Electronic Supplementary Information

Gold(I) Mediated Rearrangement of [7]-Helicene to Give a Benzo[cd]pyrenium Cation Embedded in a Chiral Framework

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Supplementary Figures

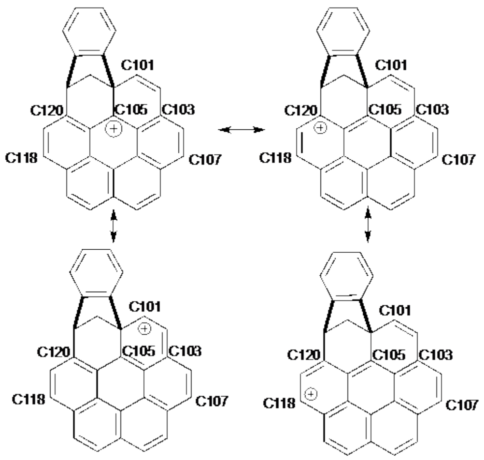


Figure S1. Selected mesomeric forms of **3**.

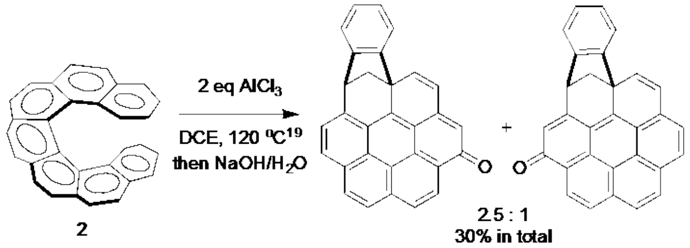


Figure S2. Previous rearrangement of [7]-helicene.[S1]

Synthesis of $[C_{30}H_{17}][Al(OC(CF_3)_3)_4]$ (3)

$Ag[Al(OC(CF_3)_3)_4]$ (56.8 mg, 0.0528 mmol), [7]-helicene[S1] (20.0 mg, 0.0528 mmol) and AuCl (12.3 mg 0.0528 mmol) were weighed in a glove box into a special two-flask fritplate vessel with J. Young valves. CH_2Cl_2 was condensed to the reaction mixture at –40 °C. The mixture was stirred for 48 h at room temperature. The colour of the solution turned from colorless to green and the reaction was sonicated for further 50 h. A grayish precipitate was observed and after filtration black crystals of **3** (60 mg, 0.045 mmol, 85 % yield) precipitated at –20 °C. The product was observed to be dark green in dilute solution. IR (crystals): ν (intensity) = 447 (vw), 512 (vw), 537 (vw), 572 (vw), 727 (w), 742 (vw), 758 (vw), 834 (vw), 860 (vw), 875 (vw), 973 (vs), 1080 (vw), 1169 (vw), 1221 (vs), 1242 (vs), 1276 (vs), 1299 (vs), 1352 (w), 1378 (w), 1390 (vw), 1455 (vw), 1421 (vw), 1455 (vw), 1512 (vw), 1541 (vw), 1590 (w), 1604 (vw), 1631(vw) cm^{-1}. ^{19}F NMR (376.49 MHz, CD_2Cl_2, 298 K): $\delta = -75.8$ (s, 36 F, 4 × CCF_3). ^{27}Al (104.27 MHz, CD_2Cl_2, 298 K): 34.6 (s, $Al(OC(CF_3)_3)_4$). ^1H and ^{13}C NMR and assignments are shown in the Table below.

X-ray data

The following Figures show some additional views of the molecular and crystal structure of **3**.

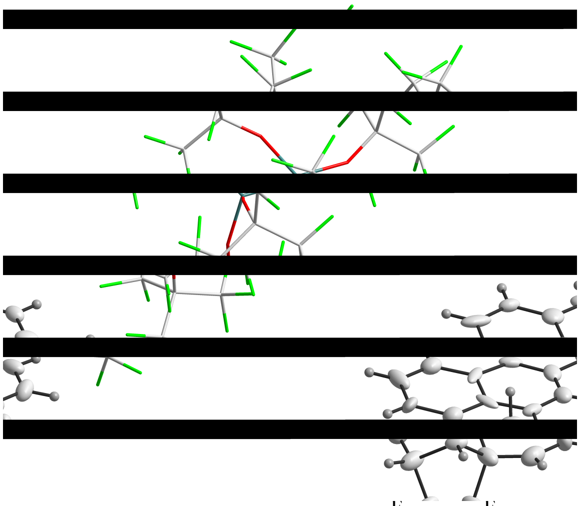


Figure S3. Solid state structure $[C_{30}H_{17}][Al(OR^F)_4]$ ($R^F = C(CF_3)_3$) (**3**). Thermal ellipsoids of the cation are drawn at the 50% probability level. The co-crystallised solvent molecule (CH_2Cl_2) was omitted for clarity.

