

Supporting Information

**Short and Linear Intermolecular Tetrel Bonds to Tin. Cocrystal Engineering
with Triphenyltin Chloride**

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S.1. Materials and methods

Starting materials were purchased from Sigma–Aldrich, TCI, or Apollo Scientific. Reactions were carried out under argon atmosphere with standard Schlenk techniques. Commercially available anhydrous solvents were used for the synthesis of tetrel-bonded complexes and for recrystallization. Melting points were measured with a MEL-TEMP electro thermal instrument. ^{119}Sn NMR spectra were recorded at ambient temperature on a Bruker AVII-300 spectrometer, with $B_0 = 7.05$ T. CDCl_3 was used as the solvent. A 0.5 M solution of trimethyl tin chloride in C_6D_6 was used as a secondary external chemical shift reference at 164.2 ppm relative to 20% Me_3SnBr in C_6D_6 .¹

S.2. Preparation of cocrystals

Complex 1·BP·CH₂Cl₂: Triphenyltin chloride **1** (500 mg, 1 equivalent) and 4,4-dipyridyl (BP) (102 mg, 0.5 equivalent) were placed in a round-bottom flask and ethanol (20 mL) was added. The resulting solution was refluxed for 1 h under argon. The solution was cooled to room temperature and the solvent was removed under reduced pressure. The resulting white solid material was further dissolved in 1:1 diethyl ether:dichloromethane (10 mL) and filtered. The supernatant was held between 0 and 5° C for 48 h to obtain pure crystalline **1**·BP. Melting point: **1**, 108-109 °C; BP, 109-112 °C; complex **1**·BP·CH₂Cl₂, 132-134° C.

Complex 1·DPNO: Triphenyltin chloride **1** (500 mg, 1 equivalent) and 4,4-dipyridyl N, N-dioxide (DPNO) (122 mg, 0.5 equivalent) were placed in a round-bottom flask and ethanol (25 mL) was added. The resulting solution was refluxed overnight under argon. The solution was cooled to room temperature and the solvent was removed under reduced pressure. The resulting white solid was further dissolved in 1:1 methanol:dichloromethane (10 mL) and filtered. The supernatant was held at 0° C for 48 h to obtain pure crystalline **1**·DPNO. Melting point: **1**, 108-109 °C; DPNO, 306-308 °C; complex **1**·DPNO, 235-244 °C.

Complex 1·DABCO·CH₃OH: Triphenyltin chloride **1** (500 mg, 1 equivalent) and 1,4-diazabicyclo[2.2.2]octane (DABCO) (73 mg, 0.5 equivalent) were placed in a round-bottom flask and ethanol (20 mL) was added. The resulting solution was refluxed for 1 h under argon. The solution was cooled to room temperature and the solvent was removed under reduced pressure. The resulting white solid was further dissolved in 1:1 methanol:dichloromethane (25 mL) and filtered. The supernatant was held at 0-5 °C for 48 h to obtain pure crystalline **1·DABCO·CH₃OH**. Melting point: **1**, 108-109 °C; DABCO, 155-160 °C; complex **1·DABCO·CH₃OH**, 120-126 °C.

Complex 1·PNO: Triphenyltin chloride **1** (500 mg, 1 equivalent) and pyridine N-oxide (PNO) (123 mg, 1 equivalent) were placed in a round-bottom flask and ethanol (20 mL) was added. The resulting solution was refluxed for 1 h under argon. The solution was cooled to room temperature and the solvent was removed under reduced pressure. The resulting white solid was further dissolved in 1:1 methanol:dichloromethane (20 mL) and filtered. The supernatant was held at 0-5 °C for 48 h to obtain pure crystalline **1·PNO**. Melting point: **1**, 108-109 °C; PNO, 60-66 °C; complex **1·PNO**, 137-139 °C.

Complex 1·DPSO: Triphenyltin chloride **1** (500 mg, 1 equivalent) and diphenyl sulfoxide (DPSO) (262 mg, 1 equivalent) were placed in a round-bottom flask and ethanol (20 mL) was added. The resulting solution was refluxed for 1 h under argon. The solution was cooled to room temperature and the solvent was removed under reduced pressure. The resulting white solid was further dissolved in 1:1 methanol:dichloromethane (20 mL) and held at 0-5 °C for 48 h to obtain pure crystalline **1·DPSO**. Melting point: **1**, 108-109 °C; DPSO, 69-71 °C; complex **1·DPSO**, 102-104 °C.

