

SUPPORTING INFORMATION FOR

Isolation and X-ray structural characterization of tetraisopropylpyrene cation radical

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Table of Contents

General experimental methods	page S2-S3
Figure S1: Cyclic and square-wave voltammograms of 3	page S3
Synthesis of Compounds.....	page S4-S5
¹ H and ¹³ C spectra of the Synthesized Compounds.....	page S6-S8
Preparation of 3^{•+} SbCl₆⁻ single crystals using NO ⁺ SbCl ₆ ⁻	page S9
Figure S2: ORTEP diagram of 3	page S9
X-ray structural data for 3	page S10
X-ray structural data for 3^{•+} SbCl₆⁻	page S11

General Experimental Methods and Materials:

All reactions were performed under argon atmosphere unless otherwise noted. All commercial reagents were used without further purification unless otherwise noted. Dichloromethane was repeatedly stirred with fresh aliquots of conc. sulfuric acid (~10 % by volume) until the acid layer remained colorless. After separation it was washed successively with water, aqueous sodium bicarbonate, water, and aqueous sodium chloride and dried over anhydrous calcium chloride. The dichloromethane was distilled twice from P₂O₅ under an argon atmosphere and stored in a Schlenk flask equipped with a Teflon valve fitted with Viton O-rings. The hexanes and toluene were distilled from P₂O₅ under an argon atmosphere and then refluxed over calcium hydride (~12 h). After distillation from CaH₂, the solvents were stored in Schlenk flasks under an argon atmosphere. Tetrahydrofuran (THF) was dried initially by distilling over lithium aluminum hydride under an argon atmosphere. The THF was further refluxed over metallic sodium in the presence of benzophenone until a persistent blue color was obtained and then it was distilled under an argon atmosphere and stored in a Schlenk flask equipped with a Teflon valve fitted with Viton O-rings. NMR spectra were recorded on 300 and 400 MHz NMR spectrometers.

Cyclic Voltammetry (CV) :

The CV cell was of an air-tight design with high vacuum Teflon valves and Viton O-ring seals to allow an inert atmosphere to be maintained without contamination by grease. The working electrode consisted of an adjustable platinum disk embedded in a glass seal to allow periodic polishing (with a fine emery cloth) without changing the surface area (~1 mm²) significantly. The reference SCE electrode (saturated calomel electrode) and its

salt bridge were separated from the catholyte by a sintered glass frit. The counter electrode consisted of a platinum gauze that was separated from the working electrode by ~3 mm. The CV measurements were carried out in a solution of 0.1 to 0.2 M supporting electrolyte (tetra-*n*-butylammonium hexafluorophosphate, TBAH) and $2-5 \times 10^{-3}$ M substrate in dry dichloromethane under an argon atmosphere. All the cyclic voltammograms were recorded at a sweep rate of 200 mV sec^{-1} , unless otherwise specified and were IR compensated. The oxidation potentials ($E_{1/2}$) were referenced to SCE, which was calibrated with added (equimolar) ferrocene ($E_{1/2} = 0.450 \text{ V vs. SCE}$). The $E_{1/2}$ values were calculated by taking the average of anodic and cathodic peak potentials in the reversible cyclic voltammograms.