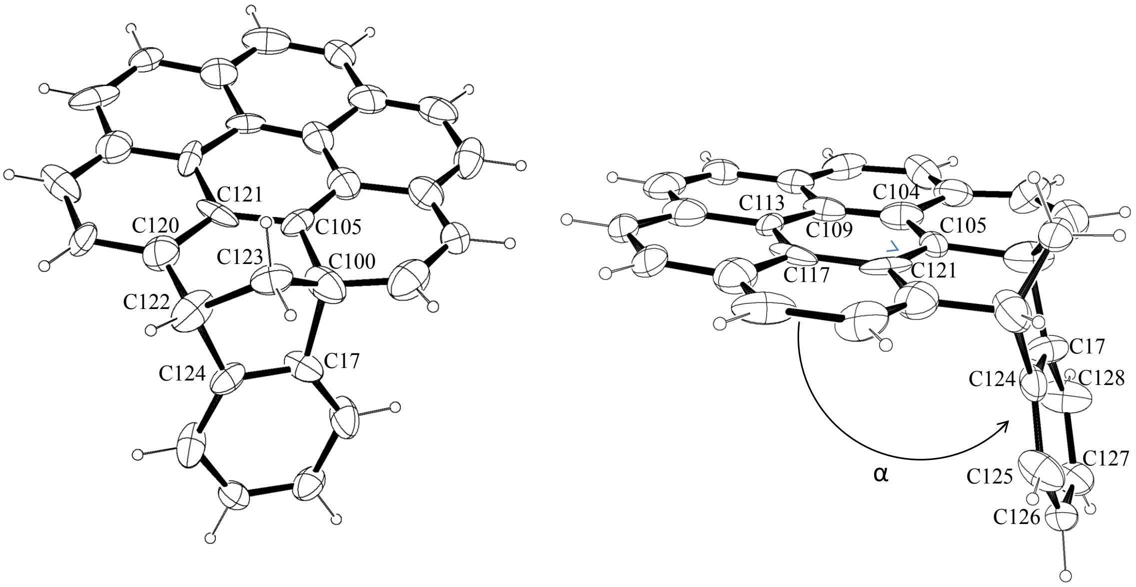


Figure S4. left: front view of the $[C_{30}H_{17}]^+$ cation; right: side view of the carbocation. α describes the angle between the two planes (plane 1 containing C104, C105, C121, C117, C113, C109; plane 2 containing C124, C125, C126, C127, C128, C129.) Thermal ellipsoids of the cation are drawn at the 50% probability level. The counterion and the co-crystallized solvent molecule were omitted for clarity. Selected bond length [pm] and angles [°]: C122-C123 157.6(8), C123-C100 151.2(7), C122-C124 154.2(7), C100-C17 155.1(7), C122-C120 146.6(8), C100-C105 159.4(8); C120-C122-C123 111.3(8), C105-C100-C123 108.3(5), C122-C123-C100 100.0(4).

