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Supporting Information

Synthesis, Crystallization, Electrochemistry and Single Crystal X-ray Analysis of a Methoxy-Substituted-Tris-Phenalenyl Based Neutral Radical

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Detail of X-ray structure determination of $18^+BPh_4^-$:

An orange prism fragment (0.43 x 0.30 x 0.19 mm^3) was used for the single crystal x-ray diffraction study of $[C_{45}H_{33}O_{12}Si]^+[C_{24}H_{20}B]^-.[CH_2Cl_2]_{1.72}$ (sample rh140_0m). The crystal was coated with paratone oil and mounted on to a cryo-loop glass fiber. X-ray intensity data were collected at 100(2) K on a Bruker APEX2 (version 2.0-22)[1] platform-CCD x-ray diffractometer system (Mo-radiation, λ = 0.71073 Å, 50KV/40mA power). The CCD detector was placed at a distance of 6.0475 cm from the crystal.

A total of 4800 frames were collected for a hemisphere of reflections (with scan width of 0.3° in ω, starting ω and 2θ angles at –30° and –45°, and ϕ angles of 0°, 90°, 180°, and 270° for every 600 frames, 20 sec/frame exposure time). The frames were integrated using the Bruker SAINT software package (version V7.23A)[2] and using a narrow-frame integration algorithm. Based on a monoclinic crystal system, the integrated frames yielded a total of 159213 reflections at a maximum 2θ angle of 63.02° (0.68 Å resolution), of which 20371 were independent reflections (R_{int} = 0.0470, R_{sig} = 0.0298, redundancy = 7.8, completeness = 99.8%) and 15082 (74.0%) reflections were greater than $2\sigma(I)$. The unit cell parameters were, **a** = 13.1909(2) Å, **b** = 41.2909(5) Å, **c** = 11.6570(2) Å, β = 105.1662(4)°**,** V = 6128.01(16) Å^3, Z = 4, calculated density D_c = 1.365 g/cm^3. Absorption corrections were applied (absorption coefficient μ = 0.254 mm^{-1}; max/min transmission = 0.9536/0.8985) to the raw intensity data using the SADABS program (version 2004/1)[3].

The Bruker SHELXTL software package (Version 6.14)[4] was used for phase determination and structure refinement. The distribution of intensities (E^2-1 = 0.983) and systematic absent reflections indicated one possible space group, P2(1)/c. The space group P2(1)/c (#14) was later determined to be correct. Direct methods of phase determination followed by two Fourier cycles of refinement led to an electron density map from which most of the non-hydrogen atoms were identified in the asymmetry unit of the unit cell. With subsequent isotropic refinement, all of the non-hydrogen atoms were identified. There were one cation of $[C_{45}H_{33}O_{12}Si]^+$, one anion of $[C_{24}H_{20}B]^-$, and two partially occupied disordered solvent molecules of CH_2Cl_2 present in the asymmetry unit of the unit cell. The two partially occupied disordered CH_2Cl_2 site occupancy factor ratios were 61%/26% and 47%/38%, crystal had lost solvent with a total of 87% and 85% solvent occupancy sites, respectively).

Atomic coordinates, isotropic and anisotropic displacement parameters of all the non-hydrogen atoms were refined by means of a full matrix least-squares procedure on F^2. The H-atoms were included in the refinement in calculated positions riding on the atoms to which they were attached. The refinement converged at R1 = 0.0557, wR2 = 0.1408, with intensity $I>2\sigma(I)$. The largest peak/hole in the final difference map was 0.927/-0.345 e/Å^3.

Detail of X-ray structure determination of 18:

A black color thin plate fragment (0.21 x 0.10 x 0.01 mm^3) was used for the single crystal x-ray diffraction study of for $C_{45}H_{33}O_{12}Si.[CH_3CN]_{2.92}$ (sample rh141_0m). The crystal was coated with paratone oil and mounted on to a cryo-loop glass fiber. X-ray intensity data were collected at 100(2) K on a Bruker APEX2 (version 2.0-22)[1] platform-CCD x-ray diffractometer system (Mo-radiation, λ = 0.71073 Å, 50KV/40mA power). The CCD detector was placed at a distance of 5.0550 cm from the crystal.

