

Supporting Information

Reversible Sn-Sn Triple Bond Dissociation in a Distannyne: Support for Charge Shift Bonding Character

Ting Yi Lai, Lizhi Tao, R. David Britt and Philip P. Power*

*Department of Chemistry, University of California, One Shields Avenue, Davis, California 95616, United States

Fax: +1-520-752-8995

E-mail: pppower@ucdavis.edu

Table of Contents

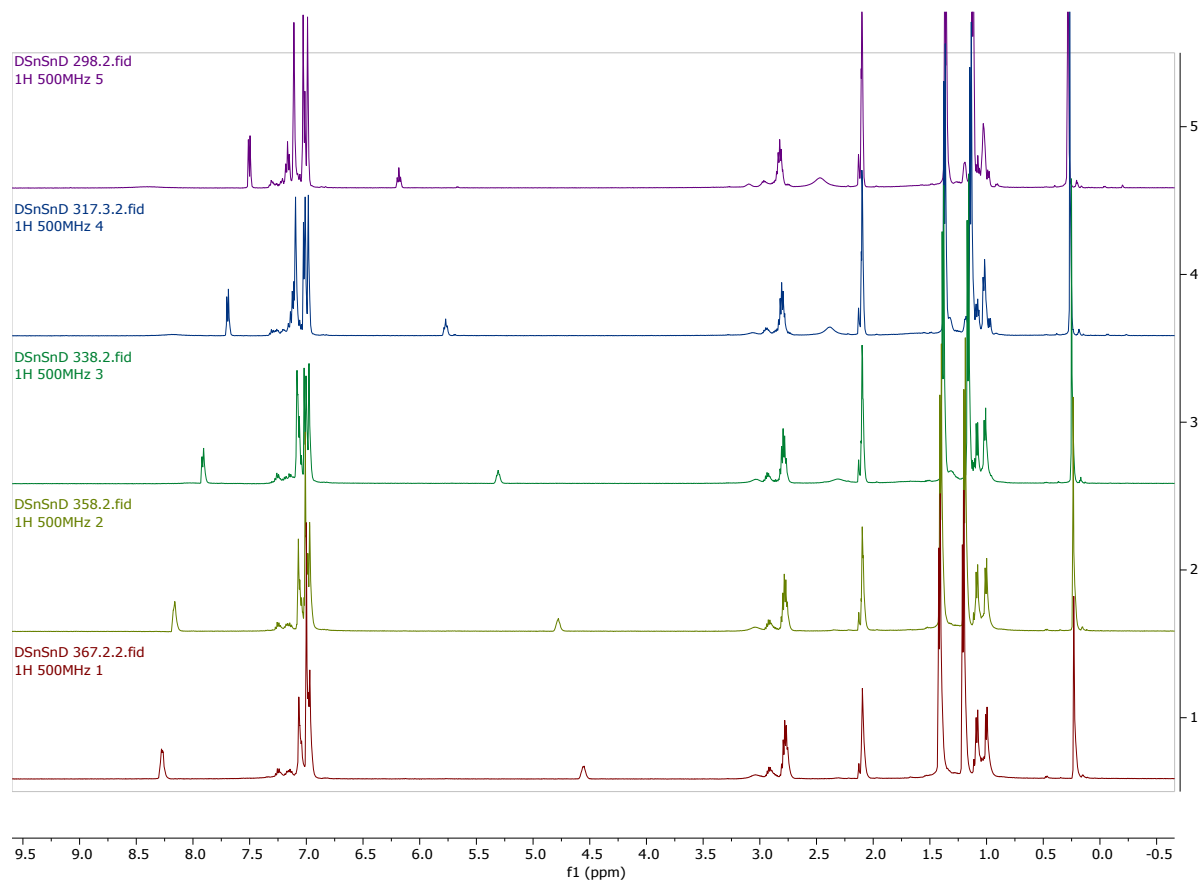
Page	
S1	Table of Contents
S2	General Experimental Procedures
S4	Figure S1. VT ^1H NMR Spectrum of $\text{Ar}^{i\text{Pr}_4}\text{SnSnAr}^{i\text{Pr}_4}$ (500 MHz, C_6D_6 , 298K to 358K ppm)
S5	van't Hoff Analysis Figure S1

