Electronic Supplementary Information for Dalton Transactions

Molecular structures of $Se(SCH_3)_2$ and $Te(SCH_3)_2$ using gas-phase electron diffraction and *ab initio* and DFT geometry optimisations

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Electronic Supplementary Information

Table S1 Nozzle-to-film distances (mm), weighting functions (nm^{-1}), scale factors, correlation parameters and electron wavelengths, λ (pm) used in the electron diffraction studies of $Se(SCH_3)_2$ and $Te(SCH_3)_2$.

	Nozzle-to-film distance [a]	Δs	s_{min}	sw_1	sw_2	s_{max}	Scale factor [b]	Correlation parameter	λ
$Se(SCH_3)_2$	94.89	2	80	100	292	320	0.798(22)	0.444	6.020
	293.46	2	20	40	104	120	0.736(6)	0.436	6.020
$Te(SCH_3)_2$	97.51	4	88	108	220	250	0.742(22)	0.161	6.020
	259.65	2	20	40	104	120	0.644(8)	–0.124	6.020

[a] Determined by reference to the scattering pattern of benzene. [b] Values in parentheses are the estimated standard deviations.

Table S2 Comparison of *r*C–C and various amplitudes of vibration for the fractional weight (frac) and bilinear (lin) methods of digital pixel interpolation for the GED scattering pattern for benzene. [a]

	HT-L (frac)	HT-L (lin)	HT-S (frac)	HT-S (lin)	RT-L (frac)	RT-L (lin)	RT-S (frac)	RT-S (lin)
*r*C–C	1.3955(2)	1.3959(2)	1.3991(4)	1.3992(4)	1.3930(8)	1.3937(9)	1.3971(5)	1.3970(6)
*u*C–C	0.0500(10)	0.0494(8)	0.0429(11)	0.0430(12)	0.0284(95)	0.0469(63)	0.0445(14)	0.0466(15)
*u*C–H	0.0727(23)	0.0709(20)	0.0672(33)	0.0706(35)	0.0322(263)	0.0676(150)	0.0969(73)	0.0910(60)
*u*C···C_m	0.0643(13)	0.0654(11)	0.0608(11)	0.0603(14)	0.0569(66)	0.0608(68)	0.0588(14)	0.0598(17)
*u*C···C_p	0.0642(19)	0.0676(18)	0.0707(23)	0.0708(32)	0.0493(119)	0.0550(118)	0.0659(25)	0.0647(33)
*u*C···H_o	0.1067(23)	0.1078(20)	0.0946(36)	0.0895(42)	0.0951(91)	0.0892(98)	0.1053(44)	0.1052(55)
*u*C···H_m	0.1141(23)	0.1139(22)	0.1181(56)	0.1139(82)	0.1292(92)	0.1329(104)	0.1169(52)	0.1280(83)
*u*C···H_p	0.1105(47)	0.1146(48)	0.1093(102)	0.0933(139)	0.1275(184)	0.1320(216)	0.0925(85)	0.0891(124)
R_G	0.0120	0.0110	0.0612	0.0693	0.0442	0.0456	0.0690	0.0777

[a] HT and RT refer to data collected at high temperature and room temperature respectively. L denotes the use of the long nozzle-to-camera distance, small angle scattering and higher signal-to-noise ratio (S/N). S denotes the use of the short nozzle-to-camera distance, large angle scattering and lower S/N. Frac refers to the assignment of fractional weight to pixels on boundaries of circular *s*-value bins and lin to a bilinear interpolation to evaluate data at fixed grid of points.

The following notes explain the contents of Table S2 in more detail.
Fractional weight method provides a significantly better fit to data for 3 of the 4 cases (exception HT-L). The method uses data from each pixel, all with the same weight. It requires more computation than the interpolation method and is therefore slower, though not prohibitively so.
Bilinear interpolation method chooses a circular grid of points spaced in 1 degree intervals (same method as Joyce-Loebl densitometer), so points are closer together at small scattering angles with better S/N. Hence this small angle data is used more often, giving it more weight. The interpolation algorithms are fast and so the computations are quicker than with the fractional weight method.

