7654(1)	6389(1)	4410(1)	29(1)
Cl(1)	5935(1)	7691(1)	3909(1)	38(1)
Cl(2)	6450(2)	7020(1)	2443(1)	42(1)
Cl(3)	6639(1)	4173(1)	2688(1)	41(1)
Cl(4)	8946(1)	7698(1)	4164(1)	36(1)
Cl(5)	6171(1)	4761(1)	4409(1)	32(1)
Cl(6)	8904(1)	4979(1)	4638(1)	38(1)
O(1)	7473(3)	5950(3)	3591(2)	32(1)
C(1)	615(4)	4904(5)	2055(3)	33(1)
N(1)	329(4)	5534(4)	3040(2)	24(1)
C(2)	1074(4)	5018(5)	2688(3)	28(1)
N(2)	1723(4)	5960(4)	3788(2)	27(1)
C(3)	134(5)	6697(5)	2832(2)	30(1)
N(3)	3639(4)	6699(4)	4212(2)	28(1)
C(4)	726(5)	5532(5)	3693(3)	29(1)
C(5)	1843(5)	7001(5)	4111(3)	29(1)
C(6)	2489(4)	5167(5)	4005(3)	27(1)
C(7)	2843(5)	7496(5)	4025(3)	31(1)
C(8)	3509(5)	5600(5)	3936(3)	30(1)
C(9)	4381(5)	6930(5)	4589(3)	31(1)

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Interatomic distances [Å] and angles [°] for LB112TW4C1.

Sb(1)-O(1)	1.951(5)	C(5)-H(5A)	0.9900
Sb(1)-Cl(2)	2.4317(16)	C(5)-H(5B)	0.9900
Sb(1)-Cl(3)	2.4645(16)	C(6)-C(8)	1.503(8)
Sb(1)-Cl(1)	2.8359(16)	C(6)-H(6A)	0.9900
Sb(2)-O(1)	1.954(4)	C(6)-H(6B)	0.9900
Sb(2)-Cl(6)	2.4197(16)	C(7)-H(7A)	0.9900
Sb(2)-Cl(4)	2.4774(16)	C(7)-H(7B)	0.9900
Sb(2)-Cl(5)	2.8151(16)	C(8)-H(8A)	0.9900
C(1)-N(1)#1	1.483(7)	C(8)-H(8B)	0.9900
C(1)-C(2)	1.525(9)	C(9)-H(9A)	0.98(6)
C(1)-H(1A)	0.9900	C(9)-H(9B)	1.00(8)
C(1)-H(1B)	0.9900		
N(1)-C(2)	1.505(7)	O(1)-Sb(1)-Cl(2)	90.33(13)
N(1)-C(3)	1.505(7)	O(1)-Sb(1)-Cl(3)	89.11(13)
N(1)-C(4)	1.540(8)	Cl(2)-Sb(1)-Cl(3)	91.48(6)
C(2)-H(2A)	0.9900	O(1)-Sb(1)-Cl(1)	78.84(13)
C(2)-H(2B)	0.9900	Cl(2)-Sb(1)-Cl(1)	86.89(5)
N(2)-C(4)	1.436(8)	Cl(3)-Sb(1)-Cl(1)	167.82(6)
N(2)-C(6)	1.459(7)	O(1)-Sb(2)-Cl(6)	91.22(13)
N(2)-C(5)	1.468(7)	O(1)-Sb(2)-Cl(4)	87.86(13)
C(3)-C(3)#1	1.534(11)	Cl(6)-Sb(2)-Cl(4)	90.60(6)
C(3)-H(3A)	0.9900	O(1)-Sb(2)-Cl(5)	78.50(13)
C(3)-H(3B)	0.9900	Cl(6)-Sb(2)-Cl(5)	89.01(5)
N(3)-C(9)	1.281(8)	Cl(4)-Sb(2)-Cl(5)	166.34(5)
N(3)-C(7)	1.473(8)	Sb(1)-O(1)-Sb(2)	117.1(2)
N(3)-C(8)	1.480(7)	N(1)#1-C(1)-C(2)	109.9(5)
C(4)-H(4A)	0.9900	N(1)#1-C(1)-H(1A)	109.7
C(4)-H(4B)	0.9900	C(2)-C(1)-H(1A)	109.7
C(5)-C(7)	1.514(8)	N(1)#1-C(1)-H(1B)	109.7