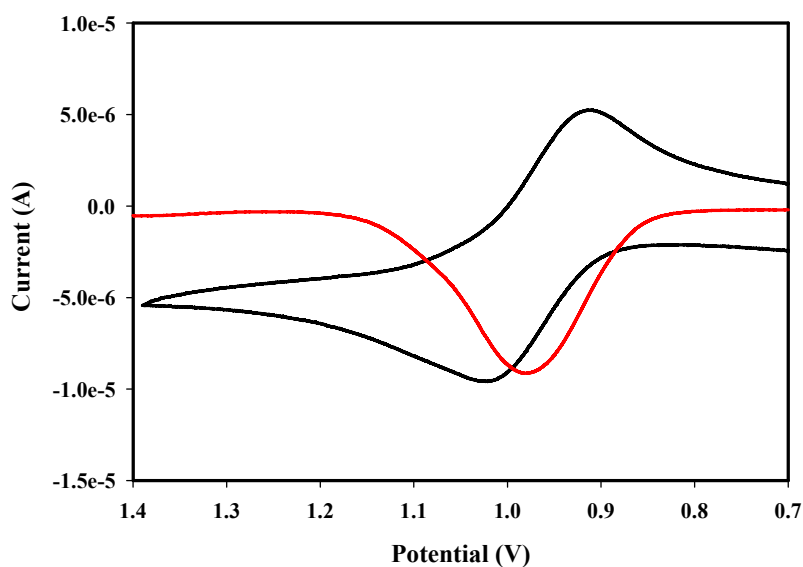


Fig. S1: Cyclic and square-wave voltammograms of $2 \times 10^{-3} \text{ M } \mathbf{3}$ in CH_2Cl_2 ($0.1 \text{ M } n\text{-Bu}_4\text{NPF}_6$) at a scan rate of 200 mVs^{-1} .

1,3,6,8-Tetrabromopyrene (1). 1,3,6,8-Tetrabromopyrene was synthesized in 95 % yield by a reaction of pyrene with bromine in nitrobenzene according to a literature procedure (G. Venkataramana, S. Sankararaman, *Eur. J. Org. Chem.*, 2005, 4162).

Isopropenyl boronic acid. Trimethyl borate (40.88 mL, 360 mmol) was dissolved in 50 mL dry THF and cooled to -78 °C and a 0.5 M solution of isopropenylmagnesium bromide in THF (300 mL, 150 mmol) was added to it dropwise. The resulting white slurry was allowed to stir and warm to room temperature overnight. The reaction was then quenched with addition of 50 mL of water and most of the THF was evacuated by rotary evaporation. The remaining slurry was cooled to 0 °C and 150 mL of 2N HCl was added and stirred for 30 min under argon. It was then extracted with diethyl ether and the organic layer was dried with MgSO₄ to remove traces of water and concentrated to give the boronic acid (11.34 g, 88 % yield) as white powder. It was stored under argon with complete exclusion of moisture. M.p. 77-79 °C (dec); ¹H NMR (DMSO-d₆, 300 MHz): δ 1.70 (t, *J* = 1.35 Hz, 3H), 5.42-5.44 (m, 1H), 5.56-5.58 (m, 1H); ¹³C NMR (DMSO-d₆, 75 MHz) δ 22.5, 127.6, 142.2.

