The Structure of a Seven-Bladed Propeller: $C_7Ph_7^+$ is Not Planar

Stacey Brydges, James F. Britten, Lisa C. F. Chao, Hari K. Gupta, Michael J. McGlinchey,* and David L. Pole

Abstract: The heptaphenylcycloheptatrienyl cation, $C_7Ph_7^+$, in $[C_7Ph_7^+][CF_3CO_2^-] \cdot 2\,CF_3CO_2H$ (**1**), is the last species in the series of $C_nPh_n^{x\pm}$ ($n = 3-7$) molecular paddle wheels to be structurally characterized. In the solid state, the C_7 central ring of the 6-π-electron perphenylated tropylium cation adopts a shallow boat conformation, with the peripheral phenyl groups possessing an average dihedral angle of 80° relative to the plane containing their attached central ring carbon and neighboring ring atoms. This geometry has been rationalized by semiempirical (AM1) calculations, and represents a compromise between steric congestion and the fractional loss in aromaticity as the central ring distorts from planarity. A correlation of the ^{13}C NMR chemical shift with the calculated electron density for $C_nH_n^{x\pm}$ and $C_nPh_n^{x\pm}$ species ($n = 3$ to 7) yields proportionality factors of approximately 21 and 22 ppm per extra 0.1 electron at the central ring carbons, respectively.

Keywords: aromaticity · chirality · hydrogen bonds · semiempirical calculations · steric hindrance

Introduction

Ions or molecules of the type $C_nPh_n^{x\pm}$ continue to attract attention, not only for their relevance to the Hückel $4N+2$ rule but also as ligands bonded to organometallic fragments. One might anticipate that $C_3Ph_3^+$, $C_4Ph_4^{2+}$, $C_5Ph_5^-$, C_6Ph_6, and $C_7Ph_7^+$ should exist as stable, planar aromatic species. Indeed, the ligands C_nPh_n ($n = 1-6$) have all been characterized crystallographically.[1] In the solid state, the ligands or complexes possessing a cyclic array of C_nPh_n fragments adopt propeller-type conformations in which the external phenyls make a dihedral angle, θ, with the plane of the central ring. Such a geometry provides a compromise between the coplanar arrangement, $\theta = 0°$, which maximizes π overlap but may induce severe steric strain, and the orthogonal rotamer, $\theta = 90°$, in which interactions between bulky groups are minimized and π conjugation is disrupted. Moreover, for the series C_nPh_n ($n = 3-7$), the angle subtended at the center of the internal ring by adjacent phenyls ($\omega = 360°/n$) decreases in value from 120°, 90°, 72°, 60°, to 51.4°, respectively. Although increasing the ring size lengthens the radial distance of the external phenyls from the center of the molecule, this is more than compensated for by the diminishing value of ω. The net result of going to a larger ring is to place the phenyls in a more restricted locale.

Despite the fact that $C_7Ph_7^+$ has been known for almost three decades,[2] it is the last species in this series of $C_nPh_n^{x\pm}$ ($n = 3-7$) molecular paddle wheels to be structurally characterized, either as a free ion or molecule, or as an organometallic ligand. The quest to determine the solid-state structure of this cation has proven to be a formidable crystallographic challenge, and its solution has revealed an exceptionally crowded system.

Results and Discussion

Heptaphenylcycloheptatriene, C_7Ph_7H, originally synthesized by Battiste in 1961,[3] was structurally characterized only in 1995, as was its precursor, the Diels–Alder adduct of tetraphenylcyclopentadienone and triphenylcyclopropene.[4] In accordance with an earlier report,[2] treatment of C_7Ph_7H with bromine yields the salt $C_7Ph_7^+Br^-$. Hydrolysis (or methanolysis) and subsequent reaction with HBF_4/ether gave crystals of $C_7Ph_7^+BF_4^-$. Several X-ray data sets were acquired for both the bromide and tetrafluoroborate salts but, despite the determined efforts of a number of crystallographers in Europe and in North America, no structural information was forthcoming because of an unresolvable disorder problem. Later, counterion exchange by slow solvent evaporation from a solution containing $C_7Ph_7^+Br^-$ in trifluoroacetic acid produced crystals of X-ray quality of the trifluoroacetate salt $[C_7Ph_7^+][CF_3CO_2^-] \cdot 2\,CF_3CO_2H$ (**1**).