C(2)-C(1)-H(1B)	109.7	H(4A)-C(4)-H(4B)	108.0
H(1A)-C(1)-H(1B)	108.2	N(2)-C(5)-C(7)	108.8(5)
C(1)#1-N(1)-C(2)	109.0(5)	N(2)-C(5)-H(5A)	109.9
C(1)#1-N(1)-C(3)	108.7(5)	C(7)-C(5)-H(5A)	109.9
C(2)-N(1)-C(3)	108.7(4)	N(2)-C(5)-H(5B)	109.9
C(1)#1-N(1)-C(4)	109.8(4)	C(7)-C(5)-H(5B)	109.9
C(2)-N(1)-C(4)	110.6(4)	H(5A)-C(5)-H(5B)	108.3
C(3)-N(1)-C(4)	110.0(4)	N(2)-C(6)-C(8)	110.9(5)
N(1)-C(2)-C(1)	109.5(5)	N(2)-C(6)-H(6A)	109.5
N(1)-C(2)-H(2A)	109.8	C(8)-C(6)-H(6A)	109.5
C(1)-C(2)-H(2A)	109.8	N(2)-C(6)-H(6B)	109.5
N(1)-C(2)-H(2B)	109.8	C(8)-C(6)-H(6B)	109.5
C(1)-C(2)-H(2B)	109.8	H(6A)-C(6)-H(6B)	108.1
H(2A)-C(2)-H(2B)	108.2	N(3)-C(7)-C(5)	109.5(5)
C(4)-N(2)-C(6)	115.4(4)	N(3)-C(7)-H(7A)	109.8
C(4)-N(2)-C(5)	115.8(5)	C(5)-C(7)-H(7A)	109.8
C(6)-N(2)-C(5)	111.3(5)	N(3)-C(7)-H(7B)	109.8
N(1)-C(3)-C(3)#1	109.4(3)	C(5)-C(7)-H(7B)	109.8
N(1)-C(3)-H(3A)	109.8	H(7A)-C(7)-H(7B)	108.2
C(3)#1-C(3)-H(3A)	109.8	N(3)-C(8)-C(6)	109.5(5)
N(1)-C(3)-H(3B)	109.8	N(3)-C(8)-H(8A)	109.8
C(3)#1-C(3)-H(3B)	109.8	C(6)-C(8)-H(8A)	109.8
H(3A)-C(3)-H(3B)	108.2	N(3)-C(8)-H(8B)	109.8
C(9)-N(3)-C(7)	122.8(5)	C(6)-C(8)-H(8B)	109.8
C(9)-N(3)-C(8)	122.3(5)	H(8A)-C(8)-H(8B)	108.2
C(7)-N(3)-C(8)	114.9(5)	N(3)-C(9)-H(9A)	118(3)
N(2)-C(4)-N(1)	111.2(4)	N(3)-C(9)-H(9B)	117(4)
N(2)-C(4)-H(4A)	109.4	H(9A)-C(9)-H(9B)	124(5)
N(1)-C(4)-H(4A)	109.4		
N(2)-C(4)-H(4B)	109.4		
N(1)-C(4)-H(4B)	109.4		

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Symmetry transformations used to generate equivalent atoms:

#1  $-x, y, -z + 1/2$

Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for LB112TW4C1. The anisotropic displacement factor exponent takes the form:  $-2 \sin^2 \theta [ h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12} ]$

	U11	U22	U33	U23	U13	U12
Sb(1)	30(1)	19(1)	37(1)	2(1)	6(1)	-1(1)
Sb(2)	32(1)	22(1)	34(1)	-1(1)	7(1)	1(1)
Cl(1)	43(1)	19(1)	56(1)	4(1)	17(1)	3(1)
Cl(2)	64(1)	28(1)	36(1)	4(1)	12(1)	-3(1)
Cl(3)	45(1)	23(1)	58(1)	-7(1)	16(1)	-5(1)
Cl(4)	37(1)	22(1)	50(1)	-1(1)	6(1)	-3(1)
Cl(5)	32(1)	22(1)	42(1)	6(1)	7(1)	1(1)
Cl(6)	36(1)	28(1)	50(1)	5(1)	3(1)	2(1)
O(1)	33(2)	27(2)	37(2)	-3(2)	8(2)	0(2)
C(1)	22(3)	31(3)	46(4)	-9(3)	3(3)	4(2)
N(1)	27(2)	14(2)	33(2)	1(2)	6(2)	-2(2)
C(2)	23(3)	26(3)	35(3)	-3(2)	7(2)	7(2)
N(2)	30(3)	15(2)	36(3)	0(2)	-2(2)	4(2)
C(3)	44(4)	13(2)	33(3)	1(2)	2(3)	-5(3)
N(3)	27(3)	23(2)	34(3)	3(2)	5(2)	0(2)
C(4)	35(3)	19(3)	33(3)	4(2)	4(2)	-2(2)
C(5)	32(3)	20(3)	33(3)	-5(2)	-1(2)	3(2)
C(6)	23(3)	22(3)	37(3)	2(2)	5(2)	1(2)
C(7)	38(3)	19(3)	35(3)	0(2)	5(3)	-2(2)
C(8)	31(3)	19(3)	41(3)	1(2)	8(3)	0(2)
C(9)	30(3)	30(3)	34(3)	3(2)	8(3)	-2(3)

Hydrogen coordinates ( $\times 10^4$ ) and isotropic displacement parameters ( $\text{\AA}^2 \times 10^{-3}$ )  
for LB112TW4C1.