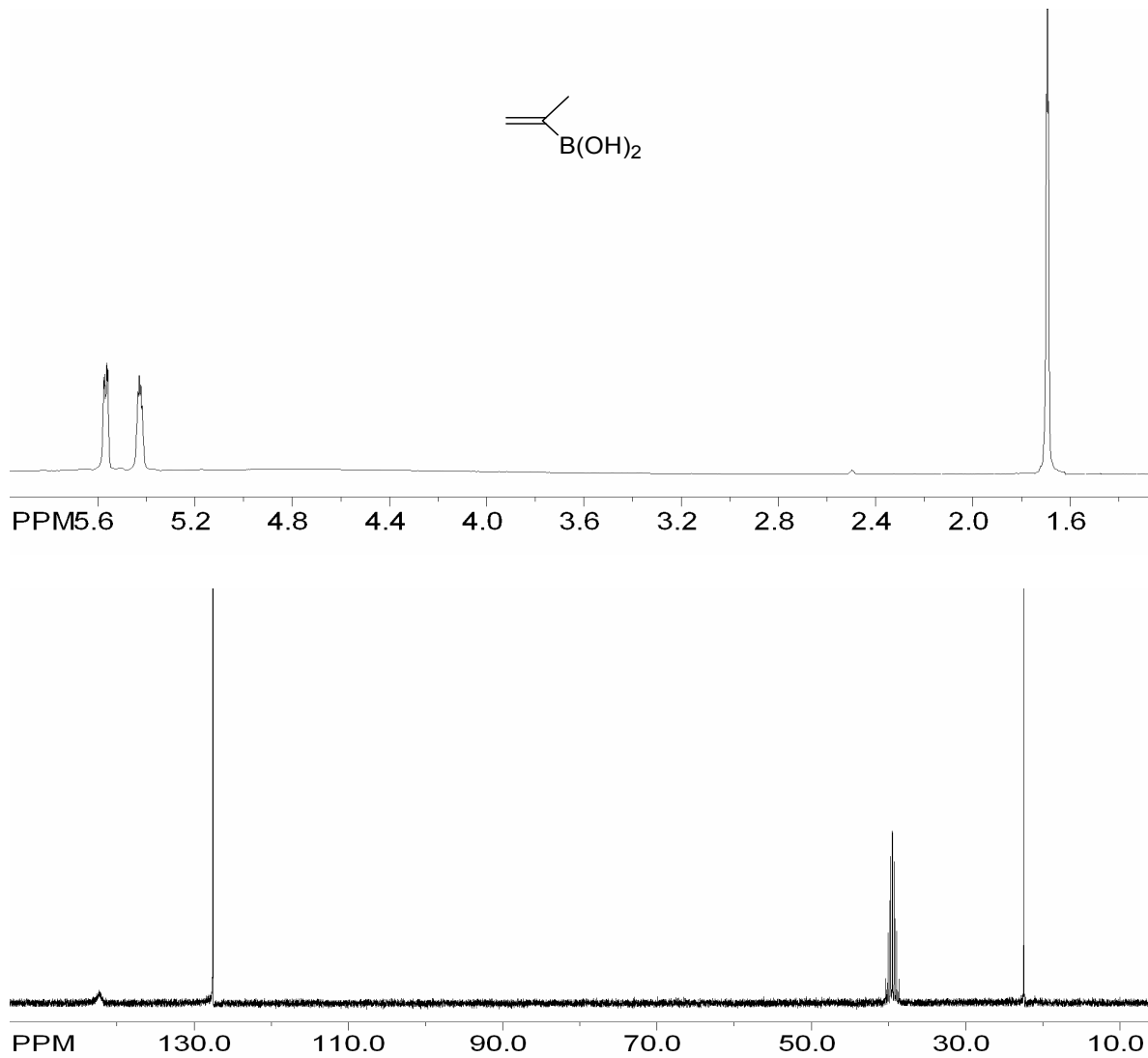
1,3,6,8-Tetraisopropenylpyrene (2). Tetrabromopyrene (2.07 g, 4 mmol), isopropenylboronic acid (2.38 g, 28 mmol), potassium carbonate (4.42 g, 32 mmol) and Pd(PPh₃)₄ (250 mg) was added to 50 mL of dioxane which was repeatedly degassed by evacuation and purging with argon gas. The mixture was refluxed in an argon atmosphere under the complete exclusion of light for 4 days after which it was quenched with the addition of water. The organic layer was extracted with dichloromethane, washed consecutively with water and brine before being dried over MgSO₄ and concentrated. The crude product was then chromatographed over silica gel pretreated with 2 %

triethylamine, using hexanes as eluent to afford 1.33 g of alkenylpyrene in 92 % yield. M.p. 268-270 °C ; ¹H NMR (CDCl₃, 400 MHz): δ 2.38 (t, *J* = 1.06 Hz, 12H), 5.22-5.23 (m, 1H), 5.58-5.59 (m, 1H), 7.75 (s, 2H), 8.30 (s, 4H); ¹³C NMR (CDCl₃, 100 MHz) δ 25.9, 117.1, 124.8, 125.1, 126.1, 127.2, 139.3, 145.3.

