1	On-Surface Synthesis of a Doubly Anti-Aromatic Carbon Allotrope:
2	Cyclo[16]carbon
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15	The synthetic carbon allotropes graphene ¹ , carbon nanotubes ² and fullerenes ³ have
16	revolutionised materials science and led to new technologies. Recently, unconventional
17	synthetic strategies such as dynamic covalent chemistry ⁴ and on-surface synthesis ⁵ have
18	been used to create new forms of carbon, including γ -graphyne ⁶ , covalent fullerene
19	polymers ⁷ , and biphenylene networks ⁸ , as well as cyclo[10]carbon, cyclo[14]carbon ⁹ and
20	cyclo[18]carbon ¹⁰ . Here, by using tip-induced on-surface chemistry ⁵ , we report the synthesis
21	and characterisation of an anti-aromatic carbon allotrope, cyclo[16]carbon. In addition to
22	structural information from atomic force microscopy (AFM), we probed its electronic
23	structure by recording orbital density maps ¹¹ with scanning tunnelling microscopy (STM),
24	which have not been reported previously for any cyclocarbon. The observation of bond-
25	length alternation in cyclo[16]carbon confirms its double anti-aromaticity, in concordance
26	with theory. The simple structure of C_{16} renders it an interesting model system for studying
27	the limits of aromaticity ¹² , and its high reactivity makes it a promising precursor to novel
28	carbon allotropes ¹³ .

29 Cyclo[*N*]carbons are reactive carbon allotropes consisting of rings of *N* carbon atoms^{14,15}. 30 They are intermediates in the formation of fullerenes¹⁶, and they constitute possible building 31 blocks for other carbon allotropes such as graphyne¹³. Many cyclocarbons (N = 6-40) have been

- detected in the gas-phase^{17,18}, and two examples (C_6 and C_8) have been trapped in solid argon and 32 characterised by infrared spectroscopy^{19,20}. Cyclo[10]carbon, cyclo[14]carbon and 33 cyclo[18]carbon have been definitively characterised by scanning probe microscopy of individual 34 molecules on NaCl surfaces at low temperature^{9,10,21}. AFM images revealed cumulenic structures 35 36 for C_{10} and C_{14} (ref. 9) and a polyynic structure for C_{18} (refs. 10, 21). Cyclo[N]carbons with N =4n + 2 (where *n* is an integer), such as C₁₀, C₁₄ and C₁₈, are expected to be doubly aromatic and to 37 have special stability, due to their closed-shell electronic configurations, relating to the presence 38 of in-plane and out-of-plane aromatic Hückel circuits of $4n + 2\pi$ -electrons^{22–27}. In contrast, 39 cyclo[4n]carbons have been predicted to be less stable and doubly anti-aromatic^{24–29}. This raises 40 the question whether a cyclo [4n] carbon can be prepared and characterised. Here we report 41 synthesis of the cyclo [4n] carbon C_{16} on a NaCl surface by tip-induced chemistry from a 42 C₁₆(CO)₄Br₂ precursor. AFM and STM provide insight into the geometry and electronic 43 structure, respectively, of neutral C_{16} and anionic C_{16} . We find that neutral C_{16} is circular, with 44 significant bond-length alternation (BLA). This geometry confirms its double anti-aromaticity. 45 Our experimental results are complemented by state-of-the-art quantum mechanical calculations, 46 as well as by methods suitable for execution on a quantum computer. 47
- 48 Cyclocarbons have two orthogonal π -systems, one with orbitals in the ring plane and the other orthogonal to the ring plane. In an infinitely large cyclocarbon these two π -systems are 49 degenerate, but in a finite ring, in-plane orbitals will be slightly higher in energy than their out-50 of-plane counterparts¹⁵. This pattern of orbitals can lead to several possible electronic states. In 51 the D_{16h} geometry of C₁₆ with no BLA, the ground state may be a doubly aromatic |2200> state 52 (Fig. 1, left), with 18 (4n + 2) and 14 (4n - 2) electrons in out-of-plane and in-plane π -systems, 53 respectively. In this state, there are two degenerate pairs of frontier orbitals (out-of-plane A" and 54 B" are occupied, and in-plane A' and B' are unoccupied). If we introduce BLA (D_{8h} symmetry), 55 these orbital pairs will no longer be degenerate, with one member of each pair (A in Fig. 1, right) 56 becoming stabilised relative to the other (B). This symmetry breaking leads to a doubly anti-57 aromatic $|2020\rangle$ configuration with 16 electrons in both in-plane and out-of-plane π -systems. A 58 third possible state would be $|1111\rangle$, with D_{16h} symmetry, but such open-shell configurations are 59 known to be unstable relative to closed-shell alternatives^{30,31}. 60
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Fig. 1. Frontier orbitals of two electronic states of C₁₆. In-plane orbitals are labelled as A' and B', and out-of-plane
 orbitals as A" and B". Orbitals A', B' (and A", B") are related by a rotation and have equal energy when all bonds are
 of equal length. Introducing bond-length alternation lifts this degeneracy, resulting in orbital reordering and a doubly
 anti-aromatic ground state.