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	x	y	z	U(eq)
H(1A)	1086	5186	1794	50(20)
H(1B)	485	4118	1962	27(16)
H(2A)	1269	4283	2848	80(30)
H(2B)	1679	5482	2709	22(15)
H(3A)	735	7154	2938	38(19)
H(3B)	-420	7015	3020	70(30)
H(4A)	285	5986	3908	50(20)
H(4B)	719	4770	3845	18(14)
H(5A)	1808	6867	4531	50(20)
H(5B)	1302	7517	3967	33(18)
H(6A)	2377	4467	3787	27(16)
H(6B)	2443	5014	4421	40(20)
H(7A)	2856	7683	3610	38(19)
H(7B)	2951	8180	4257	41(19)
H(8A)	4021	5088	4121	14(13)
H(8B)	3591	5657	3517	38(19)
H(9A)	4440(40)	7690(50)	4740(20)	11(13)
H(9B)	4860(60)	6320(60)	4710(30)	40(20)

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Torsion angles [°] for LB112TW4C1.

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C(1)#1-N(1)-C(2)-C(1)	52.5(5)
C(3)-N(1)-C(2)-C(1)	-65.9(6)
C(4)-N(1)-C(2)-C(1)	173.3(5)
N(1)#1-C(1)-C(2)-N(1)	11.4(6)
C(1)#1-N(1)-C(3)-C(3)#1	-66.8(8)
C(2)-N(1)-C(3)-C(3)#1	51.7(8)
C(4)-N(1)-C(3)-C(3)#1	173.0(6)
C(6)-N(2)-C(4)-N(1)	-113.2(5)
C(5)-N(2)-C(4)-N(1)	114.2(5)
C(1)#1-N(1)-C(4)-N(2)	169.6(5)
C(2)-N(1)-C(4)-N(2)	49.3(6)
C(3)-N(1)-C(4)-N(2)	-70.8(6)
C(4)-N(2)-C(5)-C(7)	-164.0(5)
C(6)-N(2)-C(5)-C(7)	61.6(6)
C(4)-N(2)-C(6)-C(8)	164.6(5)
C(5)-N(2)-C(6)-C(8)	-60.8(6)
C(9)-N(3)-C(7)-C(5)	-125.2(6)
C(8)-N(3)-C(7)-C(5)	54.0(6)
N(2)-C(5)-C(7)-N(3)	-56.6(6)
C(9)-N(3)-C(8)-C(6)	127.2(6)
C(7)-N(3)-C(8)-C(6)	-51.9(6)
N(2)-C(6)-C(8)-N(3)	53.6(6)

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Symmetry transformations used to generate equivalent atoms:

#1 -x,y,-z+1/2

Hydrogen bonds for LB112TW4C1 [ $\text{\AA}$  and  $^\circ$ ].

D-H...A	d(D-H)	d(H...A)	d(D...A)	$\angle(\text{DHA})$
C(1)-H(1A)...O(1)#2	0.99	2.42	3.383(8)	164
C(2)-H(2A)...Cl(2)#3	0.99	2.92	3.729(6)	139
C(3)-H(3A)...Cl(3)#4	0.99	2.83	3.668(6)	143
C(4)-H(4A)...Cl(4)#5	0.99	2.86	3.811(6)	160
C(4)-H(4A)...Cl(6)#5	0.99	2.93	3.547(6)	122
C(4)-H(4B)...Cl(1)#3	0.99	2.54	3.492(6)	161
C(5)-H(5B)...Cl(5)#4	0.99	2.92	3.561(6)	123
C(6)-H(6A)...Cl(1)#3	0.99	2.94	3.659(6)	130
C(7)-H(7A)...Cl(2)#2	0.99	2.83	3.681(6)	145
C(7)-H(7B)...Cl(6)#4	0.99	2.63	3.560(6)	156
C(8)-H(8A)...Cl(4)#3	0.99	2.91	3.602(6)	128
C(8)-H(8A)...Cl(5)	0.99	2.93	3.777(7)	144
C(8)-H(8B)...Cl(2)#2	0.99	2.76	3.630(6)	146
C(9)-H(9A)...Cl(6)#4	0.98(6)	2.88(6)	3.761(7)	150(4)
C(9)-H(9B)...Cl(5)	1.00(8)	2.74(8)	3.635(7)	149(5)

Symmetry transformations used to generate equivalent atoms:

#1  $-x, y, -z+1/2$  #2  $-x+1, y, -z+1/2$  #3  $x-1/2, y-1/2, z$

#4  $x-1/2, y+1/2, z$  #5  $x-1, y, z$

Table SI3. X-Ray data collection parameters and crystallographic details of (2)

Crystal data and structure refinement for $[(\text{N}_2\text{C}_6\text{H}_{12})^{2+}(\text{Sb}_2(\mu\text{-Cl})_2\text{Cl}_6)^{2-}]$ trimer (2)		
Identification code	LB106	
Empirical formula	C18 H36 Cl8 N6 Sb2	
Formula weight	863.63	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2 <sub>1</sub> /c	
Unit cell dimensions	a = 8.7273(5) Å	$\alpha = 90^\circ$ .
	b = 12.6462(7) Å	$\beta = 107.2990(10)^\circ$ .
	c = 14.0441(9) Å	$\gamma = 90^\circ$ .
Volume	1479.89(15) Å <sup>3</sup>	
Z	2	
Density (calculated)	1.938 Mg/m <sup>3</sup>	
Absorption coefficient	2.569 mm <sup>-1</sup>	
F(000)	848	
Crystal size	0.205 x 0.186 x 0.075 mm <sup>3</sup>	
Crystal color and habit	Colorless Plate	
Diffractometer	Bruker Photon2 CMOS	
Theta range for data collection	2.214 to 27.505°.	
Index ranges	-11 ≤ h ≤ 11, -16 ≤ k ≤ 16, -18 ≤ l ≤ 18	
Reflections collected	35168	
Independent reflections	3398 [R(int) = 0.0276]	
Observed reflections (I > 2σ(I))	3179	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Solution method	SHELXT 2014/5 (Sheldrick, 2014)	
Refinement method	SHELXL-2018/3 (Sheldrick, 2018) Full-matrix	
least-squares on F <sup>2</sup>		