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Figure 1 depicts the structure of the cation and reveals that the seven-membered ring is not flat but rather adopts a shallow boat conformation. The bend angles, γ and ϕ, are most pronounced for the planes containing C(6)-C(7)-C(1) [plane 1], C(1)-C(2)-C(5)-C(6) [plane 2], and C(2)-C(3)-C(4)-C(5) [plane 3], and yield values of 13° ([plane 1]/[plane 2]) and 18° ([plane 2]/[plane 3]), respectively. These may be compared with the corresponding interplanar angles in C_7Ph_7H (or C_7Cl_8), for which γ is 55° (52°) and ϕ is 35° (32°).[4, 5] Thus, $C_7Ph_7^+$ retains some vestiges of its boatlike precursor, C_7Ph_7H. It is noteworthy that this distortion from planarity has been previously observed in the molecular structures of [7]circulene[6] and the bis[tris(bicyclo[2.2.2]octeno)tropylium]acetylene dication.[7]

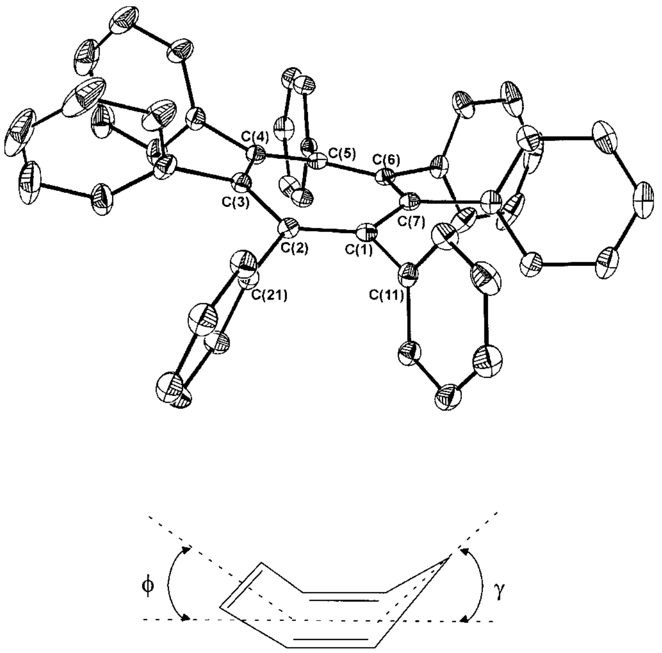

Figure 1. Structure of cation in **1** (ORTEP, thermal ellipsoids at 20% probability) with hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: C_7-ring [C1–C2 1.404(4), C2–C3 1.412(4), C3–C4 1.411(4), C4–C5 1.415(4), C5–C6 1.411(4), C6–C7 1.414(4), C1–C7 1.414(4); C2-C1-C7 127.4(3), C1-C2-C3: 127.7(3), C4-C3-C2 127.5(3), C3-C4-C5 127.1, C6-C5-C4 127.1(3), C5-C6-C7 128.5(3), C1-C7-C6 126.8(3)]; typical C_7-ring to Ph [C1–C11 1.510(4); C1-C2-C21 117.0(3), C3-C2-C21 115.2(3)]. The average interplanar angles for γ ([plane 1]/[plane 2]) and ϕ ([plane 3]/[plane 2]) are 12.8° and 10.7°, respectively.