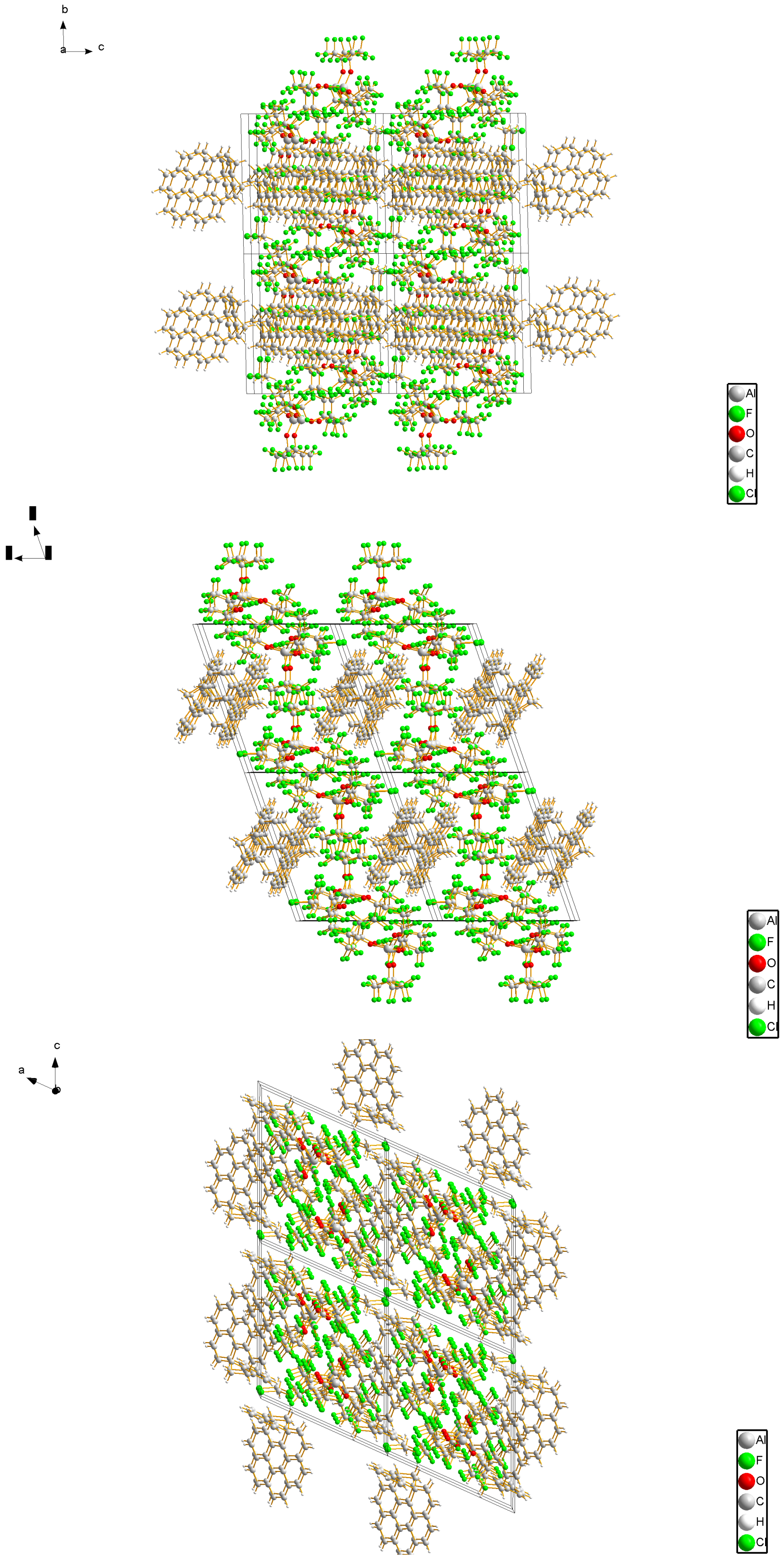


Figure S5. Views of the solid state arrangement of **3** along the axis a, b and c.

Details of the Crystal Structure Determination:

Single crystals were mounted on MicroMounts between room temperature and –25 °C in perfluoroether oil under N_2, using a custom-built low-temperature mounting device. Crystallographic data were collected on a Bruker APEX2 Quazar CCD area detector diffractometer using sealed-tube Mo-Kα X-ray (0.71073Å) sources. Structures were solved by direct methods in the SHELXS/XL[S2] program or with OLEX2[S3] and refined by least squares on weighted F2 values for all reflections. If hydrogens were not found on the difference Fourier map, they were restrained to calculated positions and refined isotropically based on a riding model (HFIX). ORTEP[S4] and DIAMOND[S5] were used for the graphical representation of the crystal structure. The CCDC number 865402 contains the supplementary crystallographic data for this paper. The data can be obtained from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Refinement details of the crystal structure determination of **3**.

Compound number	**3**
CCDC	865402
Empirical formula	C47H19AlCl2F36O4
Formula weight	1429.50
Temperature/K	100(2)
Crystal system	triclinic
Space group	*P1*
a/Å	14.1452(6)
b/Å	14.4666(5)
c/Å	14.8725(6)
α/°	80.425(2)
β/°	63.572(2)
γ/°	68.429(2)
Volume/Å3	2534.46(17)
Z	2
ρcalcmg/mm3	1.873
m/mm–1	0.325
F(000)	1408,0
Crystal size/mm3	0.07 × 0.06 × 0.02
2Θ range for data collection	4.3 to 51.36°
Index ranges	–15 ≤ h ≤ 17, –17 ≤ k ≤ 17, –16 ≤ l ≤ 18
Reflections collected	29651
Independent reflections	9551 [R(int) = 0.0402]
Data/restraints/parameters	9551/0/811
Goodness-of-fit on F2	1.042
Final R indexes [I > = 2σ (I)]	R1 = 0.0710, wR2 = 0.1683
Final R indexes [all data]	R1 = 0.1164, wR2 = 0.1923
Largest diff. peak/hole [e Å–3]	1.64/–0.54