General Experimental Procedures

General Procedures. All operations were carried out under anaerobic and anhydrous conditions using modified Schlenk techniques. All solvents were dried over alumina columns, stored over an Na mirror and degassed prior to use. $\text{Ar}^{i\text{Pr}_4}\text{SnSnAr}^{i\text{Pr}_4}$ was synthesized via the reported literature procedure.¹ The ^1H NMR spectroscopic data were collected on a Bruker 500MHz spectrometer. van't Hoff analysis was calculated with reported procedure.²

EPR Spectroscopy. The thermolysis-treated $\text{Ar}^{i\text{Pr}_4}\text{SnSnAr}^{i\text{Pr}_4}$ EPR samples was prepared by heating at 80 °C for ~30 min before being flash frozen in liquid nitrogen. The X-band (9.38 GHz) continuous-wave (CW) EPR spectra were recorded on a Bruker (Billerica, MA) Biospin EleXsys E500 spectrometer equipped with a super-high Q resonator (ER4122SHQE). Cryogenic temperatures were achieved and controlled using an ESR900 liquid helium cryostat in conjunction with a temperature controller (Oxford Instruments ITC503) and gas flow controller. CW EPR data were collected under slow-passage, non-saturating conditions. The spectrometer settings were as follows: conversion time = 40 ms, modulation amplitude = 0.5 mT, and modulation frequency = 100 kHz.

Figure S1. VT ^1H NMR Spectrum of $\text{Ar}^{i\text{Pr}_4}\text{SnSnAr}^{i\text{Pr}_4}$ (500 MHz, C_6D_6 , 298K to 358K ppm)

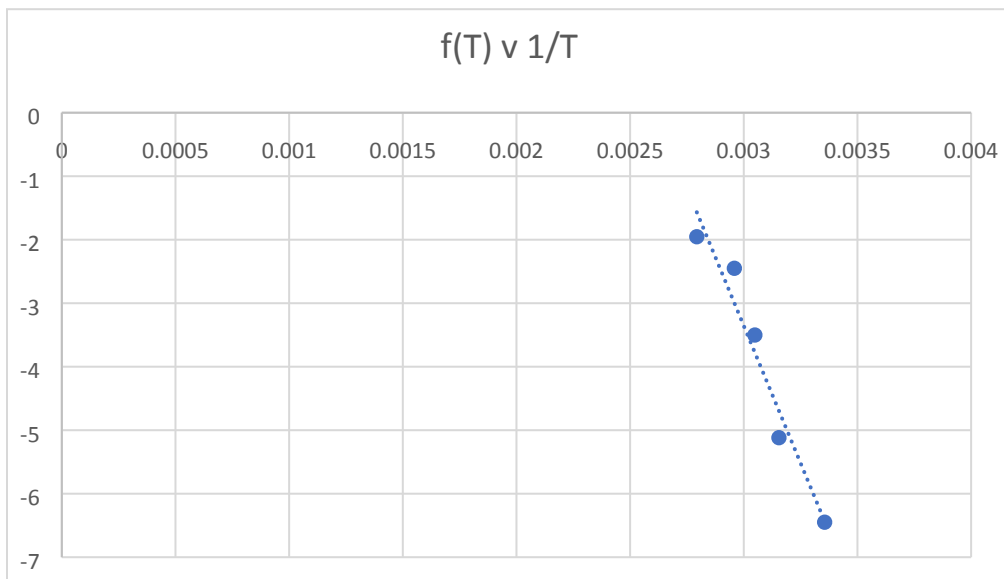


Variable temperature ^1H NMR spectroscopy and Van't Hoff analysis of $\text{Ar}^{i\text{Pr}_4}\text{SnSnAr}^{i\text{Pr}_4}$