The space-filling representation of the cation in **1** in Figure 2 shows how each peripheral phenyl group is twisted very markedly out of the plane containing its attached central ring carbon and neighboring ring atoms. These dihedral angles are 76–82° (average 80°), and may be compared to the mean θ values of 75° (67°) for C_6Ph_6,[8a,b] approximately 50° for (η^5-C_5Ph_5)ML_n complexes,[1e, 9] approximately 36° (15.3–81.5°) for various (η^4-C_4Ph_4)ML_n complexes,[1d, 10] and approximately 5° for the free $C_3Ph_3^+$ cation.[11]

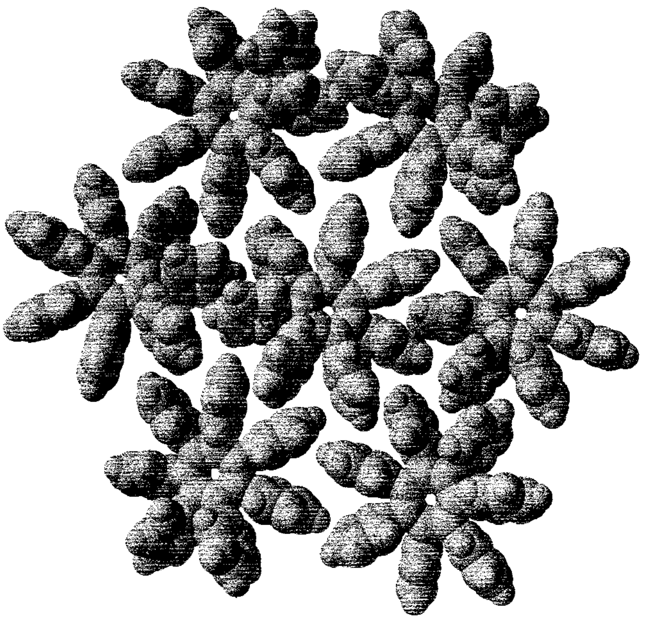

Figure 2. Space-filling representation of a section of a cationic layer, showing the hexagonal packing of $C_7Ph_7^+$ ions, in **1**.

The propensity of this system to form well-defined single crystals can be rationalized in terms of a hydrogen-bonded network of trifluoroacetates and trifluoroacetic acid molecules which lies between the layers of close-packed disks of cations and stabilizes the crystalline edifice.[12] This interlocking motif between the anion, solvates, and cation can be seen in Figure 3. It is likely that the relatively strong and directional O–H···O interactions between each anion and two separate trifluoroacetic acid molecules (2.52 Å and 2.60 Å) that lie parallel to the (101) plane are responsible for the cohesion in the molecular salt. It is of interest that many of the previous X-ray crystallographic determinations of tropylium salts have been of disordered crystals.[13] Only those complexes that involve transannular stabilization of the tropylium moiety by charge-transfer interactions[14] or the encapsulation of $C_7H_7^+$ into the large cavity of a crown ether in order to fix the ion orientation[15] have avoided the structurally unfavorable disorder that seems to be associated with the tropylium cation and its analogues.

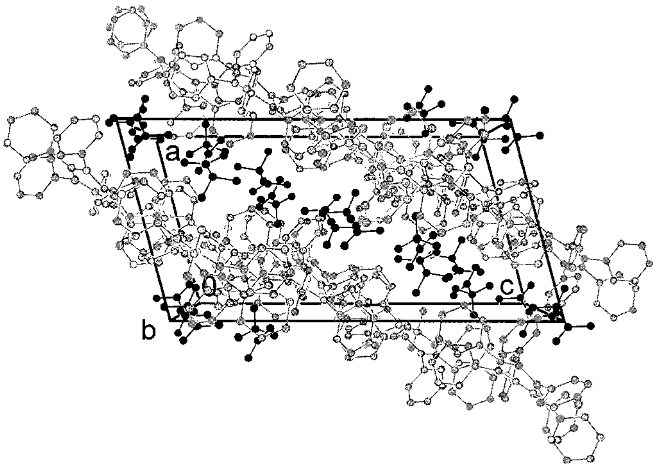

Figure 3. View of the unit cell of **1** depicting the alternating layers of cations and anions/solvates parallel to the (101) plane.