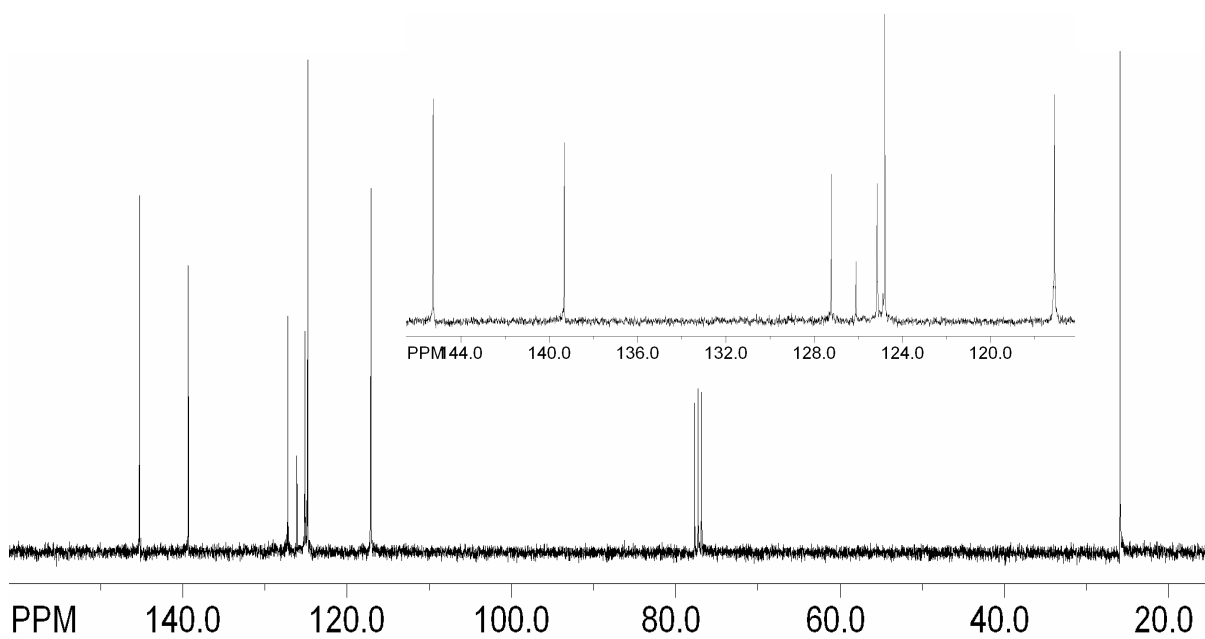
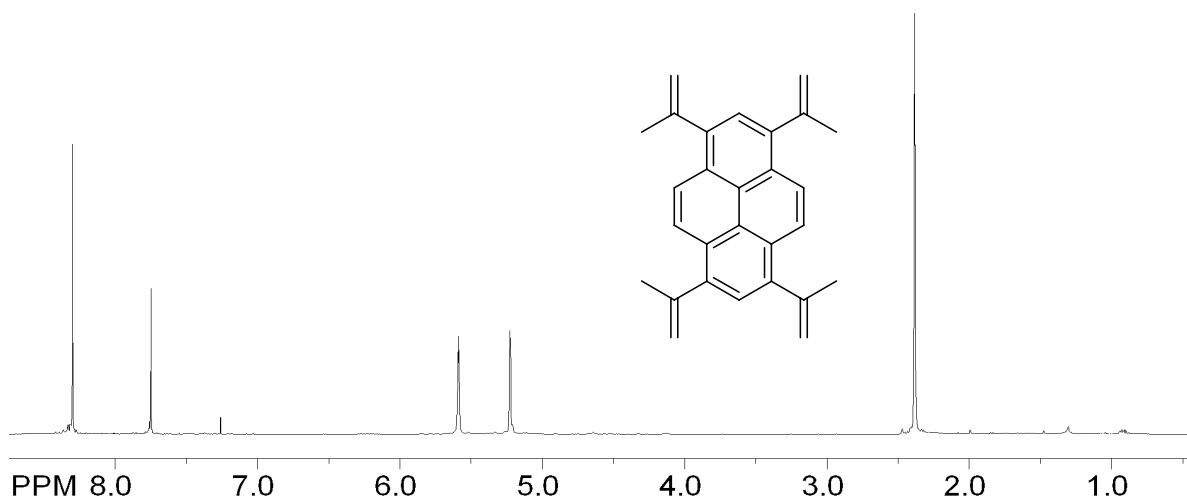
1,3,6,8-Tetraisopropylpyrene (3). Tetraisopropenylpyrene (520 mg, 1.44 mmol) was suspended in 100 mL of a 4:1 mixture of ethyl acetate and ethanol and mixed with 400 mg of 10% Pd on charcoal. The resulting suspension was subjected to a pressure of 2-3 psi hydrogen gas for 3 h in a high pressure bottle after which an aliquot showed complete alkene reduction as adjudged by ¹H NMR. The mixture was then passed through a pad of silica gel and the pad was further washed with dichloromethane (3 x 25 mL). The solvent was evaporated and the resulting solid was further purified by column chromatography using silica gel and hexanes as eluent to afford 523 mg of tetraisopropylpyrene in 98 % yield. M.p. 278-280 °C; ¹H NMR (CDCl₃, 400 MHz): δ 1.64 (d, *J* = 6.88 Hz, 24H), 4.15-4.22 (m, 4H), 8.07 (s, 2H), 8.43 (s, 4H); ¹³C NMR (CDCl₃, 100 MHz) δ 24.3, 29.4, 119.2, 121.9, 126.4, 126.7, 141.9.

