Quantum mechanical alternative to Arrhenius equation in the interpretation of proton spin-lattice relaxation data for the methyl groups in solids

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EXPERIMENTAL AND COMPUTATIONAL PROCEDURES

Syntheses

Methyltriphenylsilane-d$_{15}$ (MTPSi-d$_{15}$). Reaction was carried out under an inert atmosphere. A dispersion of phenyllithium-d$_5$ (0.656g, 7.35mmol) in anhydrous diethyl ether (5 ml) placed in a 25 ml flask equipped with a refluxing condenser, methyltrichlorosilane purchased from Sigma Aldrich (0.367, 2.45 mmol) was added dropwise for 1 hour with stirring. During the addition, the temperature of the mixture was kept at 0° C ± 5° by an outer cooling. After the addition was complete, stirring was continued for 2 h at room temperature, and H_2O (5 ml) was then added cautiously to the reaction mixture. The post-reaction slurry was filtrated, the filtrate was transferred to a separatory funnel and extracted with CH_2Cl_2 several times. The combined organic layers were dried over $MgSO_4$, filtrated, and the filtrate was concentrated. The product was purified by DCVC chromatography carried out on silica gel in hexane. Yield 0.267 g (32 %). Crystallization from methanol-d$_4$.

^{1}H NMR (400 MHz, CDCl3) 0.83 (s, 3H, Me),
^{13}C NMR (400MHz, $CDCl_3$) -3.37 (Me), 127.31 (t, 2C, $^1J_{CD}$ = 24 Hz), , 128.84 (t, 2C, $^1J_{CD}$ = 24 Hz), 134.81 (t, 2C, $^1J_{CD}$ = 24 Hz), 135.89 (s, 1C).

Methyltriphenylgermanium-d$_{15}$ (MTPSi-d$_{15}$). Reaction was carried out under an inert atmosphere. To a mixture of phenyllithium-d$_5$ in anhydrous ethyl ether (5 ml) methylgermanium trichloride purchased from Santa Cruz Biotechnology (0.20 g, 1.03 mmol) in anhydrous Et_2O (1.5 ml) was added dropwise at -50° C. After the reaction mixture was warmed to room temperature for 1 hour, the reaction mixture was quenched with water, extracted with CH_2Cl_2 three times, and dried over Na_2SO_4. The solvent was evaporated under reduced pressure. Purification by DCVC chromatography carried out on silica gel (hexane : CH_2Cl_2, 90:10 v/v) gave the desired product as a white solid (0.259 g, yield = 75%). Crystallization from methanol-d_4.

^{1}H NMR (400 MHz, $CDCl_3$) 0.82 (s, 3H, Me)
^{13}C NMR (400 MHz, $CDCl_3$) -3.99 (Me), 127.82 (t, 2C, J_{CD} = 31 Hz), 128.50 (t, 2C, J_{CD} = 31 Hz), 134.21 (t, 2C, J_{CD}= 31 Hz), 137.89 (s, 1C),

HR MS-ESI calculated for $C_{18}{}^2H_{15}{}^{74}Ge$ (M-CH_3+H) 320.1327; found: 320.1339

X-ray diffraction measurements

X-Ray diffraction data methyltriphenylgermanium (MTPGe) were collected at 100 K on Agilent SuperNova diffractometer equipped with a Mo-$K\alpha$ micro-focus X-ray source. Experimental temperatures were regulated using an Oxford Cryosystems open-flow nitrogen cryostat. The raw data were treated with the CrysAlisPro[S1] (version 1.171.37.35g) crystallographic package. Structures were solved by direct methods with SHELXS-97[S2] and refined against F^2 with full-matrix least-squares using the SHELXL-2014[S3]. All non-H atoms were refined with anisotropic atomic displacement parameters, while the hydrogen atoms were placed in geometrically calculated positions refined using a riding model, with default distances of methyl C–H = 0.98 Å and aromatic C–H = 0.95 Å. The thermal parameters of all H atoms were set as $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl groups, or $1.2U_{eq}$ otherwise. The parameters characterizing data collection and refinement, as well as crystal data are summarized in Table S1. Mercury[S4] and PLATON[S5] were used for visualization and analysis of the crystal structures. Crystallographic data for the structural analysis of MTPGe have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 1416891.