Braga and Grepioni have emphasised that in crystals of ionic species, the distribution of anions and cations is controlled primarily by the relative size and shape of component ions.[12] Bromide and tetrafluoroborate anions may be likened to molecular ball bearings and, when such species are introduced into a crystal lattice that contains layers of disc-shaped $C_7Ph_7^+$ cations, it is reasonable to infer that the coulombic interactions lack directionality and are insufficient in providing cohesion. On the other hand, the intermolecular links afforded by the trifluoroacetate anions and trifluoroacetic acid molecules serve to more efficiently fix the discoidal cations in the crystal lattice, resulting in a discrete, ordered, low-energy solid-state structure.

In order to ascertain whether the conformational anomalies observed in the solid-state structure are a response to steric or electronic factors, we conducted semiempirical MO calculations using the AM1 Hamiltonian[16] available in the Spartan computational package.[17] The general features of the X-ray structure were reproduced in the ground-state optimized C_1 geometry of $C_7Ph_7^+$, with average (maximum) interplanar angles of 9° (12°) and 11° (16°) for γ and ϕ, respectively. It is noteworthy that a search of conformational space also yielded a separate potential minimum corresponding to the D_{7h} structure of $C_7Ph_7^+$, which is only 0.2 kcal mol^{-1} higher in energy than the C_1 isomer. The existence of two energetically accessible equilibrium structures, one planar and one nonplanar, implies that the system is conformationally flexible and that solid-state packing effects may influence the geometry of the seven-membered ring in $C_7Ph_7^+$.

Further calculations (Table 1) revealed that consecutive replacement of the phenyl substituents with hydrogens results in a decrease in the dihedral angle between the peripheral phenyls and the central C_7 ring (from 88° for $C_7Ph_7^+$ to 42° for $C_7PhH_6^+$), and an increase in the planarity of the tropylium ring. For example, in the C_2-optimized structure of the 1,2,4,6-tetraphenyltropylium cation, the central ring is essentially planar and the phenyl-to-central ring dihedral angles are 58° and 45° for the two adjacent phenyl moieties, **1** and **2**, and phenyls **4** and **6**, respectively. Steric repulsions between the central C_7-ring hydrogens and the *ortho*-hydrogens of the phenyl moieties prevent the electronically optimal coplanar arrangement between the two types of π systems. In fact, one might surmise that any nonplanar substituent would pucker the central C_7 ring, as shown by the average calculated (AM1) interplanar angles of 18° (γ) and 22° (ϕ) for the ground-state C_s-optimized structure of the permethylated derivative, $C_7Me_7^+$, which is almost 15 kcal mol^{-1} more stable than its planar conformer. We are unaware of any synthetic or crystallographic studies on this latter system. Ultimately, these results indicate that the geometrical features observed in the solid-state structure of $C_7Ph_7^+$ arise because of a compromise between steric congestion and the fractional loss in aromaticity one might anticipate as the ring distorts from planarity.[18, 19] Given the complex interaction between molecular structure and crystal packing forces, it is plausible that a planar crystal form of $C_7Ph_7^+$ may eventually be realized.

Table 1. Structural features of **1** and its derivatives.

Species	Point Symmetry	Mean γ [°]	Mean ϕ [°]	Mean propeller angle [°]	Enthalpy of formation [kcal mol^{-1}]
C_7Ph_7H[a]		55	35	–	–
C_7Ph_7H[b]	C_1	50	35	–	248.01
$C_7Ph_7^+$[a]		11	13	79	–
$C_7Ph_7^+$[b]	C_1	9	11	88	419.52
$C_7Ph_7^+$[b]	D_{7h}	0	0	90	419.71
1,2,4,6-$C_7H_3Ph_4^+$[b]	C_2	≈0	≈0	45, 58	309.24
1,2,4,6-$C_7H_3Ph_4^+$[b]	C_1	3	3	46, 56	309.48
1,3,5-$C_7H_4Ph_3^+$[b]	C_1	0	0	46	279.35
$C_7H_6Ph^+$[b]	C_1	0	0	42	232.52
$C_7Me_7^+$[b]	C_s	18	22	n.a.	168.53
$C_7Me_7^+$[b]	C_{7h}	0	0	n.a.	183.47
1,3,5-$C_7H_4Me_3^+$[b]	C_s	0	0	n.a.	182.46

[a] Structure data obtained from X-ray crystallographic data. [b] Structure data obtained from AM1 calculations.

