Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Site-selective stepwise reduction of a corannulene-based chiral molecular nanographene with Na metal: An X-ray diffraction and computational study

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Content

I. Materials and Methods

All manipulations were carried out using break-and-seal and glove-box techniques under an atmosphere of argon.[1] Tetrahydrofuran (THF) and hexanes (Sigma Aldrich) were dried over Na/benzophenone and distilled prior to use. Tetrahydrofuran-d_8 (≥99.5 atom %D, Sigma Aldrich) was dried over NaK_2 alloy and vacuum-transferred. Sodium (99.9 %) and 18-crown-6 ether (99 %) were purchased from Sigma Aldrich and used as received. $C_{76}H_{64}$ (**1**) was prepared and purified according to the previously reported procedures.[2] Crystals of **1**·0.5(CH_3NO_2) were obtained by sublimation of **1** at 270 °C over two weeks in 70% yield. The UV-Vis spectra were recorded on a Thermo Scientific Evolution 201 UV-Visible spectrophotometer. The ^{1}H NMR spectra were recorded on a Bruker Ascend-500 spectrometer (500 MHz for ^{1}H). Chemical shifts (δ) are reported in parts per million (ppm) and referenced to the resonances of the corresponding solvent used. The low-temperature NMR experiment was controlled by a Cryo Diffusion cryogenic tank probe, and liquid N_2 was used as a cooling source. The presence of the interstitial hexane molecules coupled with extreme air- and moisture sensitivity of the crystals prevented obtaining elemental analysis data for **2**·0.5C_6H_{14}.

[{Na^+(18-crown-6)(THF)}$_2$(1^{2-})]·0.5C_6H_{14} (2·0.5C_6H_{14})

THF (1.5 mL) was added to a customized glass system containing excess Na (0.5 mg, 0.022 mmol), 18-crown-6 ether (1.2 mg, 0.005 mmol), and **1** (2.0 mg, 0.002 mmol). The reaction mixture was allowed to stir under argon at 25 °C for 24 hours in a closed system. The initial yellow color of the solution turned to green after 20 minutes, further deepened to dark brown after 1 hour and remained the same until the reaction was stopped. The mixture was filtered, and the dark-brown filtrate was layered with 1.2 mL of anhydrous hexanes. The ampule was sealed and stored at 5 °C. After 5 days, dark-brown block-shaped crystals were present in good yield. Yield: 4.8 mg, 70%. UV-Vis (THF, λ_{max}, nm): 330, 495, 646. ^{1}H NMR (THF-d_8, –80 °C, δ, ppm): 0.83 (9H, $\mathbf{1}^{2-}$), 1.16 (18H, $\mathbf{1}^{2-}$), 1.19 (9H, $\mathbf{1}^{2-}$), 1.32 (9H, $\mathbf{1}^{2-}$), 3.82 (1H, $\mathbf{1}^{2-}$), 4.02 (1H, $\mathbf{1}^{2-}$), 4.16 (1H, $\mathbf{1}^{2-}$), 4.39 (1H, $\mathbf{1}^{2-}$), 4.57 (1H, $\mathbf{1}^{2-}$), 4.69 (1H, $\mathbf{1}^{2-}$), 5.00 (1H, $\mathbf{1}^{2-}$), 5.25 (2H, $\mathbf{1}^{2-}$), 5.42 (1H, $\mathbf{1}^{2-}$), 6.37 (1H, $\mathbf{1}^{2-}$), 6.54 (1H, $\mathbf{1}^{2-}$), 6.65 (3H, $\mathbf{1}^{2-}$), 6.89 (1H, $\mathbf{1}^{2-}$), 7.21 (2H, $\mathbf{1}^{2-}$), 7.52 (1H, $\mathbf{1}^{2-}$).

II. UV-Vis Spectroscopic Investigation

Sample preparation: THF (2.0 mL) was added to an airtight storage ampule containing Na metal (0.50 mg, 0.022 mmol), 18-crown-6 (0.20 mg, 7.5×10^{-4} mmol), and **1** (0.30 mg, 3.0×10^{-4} mmol); and UV-Vis spectra were monitored at different reaction times (total 24 hours) at room temperature.

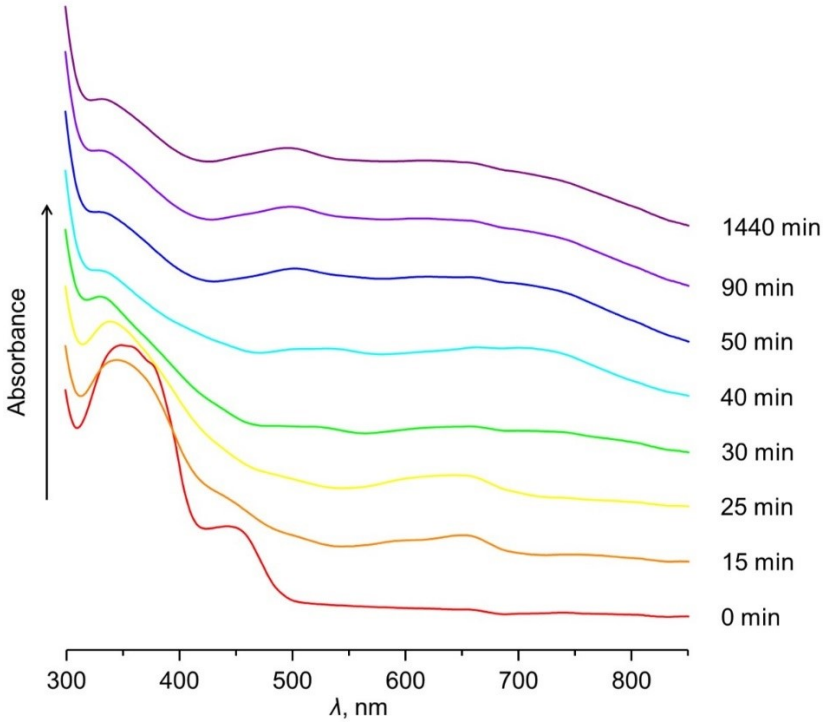


Figure S1. UV-Vis spectra of Na/18-crown-6/**1** in THF at 25 ℃.

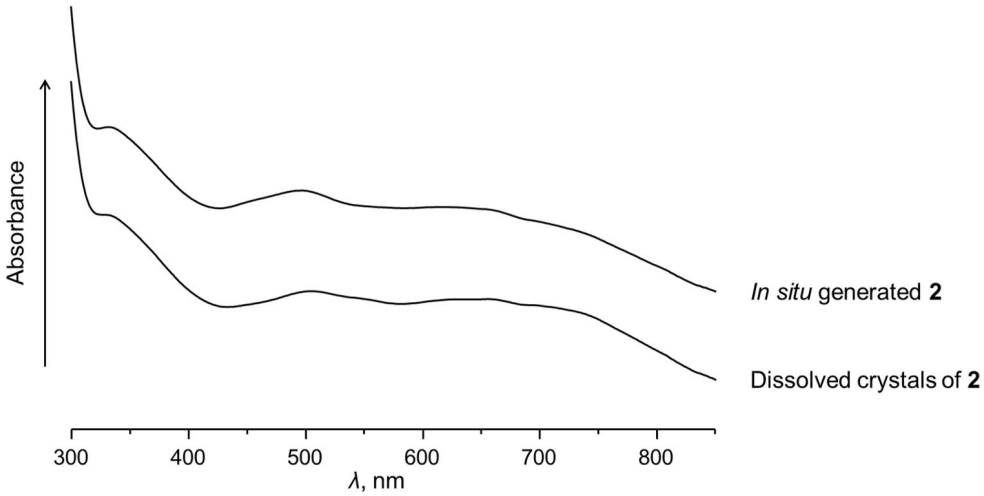


Figure S2. UV-Vis spectra of i*n situ* generated **2** and crystals of **2** dissolved in THF at 25 ℃.

III. NMR Spectroscopic Investigation

Sample preparation: Crystals of **2** (3.0 mg) were washed several times with hexanes, dried *in-vacuo*, and dissolved in THF-d_8 (0.70 mL). The resulting solution was transferred to an NMR tube that was sealed under argon.