A total of 3600 frames were collected for a sphere of reflections (with scan width of 0.3° in ω, starting ω and 2θ angles of –30°, and ϕ angles of 0°, 90°, 120°, 180°, 240°, and 270° for every 600 frames, 80 sec/frame exposure time). The frames were integrated using the Bruker SAINT software package (version V7.23A)[2] and using a narrow-frame integration algorithm. Based on a triclinic crystal system, the integrated frames yielded a total of 20412 reflections at a maximum 2θ angle of 40.78° (1.02 Å resolution), of which 4292 were independent reflections (R_{int} = 0.0970, R_{sig} = 0.0727, redundancy = 4.8, completeness = 100%) and 2587 (60.3%) reflections were greater than 2σ(I). The unit cell parameters were, **a** = 12.357(2) Å, **b** = 12.711(2) Å, **c** = 14.644(3) Å, α = 91.192(3)°, β = 104.382(3)°, γ = 101.723(3)°, V = 2175.4(7) Å^3, Z = 2, calculated density D_c = 1.395 g/cm^3. Absorption corrections were applied (absorption coefficient μ = 0.126 mm^{-1}; max/min transmission = 0.9987/0.9741) to the raw intensity data using the SADABS program (version 2004/1)[3].

The Bruker SHELXTL software package (Version 6.14)[4] was used for phase determination and structure refinement. The distribution of intensities (E^2-1 = 1.010) and no systematic absent reflections indicated two possible space groups, P-1 and P1. The space group P-1 (#2) was later determined to be correct. Direct methods of phase determination followed by two Fourier cycles of refinement led to an electron density map from which most of the non-hydrogen atoms were identified in the asymmetry unit of the unit cell. With subsequent isotropic refinement, all of the non-hydrogen atoms were identified. There was one molecule of $C_{45}H_{33}O_{12}Si$ and 2.92 solvent molecule of CH_3CN present in the asymmetry unit of the unit cell. Attempt to model the possible disorder in the partially occupied (92% site occupied) solvent molecule was not successful. Note that Alert level A (lower sin(theta_max)/wavelength = 0.49) and B (ratio reflections to parameters = 7.0) is due to the very thin crystal size (10 micron thickness for the smallest dimension) and possible solvent disorder. Although data quality is not very good, the atom connectivity of the structure is accurate even though the standard uncertainty of the bond lengths and angles are higher.

Atomic coordinates, isotropic and anisotropic displacement parameters of all the non-hydrogen atoms were refined by means of a full matrix least-squares procedure on F^2. The H-atoms were included in the refinement in calculated positions riding on the atoms to which they were attached. The refinement converged at R1 = 0.0547, wR2 = 0.1258, with intensity, $I > 2\sigma(I)$. The largest peak/hole in the final difference map was 0.339/-0.258 e/Å^3.

Table S1. Bond lengths of **18** and **18**$^+$, together with Δr_{kl} (Å) and Δ BO **(** p_{kl}^{f} **)** at different temperatures