In his pioneering studies, Olah noted that a plot of the ^{13}C NMR chemical shifts of the central ring carbons in the aromatic species $C_nH_n^{x\pm}$ ($n = 3-9$) established a linear correlation with the local π-electron density at these carbons.[20] Moreover, these data indicate a ^{13}C NMR shielding of about 14 ppm per extra 0.1 electron at these carbons. At the semiempirical level (using the AM1 Hamiltonian and Mulliken charges for the ring carbons) we have found that this correlation still holds, but that the proportionality factor is approximately 21 ppm per extra 0.1 electron. We also extended this quantitative relationship to the $C_nPh_n^{x\pm}$ series ($n = 3-7$), since phenyl substitution is apt to influence the charge delocalization within each system. In contrast to the earlier studies,[20] all calculations were performed on energy-minimized (AM1 Hamiltonian) structures, since for the larger rings, the peripheral phenyls are clearly not coplanar with the central ring. Computation of the Mulliken charges in the perphenylated series again revealed a reasonable correlation, with a ^{13}C NMR shielding of approximately 22 ppm per extra 0.1 electron at the central-ring carbons. In improving the level of theory from simple Hückel to semiempirical calculations, the results indicate that a particular change in ^{13}C chemical shift corresponds to a smaller change in total electron density (π and σ inclusive). We emphasize that the NMR data for such a series of anionic, neutral and cationic species cannot be acquired in the same solvent medium, a factor which introduces a degree of uncertainty in the relationship between ^{13}C resonances and electron density.

A further structural attribute of $C_nPh_n^{x\pm}$ ($n = 3-7$) molecular paddle-wheels that we have not yet addressed is the ability of the peripheral phenyl substituents to adopt either clockwise or anticlockwise orientations, a phenomenon which confers chirality on the system.[21] The interconversion of enantiomers of the pentaisopropylcobalticenium cation reported by Astruc et al. is a striking example of metallocenic chirality.[22] The pursuit of organometallic derivatives of $C_7Ph_7^+$, a logical extension of the studies conducted so far, remains an engaging challenge in view of the chiral nature of the $C_7Ph_7^+$ ligand and the severe steric effects in this highly hindered system. The application of the $C_7Ph_7^+$ ligand to various facets of organometallic chemistry is a focus of current research and will be reported in a forthcoming paper.

Experimental Section

All syntheses were performed under an atmosphere of dry nitrogen utilizing conventional benchtop and glovebag techniques. Solvents were dried and distilled according to standard procedures.[23] ^{1}H and ^{13}C NMR spectra were recorded on spinning samples, locked to a solvent signal, with a Bruker Avance DRX-500 spectrometer (^{1}H: 500.13 MHz, ^{13}C: 125.76 MHz). ^{19}F NMR spectra were acquired with a Bruker AC 300 spectrometer (^{19}F: 282.4 MHz). All NMR resonances were referenced to a residual proton signal of the solvent, to a ^{13}C solvent signal, or to an external trichlorofluoromethane signal. Electrospray ionization (ESI) and MS/MS spectra were acquired by a Micromass Quattro-LC triple-quadrupole mass spectrometer. For pneumatically assisted electrospray, samples were injected into a mobile phase consisting of 50/50 CH_3CN/H_2O flowing at 10 μL min^{-1}. Typical experimental conditions included a source temperature of 80 °C, an ESI probe voltage of 3.1 kV, and gas flow rates (N_2 at 100 psi) of approximately 60 L h^{-1} for the drying gas and 60 L h^{-1} for the ESI nebulizing gas. MS/MS experiments were performed with argon as the target gas, at a pressure of 1.9×10^{-3} mbar and a collision energy of 20 eV. Melting points (uncorrected) were determined on a Thomas Hoover melting point apparatus.