^1H and ^{13}C spectra of the various synthesized compounds

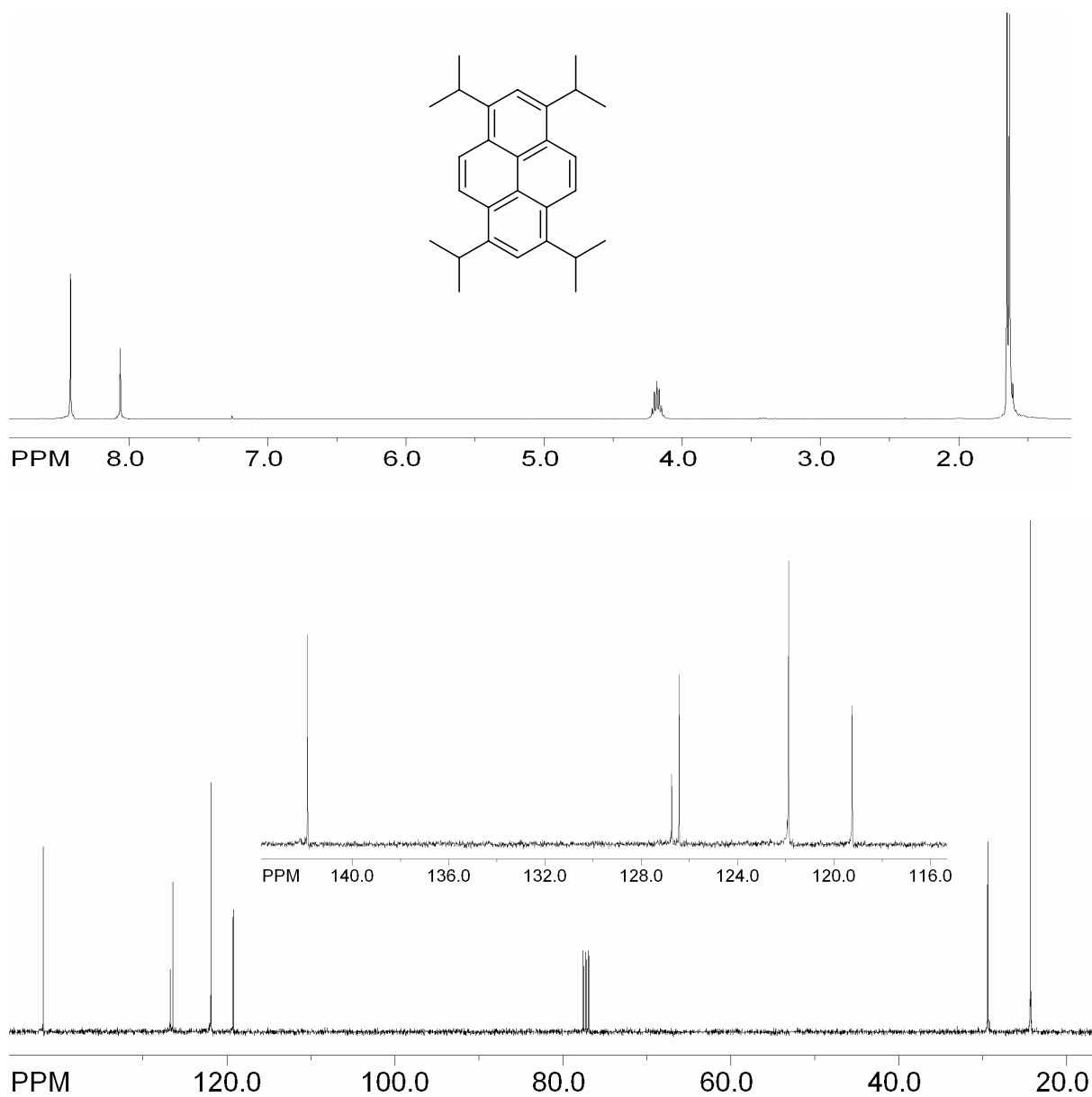
Isopropenyl boronic acid:



1,3,6,8-Tetraisopropenylpyrene (2):



1,3,6,8-Tetraisopropylpyrene (3):



Preparation of $3^{\bullet+}$ SbCl₆⁻ single crystals using NO⁺SbCl₆⁻. A 50-mL flask fitted with a Schlenk adaptor was charged with nitrosonium hexachloroantimonate (44 mg, 0.12 mmol), and a cold solution of 1,3,6,8-tetraisopropylpyrene **3** (45 mg, 0.12 mmol) in anhydrous dichloromethane (20 mL) was added under an argon atmosphere at -10 °C. The solution immediately took on a green coloration and the solution was stirred (while slowly bubbling argon through the solution to entrain gaseous NO) for 30 min to yield a greenish-blue solution of cation radical [**3**^{•+} SbCl₆⁻]. The solution was carefully layered with dry toluene (30 mL) and placed in a refrigerator (-20 °C) which after 2 days, produced greenish-blue needle shaped crystals of the cation radical suitable for X-ray structure analysis.

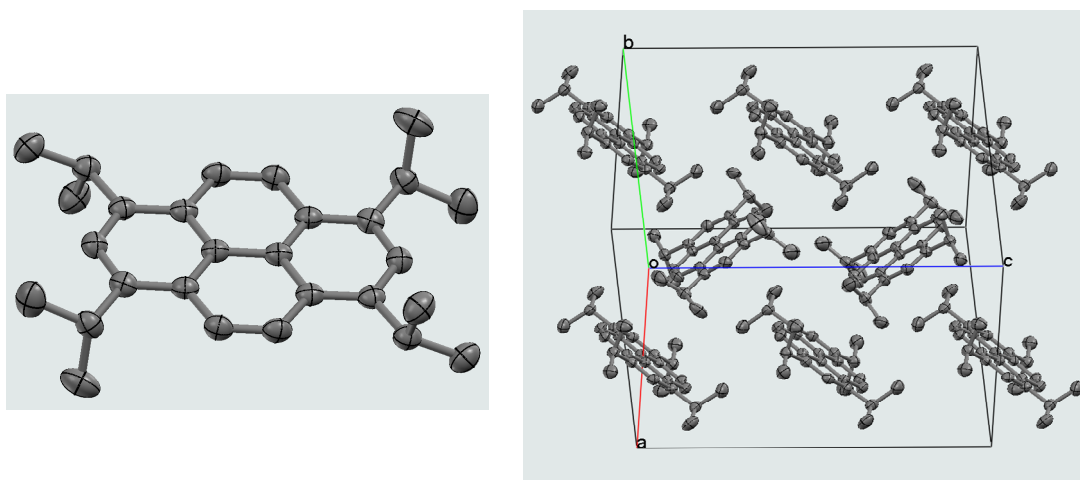


Fig. S2. The ORTEP diagram of **3** (**right**), with the packing diagram (**left**) with the ellipsoids shown in 50% probability.

Crystal data and structure refinement for 1,3,6,8-Tetraisopropylpyrene (3)

Identification code		
Empirical formula	C ₂₈ H ₃₄	
Formula weight	370.55	
Temperature	200(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 11.3272(7) Å	α = 94.595(4)°.
	b = 12.6764(7) Å	β = 92.311(4)°.
	c = 16.9660(12) Å	γ = 115.064(3)°.
Volume	2192.2(2) Å ³	
Z	4	
Density (calculated)	1.123 Mg/m ³	
Absorption coefficient	0.463 mm ⁻¹	
F(000)	808	
Crystal size	0.20 x 0.18 x 0.06 mm ³	
Theta range for data collection	2.62 to 67.24°.	
Index ranges	-13 ≤ h ≤ 13, -15 ≤ k ≤ 15, 0 ≤ l ≤ 19	