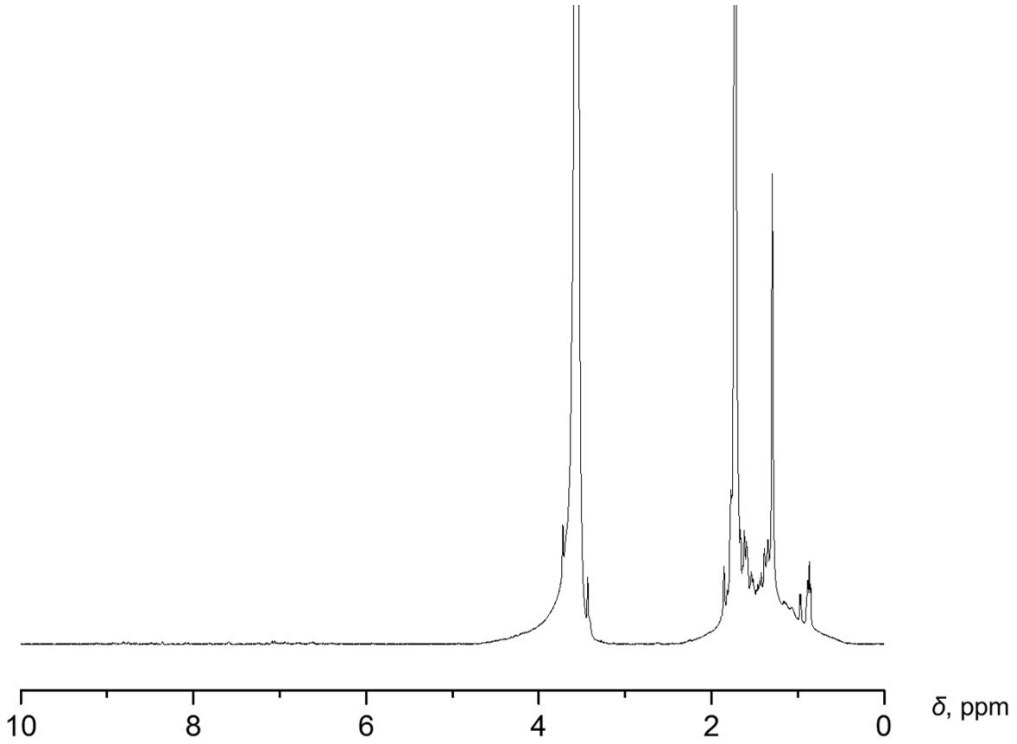


Figure S3. ^{1}H NMR spectrum of **2** in THF-d_8 at 25 °C.

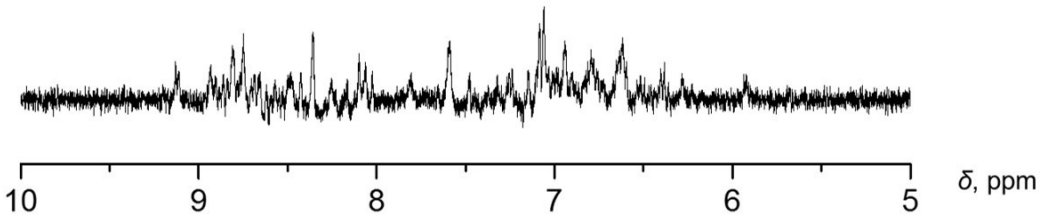


Figure S4. ^{1}H NMR spectrum of **2** in THF-d_8 at 25 °C, aromatic region.

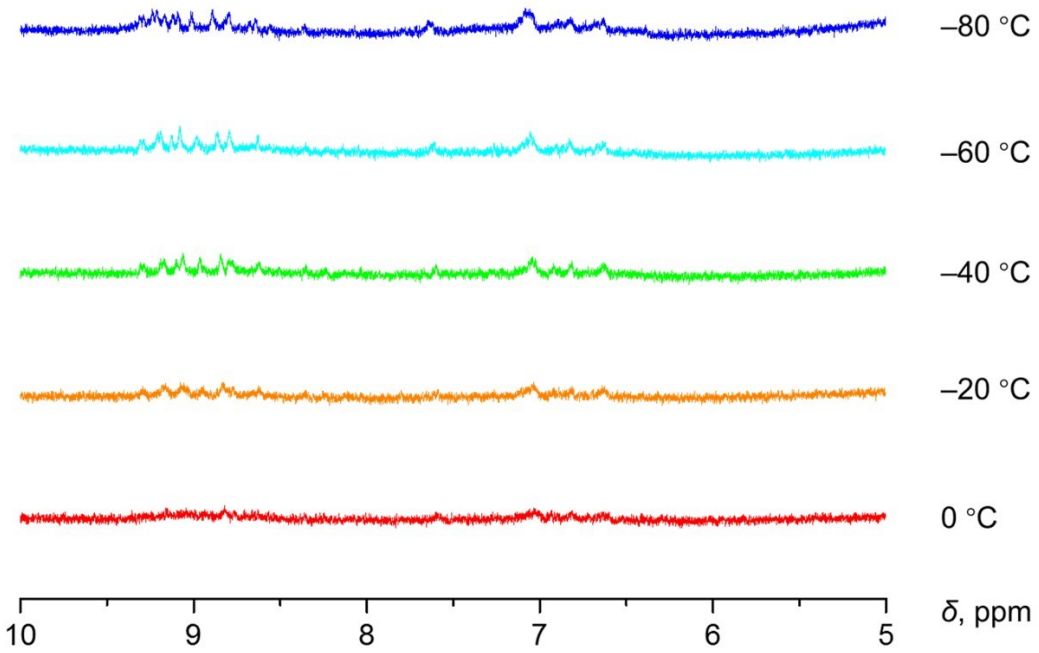


Figure S5. Variable temperature ^{1}H NMR spectra of **2** in THF-d_8, aromatic region.

Sample preparation: THF-d_8 (0.60 mL) was added to an NMR tube containing excess Na metal (2.0 mg, 0.087 mmol) and **1** (2.0 mg, 0.002 mmol). The tube was sealed under argon. After 50 minutes, the ^{1}H NMR spectrum of *in situ* generated $\mathbf{1}^{2-}$ was collected.

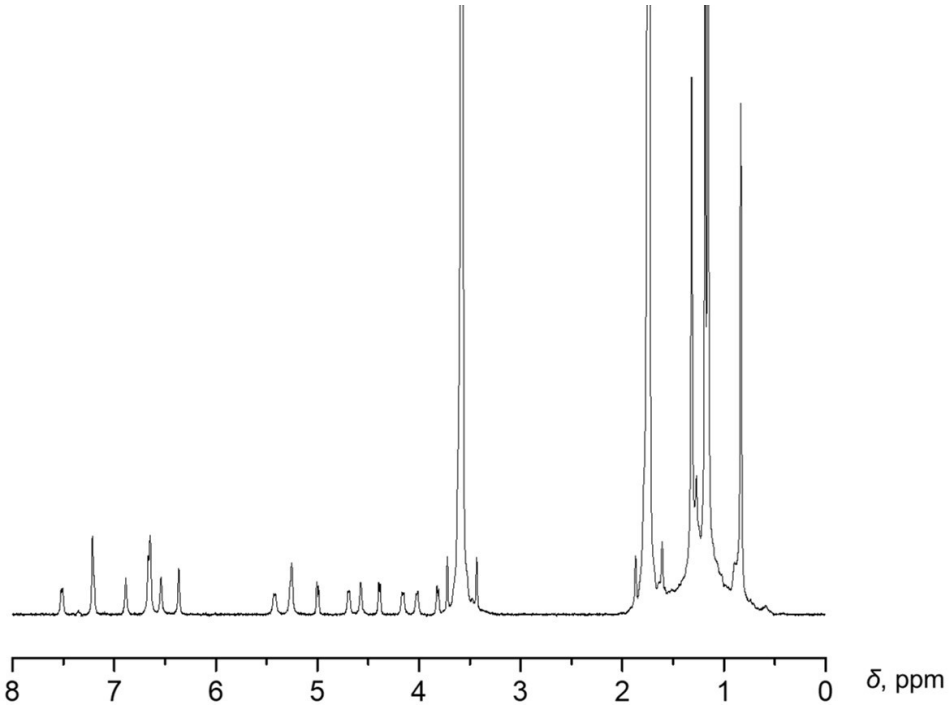


Figure S6. ^{1}H NMR spectrum of *in situ* generated $\mathbf{1}^{2-}$ in THF-d_8 at –80 °C.