Complex 1·DMU: Triphenyltin chloride **1** (500 mg, 1 equivalent) and dimethyl urea (DMU) (114 mg, 1 equivalent) were placed in a round-bottom flask and ethanol (20 mL) was added. The resulting solution was refluxed for 1 h under argon. The solution was cooled to room temperature and the solvent was removed under reduced pressure. The resulting light yellow oil was further dissolved in

diethyl ether (10 mL) and held at 0-5 °C for 48 h to obtain pure crystalline **1**·DMU. Melting point: **1**, 108-109 °C; DMU, 101-104 °C; complex **1**·DMU, 95-97°C.

Complex 1·PPNO: Triphenyltin chloride **1** (250 mg, 1 equivalent) and 4-phenylpyridine *N*-oxide (PPNO) (111 mg, 1 equivalent) were placed in a round-bottomed flask and ethanol (25 mL) was added. The resulting solution was refluxed for 4 h under argon. The solution was cooled to room temperature and the solvent was removed under reduced pressure. The resulting white solid was further dissolved in 1:1 methanol:dichloromethane (10 mL) and filtered. The supernatant was kept at 0° C for 48 h to obtain pure crystalline **1**·PPNO. Melting point: **1**, 108-109 °C; PPNO, 153-155 °C; complex **1**·PPNO, 126-128 °C.

Complex 1·2MPNO: Triphenyltin chloride **1** (250 mg, 1 equivalent) and 2-methylpyridine *N*-oxide (2MPNO) (71 mg, 1 equivalent) were placed in a round-bottom flask and ethanol (20 mL) was added. The resulting solution was refluxed for 1 h under argon. The solution was cooled to room temperature and the solvent was removed under reduced pressure. The resulting white semi-solid material was further dissolved in 1:1 methanol:dichloromethane (10 mL) and filtered. The supernatant was kept at 0 °C for 48 h to obtain pure crystalline **1**·2MPNO. Melting point: **1**, 108-109 °C; 2MPNO, 41-45 °C; complex **1**·2MPNO, 77-79 °C.

Complex 1·26DMPNO·H₂O: Triphenyltin chloride **1** (250 mg, 1 equivalent) and 2,6-dimethylpyridine *N*-oxide (26DMPNO) (86 mg, 1 equivalent) were placed in a round-bottom flask and ethanol (20 mL) was added. The resulting solution was refluxed for 1 h under argon. The solution was cooled to room temperature and the solvent was removed under reduced pressure. The resulting white solid material was further dissolved in 1:1 methanol:dichloromethane (10 mL) and filtered. The supernatant was kept at 0° C for 48 h to obtain pure crystalline **1**·26DMPNO·H₂O. Melting point: **1**, 108-109 °C; boiling point of 26DMPNO, 108-111 °C / 10 mmHg; complex **1**·26DMPNO, 55-57 °C.

Complex 1·35DMPNO: Triphenyltin chloride **1** (250 mg, 1 equivalent) and 3,5-dimethylpyridine *N*-oxide (35DMPNO) (80 mg, 1 equivalent) were placed in a round-bottom flask and ethanol (20 mL) was added. The resulting solution was refluxed for 1 h under argon. The solution was cooled to room temperature and the solvent was removed under reduced pressure. The resulting solid material was further dissolved in 1:1 methanol:dichloromethane (10 mL) and filtered. The supernatant was kept at 0 °C to obtain pure crystalline **1·35DMPNO**. Melting point: **1**, 108-109 °C; 3,5-DMPNO, 100-104 °C; complex **1·35DMPNO**, 90-92 °C.

S.3. Powder X-ray diffraction (PXRD) analysis

Selected cocrystals were individually packed in an aluminium or glass sample holder and data sets were collected on a Rigaku Ultima IV powder diffractometer at 293 K (± 2) (CuK α_1 radiation with a wavelength of $\lambda = 1.54056$ Å). The measurements were carried out in focused beam geometry with a step-scan technique in 2θ range of 5–50°. Data were acquired by scintillation counter detector in continuous scanning mode with a step size of 0.02°. The experimental PXRD patterns of selected tetrel-bonded cocrystals and simulated patterns generated from single-crystal X-ray data are shown below. The comparison of simulated and experimental PXRD patterns confirms the structural uniformity of bulk co-crystal powders. See also Figure 3 of the main text.