Reflections collected	25845	
Independent reflections	7547 [R(int) = 0.0397]	
Completeness to theta = 67.24°	96.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9727 and 0.9130	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	7547 / 0 / 506	
Goodness-of-fit on F ²	1.064	
Final R indices [I > 2σ(I)]	R1 = 0.0644, wR2 = 0.1740	
R indices (all data)	R1 = 0.0981, wR2 = 0.1900	
Extinction coefficient	0.0007(2)	
Largest diff. peak and hole	0.243 and -0.188 e.Å ⁻³	

Crystal data and structure refinement for the 1,3,6,8-Tetraisopropylpyrene Cation Radical

Table 1. Crystal data and structure refinement for raj9wa.

Identification code	raj9wa	
Empirical formula	C ₄₂ H ₅₀ Cl ₆ Sb	
Formula weight	889.27	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	P nma	
Unit cell dimensions	a = 13.8054(3) Å	α = 90°.
	b = 12.5572(3) Å	β = 90°.
	c = 23.6942(6) Å	γ = 90°.
Volume	4107.56(17) Å ³	
Z	4	
Density (calculated)	1.438 Mg/m ³	
Absorption coefficient	9.129 mm ⁻¹	
F(000)	1820	
Crystal size	0.51 x 0.23 x 0.14 mm ³	
Theta range for data collection	3.71 to 67.39°.	
Index ranges	0 ≤ h ≤ 16, 0 ≤ k ≤ 15, 0 ≤ l ≤ 28	
Reflections collected	34504	
Independent reflections	3746 [R(int) = 0.0324]	
Completeness to theta = 67.39°	96.7 %	
Absorption correction	Numerical	
Max. and min. transmission	0.3613 and 0.0897	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3746 / 50 / 255	
Goodness-of-fit on F ²	1.013	
Final R indices [I > 2σ(I)]	R1 = 0.0268, wR2 = 0.0659	
R indices (all data)	R1 = 0.0272, wR2 = 0.0662	
Extinction coefficient	0.00017(2)	
Largest diff. peak and hole	1.105 and -1.104 e.Å ⁻³	