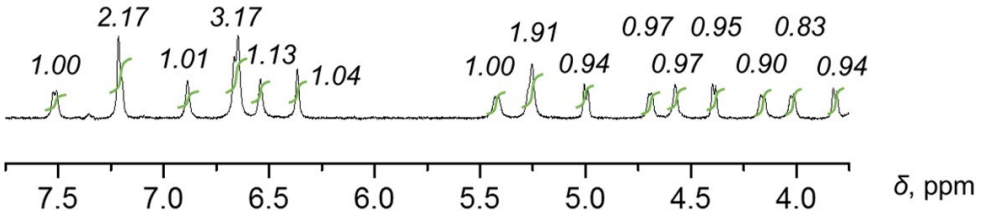


Figure S7. ^{1}H NMR spectrum of *in situ* generated $\mathbf{1}^{2-}$ in THF-d_8 at –80 °C, aromatic region.

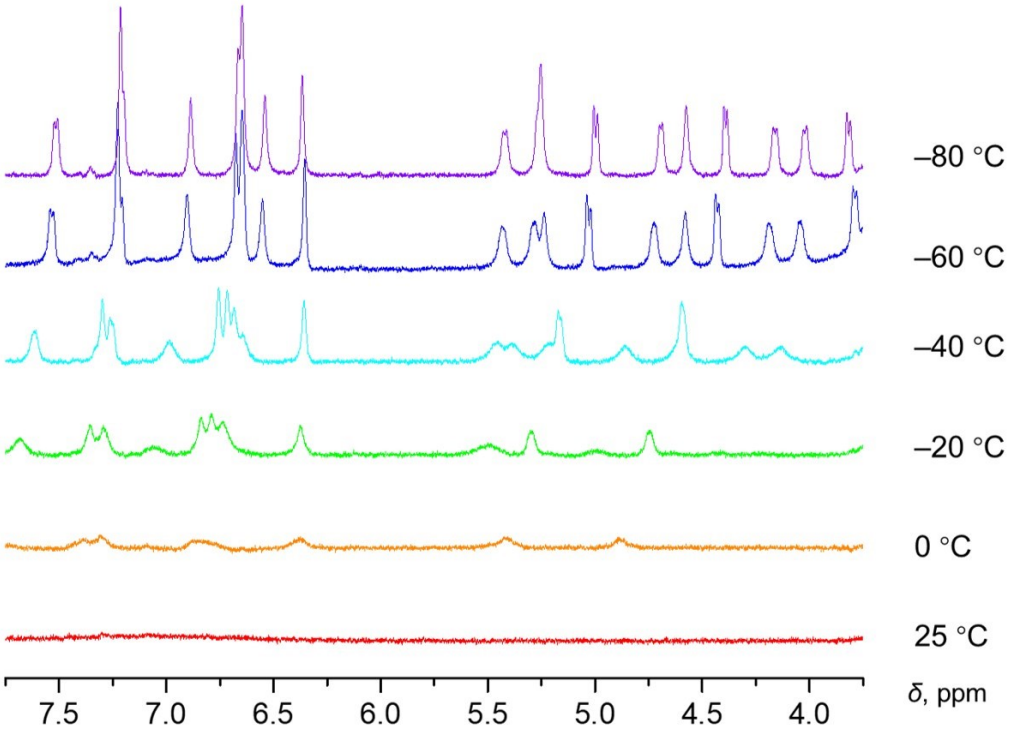


Figure S8. Variable-temperature ^{1}H NMR spectra of *in situ* generated $\mathbf{1}^{2-}$ in THF-d_8, aromatic region.

IV. Redox Reversibility Study

Sample preparation: THF-d_8 (0.60 mL) was added to an NMR tube containing excess Na metal (2.0 mg, 0.087 mmol) and **1** (2.0 mg, 0.002 mmol). The tube was sealed under argon. The ^{1}H NMR spectra of **1** were collected immediately, and that of *in situ* generated $\mathbf{1}^{2-}$ were collected after 50 minutes. The solution was then exposed to dry oxygen by opening the tube. The resulting off-white solution was checked as the spectrum of a quenched product.

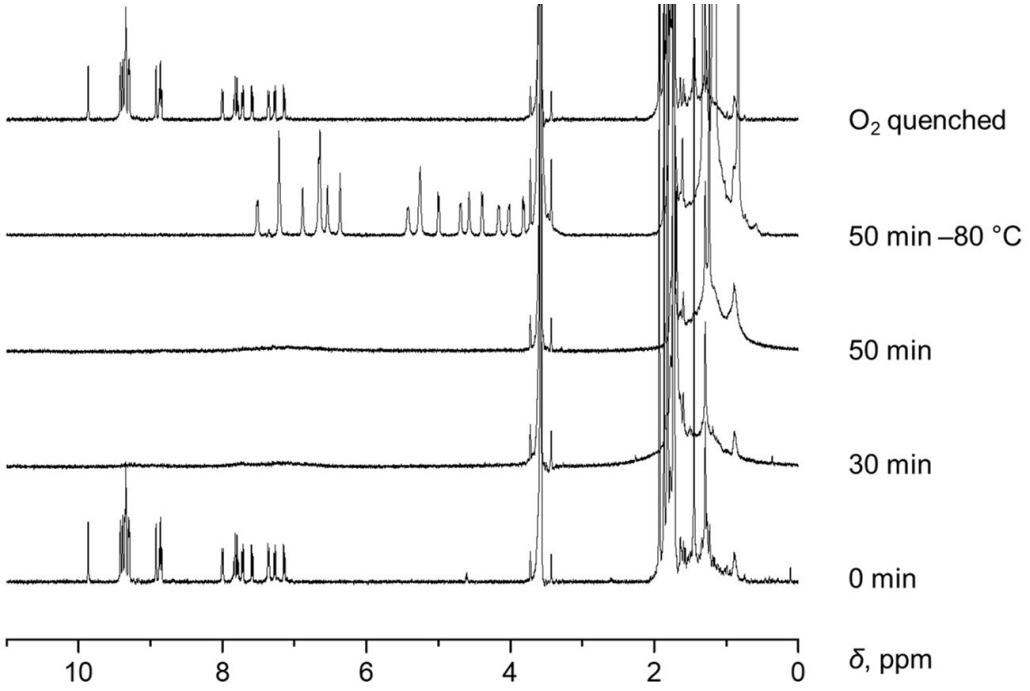


Figure S9. ^{1}H NMR spectra of **1**, *in situ* generated $\mathbf{1}^{2-}$, and its quenched product in THF-d_8 at 25 °C and –80 °C.