Data / restraints / parameters	3398 / 0 / 178
Goodness-of-fit on $F^2$	1.113
Final R indices [ $I > 2\sigma(I)$ ]	R1 = 0.0211, wR2 = 0.0517
R indices (all data)	R1 = 0.0232, wR2 = 0.0526
Extinction coefficient	n/a
Largest diff. peak and hole	0.766 and -0.338 e.Å <sup>-3</sup>

Atomic coordinates (  $\times 10^4$ ) and equivalent isotropic displacement parameters (Å<sup>2</sup> $\times 10^3$ ) for lb106.  $U(eq)$  is defined as one third of the trace of the orthogonalized  $U^{ij}$  tensor.

	x	y	z	U(eq)
Sb(1)	5412(1)	6421(1)	5721(1)	21(1)
Cl(1)	4221(1)	8177(1)	5403(1)	29(1)
Cl(2)	7223(1)	7100(1)	7308(1)	33(1)
Cl(3)	7451(1)	6807(1)	4869(1)	40(1)
Cl(4)	3157(1)	5766(1)	3826(1)	38(1)
C(1)	858(3)	5201(2)	6660(2)	29(1)
N(1)	1484(2)	5491(2)	7744(1)	22(1)
C(2)	1884(3)	5773(2)	6101(2)	28(1)
N(2)	3423(2)	6113(2)	6810(1)	23(1)
C(3)	3099(3)	4987(2)	8177(2)	26(1)
N(3)	868(3)	5342(2)	9327(2)	28(1)
C(4)	4116(3)	5218(2)	7478(2)	29(1)
C(5)	1686(3)	6673(2)	7827(2)	23(1)
C(6)	3098(3)	6976(2)	7426(2)	27(1)
C(7)	1465(3)	4472(2)	10035(2)	29(1)
C(8)	-108(3)	6085(2)	9702(2)	28(1)
C(9)	310(3)	5094(2)	8300(2)	28(1)

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Interatomic distances [Å] and angles [°] for lb106.

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Sb(1)-Cl(1)	2.4373(6)
Sb(1)-Cl(3)	2.4706(6)
Sb(1)-Cl(2)	2.4709(6)
C(1)-N(1)	1.501(3)
C(1)-C(2)	1.536(3)
C(1)-H(1A)	0.9900
C(1)-H(1B)	0.9900
N(1)-C(3)	1.501(3)
N(1)-C(5)	1.506(3)
N(1)-C(9)	1.546(3)
C(2)-N(2)	1.478(3)
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900
N(2)-C(6)	1.473(3)
N(2)-C(4)	1.480(3)
C(3)-C(4)	1.535(3)
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
N(3)-C(9)	1.414(3)
N(3)-C(8)	1.467(3)
N(3)-C(7)	1.470(3)
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900
C(5)-C(6)	1.547(3)
C(5)-H(5A)	0.9900
C(5)-H(5B)	0.9900
C(6)-H(6A)	0.98(3)

C(6)-H(6B)	1.00(3)
C(7)-C(8)#1	1.515(4)
C(7)-H(7A)	1.04(3)
C(7)-H(7B)	1.00(3)
C(8)-H(8A)	0.98(3)
C(8)-H(8B)	1.04(3)
C(9)-H(9A)	0.9900
C(9)-H(9B)	0.9900
Cl(1)-Sb(1)-Cl(3)	93.46(2)
Cl(1)-Sb(1)-Cl(2)	88.39(2)
Cl(3)-Sb(1)-Cl(2)	90.49(3)
N(1)-C(1)-C(2)	108.11(18)
N(1)-C(1)-H(1A)	110.1
C(2)-C(1)-H(1A)	110.1
N(1)-C(1)-H(1B)	110.1
C(2)-C(1)-H(1B)	110.1
H(1A)-C(1)-H(1B)	108.4
C(1)-N(1)-C(3)	108.78(18)
C(1)-N(1)-C(5)	108.73(18)
C(3)-N(1)-C(5)	108.40(18)
C(1)-N(1)-C(9)	109.68(18)
C(3)-N(1)-C(9)	109.89(17)
C(5)-N(1)-C(9)	111.30(17)
N(2)-C(2)-C(1)	110.14(19)
N(2)-C(2)-H(2A)	109.6
C(1)-C(2)-H(2A)	109.6
N(2)-C(2)-H(2B)	109.6
C(1)-C(2)-H(2B)	109.6
H(2A)-C(2)-H(2B)	108.1
C(6)-N(2)-C(2)	108.39(19)