$[C_7Ph_7^+][CF_3CO_2^-] \cdot 2CF_3CO_2H$ (1): Bright orange-red needles of $C_7Ph_7^+Br^-$ were prepared from C_7Ph_7H and bromine in CCl_4, followed by treatment with acetonitrile containing 6% acetone, as outlined in the literature.[2] Subsequent digestion of $C_7Ph_7^+Br^-$ (352 mg, 0.50 mM) in a solution of trifluoroacetic acid followed by filtration and slow solvent evaporation over several days produced red plates of the title compound **1**. Yield: 260 mg (0.27 mmol, 54%, based on $C_7Ph_7^+Br^-$); m.p. 160 °C; ^{1}H NMR (CD_3CN, 500 MHz, 25 °C): $\delta = 6.89$ (d of d, $^1J = 8.1$ Hz, $^2J = 1.6$ Hz, 14 H, H(*ortho*)), 6.83 (m, 21 H, H(*meta*) and H(*para*); ^{13}C NMR (CD_3CN, 125 MHz, 25 °C): $\delta = 167.2$ (C_7-ring)), 141.5 (C-*ipso*)), 130.4 (C-*ortho*), 127.8 (C-*para*), 127.5 (C-*meta*); ^{19}F NMR (CD_3CN, 282.4 MHz, 25 °C): $\delta = -76.2$ (s); MS (+ESI): m/z (%) = 623.2 (100) $[M^+]$; MS (ESI MS/MS of $[M^+]$ ion): m/z (%) = 545.2 (100) $[M - C_6H_6]^+$, 533.2 (7) $[M - C_7H_6]^+$, 467.2 (18) $[M - 2C_6H_6]^+$, 455.2 (8) $[M - 2C_7H_6]^+$, 367.1 (11), 343.1 (6), 291.1 (8), 166.9 (35); $C_{55}H_{37}F_9O_6$ (964.85): calcd C 68.47, H 3.86; found C 68.49, H 4.00.

Crystallographic data for $[C_7Ph_7^+][CF_3CO_2^-] \cdot 2CF_3CO_2H$: X-ray crystallographic data for **1** were obtained from a single crystal sample, which was mounted on a glass fiber. Data were collected on a P4 Siemens diffractometer, equipped with a Siemens SMART 1K charge-coupled device (CCD) area detector (employing the program SMART[24]) and a rotating anode utilizing graphite-monochromated Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The crystal-to-detector distance was 39.91 mm, and the data collection was carried out in 512 × 512 pixel mode, by 2 × 2 pixel binning. The initial unit cell parameters were determined by a least-squares fit of the angular settings of the strong reflections, collected by 4.5° scans in 15 frames over three different parts of reciprocal space (45 frames total). One complete hemisphere of data was collected, to better than 0.8 Å resolution. On completion of the data collection, the first 50 frames were recollected in order to improve the decay analysis. Processing was carried out by the program SAINT,[25] which applied Lorentz and polarization corrections to three-dimensionally integrated diffraction spots. The program SADABS[26] was utilized for the scaling of diffraction data, the application of a decay correction, and an empirical absorption correction based on redundant reflections. The structure was solved by use of the direct method (procedure outlined in the Siemens SHELXTL program library[27]) followed by full-matrix least-squares refinement on F^2 with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were added as fixed contributors at calculated positions, with isotropic thermal parameters based on the atoms to which they were bonded. (For cell parameters and intensity collection refer to Table 2.)