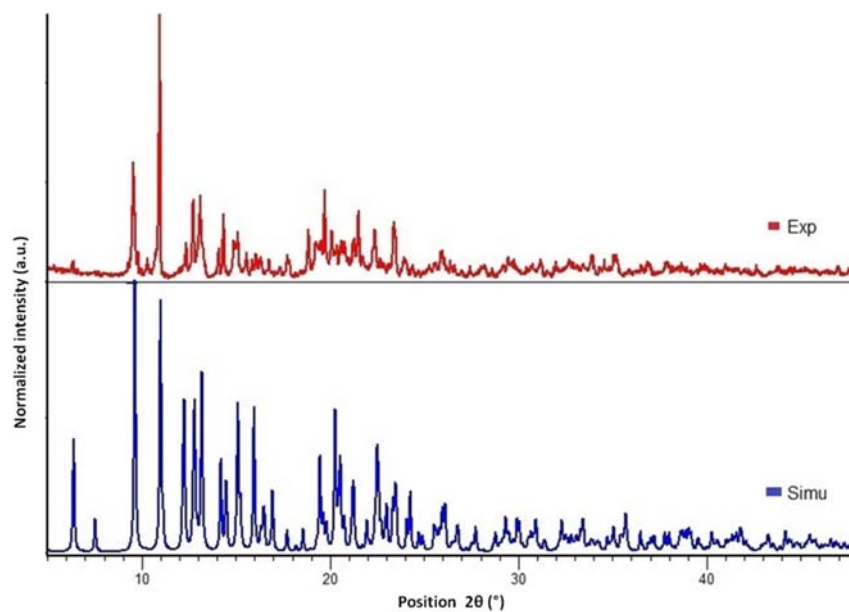


Fig. S1. Comparison of the experimental PXRD pattern of **1**·BP·CH₂Cl₂ obtained by solution crystallization (top, red) and the simulated pattern generated from the single-crystal X-ray structure (bottom, blue).

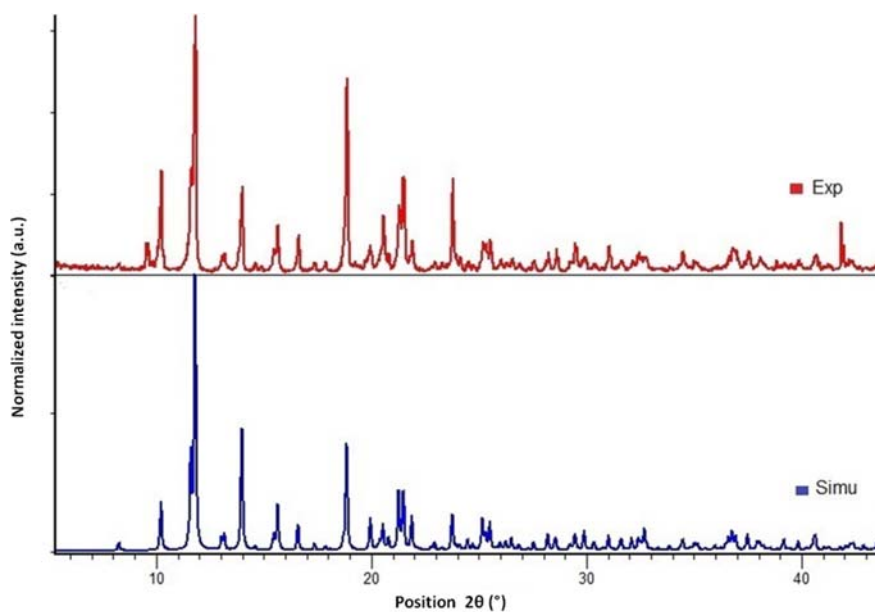


Fig. S2. Comparison of the experimental PXRD pattern of **1**·DPNO obtained by solution crystallization (top, red) and the simulated pattern generated from the single-crystal X-ray structure (bottom, blue).