C(6)-N(2)-C(4)	107.96(18)
C(2)-N(2)-C(4)	108.83(19)
N(1)-C(3)-C(4)	108.15(18)
N(1)-C(3)-H(3A)	110.1
C(4)-C(3)-H(3A)	110.1
N(1)-C(3)-H(3B)	110.1
C(4)-C(3)-H(3B)	110.1
H(3A)-C(3)-H(3B)	108.4
C(9)-N(3)-C(8)	116.6(2)
C(9)-N(3)-C(7)	117.9(2)
C(8)-N(3)-C(7)	111.28(19)
N(2)-C(4)-C(3)	110.25(18)
N(2)-C(4)-H(4A)	109.6
C(3)-C(4)-H(4A)	109.6
N(2)-C(4)-H(4B)	109.6
C(3)-C(4)-H(4B)	109.6
H(4A)-C(4)-H(4B)	108.1
N(1)-C(5)-C(6)	107.77(18)
N(1)-C(5)-H(5A)	110.2
C(6)-C(5)-H(5A)	110.2
N(1)-C(5)-H(5B)	110.2
C(6)-C(5)-H(5B)	110.2
H(5A)-C(5)-H(5B)	108.5
N(2)-C(6)-C(5)	110.13(19)
N(2)-C(6)-H(6A)	107.9(16)
C(5)-C(6)-H(6A)	109.6(15)
N(2)-C(6)-H(6B)	110.1(16)
C(5)-C(6)-H(6B)	111.3(16)
H(6A)-C(6)-H(6B)	108(2)
N(3)-C(7)-C(8)#1	111.6(2)
N(3)-C(7)-H(7A)	108.6(15)

C(8)#1-C(7)-H(7A)	106.7(15)
N(3)-C(7)-H(7B)	110.2(18)
C(8)#1-C(7)-H(7B)	110.2(19)
H(7A)-C(7)-H(7B)	109(2)
N(3)-C(8)-C(7)#1	111.7(2)
N(3)-C(8)-H(8A)	108.6(16)
C(7)#1-C(8)-H(8A)	109.0(16)
N(3)-C(8)-H(8B)	110.5(16)
C(7)#1-C(8)-H(8B)	101.4(17)
H(8A)-C(8)-H(8B)	116(2)
N(3)-C(9)-N(1)	111.37(19)
N(3)-C(9)-H(9A)	109.4
N(1)-C(9)-H(9A)	109.4
N(3)-C(9)-H(9B)	109.4
N(1)-C(9)-H(9B)	109.4
H(9A)-C(9)-H(9B)	108.0

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Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+1,-z+2

Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for lb106. The anisotropic displacement factor exponent takes the form:  $-2p^2 [ h^2 a^*2U^{11} + \dots + 2 h k a^* b^* U^{12} ]$

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	U11	U22	U33	U23	U13	U12
Sb(1)	21(1)	19(1)	25(1)	-1(1)	10(1)	-2(1)
Cl(1)	31(1)	23(1)	30(1)	2(1)	4(1)	4(1)
Cl(2)	29(1)	32(1)	32(1)	-4(1)	-3(1)	3(1)
Cl(3)	46(1)	29(1)	60(1)	0(1)	37(1)	-6(1)
Cl(4)	30(1)	43(1)	40(1)	14(1)	10(1)	-3(1)
C(1)	27(1)	34(1)	27(1)	-6(1)	10(1)	-8(1)

N(1)	24(1)	20(1)	24(1)	1(1)	12(1)	0(1)
C(2)	29(1)	33(1)	23(1)	-3(1)	10(1)	-5(1)
N(2)	22(1)	24(1)	24(1)	-1(1)	11(1)	-1(1)
C(3)	30(1)	24(1)	28(1)	4(1)	13(1)	8(1)
N(3)	33(1)	26(1)	28(1)	6(1)	15(1)	6(1)
C(4)	27(1)	30(1)	32(1)	4(1)	13(1)	6(1)
C(5)	28(1)	18(1)	27(1)	1(1)	13(1)	3(1)
C(6)	32(1)	23(1)	30(1)	-2(1)	16(1)	-3(1)
C(7)	30(1)	30(1)	32(1)	9(1)	14(1)	7(1)
C(8)	36(1)	25(1)	29(1)	5(1)	16(1)	6(1)
C(9)	29(1)	24(1)	35(1)	2(1)	18(1)	-3(1)

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Hydrogen coordinates ( $\times 10^4$ ) and isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ )  
for lb106.