V. Crystal Structure Solution and Refinement

Data collection of **2**·0.5C_6H_{14} was performed at 100 K on a Bruker D8 fixed-χ system with a Pilatus 3×2M detector using ϕ scans (synchrotron radiation at λ = 0.61992 Å) located at the Advanced Photon Source, Argonne National Laboratory (ChemMatCARS, Sector 15). Data collection of **1**·0.5CH_3NO_2 was performed on a Bruker D8 VENTURE X-ray diffractometer equipped with a PHOTON 100 CMOS shutterless mode detector and a INCOATEC IμS micro-focus Cu-target X-ray tube (λ = 1.54178 Å) at T = 100(2) K. Data reduction and integration were performed with SAINT (version 8.38A)[3] and corrected for absorption effects using the empirical methods as implemented in SADABS (version 2016/2).[4] The structures were solved by SHELXT (version 2018/2)[5] and refined by full-matrix least-squares procedures using the SHELXL program (version 2018/3)[6] through the OLEX2[7] graphical interface. All non-hydrogen atoms, including those in disordered parts, were refined anisotropically. All H-atoms were included at calculated positions and refined as riders, with U_{iso}(H) = 1.2 U_{eq}(C) and U_{iso}(H) = 1.5 U_{eq}(C) for methyl groups. In the asymmetric unit of **2**·0.5C_6H_{14}, two {Na^+(18-crown-6)(THF)} units and two *tert*-butyl groups were found to be disordered and modeled with two orientations. In the asymmetric unit of **1**·0.5CH_3NO_2, two *tert*-butyl groups and the corannulene core were found to be disordered and modeled with two orientations. The geometries of the disordered parts were restrained to be similar. The anisotropic displacement parameters of the disordered molecules in the direction of the bonds were restrained to be equal with a standard uncertainty of 0.004 Å^2. They were also restrained to have the same U_{ij} components, with a standard uncertainty of 0.01 Å^2. Besides, in each unit cell of **2**·0.5C_6H_{14}, one hexane molecule was found to be severely disordered and removed by the Olex2's solvent mask.[7] The total void volume was 548.1 Å^3, equivalent to 11.44% of the unit cell's total volume. In each unit cell of **1**·0.5CH_3NO_2, two nitromethane molecules were found to be severely disordered and removed by the Olex2's solvent mask.[7] The total void volume was 798.0 Å^3, equivalent to 13.92% of the unit cell's total volume. Crystallographic data and details of the data collections and structure refinements are listed in Table S1.

Table S1. Crystallographic data of **1** and **2**

Compound	**1**·0.5CH_3NO_2	**2**·0.5C_6H_{14}
Empirical formula	$C_{76.50}H_{65.50}N_{0.5}O$	$C_{111}H_{135}Na_2O_{14}$
Formula weight	1007.79	1739.16
Temperature (K)	100(2)	100(2)
Wavelength (Å)	1.54178	0.61992
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
a (Å)	16.2936(3)	16.9258(9)
b (Å)	21.0583(4)	16.9445(8)
c (Å)	17.2056(3)	17.9330(9)
α (°)	90.00	105.9780(10)
β (°)	103.8220(9)	93.6390(10)
γ (°)	90.00	102.3500(10)
V (Å^3)	5732.56(18)	4788.9(4)
Z	4	2
ρ_{calcd} (g·cm^{-3})	1.168	1.206
μ (mm^{-1})	0.510	0.064
F(000)	2144	1870
Crystal size (mm)	0.03×0.05×0.08	0.003×0.004×0.095
θ range for data collection (°)	3.36-74.26	1.039-23.500
Reflections collected	45846	92339
Independent reflections	11455 [R_{int} = 0.0868]	19673 [R_{int} = 0.0435]
Transmission factors (min/max)	0.5018/0.6549	0.5429/0.7451
Data/restraints/params.	11455/2306/925	19673/2667/1691
$R1$,[a] $wR2$[b] ($I > 2\sigma(I)$)	0.0793, 0.1997	0.0977, 0.3173
$R1$,[a] $wR2$[b] (all data)	0.1226, 0.2310	0.1083, 0.3347
Quality-of-fit[c]	1.009	1.463

[a]$R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b]$wR2 = [\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]]$.
[c]Quality-of-fit = $[\Sigma[w(F_o^2-F_c^2)^2]/(N_{obs}-N_{params})]^{1/2}$, based on all data.

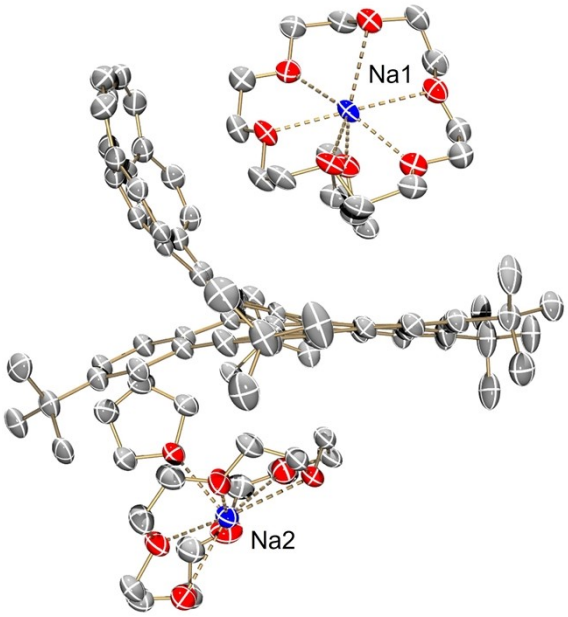


Figure S10. ORTEP drawing of the asymmetric unit of **2**, drawn with thermal ellipsoids at the 40% probability level. H-atoms are omitted for clarity. The color scheme used: C grey, H white, O red, Na blue.

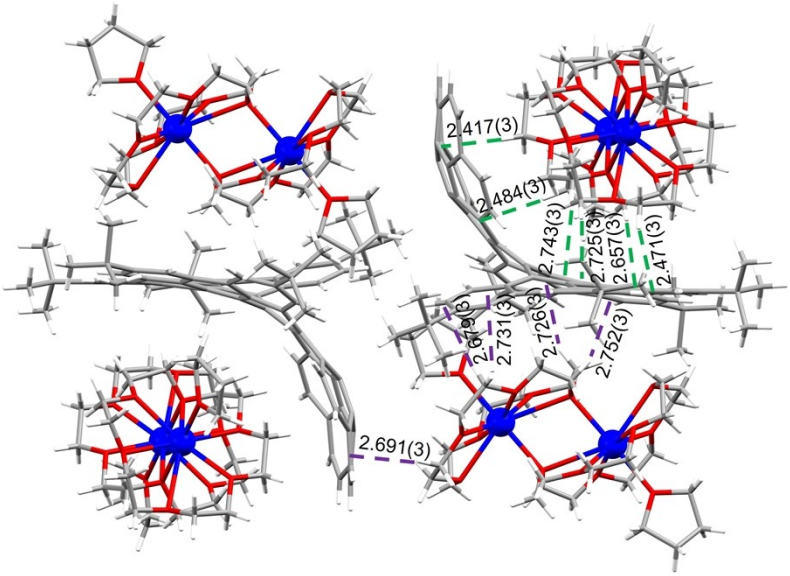


Figure S11. C–H···π interactions in **2**, mixed models.

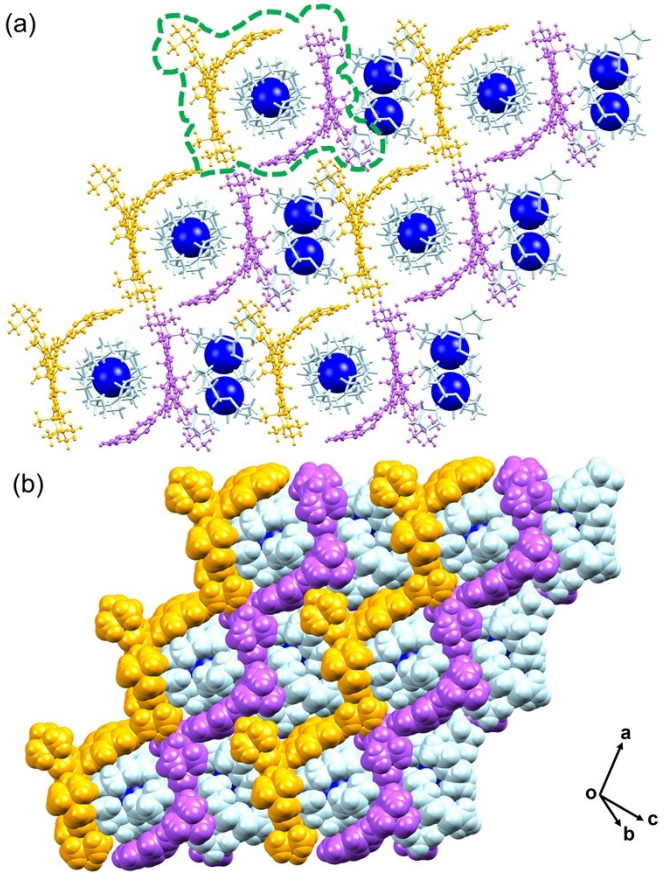
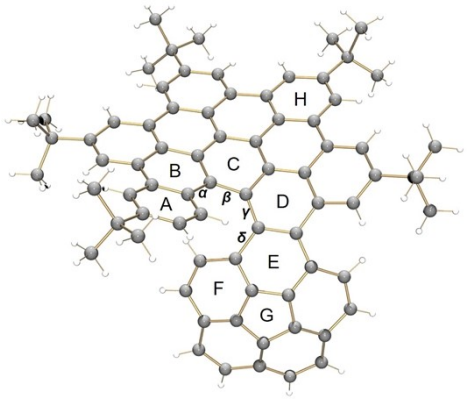


Figure S12. Solid-state packing in **2**, (a) ball-and-stick and (b) space-filling models. The *P*- and *M*- isomers are shown in orange and purple, respectively, and the $\{Na^{+}(18\text{-crown-6})(THF)\}_2$ moieties are shown in blue.