NMR data

Table S2 NMR assignments for cation **3**

δ ^{1}H (ppm)[a]	δ ^{13}C (ppm)[b]	Assignment[c]	δ ^{1}H (ppm)[a]	δ ^{13}C (ppm)[b]	Assignment[c]
5.53 (1H, dd, J = 4.2 Hz	51.4	C122	7.20 (1H, ddd, J = 2 x 7.3, 1.4 Hz)	129.5	C126
-	57.9	C100	8.75 (1H, d, J = 8.5 Hz)	129.6	C116
3.98 (1H, dd, J = 10.9, 4.3 Hz), 3.26 (1H, dd, J = 10.9, 0.7 Hz)	70.4	C123	-	129.6	C111
-	121.2	C104	-	129.8	C108
-	121.5	C113	8.9 (1H, d, J = 8.5 Hz)	134.2	C110
-	122.3	C109	8.78 (1H, d, J = 8.7 Hz)	134.4	C115
6.90 (1H, m)	123.3	C128	-	139.9	C124
-	123.5	C121	-	140.4	C112
-	123.9	C117	9.13 (1H, d, J = 7.8 Hz)	144.8	C118
8.58 (1H, d, J = 7.8 Hz)	126.5	C119	-	146.6	C103
6.86 (1H, ddd, J = 2 x 7.3, 1.1 Hz)	126.7	C127	9.38 (1H d, J = 8.1 Hz)	148.7	C107
7.72 (1H, m)	128.5	C125	7.98 (1H, d, J = 9.3 Hz)	149.6	C101
8.60 (1H, d, J = 8.1 Hz)	128.7	C106	-	154.9	C120
8.63 (1H, d, J = 8.7 Hz)	128.9	C114	-	167.7	C105
8.25 (1H, d, J = 9.3 Hz)	129.4	C102			

[a] Measured at 400 MHz in CD_2Cl_2; [b] Measured at 100 MHz in CD_2Cl_2; [c] Numbering based on the scheme of the crystal structure (see Figure 1).

Computational details – NMR and CM5 charges

Calculations were carried out using Gaussian 09 Revision D.1.[S6] Full details of the B3LYP/6-311++G(d,p)/GAIO/SCRF=dichloromethane calculation are available *via* the doi: 10.6084/m9.figshare.745374 and at the ωB97Xd/6-311++G(d,p)/SCRF=dichloromethane level at doi: 10.6084/m9.figshare.745376

CM5 charges were computed at the ωB97Xd/6-311++G(d,p)/SCRF=dichloromethane level using the method reported in A. V. Marenich, S. V. Jerome, C. J. Cramer, D. G. Truhlar, *J. Chem. Theor. Comput.* **2012**, *8*, 527-541 and are archived at doi: 10.6084/m9.figshare.748776

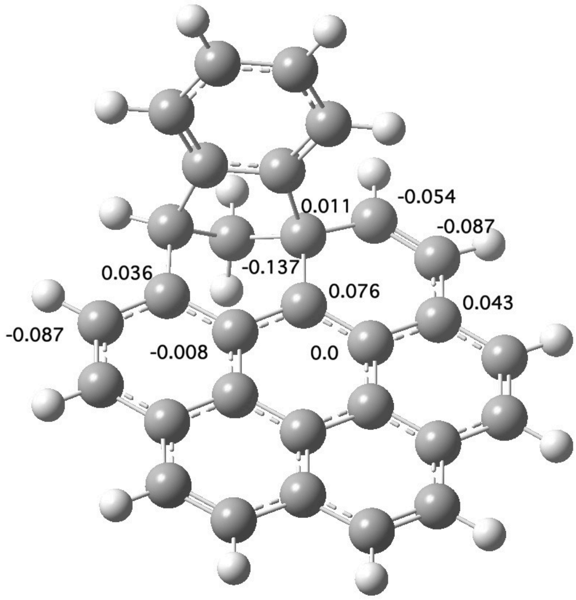


Figure S6. Selected CM5 charges.