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	x	y	z	U(eq)
H(1A)	-279	5417	6389	35
H(1B)	925	4426	6579	35
H(2A)	2093	5293	5597	33
H(2B)	1296	6398	5750	33
H(3A)	2977	4214	8241	32
H(3B)	3628	5280	8848	32
H(4A)	5227	5392	7877	35
H(4B)	4154	4582	7074	35
H(5A)	1919	6896	8532	28
H(5B)	690	7029	7432	28
H(6A)	4070(30)	7090(20)	7990(20)	23(7)

H(6B)	2870(30)	7640(20)	7030(20)	29(7)
H(7A)	2210(30)	4790(20)	10700(20)	23(7)
H(7B)	2080(40)	3960(30)	9750(20)	39(8)
H(8A)	-560(30)	6610(20)	9180(20)	28(7)
H(8B)	550(30)	6390(20)	10390(20)	29(7)
H(9A)	-755	5423	8004	33
H(9B)	183	4318	8218	33

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Torsion angles [°] for lb106.

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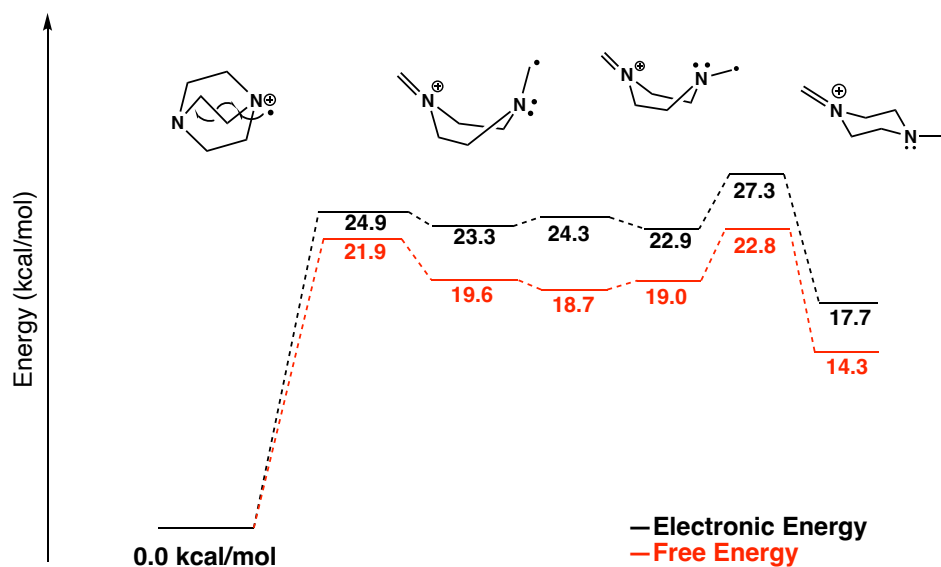
C(2)-C(1)-N(1)-C(3)	-69.7(2)
C(2)-C(1)-N(1)-C(5)	48.2(2)
C(2)-C(1)-N(1)-C(9)	170.08(19)
N(1)-C(1)-C(2)-N(2)	18.9(3)
C(1)-C(2)-N(2)-C(6)	-70.1(2)
C(1)-C(2)-N(2)-C(4)	47.1(2)
C(1)-N(1)-C(3)-C(4)	48.4(2)
C(5)-N(1)-C(3)-C(4)	-69.6(2)
C(9)-N(1)-C(3)-C(4)	168.53(19)
C(6)-N(2)-C(4)-C(3)	48.5(3)
C(2)-N(2)-C(4)-C(3)	-68.9(2)
N(1)-C(3)-C(4)-N(2)	18.1(3)
C(1)-N(1)-C(5)-C(6)	-69.4(2)
C(3)-N(1)-C(5)-C(6)	48.7(2)
C(9)-N(1)-C(5)-C(6)	169.67(18)
C(2)-N(2)-C(6)-C(5)	47.8(2)
C(4)-N(2)-C(6)-C(5)	-69.9(2)
N(1)-C(5)-C(6)-N(2)	18.4(3)
C(9)-N(3)-C(7)-C(8)#1	-84.1(3)
C(8)-N(3)-C(7)-C(8)#1	54.6(3)

C(9)-N(3)-C(8)-C(7)#1	84.6(3)
C(7)-N(3)-C(8)-C(7)#1	-54.6(3)
C(8)-N(3)-C(9)-N(1)	115.1(2)
C(7)-N(3)-C(9)-N(1)	-108.4(2)
C(1)-N(1)-C(9)-N(3)	179.33(19)
C(3)-N(1)-C(9)-N(3)	59.8(2)
C(5)-N(1)-C(9)-N(3)	-60.3(2)