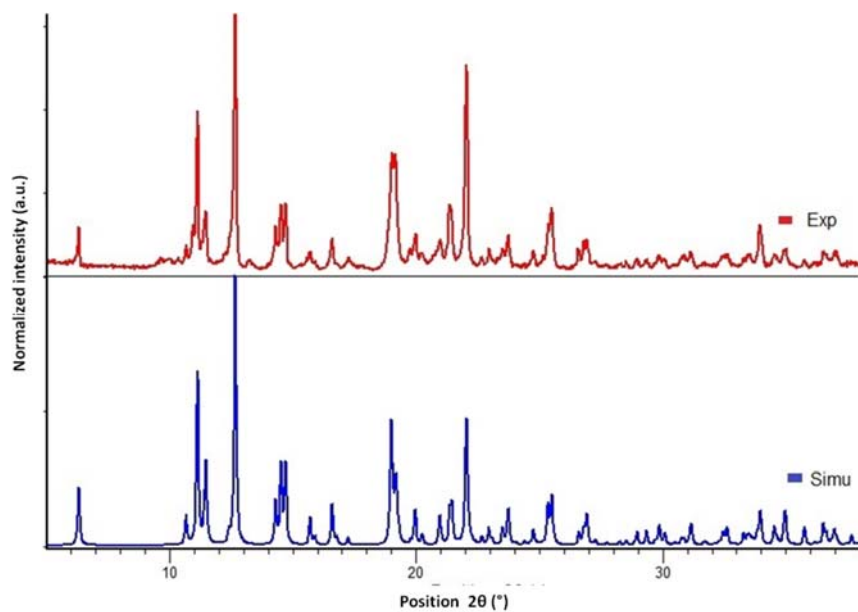


Fig. S3. Comparison of the experimental PXRD pattern of **1**·DABCO·MeOH cocrystal obtained by solution crystallization (top, red) and the simulated pattern generated from the single-crystal X-ray structure (bottom, blue).

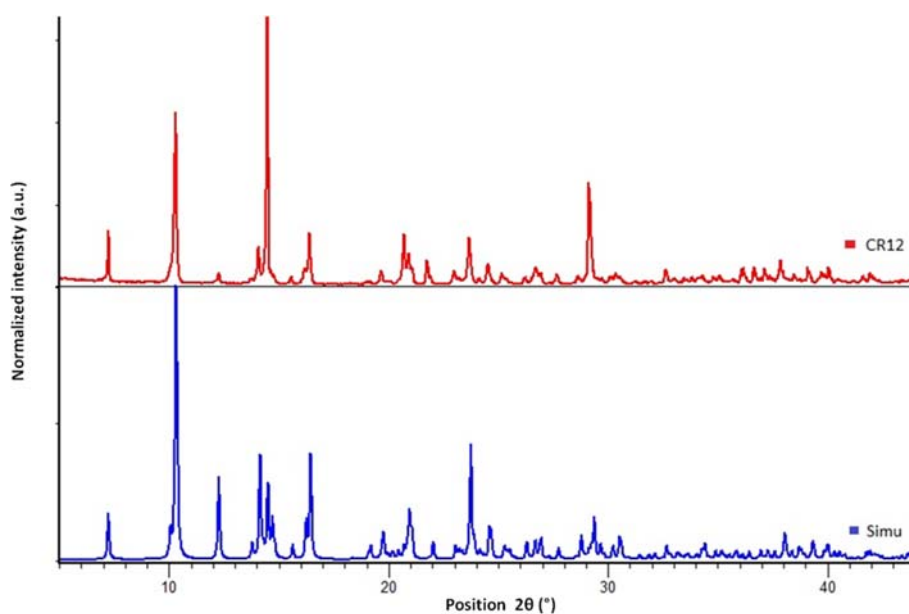


Fig. S4. Comparison of the experimental PXRD pattern of **1**·DMU obtained by solution crystallization (top, red) and the simulated pattern generated from the single-crystal X-ray structure (bottom, blue).