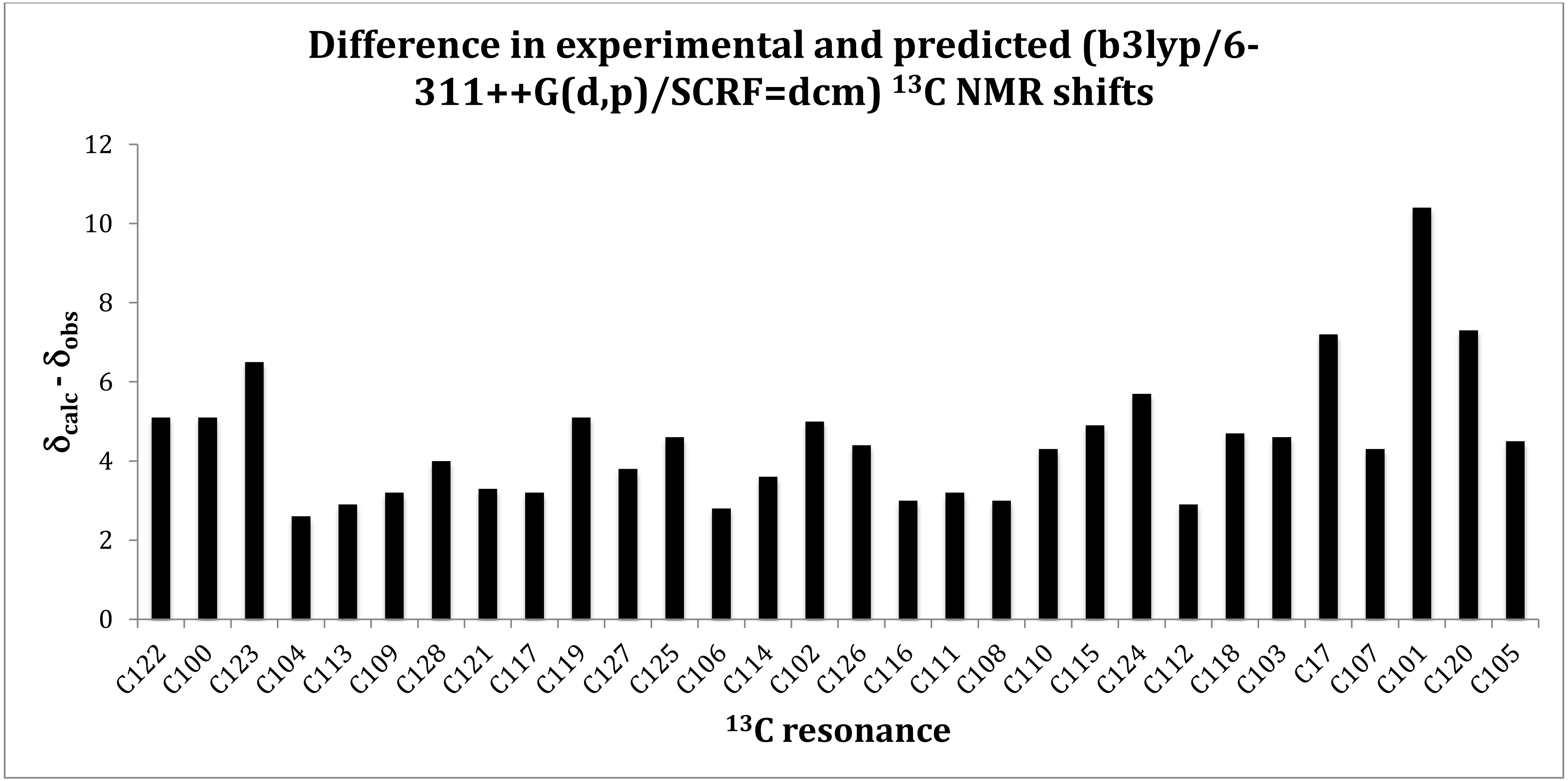
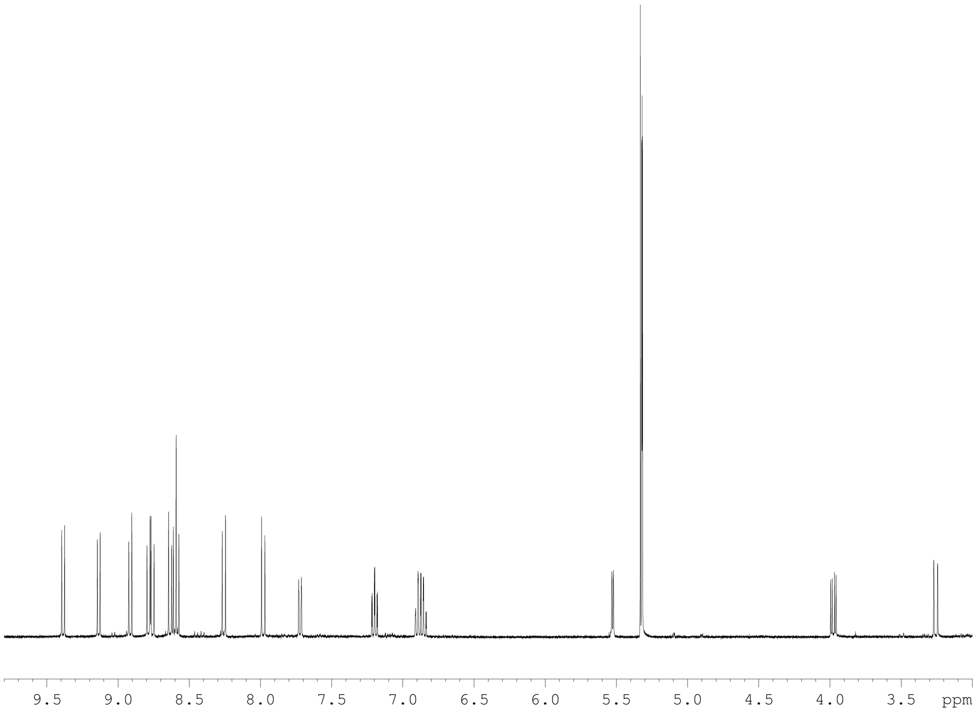