Table S2. Selected dihedral and torsion angles (°) in **1** and $\mathbf{1}^{2-}$ along with a labelling scheme



		1	$\mathbf{1}^{2-}$
Dihedral angle	A/H	12.2	28.5
	F/H	48.2	54.6
	A/F	47.0	80.8
	G/H	48.9	64.4
Torsion angle	α	22.4	11.5
	β	27.7	36.6
	γ	25.3	25.6
	δ	19.3	7.6

Table S3. Sum of the interior angles (°) for selected rings in **1** and $\mathbf{1}^{2-}$

	1	$\mathbf{1}^{2-}$
A	719.4	720.0
B	715.8	716.6
C	716.5	714.4
D	713.5	712.0
E	712.4	719.0
F	719.5	719.0

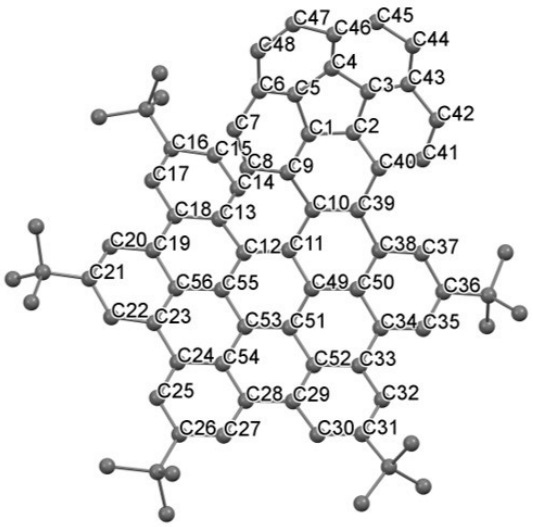
Table S4. Selected C–C bond distances (Å) in **1** and $\mathbf{1}^{2-}$

	1	$\mathbf{1}^{2-}$		**1**	$\mathbf{1}^{2-}$
C1–C2	1.410(11)	1.414(3)	C23–C24	1.465(4)	1.459(3)
C1–C5	1.420(10)	1.413(4)	C23–C56	1.422(4)	1.411(3)
C1–C9	1.376(11)	1.377(3)	C24–C25	1.398(4)	1.391(3)
C2–C3	1.431(10)	1.396(4)	C24–C54	1.423(4)	1.425(3)
C2–C40	1.362(11)	1.395(3)	C25–C26	1.393(4)	1.382(3)
C3–C4	1.404(11)	1.399(4)	C26–C27	1.398(4)	1.389(3)
C3–C43	1.375(11)	1.388(3)	C27–C28	1.395(4)	1.383(3)
C4–C5	1.414(10)	1.419(3)	C28–C29	1.476(4)	1.468(3)
C4–C46	1.384(10)	1.384(4)	C28–C54	1.412(4)	1.426(3)
C5–C6	1.374(10)	1.370(4)	C29–C30	1.390(4)	1.388(3)
C6–C7	1.434(10)	1.395(4)	C29–C52	1.413(4)	1.416(3)
C6–C48	1.447(10)	1.452(4)	C30–C31	1.390(4)	1.395(3)
C7–C8	1.393(11)	1.383(3)	C31–C32	1.397(4)	1.364(3)
C8–C9	1.444(11)	1.429(3)	C32–C33	1.384(4)	1.407(3)
C9–C10	1.482(10)	1.477(3)	C33–C34	1.465(4)	1.434(3)
C10–C11	1.462(4)	1.392(3)	C33–C52	1.425(4)	1.434(3)
C10–C39	1.422(4)	1.471(3)	C34–C35	1.402(4)	1.411(3)
C11–C12	1.429(4)	1.461(3)	C34–C50	1.415(4)	1.407(3)
C11–C49	1.407(4)	1.433(3)	C35–C36	1.396(4)	1.371(3)
C12–C13	1.466(4)	1.436(3)	C36–C37	1.380(4)	1.386(3)
C12–C55	1.466(4)	1.409(3)	C37–C38	1.406(4)	1.403(3)
C13–C14	1.404(4)	1.405(3)	C38–C39	1.450(4)	1.432(3)
C13–C18	1.408(4)	1.415(3)	C38–C50	1.413(4)	1.401(3)
C14–C15	1.369(4)	1.361(3)	C39–C40	1.493(10)	1.427(3)
C15–C16	1.402(4)	1.396(3)	C40–C41	1.446(11)	1.452(3)
C16–C17	1.385(4)	1.372(3)	C41–C42	1.376(11)	1.385(4)
C17–C18	1.398(4)	1.404(3)	C42–C43	1.436(11)	1.446(4)
C18–C19	1.464(4)	1.438(3)	C43–C44	1.456(11)	1.405(5)
C19–C20	1.400(4)	1.395(3)	C44–C45	1.388(12)	1.404(5)
C19–C56	1.417(4)	1.421(3)	C45–C46	1.425(12)	1.415(4)
C20–C21	1.373(4)	1.373(3)	C46–C47	1.443(12)	1.425(5)
C21-C22	1.396(4)	1.386(3)	C47–C48	1.376(12)	1.382(5)
C22–C23	1.398(4)	1.396(3)			

Table S5. Selected C–C bond lengths (Å) of the corannulene cores in **1** and $\mathbf{1}^{2-}$ compared to $C_{20}H_{10}$, and $C_{20}H_{10}^{2-}$

	$C_{20}H_{10}$	$C_{20}H_{10}^{2-}$	**1**	$\mathbf{1}^{2-}$
hub	1.411(2)–1.417(2)	1.390(3)–1.428(2)	1.405(4)–1.430(4)	1.401(3)–1.420(3)
spoke	1.376(2)–1.381(2)	1.404(3)–1.419(3)	1.363(4)–1.384(4)	1.373(3)–1.392(3)
flank	1.441(2)–1.450(2)	1.405(3)–1.460(3)	1.441(4)–1.493(4)	1.396(3)–1.477(3)
rim	1.377(2)–1.387(2)	1.390(3)–1.445(3)	1.376(4)–1.422(4)	1.385(3)–1.471(3)
B.D.	0.875(2)	0.795(3)	0.829(4)	0.859(3)

Table S6. Average *p*-orbital axis vector (POAV) angles (°) in **1** and $\mathbf{1}^{2-}$

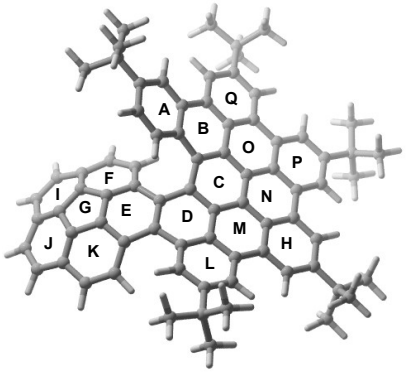


	1	$\mathbf{1}^{2-}$		**1**	$\mathbf{1}^{2-}$
C1	8.117	7.551	C39	2.753	2.131
C2	8.496	8.589	C40	0.925	4.743
C3	8.011	7.263	C41	0	0
C4	7.757	8.122	C42	0	0
C5	8.662	7.204	C43	3.842	4.624
C6	3.239	4.297	C44	0	0
C7	0	0	C45	0	0
C8	0	0	C46	3.646	4.194
C9	1.403	4.476	C47	0	0
C10	2.763	3.253	C48	0	0

VI. Computational Details

All the calculations reported in this paper were obtained with the GAUSSIAN 09 suite of programs. Electron correlation was partially taken into account using the (u)B3LYP functional in conjuction with the D3 dispersion correction suggested by Grimme *et al.* and the double-ζ quality plus polarization functions def2-SVP basis set for all atoms. All species were characterized by frequency calculations and have positive definite Hessian matrices. This level is denoted B3LYP-D3/def2-SVP, which was proven to provide good results for strongly related systems.