Table S3 Calculated [HF/6-31G(d)] coordinates for $Se(SCH_3)_2$.

	g^+g^+			g^+g^-		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Se(1)	0.0000	0.0000	0.9131	0.7851	–0.5180	0.0000
S(2)	0.0000	1.7226	–0.4399	–0.5327	–0.3343	1.7392
S(3)	0.0000	–1.7226	–0.4399	–0.5327	–0.3343	–1.7392
C(4)	1.7525	1.8317	–0.9083	–0.5327	1.4560	2.0579
C(5)	–1.7525	–1.8317	–0.9083	–0.5327	1.4560	–2.0579
H(6)	1.8519	2.7117	–1.5315	–1.0023	1.5946	3.0239
H(7)	2.0494	0.9590	–1.4722	–1.1035	1.9863	1.3094
H(8)	2.3749	1.9370	–0.0317	0.4772	1.8383	2.0932
H(9)	–1.8519	–2.7117	–1.5315	–1.0023	1.5946	–3.0239
H(10)	–2.0494	–0.9590	–1.4722	–1.1035	1.9863	–1.3094
H(11)	–2.3749	–1.9370	–0.0317	0.4772	1.8383	–2.0932

Sum of electronic and zero-point energies = –3271.7673 Hartree for g^+g^+
Sum of electronic and zero-point energies = –3271.7648 Hartree for g^+g^-

Table S4 Calculated [B3LYP/6-31G(d)] coordinates for $Se(SCH_3)_2$.

	g^+g^+			g^+g^-		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Se(1)	0.0000	0.0000	0.9035	0.7786	–0.5343	0.0000
S(2)	0.0000	1.7671	–0.4424	–0.5284	–0.3323	1.7835
S(3)	0.0000	–1.7671	–0.4424	–0.5284	–0.3323	–1.7835
C(4)	1.7767	1.9032	–0.8869	–0.5284	1.4822	2.0796
C(5)	–1.7767	–1.9032	–0.8869	–0.5284	1.4822	–2.0796
H(6)	1.8762	2.8084	–1.4941	–0.9545	1.6326	3.0765
H(7)	2.0893	1.0370	–1.4744	–1.1477	1.9998	1.3438
H(8)	2.3931	1.9935	0.0098	0.4901	1.8749	2.0572
H(9)	–1.8762	–2.8084	–1.4941	–0.9545	1.6326	–3.0765
H(10)	–2.0893	–1.0370	–1.4744	–1.1477	1.9998	–1.3438
H(11)	–2.3931	–1.9935	0.0098	0.4901	1.8749	–2.0572

Sum of electronic and zero-point energies = –3275.5371 Hartree for g^+g^+
Sum of electronic and zero-point energies = –3275.5353 Hartree for g^+g^-

Table S5 Calculated [MP2/6-31G(d)] coordinates for $Se(SCH_3)_2$.

	g^+g^+			g^+g^-		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Se(1)	0.0000	0.0000	0.9232	0.7822	–0.5325	0.0000
S(2)	0.0000	1.7256	–0.4402	–0.5311	–0.3297	1.7499
S(3)	0.0000	–1.7256	–0.4402	–0.5311	–0.3297	–1.7499
C(4)	1.7501	1.7597	–0.9251	–0.5311	1.4725	1.9940
C(5)	–1.7501	–1.7597	–0.9251	–0.5311	1.4725	–1.9940
H(6)	1.8847	2.6288	–1.5742	–0.9423	1.6575	2.9898
H(7)	2.0079	0.8549	–1.4780	–1.1568	1.9722	1.2534
H(8)	2.3907	1.8559	–0.0479	0.4858	1.8638	1.9460
H(9)	–1.8847	–2.6288	–1.5742	–0.9423	1.6575	–2.9898
H(10)	–2.0079	–0.8549	–1.4780	–1.1568	1.9722	–1.2534
H(11)	–2.3907	–1.8559	–0.0479	0.4858	1.8638	–1.9460

Sum of electronic and zero-point energies = –3272.3901 Hartree for g^+g^+
Sum of electronic and zero-point energies = –3272.3878 Hartree for g^+g^-

Table S6 Calculated [MP2/LanL2DZ(d)] coordinates for $Se(SCH_3)_2$.

	g^+g^+			g^+g^-		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Se(1)	0.0000	0.0000	1.4507	1.1046	–1.1369	0.0000
S(2)	0.0000	1.7242	0.0700	–0.2184	–0.9287	1.7553
S(3)	0.0000	–1.7242	0.0700	–0.2184	–0.9287	–1.7553
C(4)	1.7391	1.7273	–0.4886	–0.2184	0.8792	2.0339
C(5)	–1.7391	–1.7273	–0.4886	–0.2184	0.8792	–2.0339
H(6)	1.8402	2.5629	–1.1938	–0.7258	1.0416	2.9942
H(7)	1.9719	0.7879	–1.0032	–0.7713	1.4006	1.2452
H(8)	2.4202	1.8761	0.3561	0.8044	1.2658	2.0966
H(9)	–1.8402	–2.5629	–1.1938	–0.7258	1.0416	–2.9942
H(10)	–1.9719	–0.7879	–1.0032	–0.7713	1.4006	–1.2452
H(11)	–2.4202	–1.8761	0.3561	0.8044	1.2658	–2.0966