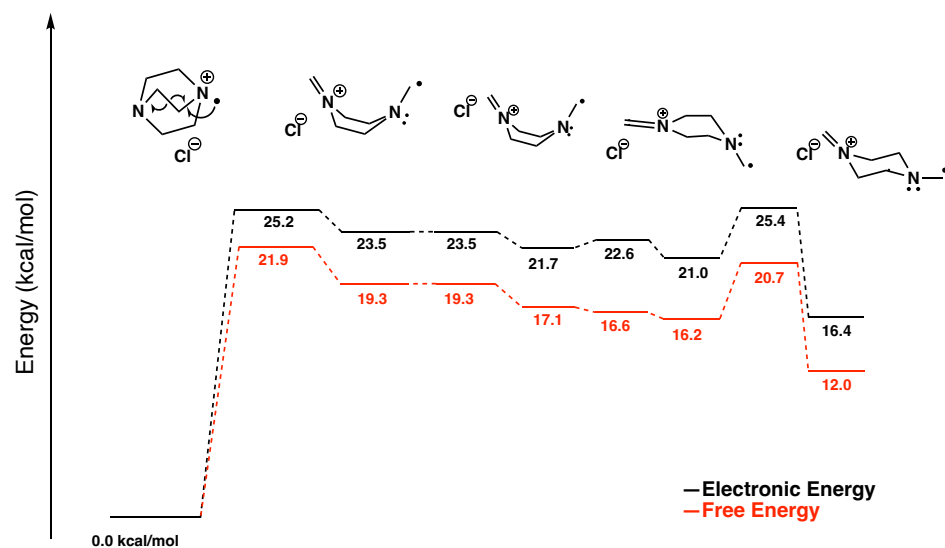
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#### 4. *In Silico* Studies continued

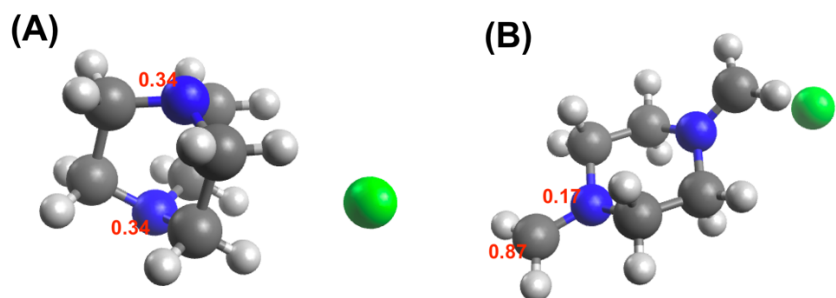
##### *DFT Study Figures*



**Figure SI5.** The potential and free energy surface for the conversion of DABCO<sup>++</sup> to MVP<sup>++</sup>.



**Figure SI6.** The potential and free energy surface for the conversion of DABCO<sup>+</sup> to MVP<sup>+</sup> with a chloride counterion.



**Figure SI7.** The optimized (unrestricted  $\omega$ B97X-D3/def2-TZVP-f) structures of DABCO<sup>+</sup> (A) and MVP<sup>+</sup> (B) with chloride counterions. Atoms with significant Mulliken spin populations are indicated.

**Table SI4 . DABCO<sup>+</sup> EPR results (def2-TZVP)**

	G <sub>x</sub>	G <sub>y</sub>	G <sub>z</sub>	G <sub>iso</sub>
G-tensor	2.002	2.005	2.005	2.004
	A <sub>x</sub>	A <sub>y</sub>	A <sub>z</sub>	A <sub>iso</sub>
H	16.2	14.5	25.5	18.7
	16.4	25.8	14.8	19.0
	16.1	25.5	14.5	18.7
	16.2	14.6	25.7	18.8
	16.0	14.3	25.4	18.5
	16.5	26.0	14.9	19.1
	16.0	25.3	14.3	18.5
	16.4	14.7	25.8	19.0
	16.2	14.6	25.6	18.8
	16.3	25.7	14.6	18.9
	16.1	25.5	14.5	18.7
	16.3	14.6	25.7	18.9
	N	76.3	27.5	27.5
76.3		27.4	27.4	43.7

**Table SI5. DABCO<sup>+</sup> EPR results (IGLO-III)**

	G <sub>x</sub>	G <sub>y</sub>	G <sub>z</sub>	G <sub>iso</sub>
G-tensor	2.002	2.006	2.006	2.004
	A <sub>x</sub>	A <sub>y</sub>	A <sub>z</sub>	A <sub>iso</sub>
H	17.0	15.4	26.2	19.5
	17.2	26.5	15.7	19.8
	17.0	26.2	15.4	19.5
	17.1	15.6	26.3	19.7
	16.8	15.3	26.0	19.4
	17.4	26.6	15.9	20.0
	16.8	26.0	15.2	19.3
	17.2	15.7	26.5	19.8
	17.0	26.3	15.5	19.6
	17.1	15.6	26.4	19.7
	17.0	15.4	26.2	19.5
	17.1	26.4	15.6	19.7
	N	78.3	28.8	28.8
78.3		28.7	28.7	45.3

**Table SI6. DABCO<sup>+</sup> EPR results with CI**

	G <sub>x</sub>	G <sub>y</sub>	G <sub>z</sub>	G <sub>iso</sub>
G-tensor	2.002	2.005	2.005	2.004
	A <sub>x</sub>	A <sub>y</sub>	A <sub>z</sub>	A <sub>iso</sub>
H	15.5	24.8	13.9	18.1
	15.7	24.9	14.0	18.2
	15.5	24.8	13.9	18.1
	15.7	25.0	14.1	18.2
	16.5	14.7	25.9	19.0
	16.2	25.7	14.5	18.8
	16.0	25.4	14.2	18.5
	16.4	14.6	25.8	18.9
	16.1	25.5	14.3	18.6
	16.5	14.8	25.9	19.1
	16.3	14.6	25.7	18.9
N	27.6	27.6	76.0	43.7
	27.5	27.5	76.4	43.8