Rotational disorder of the fluorine atoms F7, F8 and F9 in one of the CF_3CO_2H molecules and a conformational disorder involving C82, O3 and O4 in the other solvate molecule was established by refinement of the population factors F7, F8, F9 and F7A, F8A, F9A and C82, O3, O4 and C82A, O3A and O4A, respectively, with a final occupancy ratio of approximately 50:50. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100958. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Table 2. Crystallographic data for **1**.

	1
empirical formula	$C_{55}H_{37}F_9O_6$
M_r	964.85
description	red plate
crystal size	0.22 × 0.17 × 0.06 mm
T [K]	210(2)
λ [Å]	(Mo$_{K\alpha}$) 0.71073
crystal system	monoclinic
space group	$P2_1/n$
a [Å]	11.3060(2)
b [Å]	21.2346(4)
c [Å]	20.9158(1)
α [°]	90.0
β [°]	104.773(1)
γ [°]	90.0
V [Å^3]	4855.44(1)
Z	4
ρ_{calcd} [g cm^{-3}]	1.320
abs coeff [mm^{-1}]	0.108
scan mode	ϕ and ω scans
F(000)	1984
θ range for collection [°]	1.39–23.00
index ranges	$-14 \le h \le 14$
	$-26 \le k \le 24$
	$-26 \le l \le 26$
no. reflns collected	29358
no. independent reflns	6741
R(int)	0.0719
refinement method	full-matrix least-squares on F^2
weighting scheme	$w = 1/[\sigma^2 F_o^2 + (0.0496P((F_o^2 + 2F_c^2)/3))^2 + 2.9838((F_o^2 + 2F_c^2)/3))^2]$
data/restraints/parameters	6696/15/687
goodness-of-fit on F^2	1.052
final R indices ($I > 2\sigma(I)$)[a]	$R1 = 0.0613$; $wR2 = 0.1237$
R indices (all data)[a]	$R1 = 0.1102$; $wR2 = 0.1483$
mean shift/error	< 0.001
max. shift/error	< 0.001
rel. trans. (max., min.)	0.9886, 0.8122
extinction coeff	0.0037(3)
largest diff. peak [e Å^{-3}]	0.231
largest diff. hole [e Å^{-3}]	−0.302

[a] $R1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{0.5}$.

Computational methods: All computed structures were geometry-optimized with the restricted Hartree-Fock assumption using the AM1 Hamiltonian[16] found in the Spartan computational package.[17] Mulliken point charges were calculated on the resultant wavefunctions and stationary points were confirmed to be minima by vibrational frequency analysis. Planar structures were attained for all members of the $C_nH_n^{x\pm}$ ($n = 3-7$) and the $C_nPh_n^{x\pm}$ ($n = 3-6$) series. In the latter systems, all species possessed a propeller-like arrangement of the peripheral phenyl rings such that the dihedral angle between the phenyl rings and the central ring of the molecule increased as the value of n increased. Conformational searches were conducted for $C_7H_{7-n}Ph_n^+$ ($n = 1,3,4$, and 7) cations, utilizing symmetry constraints to identify the higher symmetry molecules. Two conformers of $C_7Ph_7^+$ were located (ΔH_f (C_1) = 419.52 and ΔH_f (D_{7h}) = 419.71 kJ mol^{-1})[28] and based on the energy difference between the two stationary points, the puckered C_1 structure represents the global minimum on the potential energy surface for the heptaphenylcycloheptatrienyl cation. Of the two conformers of 1,2,4,6-$C_7H_3Ph_4^+$ that were identified (ΔH_f (C_2) = 309.24 and ΔH_f (C_1) = 309.48 kJ mol^{-1}), the planar configuration is slightly preferred over the nonplanar form. It is evident from the results pertaining to $C_7Ph_7^+$ and 1,2,4,6-$C_7H_3Ph_4^+$ that the potential energy surface near each of the minima is flat, and accordingly, the convergence criteria were altered and the maximum step size reduced during the geometry optimization in order to prevent premature identification of the minima. Given the small energy differences that separate the equilibrium structures, it should be emphasized that the topology of these regions may be sensitive to changes in the level of calculation.

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