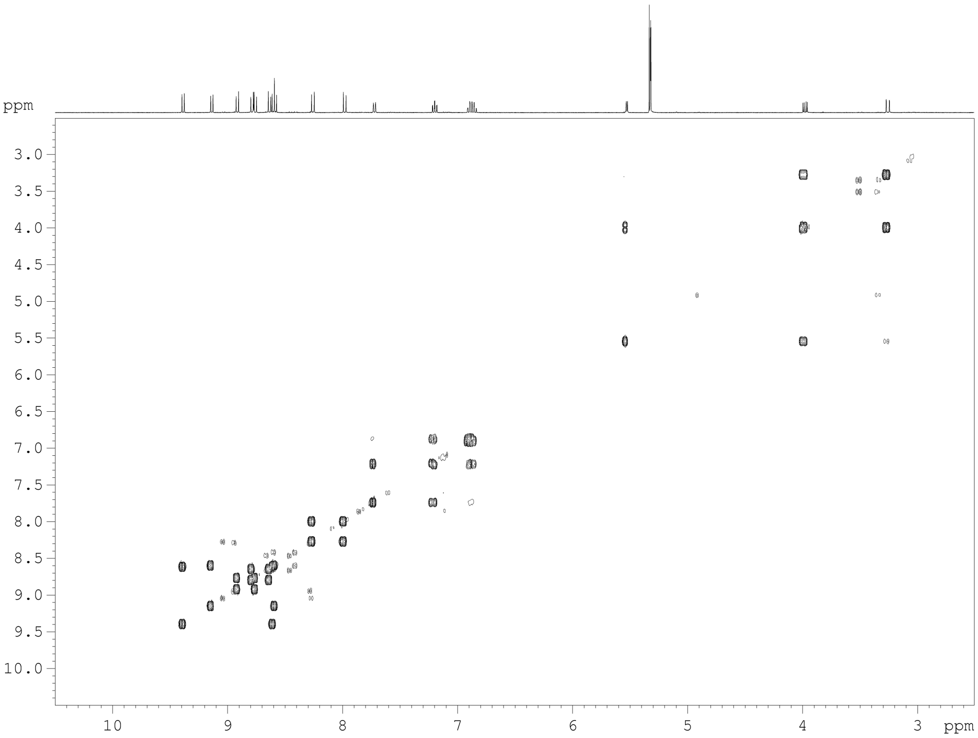