**Table SI7.** MVP<sup>++</sup> EPR results

	G <sub>x</sub>	G <sub>y</sub>	G <sub>z</sub>	G <sub>iso</sub>
G-tensor	2.002	2.003	2.003	2.003
	A <sub>x</sub>	A <sub>y</sub>	A <sub>z</sub>	A <sub>iso</sub>
H	14.0	15.1	24.3	17.8
	14.0	15.1	24.4	17.8
	-0.9	2.0	-1.1	0.0
	-0.9	2.0	-1.1	0.0
	-1.5	3.9	-1.9	0.2
	-1.5	3.9	-1.9	0.2
	0.1	1.0	11.0	4.0
	0.1	0.9	11.0	4.0
	-0.7	0.7	-0.6	-0.2
	-0.7	0.7	-0.6	-0.2
	-34.6	-66.6	-3.8	-35.0
	-34.5	-66.4	-3.8	-34.8
N	1.4	1.6	38.0	13.7
	0.0	-0.3	-0.4	-0.2

**Table SI8.** MVP<sup>++</sup> EPR results with Cl<sup>-</sup>

	G <sub>x</sub>	G <sub>y</sub>	G <sub>z</sub>	G <sub>iso</sub>
G-tensor	2.002	2.003	2.003	2.003
	A <sub>x</sub>	A <sub>y</sub>	A <sub>z</sub>	A <sub>iso</sub>
H	14.0	15.1	24.3	17.8
	14.0	15.1	24.4	17.8
	-0.9	2.0	-1.1	0.0
	-0.9	2.0	-1.1	0.0
	-1.5	3.9	-1.9	0.2
	-1.5	3.9	-1.9	0.2
	0.1	1.0	11.0	4.0
	0.1	0.9	11.0	4.0
	-0.7	0.7	-0.6	-0.2
	-0.7	0.7	-0.6	-0.2
	-34.6	-66.6	-3.8	-35.0
	-34.5	-66.4	-3.8	-34.8
N	1.4	1.6	38.0	13.7
	0.0	-0.3	-0.4	-0.2

**Table SI9.** DABCO<sup>+</sup> [SbCl<sub>5</sub>] EPR results

	G <sub>x</sub>	G <sub>y</sub>	G <sub>z</sub>	G <sub>iso</sub>
G-tensor	2.005	2.008	2.008	2.007
	A <sub>x</sub>	A <sub>y</sub>	A <sub>z</sub>	A <sub>iso</sub>
H	-1.1	6.5	-4.3	0.4
	-0.3	-3.5	7.4	1.2
	0.1	-3.1	7.7	1.6
	7.3	15.1	4.0	8.8
	7.4	4.0	15.3	8.9
	8.3	5.0	16.1	9.8
	9.3	8.8	23.4	13.8
	10.7	24.9	10.2	15.2
	10.2	24.4	9.8	14.8
	27.8	28.4	43.8	33.3
	29.4	45.5	30.0	35.0
	28.5	44.5	29.1	34.0
N	131.8	30.9	30.9	64.5
	1.1	-1.3	-1.3	-0.5

**Table SI10.** DABCO<sup>+</sup> [SbCl<sub>3</sub>] EPR results

	G <sub>x</sub>	G <sub>y</sub>	G <sub>z</sub>	G <sub>iso</sub>
G-tensor	2.002	2.005	2.005	2.004
	A <sub>x</sub>	A <sub>y</sub>	A <sub>z</sub>	A <sub>iso</sub>
H	18.6	29.5	17.7	21.9
	18.8	17.8	29.7	22.1
	18.9	17.9	29.8	22.2
	18.2	29.1	17.3	21.5
	18.2	17.3	29.1	21.5
	18.2	17.2	29.1	21.5
	12.8	10.4	21.2	14.8
	13.2	21.8	10.9	15.3
	12.9	21.4	10.6	14.9
	12.5	10.1	20.9	14.5
	12.7	21.2	10.3	14.7
	12.5	21.0	10.2	14.6
N	94.7	29.5	29.5	51.2
	51.7	20.4	20.4	30.8

**Table SI11.** DABCO<sup>+</sup> [SbCl<sub>4</sub>]<sup>-</sup> EPR results

	G <sub>x</sub>	G <sub>y</sub>	G <sub>z</sub>	G <sub>iso</sub>
G-tensor	2.002	2.004	2.005	2.004
	A <sub>x</sub>	A <sub>y</sub>	A <sub>z</sub>	A <sub>iso</sub>
H	17.8	28.1	16.6	20.8
	17.9	28.1	16.7	20.9
	17.5	16.3	27.8	20.5
	17.5	27.7	16.3	20.5
	17.8	16.6	28.1	20.8
	18.0	28.3	16.8	21.0
	14.3	12.2	23.1	16.5
	14.2	22.9	12.1	16.4
	13.9	22.5	11.8	16.1
	13.7	11.5	22.3	15.8
	14.7	12.7	23.6	17.0
	14.3	23.1	12.2	16.5
N	88.1	29.1	29.1	48.7

## 5. References

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