Bonds	Cation (**18**$^+$BPh$_4^-$) bond lengths (Å) (@ 100K)	Average cation bl (av. Over two euiv. bonds	Radical **(18)** bond lengths (Å) (@ 100K)	Radical bond length – av. cation bond length(@100K) Δr_{kl} (Å)	Δ BO (p_{kl}^{f})	
C1-C2	1.411	1.415	1.398	-0.017	0.028	Phenalenyl unit that involved in partially-superimposed π-overlap (PLY1)
C2-C3	1.369	1.371667	1.378	0.006333	-0.0301	
C3-C3A	1.445	1.445	1.438	-0.007	0.0464	
C3A-C4	1.401	1.400333	1.408	0.007667	-0.0515	
C4-C5	1.381	1.386667	1.381	-0.00567	0	
C5-C6	1.391	1.389667	1.355	-0.03467	0	
C6-C6A	1.399	1.400333	1.389	-0.01133	-0.0515	
C6A-C7	1.443	1.445333	1.423	-0.02233	0.0464	
C7-C8	1.375	1.372667	1.363	-0.00967	-0.0301	
C8-C9	1.411	1.415667	1.413	-0.00267	0.028	
C9-C9A	1.415	1.414667	1.403	-0.01167	0	
C9A-C1	1.413	1.413	1.417	0.004	0	
C9A-C9B	1.422	1.422	1.422	0	0	
C9B-C3A	1.414	1.417333	1.417	-0.00033	0	
C9B-C6A	1.415	1.415	1.429	0.014	0	
C1-O1	1.308	1.304	1.321	0.017	-0.0644	
C9-O9	1.307	1.304667	1.317	0.012333	-0.0644	
C3-O3”	1.344	1.342667	1.359	0.016333	-0.0583	
C7-O7”	1.344	1.345333	1.373	0.027667	-0.0583	
C11-C12	1.417		1.411	-0.004		Phenalenyl unit that is not involved in any interaction (PLY2)
C12-C13	1.374		1.358	-0.01367		
C13-C13A	1.442		1.431	-0.014		
C13A-C14	1.399		1.375	-0.02533		
C14-C15	1.389		1.368	-0.01867		
C15-C16	1.388		1.378	-0.01167		
C16-C16A	1.402		1.401	0.000667		
C16A-C17	1.445		1.437	-0.00833		
C17-C18	1.370		1.354	-0.01867		
C18-C19	1.419		1.395	-0.02067		
C19-C19A	1.413		1.413	-0.00167		
C19A-C11	1.412		1.419	0.006		
C19A-C19B	1.420		1.414	-0.008		
C19B-C13A	1.420		1.426	0.008667		
C19B-C16A	1.416		1.403	-0.012		
C11-O11	1.300		1.321	0.017		
C19-O19	1.302		1.331	0.026333		
C13-O13”	1.342		1.366	0.023333		
C17-O17”	1.346		1.362	0.016667		
C21-C22	1.417		1.418	0.003		Phenalenyl unit that involved in partially-superimposed π-overlap (PLY3)
C22-C23	1.372		1.368	-0.00367		
C23-C23A	1.448		1.442	-0.003		
C23A-C24	1.401		1.388	-0.01233		
C24-C25	1.390		1.355	-0.03167		
C25-C26	1.390		1.388	-0.00167		
C26-C26A	1.400		1.392	-0.00833		

C26A-C27	1.448		1.456	0.010667		
C27-C28	1.373		1.365	-0.00767		
C28-C29	1.417		1.403	-0.01267		
C29-C29A	1.416		1.414	-0.00067		
C29A-C21	1.414		1.416	0.003		
C29A-C29B	1.424		1.424	0.002		
C29B-C23A	1.418		1.424	0.006667		
C29B-C26A	1.414		1.412	-0.003		
C21-O21	1.304		1.307	0.003		
C29-O29	1.305		1.304	-0.00067		
C23-O23"	1.342		1.359	0.016333		
C27-O27"	1.346		1.350	0.004667		

REFERENCES

1. *APEX 2,* version 2010.3-0, Bruker (2010), Bruker AXS Inc., Madison, Wisconsin, USA.

2. *SAINT,* version V7.60A, Bruker (2009), Bruker AXS Inc., Madison, Wisconsin, USA.

3. *SADABS,* version 2008/1, Bruker (2008), Bruker AXS Inc., Madison, Wisconsin, USA.

4. *SHELXTL,* version 2008/4, Bruker (2008), Bruker AXS Inc., Madison, Wisconsin, USA.