Sum of electronic and zero-point energies = –108.6376 Hartree for g^+g^+
Sum of electronic and zero-point energies = –108.6348 Hartree for g^+g^-

Table S7 Calculated [HF/3-21G(d)] coordinates for $Te(SCH_3)_2$.

	g^+g^+			g^+g^-		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Te(1)	0.0000	0.0000	0.8631	0.7249	–0.4791	0.0000
S(2)	0.0000	1.8461	–0.6751	–0.7522	–0.1929	1.8735
S(3)	0.0000	–1.8461	–0.6751	–0.7522	–0.1929	–1.8735
C(4)	1.7324	1.9249	–1.2512	–0.7522	1.6096	2.1794
C(5)	–1.7324	–1.9249	–1.2512	–0.7522	1.6096	–2.1794
H(6)	1.7927	2.7595	–1.9377	–1.3144	1.7654	3.0912
H(7)	1.9986	1.0167	–1.7707	–1.2369	2.1370	1.3722
H(8)	2.4062	2.0910	–0.4245	0.2523	1.9812	2.3135
H(9)	–1.7927	–2.7595	–1.9377	–1.3144	1.7654	–3.0912
H(10)	–1.9986	–1.0167	–1.7707	–1.2369	2.1370	–1.3722
H(11)	–2.4062	–2.0910	–0.4245	0.2523	1.9812	–2.3135

Sum of electronic and zero-point energies = –7453.3400 Hartree for g^+g^+
Sum of electronic and zero-point energies = –7453.3381 Hartree for g^+g^-

Table S8 Calculated [HF/LanL2DZ(d)] coordinates for $Te(SCH_3)_2$.

	g^+g^+			g^+g^-		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Te(1)	0.0000	0.0000	1.5593	0.7158	–0.4677	0.0000
S(2)	0.0000	1.8457	0.0463	–0.7426	–0.2038	1.8714
S(3)	0.0000	–1.8457	0.0463	–0.7426	–0.2038	–1.8714
C(4)	1.7402	1.9488	–0.5096	–0.7426	1.5969	2.2006
C(5)	–1.7402	–1.9488	–0.5096	–0.7426	1.5969	–2.2006
H(6)	1.7925	2.7941	–1.1857	–1.3074	1.7346	3.1152
H(7)	2.0233	1.0497	–1.0384	–1.2281	2.1375	1.4005
H(8)	2.4050	2.1152	0.3261	0.2622	1.9687	2.3436
H(9)	–1.7925	–2.7941	–1.1857	–1.3074	1.7346	–3.1152
H(10)	–2.0233	–1.0497	–1.0384	–1.2281	2.1375	–1.4005
H(11)	–2.4050	–2.1152	0.3261	0.2622	1.9687	–2.3436

Sum of electronic and zero-point energies = –106.8570 Hartree for g^+g^+
Sum of electronic and zero-point energies = –106.8547 Hartree for g^+g^-

Table S9 Calculated [B3LYP/LanL2DZ(d)] coordinates for $Te(SCH_3)_2$.

	g^+g^+			g^+g^-		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Te(1)	0.0000	0.0000	0.8306	0.7096	–0.4695	0.0000
S(2)	0.0000	1.9006	–0.6669	–0.7362	–0.2093	1.9239
S(3)	0.0000	–1.9006	–0.6669	–0.7362	–0.2093	–1.9239
C(4)	1.7702	2.0597	–1.1756	–0.7362	1.6106	2.2542
C(5)	–1.7702	–2.0597	–1.1756	–0.7362	1.6106	–2.2542
H(6)	1.8208	2.9385	–1.8298	–1.2597	1.7446	3.2087
H(7)	2.0894	1.1749	–1.7334	–1.2762	2.1502	1.4710
H(8)	2.4177	2.2147	–0.3082	0.2823	1.9977	2.3453
H(9)	–1.8208	–2.9385	–1.8298	–1.2597	1.7446	–3.2087
H(10)	–2.0894	–1.1749	–1.7334	–1.2762	2.1502	–1.4710
H(11)	–2.4177	–2.2147	–0.3082	0.2823	1.9977	–2.3453