Table S7. Nuclear Independent Chemical Shift (NICS(0), in ppm) values computed for **1**, $\mathbf{1}^{\bullet-}$and $\mathbf{1}^{2-}$. All data have been computed at the GIAO-B3LYP/def2-SVP//B3LYP-D3/def2-SVP level.



Ring	X	$X^{\bullet-}$	X^{2-}
G	**+9.98**	**-0.14**	**+2.00**
F	-6.43	-1.71	-3.42
I	-6.49	-2.57	-3.80
J	-5.93	-1.26	-3.01
K	**-6.16**	**+1.83**	**+0.24**
E	**-2.15**	**+8.17**	**+5.64**
D	**-0.43**	**+5.52**	**+4.50**
L	**-8.18**	**+1.31**	**-0.89**
M	+2.72	-0.64	-0.82
H	-8.00	-3.69	-4.88
C	**-8.50**	**+7.62**	**+4.41**
N	+1.76	+3.65	+3.52
A	-7.23	-5.80	-5.97
B	+0.58	+1.52	-0.72
O	+2.41	+2.32	+2.00
P	-8.06	-2.61	-3.91
Q	-8.08	-2.96	-4.04

Cartesian coordinates (in Å) and total energies (in a.u., ZPVE included) of all the stationary points discussed in the text. All calculations have been performed at the B3LYP-D3/def2-SVP level.

1: E= -2931.751496

C	1.119736000	-2.045185000	1.219550000
C	0.722511000	-3.404164000	1.141210000
C	1.648883000	3.001898000	0.585952000
C	0.772343000	0.317680000	0.324855000
C	1.577595000	-4.397382000	1.675173000
H	1.268945000	-5.436036000	1.595696000
C	2.291583000	-1.741858000	1.952704000
H	2.566047000	-0.700139000	2.112705000
C	-1.569987000	1.081613000	0.161716000
C	-2.524402000	2.157333000	0.088441000
C	-2.823881000	-3.001686000	-0.134213000
C	0.295332000	-1.003175000	0.609914000
C	-1.996908000	-0.261879000	0.081041000
C	0.260612000	2.725126000	0.435764000
C	-6.078124000	-1.163480000	-0.852410000
C	2.165299000	0.641302000	0.026402000
C	-0.687712000	3.778451000	0.578472000
C	-0.181000000	1.368877000	0.273004000
C	-0.237785000	5.029601000	1.016456000
H	-0.966170000	5.824273000	1.172854000
C	-0.581677000	-3.738779000	0.562792000
C	2.617348000	1.988988000	0.179701000
C	3.055000000	-0.376317000	-0.561194000
C	-1.063020000	-1.308006000	0.339060000
C	-3.796058000	-1.918065000	-0.344260000
C	-2.102522000	3.505250000	0.288564000
C	2.735580000	-1.573474000	-1.312261000
H	1.704379000	-1.922475000	-1.353004000
C	-3.374189000	-0.565677000	-0.207379000
C	2.031346000	4.259080000	1.094816000
H	3.077327000	4.411920000	1.339662000
C	1.108914000	5.281393000	1.326538000
C	-5.138153000	-2.180758000	-0.664112000
H	-5.457625000	-3.213846000	-0.761382000
C	-1.495968000	-2.684811000	0.279309000
C	2.774852000	-4.101016000	2.317708000
C	3.096194000	-2.733088000	2.479112000
H	3.993414000	-2.440504000	3.027955000
C	4.395096000	-0.038081000	-0.583079000
C	-5.645058000	0.158738000	-0.695633000
H	-6.368772000	0.959691000	-0.834051000
C	3.677097000	-2.252768000	-2.077983000
H	3.339964000	-3.101742000	-2.679792000
C	-3.893678000	1.881408000	-0.178421000
C	3.997422000	2.365523000	-0.182013000
C	-0.979975000	-5.068319000	0.338848000
H	-0.263553000	-5.862888000	0.525743000
C	5.355996000	-0.725580000	-1.368805000
C	4.859203000	1.298799000	-0.391877000

C	-4.322130000	0.489380000	-0.369322000
C	-3.049971000	4.530370000	0.193159000
H	-2.721455000	5.561701000	0.314286000
C	-2.257675000	-5.397396000	-0.117848000
C	-3.162079000	-4.347509000	-0.329546000
H	-4.164928000	-4.593834000	-0.673041000
C	5.039517000	-1.793207000	-2.199638000
C	6.104813000	1.421371000	-1.062860000
C	6.421122000	0.167796000	-1.650436000
C	-4.404714000	4.283516000	-0.075124000
C	6.582060000	2.620475000	-1.578502000
C	4.547890000	3.643035000	-0.598311000
H	3.947314000	4.546820000	-0.505515000
C	7.243170000	0.036969000	-2.762106000
C	-4.799676000	2.955735000	-0.249423000
H	-5.845469000	2.741589000	-0.448123000
C	5.776203000	3.766137000	-1.243087000
H	6.075666000	4.756390000	-1.599034000
C	7.609690000	2.483547000	-2.590662000
H	8.083515000	3.383050000	-2.994820000
C	7.927637000	1.252818000	-3.151983000
H	8.643653000	1.222202000	-3.978710000
C	7.068931000	-1.197757000	-3.497992000
H	7.720825000	-1.408223000	-4.351095000
C	6.016911000	-2.067488000	-3.232051000
H	5.873971000	-2.932787000	-3.886139000
C	3.726991000	-5.179916000	2.857913000
C	-2.701105000	-6.847801000	-0.385044000
C	-7.548432000	-1.445126000	-1.215135000
C	-5.387639000	5.465191000	-0.173764000
C	1.515553000	6.652648000	1.897092000
C	5.093078000	-5.036296000	2.147855000
H	5.800708000	-5.797477000	2.516101000
H	4.983957000	-5.164627000	1.059339000
H	5.543316000	-4.047401000	2.322204000
C	3.913346000	-4.993287000	4.380571000
H	2.950129000	-5.083526000	4.907505000
H	4.597177000	-5.759941000	4.780663000
H	4.339139000	-4.008634000	4.625664000
C	3.200165000	-6.603757000	2.607654000
H	3.067059000	-6.806648000	1.533461000
H	3.918261000	-7.341838000	2.997954000
H	2.237377000	-6.779564000	3.112984000
C	-1.581821000	-7.863515000	-0.095039000
H	-1.262053000	-7.831002000	0.958238000
H	-1.941735000	-8.883917000	-0.300046000
H	-0.697800000	-7.691001000	-0.728668000
C	-3.908343000	-7.189282000	0.517629000
H	-4.766305000	-6.527777000	0.323783000
H	-4.240234000	-8.225633000	0.340800000
H	-3.642785000	-7.090590000	1.582073000
C	-3.110242000	-6.990137000	-1.868821000
H	-2.266413000	-6.745420000	-2.533204000
H	-3.427944000	-8.023842000	-2.083215000
H	-3.946232000	-6.323501000	-2.129978000
C	-7.874442000	-0.778254000	-2.570830000
H	-7.227858000	-1.175919000	-3.369049000