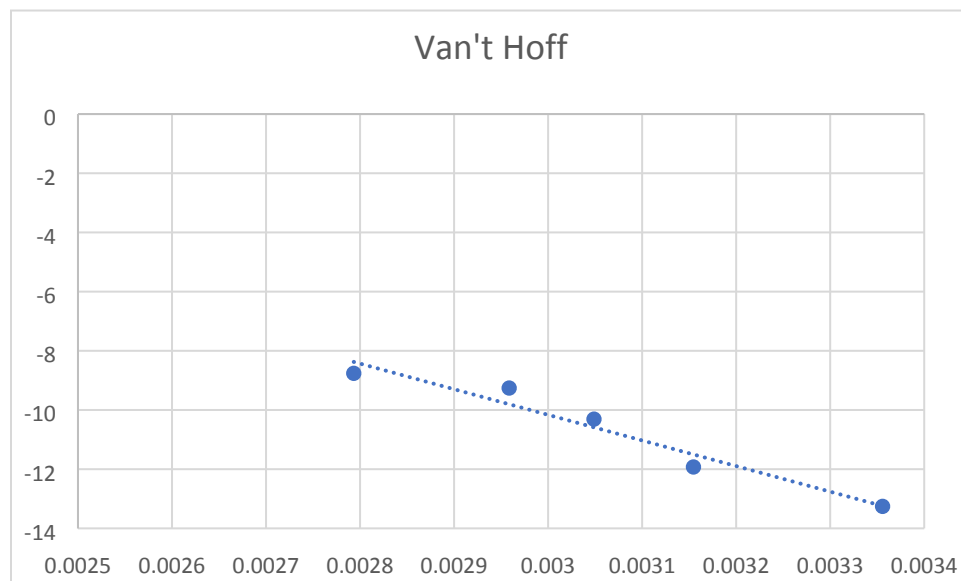
The integral for the signal atoms of the, meta aromatic hydrogen of the central ring were used for the determination of the equilibrium constant for dissociation.

$$f(T) = \ln \left[\frac{(I_0 - I_2)^2}{I_2} \right] = - \frac{\Delta H_d^{298K}}{R} \left(\frac{1}{T} \right) + \ln \left(\frac{I_0 K_0}{4C_0} \right)$$

I0	T	I2	f(T)	1/T	f(T)
2.335	298	2.275	-6.4488	0.003356	-6.4488
2.335	317	2.2197	-5.1178	0.003155	-5.117
2.335	328	2.08425	-3.5010	0.003049	-3.501
2.335	338	1.9272	-2.4500	0.002959	-2.450
2.335	358	1.8261	-1.953	0.002793	-1.953



K	lnK	1/T
1.74845E-06	-13.256	0.003356
6.61755E-06	-11.925	0.003155
3.33323E-05	-10.309	0.003049
9.53456E-05	-9.258	0.002959
0.000156702	-8.7611	0.002793



$$\Delta H_d^{298K} = 17.2 \pm 1.7 \text{ kcal mol}^{-1}$$

$$\Delta S_d = 31.4 \pm 3.14 \text{ cal mol}^{-1} \text{ K}^{-1}$$

$$\Delta G_d^{298K} = 7.84 \pm 0.78 \text{ kcal mol}^{-1}$$

Estimate of Error:

The uncertainty in the integration was estimated to be 10% due to broadening. The VT apparatus indicated an uncertainty in the temperature of 1°C. The concentration is accurate ca. 5%.

Reference:

1. Philips, A.D.; Wright, R.J.; Olmstead, M.M. and Power, P.P. Synthesis and Characterization of 2,6-Dipp₂-H₃C₆SnSnC₆H₃-2,6-Dipp₂ (Dipp = C₆H₃-2,6-*i*Pr₂): A Tin Analogue of an Alkyne *J. Am. Chem. Soc.*, **2002**, *124*, 5930-5931.
2. Rösel, S.; Becker, J.; Allen, W.D.; Schreiner, P.R. Probing the Delicate Balance between Pauli Repulsion and London Dispersion with Triphenylmethyl Derivatives *J. Am. Chem. Soc.* **2018**, *140*, 14421-14432