Chart S1 Comparison of observed and predicted ^{13}C NMR shifts.

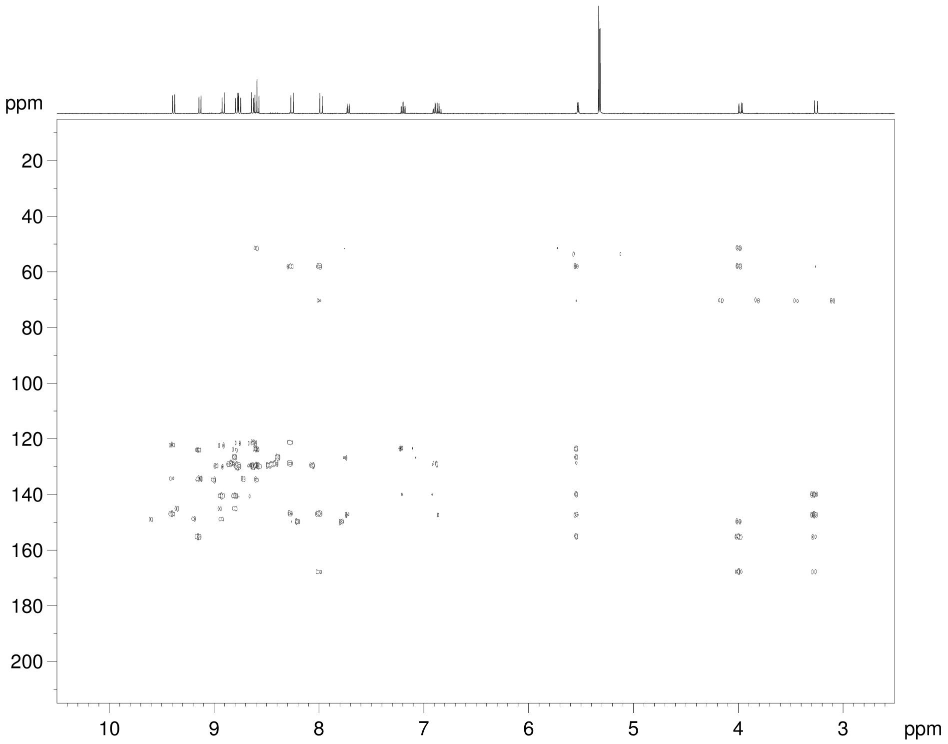
NMR spectra



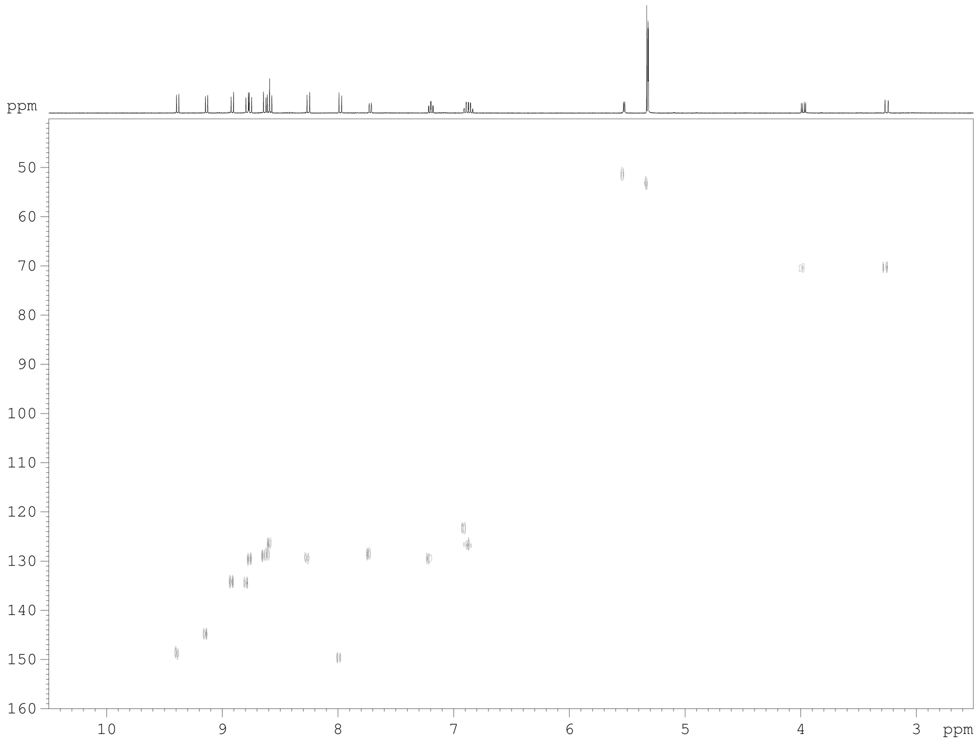
^{1}H NMR spectrum (400.17 MHz) of **3** in CD_2Cl_2 at room temperature.



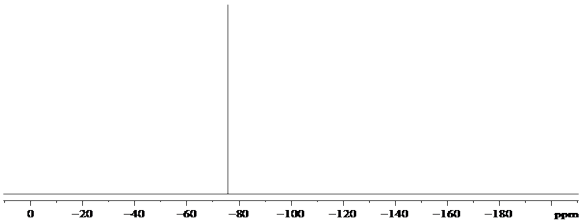
^{1}H, ^{1}H COSY NMR spectrum (400.17 MHz) of **3** in CD_2Cl_2 at room temperature.



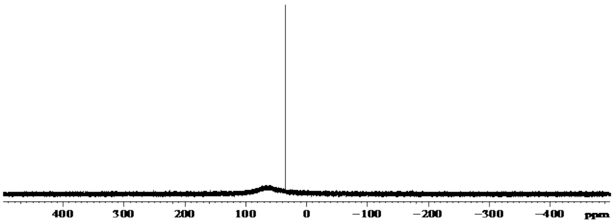
^{1}H, ^{13}C HMBC NMR (^{1}H: 400.17, ^{13}C: 100.62 MHz, optimized for 8 Hz) of **3** in CD_2Cl_2 at room temperature.



^{1}H ^{13}C HSQC NMR spectrum (^{1}H: 400.17, ^{13}C: 100.62 MHz, optimized for 145 Hz) of **3** in CD_2Cl_2 at room temperature.



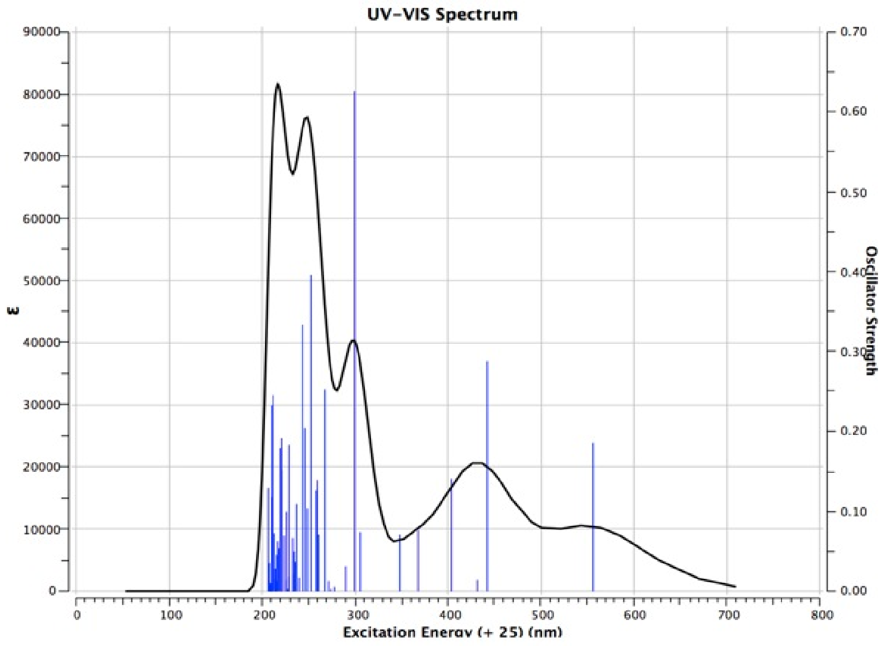
^{19}F-NMR spectrum (376.54 MHz) of **3** in CD_2Cl_2 at 298K.