H	-8.923557000	-0.968449000	-2.851474000
H	-7.731147000	0.312418000	-2.536043000
C	-8.468487000	-0.861961000	-0.118663000
H	-9.526476000	-1.055949000	-0.360731000
H	-8.250636000	-1.318410000	0.859848000
H	-8.345351000	0.226811000	-0.015430000
C	-7.842208000	-2.950820000	-1.337467000
H	-8.900927000	-3.103714000	-1.598841000
H	-7.235465000	-3.423520000	-2.125632000
H	-7.654887000	-3.483042000	-0.391717000
C	3.026477000	6.743196000	2.174652000
H	3.352778000	5.995277000	2.913840000
H	3.622053000	6.602203000	1.259072000
H	3.272427000	7.737672000	2.578559000
C	0.764313000	6.897468000	3.225557000
H	-0.327484000	6.894622000	3.086552000
H	1.010189000	6.118223000	3.964105000
H	1.044491000	7.875038000	3.651264000
C	1.144054000	7.758301000	0.883095000
H	1.669051000	7.606540000	-0.073408000
H	0.063889000	7.777726000	0.672968000
H	1.424935000	8.749604000	1.275276000
C	-4.945624000	6.399519000	-1.322835000
H	-3.934012000	6.800899000	-1.159188000
H	-4.941695000	5.862863000	-2.284765000
H	-5.634740000	7.255738000	-1.409781000
C	-5.383718000	6.248112000	1.158986000
H	-6.086325000	7.096162000	1.109337000
H	-5.687120000	5.599286000	1.995818000
H	-4.388289000	6.654550000	1.394102000
C	-6.828627000	5.004759000	-0.455800000
H	-6.905728000	4.464220000	-1.412146000
H	-7.213256000	4.350586000	0.342352000
H	-7.494531000	5.879664000	-0.516741000

1$^{\cdot-}$**:** E= -2931.804602

C	1.058019000	-2.056569000	1.230800000
C	0.618967000	-3.410482000	1.187116000
C	1.717241000	2.995876000	0.554854000
C	0.795690000	0.314781000	0.305781000
C	1.423947000	-4.416328000	1.774921000
H	1.070180000	-5.443140000	1.725877000
C	2.246881000	-1.784502000	1.957821000
H	2.570774000	-0.750779000	2.069260000
C	-1.537307000	1.124880000	0.168549000
C	-2.471932000	2.211632000	0.123618000
C	-2.878092000	-2.941146000	-0.198375000
C	0.278600000	-1.009044000	0.594633000
C	-1.994926000	-0.222729000	0.048353000
C	0.311446000	2.738837000	0.458476000
C	-6.061156000	-1.027281000	-1.013850000
C	2.168090000	0.603379000	-0.004227000
C	-0.617114000	3.805921000	0.614419000
C	-0.151174000	1.388078000	0.294184000
C	-0.138231000	5.074565000	1.014665000

H	-0.853949000	5.878527000	1.160630000
C	-0.672678000	-3.726122000	0.575803000
C	2.657998000	1.974805000	0.132051000
C	3.051278000	-0.430415000	-0.575764000
C	-1.084446000	-1.285138000	0.301479000
C	-3.812623000	-1.839111000	-0.439648000
C	-2.033828000	3.549574000	0.363605000
C	2.726413000	-1.650014000	-1.291807000
H	1.695031000	-2.000893000	-1.303520000
C	-3.362013000	-0.494030000	-0.266266000
C	2.119027000	4.253525000	1.050198000
H	3.171629000	4.401641000	1.281043000
C	1.213446000	5.299176000	1.283122000
C	-5.150451000	-2.065261000	-0.815943000
H	-5.483140000	-3.090399000	-0.951778000
C	-1.552881000	-2.651280000	0.242461000
C	2.620542000	-4.148254000	2.428435000
C	2.999775000	-2.786977000	2.533104000
H	3.905824000	-2.509191000	3.076842000
C	4.394866000	-0.101337000	-0.630270000
C	-5.607587000	0.285591000	-0.799653000
H	-6.309873000	1.105988000	-0.942238000
C	3.653139000	-2.352362000	-2.059945000
H	3.300511000	-3.217721000	-2.630096000
C	-3.853429000	1.962117000	-0.150603000
C	4.028993000	2.315931000	-0.239017000
C	-1.101070000	-5.044744000	0.356522000
H	-0.412570000	-5.861413000	0.568950000
C	5.337542000	-0.810116000	-1.415356000
C	4.880782000	1.234874000	-0.458402000
C	-4.295677000	0.582019000	-0.417063000
C	-2.984419000	4.591577000	0.338251000
H	-2.637619000	5.607558000	0.505590000
C	-2.380322000	-5.349471000	-0.128786000
C	-3.252861000	-4.289190000	-0.379181000
H	-4.256449000	-4.504606000	-0.734055000
C	5.013144000	-1.904659000	-2.214722000
C	6.112097000	1.333259000	-1.144956000
C	6.405956000	0.068030000	-1.722827000
C	-4.336326000	4.364632000	0.088691000
C	6.623256000	2.521491000	-1.667969000
C	4.615325000	3.582778000	-0.663519000
H	4.035271000	4.499743000	-0.565874000
C	7.233159000	-0.094009000	-2.828634000
C	-4.744763000	3.040776000	-0.151814000
H	-5.800386000	2.850623000	-0.341617000
C	5.837356000	3.680900000	-1.323990000
H	6.149768000	4.667560000	-1.682356000
C	7.636115000	2.352315000	-2.681058000
H	8.120587000	3.238951000	-3.103780000
C	7.936609000	1.104974000	-3.232201000
H	8.648439000	1.055648000	-4.062505000
C	7.045104000	-1.346970000	-3.532419000
H	7.692092000	-1.584094000	-4.383377000
C	5.984641000	-2.203682000	-3.242469000
H	5.835067000	-3.082480000	-3.878510000
C	3.515997000	-5.242070000	3.032151000

C	-2.773637000	-6.822456000	-0.353728000
C	-7.521670000	-1.265628000	-1.441925000
C	-5.382393000	5.495340000	0.060864000
C	1.739475000	6.640437000	1.831216000
C	4.908785000	-5.179829000	2.363541000
H	5.575240000	-5.955532000	2.778667000
H	4.826378000	-5.338317000	1.276730000
H	5.392199000	-4.203422000	2.517603000
C	3.666456000	-5.012657000	4.553138000
H	2.685578000	-5.057402000	5.053120000
H	4.317762000	-5.783086000	5.000748000
H	4.109662000	-4.030207000	4.775530000
C	2.943942000	-6.653976000	2.814861000
H	2.831675000	-6.885197000	1.744051000
H	3.622407000	-7.405639000	3.250133000
H	1.960319000	-6.775421000	3.295587000
C	-1.809105000	-7.460263000	-1.379139000
H	-0.765096000	-7.426469000	-1.033071000
H	-2.071198000	-8.517838000	-1.554372000
H	-1.858047000	-6.928647000	-2.342730000
C	-2.679693000	-7.590119000	0.984530000
H	-3.358062000	-7.151327000	1.733524000
H	-2.956348000	-8.649627000	0.846841000
H	-1.661333000	-7.560820000	1.400387000
C	-4.208106000	-6.972924000	-0.890644000
H	-4.335755000	-6.464135000	-1.858822000
H	-4.442050000	-8.039453000	-1.039934000
H	-4.951999000	-6.563913000	-0.189194000
C	-7.786739000	-0.550167000	-2.786209000
H	-7.118847000	-0.937681000	-3.571884000
H	-8.829765000	-0.705204000	-3.111743000
H	-7.616868000	0.534585000	-2.710861000
C	-8.475676000	-0.700618000	-0.364778000
H	-9.528842000	-0.858084000	-0.654782000
H	-8.306593000	-1.197516000	0.603797000
H	-8.327846000	0.379618000	-0.214959000
C	-7.841667000	-2.759874000	-1.625069000
H	-7.210407000	-3.219484000	-2.401498000
H	-7.699047000	-3.324886000	-0.690661000
H	-8.892767000	-2.884347000	-1.932233000
C	-4.764210000	6.873247000	0.356303000
H	-4.296050000	6.903872000	1.352484000
H	-3.999778000	7.145140000	-0.388048000
H	-5.546376000	7.649349000	0.329979000
C	-6.040377000	5.554458000	-1.336550000
H	-5.286448000	5.758248000	-2.113505000
H	-6.535204000	4.605766000	-1.594086000
H	-6.801404000	6.352817000	-1.375793000
C	-6.468192000	5.219969000	1.126083000
H	-6.984756000	4.264940000	0.946417000
H	-6.023164000	5.173895000	2.132760000
H	-7.229021000	6.019231000	1.120709000
C	2.835648000	7.194628000	0.893010000
H	3.211290000	8.163617000	1.264155000
H	3.695608000	6.512502000	0.819194000
H	2.439383000	7.345325000	-0.123941000
C	2.338820000	6.411756000	3.237249000