Sum of electronic and zero-point energies = –108.0849 Hartree for g^+g^+
Sum of electronic and zero-point energies = –108.0833 Hartree for g^+g^-

Table S10 Calculated [MP2/LanL2DZ(d)] coordinates for $Te(SCH_3)_2$.

	g^+g^+			g^+g^-		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Te(1)	0.0000	0.0000	1.5906	0.7151	–0.4788	0.0000
S(2)	0.0000	1.8374	0.0571	–0.7419	–0.1993	1.8775
S(3)	0.0000	–1.8374	0.0571	–0.7419	–0.1993	–1.8775
C(4)	1.7375	1.8447	–0.5247	–0.7419	1.6180	2.1307
C(5)	–1.7375	–1.8447	–0.5247	–0.7419	1.6180	–2.1307
H(6)	1.8205	2.6722	–1.2415	–1.2855	1.7955	3.0680
H(7)	1.9745	0.9021	–1.0309	–1.2623	2.1283	1.3132
H(8)	2.4312	2.0111	0.3063	0.2780	2.0051	2.2260
H(9)	–1.8205	–2.6722	–1.2415	–1.2855	1.7955	–3.0680
H(10)	–1.9745	–0.9021	–1.0309	–1.2623	2.1283	–1.3132
H(11)	–2.4312	–2.0111	0.3063	0.2780	2.0051	–2.2260

Sum of electronic and zero-point energies = –107.4617 Hartree for g^+g^+
Sum of electronic and zero-point energies = –107.4596 Hartree for g^+g^-

Table S11 Least-squares correlation matrix (×100) for $Se(SCH_3)_2$. [a]

	u_8	k_2
p_2	51	57
u_7	71	76
u_8		93

[a] Only elements with absolute values > 50% are shown; k_2 is a scale factor.

Table S12 Least-squares correlation matrix (×100) for $Te(SCH_3)_2$. [a]

	p_5	p_6	k_1	k_2
p_1		–63		
p_4	63			
u_8			62	72

[a] Only elements with absolute values > 50% are shown; k_1 and k_2 are scale factors.

Figure S1 Experimental and difference (experimental–theoretical) molecular-scattering intensities for $Se(SCH_3)_2$.

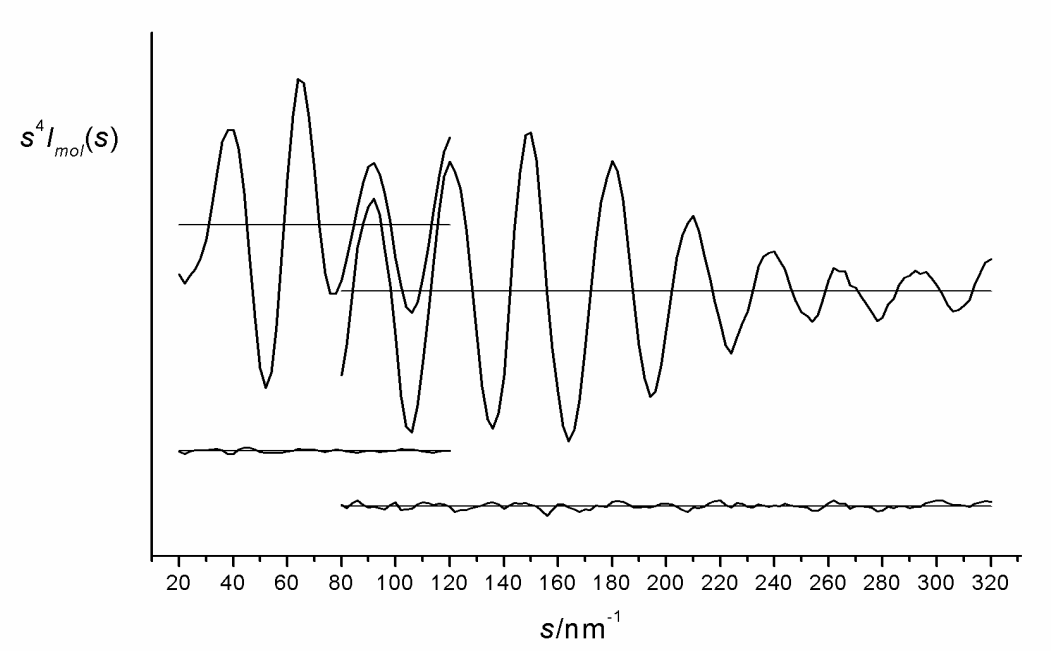

Figure S2 Experimental and difference (experimental–theoretical) molecular-scattering intensities for $Te(SCH_3)_2$.