^{27}Al-NMR spectrum (104.27 MHz) of **3** in CD_2Cl_2 at 298K (the broad resonance is a background signal from the probehead).

Computational Details - UV-vis

The UV-vis spectrum of **3** was computed using Gaussian 09 Revision D.1.[S6] Full details of the cam-B3LYP/6-311++G(d,p) scrf(cpcm,solvent=dichloromethane) calculation are available *via* the shortdoi: n6n. The ωB97XD level gave an almost identical result (shortdoi: n6p).



Computational details – ring currents

All calculations regarding the molecular ring currents have been performed with the Turbomole program package[S7] version 6.3. The structure optimization of the mono-cation **3** was carried out using RI-DFT with the BP86 density functional and def2-SV(P) basis sets on all elements. The structure of the mono-anion [**3**]$^{2-}$ was optimized starting from the minimum structure of **3**. Thereby there were only very small changes in the geometric parameters.

The current densities of **3** and [**3**]$^{2-}$ were calculated in terms of gauge independent atomic orbitals (GIAO) using Turbomoles mpshift routine with the (hidden) flag $gimic. Further non-standard settings were $denconv 1.0D-8 and $scfconv 7, and $grid m4. Current density vectors **j** have been calculated with the programme GIMIC.[S8]

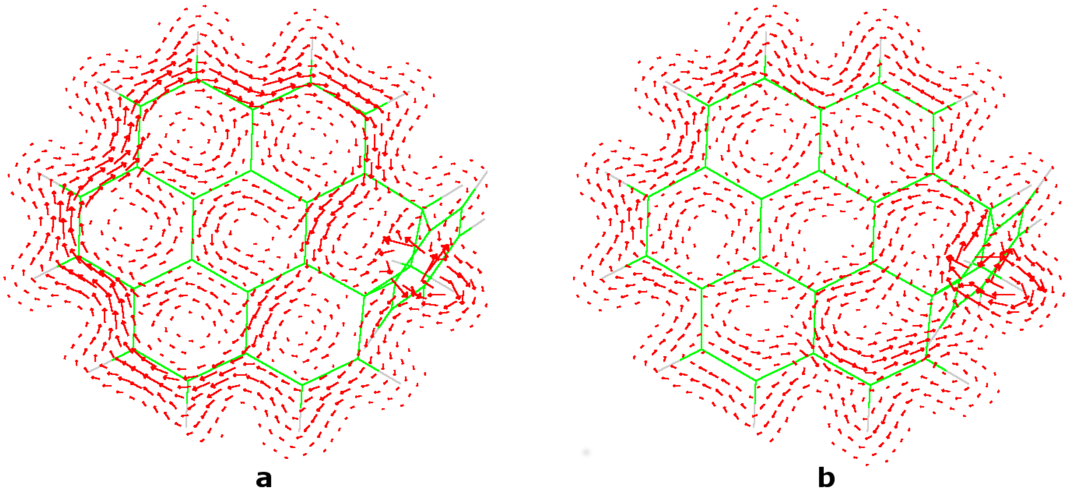


Figure S7. Magnetically induced current density vectors (red) a) in the mono-cation **3** and b) in the mono-anion [**3**]$^{2-}$ when a magnetic field perpendicular to the main molecular plane of 1 T field strength is applied. Shown are current vectors about 0.53 Å above the molecular plane, resulting mainly from the contribution from π orbitals. The total circulating current in the mono-anion [**3**]$^{2-}$ integrates to a 17 nAT^{-1} diamagnetic contribution and –14 nAT^{-1} paramagnetic contribution. Therefore overall the current is diamagnetic and amounts to 3 nAT^{-1}, which is considerably less than in the cation (in agreement with Hückel's rule). Since the paramagnetic contribution does not overly change in comparison with the cation, it should not be considered anti-aromatic.

Computational details – mechanistic study

Calculations were carried out using Gaussian 09 Revision D.01.[S6] Full details of the ωb97xd/6-311g(d,p) calculations for **2**, the transition state and **4** are archived at shortdoi: n8m, n8n and n8p respectively, and for cations **5** **7** and **3** at shortdoi: n7g n7f and n7d respectively.

References

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