S.4. Single crystal X-ray (SC-XRD) studies

The crystals were mounted on glass fibers or transparent MiTeGen MicroMounts™ precision tools prior to data collection. The data were collected on a Bruker Kappa Apex diffractometer equipped with MoK α radiation (wavelength of $\lambda = 0.7103 \text{ \AA}$) with an APEX II CCD detector at $200 \pm 2 \text{ K}$. Raw data collection and processing were performed with the Bruker APEX III software package. Crystal structures of the complexes were solved using WinGX and Olex2 software packages using the direct method and refined against F² using SHELXL97.² Packing diagrams were generated using Mercury 4.1.0 and POV-Ray.³ Intermolecular interactions were analyzed with PLATON.⁴ The non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using difference Fourier maps or positioned geometrically. In cocrystal **1**·DABCO·MeOH, DABCO shows rotational disorder. The disordered dabco molecule is modelled with the PARTs module and occupancies are refined with free variables and restraints. Crystallographic data and structural refinement details are provided in Table S1.

Table S1. Crystallographic data and structural refinement details for the tetrel-bonded complexes

Name	1 ·DPNO	1 ·DABCO·CH ₃ OH	1 ·PNO
Crystal system, space group	monoclinic, <i>P2₁/n</i>	orthorhombic, <i>Pbca</i>	monoclinic, <i>P2₁/n</i>
Temperature (K)	293(2)	293 (2)	293(2)
a (Å)	9.157(3)	9.2232(2)	10.681(15)
b (Å)	14.961(5)	16.5452(4)	14.224(15)
c (Å)	15.683(5)	27.9051(6)	14.167(15)
α (°)	90	90	90
β (°)	103.98(5)	90	93.44(2)
γ (°)	90	90	90
V (Å ³)	2084.7(12)	4258.31(17)	2149(4)
Z	2	8	4
μ (mm ⁻¹)	1.365	1.477	1.325
Crystal size (mm ³)	0.16 × 0.15 × 0.14	0.14 × 0.12 × 0.1	0.15 × 0.12 × 0.11
F(000)	956.0	1912.0	960.0
Data collection and refinement			
Diffractometer	Bruker APEX-II CCD area detector diffractometer		
Absorption correction	Based on multi-scan		
No. of reflections: measured and independent,	23131, 4102	33509, 4883	25027, 4675
R _{int}	0.0677	0.0333	0.0478
θ_{\min} (°)	1.909	1.459	2.031
θ_{\max} (°)	25.99	27.516	26.998
<i>R</i> _{all} , <i>R</i> _{obs}	0.0907, 0.0368	0.0607, 0.0458	0.0510, 0.0259
<i>wR</i> _{2_all} , <i>wR</i> _{2_obs}	0.0947, 0.0829	0.1270, 0.1176	0.0532, 0.0482
GOOF	0.905	1.051	0.931

No. of parameters	244	232	244
$\Delta\rho_{\max}, \Delta\rho_{\min}$ (e Å ⁻³)	1.29, -0.71	1.61, -0.70	0.39, -0.28
CCDC number	1969058	1969059	1969057

Name	1-DPSO	1-DMU	1-2MPNO
Crystal system, space group	monoclinic, $P2_1/n$	monoclinic, $P2_1/c$	monoclinic, $P2_1/n$
Temperature (K)	292(2)	292 (2)	292 (2)
a (Å)	10.795(7)	13.7449(5)	16.295(3)
b (Å)	18.134(11)	12.0345(4)	15.606(3)
c (Å)	13.994(7)	14.4495(5)	18.300(4)
α (°)	90	90	90.00(3)
β (°)	90.100(8)	117.4250(10)	106.26(3)
γ (°)	90	90	90.00(3)
V (Å ³)	2740(3)	2121.52(13)	4467.6(17)
Z	4	4	1
μ (mm ⁻¹)	1.126	1.342	1.277
Crystal size (mm ³)	0.18 × 0.16 × 0.12	0.21 × 0.2 × 0.12	0.21 × 0.16 × 0.14
F(000)	1184.0	952.0	1984.0
Data collection and refinement			
Diffractionmeter	Bruker APEX-II CCD area detector diffractometer		
Absorption correction	Based on multi-scan		
No. of reflections: measured and independent	38495, 5981	18869, 6479	27596, 9101
R _{int}	0.0507	0.0334	0.0532
θ_{\min} (°)	1.838	1.669	1.481
θ_{\max} (°)	26.998	30.55	26.397
$R_{\text{all}}, R_{\text{obs}}$	0.0451, 0.0276	0.0456, 0.0294	0.0923, 0.0425
$wR2_{\text{all}}, wR2_{\text{obs}}$	0.0592, 0.0551	0.0651, 0.0588	0.0960, 0.0769
GOOF	1.005	1.009	1.005
No. of parameters	307	237	507
$\Delta\rho_{\max}, \Delta\rho_{\min}$ (e Å ⁻³)	0.45, -0.29	0.44, -0.50	0.90, -0.38
CCDC number	1969061	1969064	1969056