Table S1. Crystal and Structure Refinement Data for MTPGe.

Empirical formula	$C_{19}H_{18}Ge$
Formula weight	318.92
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	18.5689(2)
b (Å)	9.5521(1)
c (Å)	18.3723(2)
α (°)	90
β (°)	107.433(1)
γ (°)	90
Volume (Å^3)	3109.05(6)
Z, calculated density (g cm^{-3})	8, 1.363
F(000)	1312
Temperature (K)	100.0(1)

Radiation type, wavelength (Å)	Mo $K\alpha$, 0.71073
Absorption correction	Multi-scan
Absorption coefficient (mm^{-1})	1.96
Crystal size (mm)	0.21 × 0.16 × 0.02
Shape, color	Plate, colourless
θ range for data collection (°)	2.8-37.7
Limiting indices	$-31 > h > 31$ $-16 > k > 16$ $-31 > l > 31$
Reflection collected / unique / observed with $I > 2\sigma(I)$	149693 / 16256 / 12859
R_{int}	0.057
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	16256 / 0 / 363
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.034$, $wR_2 = 0.074$
Final R indices (all data)	$R_1 = 0.052$, $wR_2 = 0.079$
Weighting scheme	$[\sigma^2(F_o^2) + (0.0321P)^2 + 0.4004P]^{-1}$
Goodness-of-fit	1.06
Largest diff. peak/hole / e Å^{-3}	0.59/-0.38

NMR measurements

Proton spin-lattice relaxation measurements were carried out, using the inversion-recovery method, for powdered samples of MTPSi-d$_{15}$ and MTPGe-d$_{15}$, both of about 50 mg, each packed in a ZrO_2 rotor for MAS spectra of 4 mm o.d. In the interpretation of the relaxation data, the recovery of the integral intensity of the signal was monitored. The measurements were done on a Bruker Avance II 500 MHz spectrometer equipped with a probehead dedicated to ^{1}H wide-line measurements, purchased from Bruker Company. Temperature was controlled using a liquid helium/liquid nitrogen cryostate Janis ST-200-NMR with static exchange gas, equipped with LakeShore 331 temperature control unit and Cernox CX-1050-AA 1.4L calibrated temperature sensors. The cooling medium was liquid nitrogen and, below 88 K, liquid helium.

Calculated torsional potentials for methyl groups in MTPSi

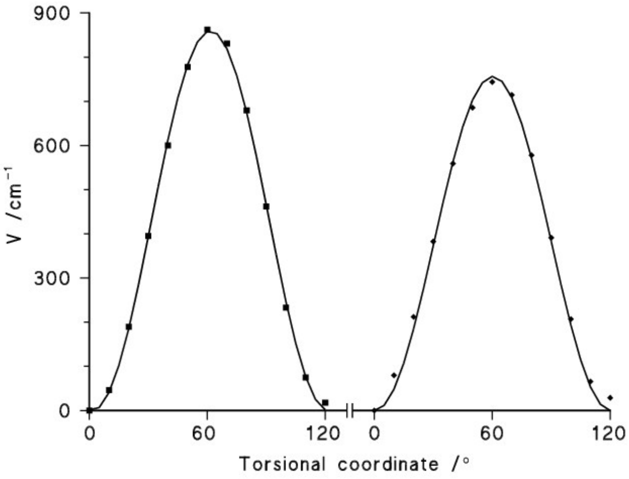

Figure S1. Squares: calculated values of the torsional energy for methyl group A in MTPSi (left plot) and B in MTPSi (right plot); for each group calculations involved a cluster of six molecules whose fragments are most proximate to the group. Solid lines: values of the expression $V[1\text{-}\cos 3(\varphi+\alpha)]/2$ fitted to the calculated values (optimized V and α), where φ is the torsional coordinate and α is a correction to the origin of the angle scale.

S1. *CrysAlisPro Software system ver. 1.171.37.35g*, Agilent Technologies UK Ltd, Oxford, UK, 2015.

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S3. G. M. Sheldrick, *Acta Crystallogr.*, *Sect. A: Found. Crystallogr.*, 2008, **64**, 112–122.

S4. C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler and J. van de Streek, *J. Appl. Cryst.*, 2006, **39**, 453-457.

S5. A.L. Spek, *Acta Cryst.*, 2009, **D65**, 148-155.