H	1.573087000	6.023539000	3.927645000
H	3.163269000	5.683506000	3.211227000
H	2.732593000	7.355830000	3.652219000
C	0.631584000	7.702605000	1.947097000
H	0.170006000	7.915440000	0.970064000
H	-0.164755000	7.387986000	2.639282000
H	1.053902000	8.645339000	2.331681000

1^{2-}: E= -2931.764550

C	0.949858000	-2.110007000	1.252080000
C	0.429233000	-3.446716000	1.243102000
C	1.877188000	2.919165000	0.545658000
C	0.842278000	0.270039000	0.300408000
C	1.171747000	-4.482372000	1.865943000
H	0.751857000	-5.485668000	1.843262000
C	2.168231000	-1.904401000	1.963925000
H	2.564059000	-0.892211000	2.034143000
C	-1.455141000	1.188735000	0.181605000
C	-2.340068000	2.309267000	0.161962000
C	-3.006117000	-2.817599000	-0.228559000
C	0.247533000	-1.043392000	0.591233000
C	-1.978697000	-0.145725000	0.018898000
C	0.455538000	2.720348000	0.494937000
C	-6.037029000	-0.734726000	-1.187054000
C	2.204137000	0.490820000	-0.022644000
C	-0.426740000	3.827399000	0.668032000
C	-0.063424000	1.389835000	0.324929000
C	0.114939000	5.084590000	1.049075000
H	-0.562535000	5.920971000	1.196958000
C	-0.859922000	-3.707399000	0.618840000
C	2.763416000	1.867656000	0.095782000
C	3.055137000	-0.581603000	-0.587399000
C	-1.122322000	-1.253963000	0.273703000
C	-3.861000000	-1.670830000	-0.517316000
C	-1.850182000	3.627910000	0.440332000
C	2.694050000	-1.814749000	-1.263794000
H	1.657397000	-2.148690000	-1.234994000
C	-3.338635000	-0.346184000	-0.318803000
C	2.338251000	4.161234000	1.042498000
H	3.399778000	4.262795000	1.259340000
C	1.479505000	5.245297000	1.286297000
C	-5.191154000	-1.819284000	-0.960151000
H	-5.564583000	-2.826193000	-1.130992000
C	-1.666885000	-2.593940000	0.231434000
C	2.380429000	-4.274399000	2.515519000
C	2.851309000	-2.933463000	2.571831000
H	3.776472000	-2.697842000	3.105146000
C	4.406060000	-0.287732000	-0.684326000
C	-5.527398000	0.554410000	-0.918104000
H	-6.179314000	1.414396000	-1.076045000
C	3.586090000	-2.557725000	-2.042326000
H	3.196686000	-3.430810000	-2.577358000
C	-3.734299000	2.126336000	-0.125550000
C	4.128610000	2.146046000	-0.288294000
C	-1.360329000	-5.016852000	0.423697000

H	-0.713251000	-5.856399000	0.662611000
C	5.313326000	-1.039721000	-1.471685000
C	4.944168000	1.031536000	-0.528462000
C	-4.225906000	0.777293000	-0.468222000
C	-2.769409000	4.703727000	0.466529000
H	-2.383355000	5.698987000	0.671430000
C	-2.646089000	-5.252279000	-0.067706000
C	-3.456476000	-4.148885000	-0.363095000
H	-4.472959000	-4.326374000	-0.712431000
C	4.950177000	-2.151067000	-2.238266000
C	6.159436000	1.079973000	-1.232942000
C	6.401460000	-0.202059000	-1.805713000
C	-4.128615000	4.534186000	0.225953000
C	6.729357000	2.245014000	-1.762573000
C	4.779349000	3.388870000	-0.717096000
H	4.245665000	4.332459000	-0.602391000
C	7.225558000	-0.408852000	-2.909552000
C	-4.587146000	3.232098000	-0.067899000
H	-5.651551000	3.082664000	-0.250443000
C	5.991905000	3.435709000	-1.398030000
H	6.340485000	4.412743000	-1.754007000
C	7.717696000	2.026643000	-2.778987000
H	8.228315000	2.890951000	-3.220730000
C	7.972051000	0.755669000	-3.326164000
H	8.672827000	0.675788000	-4.164672000
C	6.991492000	-1.675352000	-3.580892000
H	7.624552000	-1.953409000	-4.431578000
C	5.905295000	-2.494842000	-3.265213000
H	5.728542000	-3.383275000	-3.882833000
C	3.206300000	-5.403512000	3.151989000
C	-3.203429000	-6.675068000	-0.280296000
C	-7.481487000	-0.885437000	-1.697633000
C	-5.136794000	5.698701000	0.254772000
C	2.076368000	6.565089000	1.817764000
C	4.598754000	-5.454635000	2.480974000
H	5.220437000	-6.255386000	2.921018000
H	4.500322000	-5.642635000	1.400232000
H	5.138954000	-4.503351000	2.598051000
C	3.380304000	-5.140037000	4.665505000
H	2.400359000	-5.115391000	5.169171000
H	3.992456000	-5.930542000	5.136226000
H	3.875164000	-4.175297000	4.853881000
C	2.544803000	-6.782675000	2.982681000
H	2.413655000	-7.039073000	1.919829000
H	3.173811000	-7.563484000	3.443134000
H	1.555194000	-6.820487000	3.464944000
C	-2.181740000	-7.768590000	0.079420000
H	-1.878149000	-7.708175000	1.136039000
H	-2.621564000	-8.766343000	-0.088780000
H	-1.273073000	-7.692333000	-0.537577000
C	-4.451656000	-6.879040000	0.608023000
H	-5.241263000	-6.150670000	0.369930000
H	-4.871341000	-7.892102000	0.471558000
H	-4.193336000	-6.752361000	1.671605000
C	-3.597364000	-6.860607000	-1.763241000
H	-2.721763000	-6.717644000	-2.416402000
H	-4.000131000	-7.874226000	-1.939907000

H	-4.362535000	-6.132912000	-2.072576000
C	-7.644439000	-0.123274000	-3.033171000
H	-6.959862000	-0.528515000	-3.795325000
H	-8.678296000	-0.208745000	-3.414106000
H	-7.415114000	0.946969000	-2.918865000
C	-8.467047000	-0.301294000	-0.658671000
H	-9.511480000	-0.392577000	-1.008103000
H	-8.375300000	-0.833385000	0.301749000
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C	-7.868192000	-2.355179000	-1.942045000
H	-7.214151000	-2.825998000	-2.692477000
H	-7.805464000	-2.950571000	-1.017724000
H	-8.905588000	-2.417263000	-2.312291000
C	-6.230643000	5.415021000	1.309895000
H	-6.774362000	4.483479000	1.091613000
H	-5.783807000	5.310946000	2.311565000
H	-6.968085000	6.237076000	1.342165000
C	-5.798387000	5.845749000	-1.134817000
H	-5.038872000	6.064083000	-1.902498000
H	-6.316313000	4.922386000	-1.435111000
H	-6.538592000	6.666213000	-1.135350000
C	-4.474456000	7.041729000	0.609726000
H	-3.997644000	7.008063000	1.601656000
H	-3.704019000	7.320967000	-0.125562000
H	-5.231320000	7.844349000	0.625102000
C	1.023872000	7.681364000	1.943200000
H	0.557167000	7.906025000	0.971299000
H	0.223123000	7.407287000	2.647420000
H	1.496413000	8.606733000	2.314739000
C	3.184323000	7.063759000	0.862671000
H	3.614890000	8.014927000	1.224366000
H	4.005083000	6.337029000	0.774512000
H	2.778303000	7.230230000	-0.148087000
C	2.684832000	6.320398000	3.217154000
H	1.909599000	5.974424000	3.919663000
H	3.468847000	5.549475000	3.183160000
H	3.131999000	7.246996000	3.621151000

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