Name	1-PPNO	1-26DMPNO·H ₂ O	1-BP·CH ₂ Cl ₂
Crystal system, space group	monoclinic, $P2_1/c$	triclinic, $P-1$	triclinic, $P-1$
Temperature (K)	200(2)	200 (2)	200 (2)
a (Å)	16.4573(5)	9.9175(4)	9.1657(6)
b (Å)	17.8277(5)	11.3687(5)	13.9885(7)
c (Å)	18.3574(6)	11.3727(4)	18.8925(11)
α (°)	90	81.6840(10)	82.256(2)
β (°)	112.9600(10)	66.6190(10)	80.360(2)
γ (°)	90	87.2160(10)	81.292(2)
V (Å ³)	4959.3(3)	1164.54(8)	2345.6(2)
Z	4	2	2
μ (mm ⁻¹)	1.160	1.232	1.331
Crystal size (mm ³)	0.18 × 0.16 × 0.14	0.28 × 0.26 × 0.02	0.28 × 0.15 × 0.08
F(000)	2240.0	532.0	1078.0
Data collection and refinement			
Diffractionmeter	Bruker APEX-II CCD area detector diffractometer		
Absorption correction	Based on multi-scan		
No. of reflections: measured and independent	35382, 10815	8474, 4538	17665, 9614
R _{int}	0.0755	0.0194	0.0425
θ_{\min} (°)	1.344	1.81	1.1
θ_{\max} (°)	26.999	25.999	26.499
$R_{\text{all}}, R_{\text{obs}}$	0.1068, 0.0492	0.0298, 0.0260	0.0862, 0.0513
$wR2_{\text{all}}, wR2_{\text{obs}}$	0.0964, 0.0783	0.0641, 0.0624	0.1131, 0.0971

No. of parameters	595	274	550
$\Delta\rho_{\max}, \Delta\rho_{\min}$ (e Å ⁻³)	0.66, -0.56	0.65, -0.58	1.21, -1.21
CCDC number	1969063	1969055	1969060

Name	1-35DMPNO
Empirical formula	C ₂₅ H ₂₄ ClNOSn
Formula weight	508.59
Temperature/K	200(2)
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> /Å	10.6635(6)
<i>b</i> /Å	10.3627(6)
<i>c</i> /Å	21.2450(12)
α /°	90
β /°	97.983(2)
γ /°	90
Volume/Å ³	2324.9(2)
<i>Z</i>	4
ρ_{calc} /cm ³	1.453
μ /mm ⁻¹	1.229
<i>F</i> (000)	1024.0
Crystal size/mm ³	0.2 × 0.16 × 0.13
Radiation	MoK α (λ = 0.71073)
2 θ range for data collection/°	3.856 to 53.05
Index ranges	-13 ≤ <i>h</i> ≤ 13, -12 ≤ <i>k</i> ≤ 13, -26 ≤ <i>l</i> ≤ 26
Reflections collected	23348
Independent reflections	4794 [<i>R</i> _{int} = 0.0366, <i>R</i> _{sigma} = 0.0306]
Data/restraints/parameters	4794/0/264
Goodness-of-fit on <i>F</i> ²	1.027
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0282, <i>wR</i> ₂ = 0.0606
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0405, <i>wR</i> ₂ = 0.0656
Largest diff. peak/hole / e Å ⁻³	0.42/-0.32
CCDC number	1969062

S.5 References

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- ⁴ A. L. Spek, *Acta Crystallogr. Sect. D*, 2009, **65**, 148.