The unique structure, small size, and high symmetry of cyclocarbons has made them a target of many theoretical studies, which have sometimes produced conflicting results¹⁵. Here, we investigate C_{16} using both state-of-the-art computational methods and a variational quantum eigensolver³² paired with the quantum unitary coupled clusters singles doubles (q-UCCSD)³³ ansatz. These calculations confirm that the doubly anti-aromatic configuration is the ground state of C_{16} , with strong BLA.

73 **Results**

Precursor synthesis: We explored two routes to C₁₆, as summarised in Fig. 2. Glaser-Hay 74 coupling of a mixture of alkynes 1 and 2 gave macrocycle 3 in 20% yield. This macrocycle has a 75 circuit of 16 sp^1 or sp^2 hybridised carbon atoms and it is anti-aromatic, in contrast to the 76 corresponding C_{18} -precursor, which features a ring of 18 sp¹ or sp² hybridised carbon atoms and 77 is aromatic. This difference in electronic structure is reflected by the ¹H NMR spectra and 78 reactivities of these compounds (see Fig. S1). Deprotection of 3 to give 4 proved difficult because 79 of the high reactivity of these compounds (e.g., using concentrated sulfuric acid, as in case of C₁₈, 80 was not viable). After testing many reaction conditions, we found that 3 can be converted to 4 81 using trifluoracetic acid containing water (2.5% by volume), but unfortunately the anti-aromatic 82 cyclocarbon oxide 4 is too unstable for sublimation, preventing further work on this route to C_{16} . 83

We encountered the same problem when attempting to prepare other cyclo[4*n*]carbons, C_{20} and C₂₄, from their anti-aromatic carbon oxide precursors $C_{20}(CO)_8$ and $C_{24}(CO)_8$ (see Supplementary Information for details). Fortunately, we were able to get round this problem in the case of C16 by using $C_{16}(CO)_4Br_2$ as a precursor.

Glaser-Hay coupling of a mixture of compounds 1 and 5 gave the dibromo macrocycle 6 88 (20% yield), and the structure of this compound was confirmed by single-crystal X-ray 89 diffraction (Fig. S2). Deprotection of 6 with aqueous trifluoracetic acid gave 7 (94% yield). 90 Although 7 is antiaromatic, like 4, it is substantially more stable. At room temperature in the 91 dark, solid samples of precursor 4 decompose to an extent of about 50% in 5 minutes, whereas 92 93 under the same conditions, the extent of decomposition of 7 is only about 10% (Fig. S3 and S4). The greater thermal stability of 7 made it possible to deposit this compound on a surface by 94 sublimation under ultra-high vacuum. 95



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Fig. 2. Two approaches to the synthesis of C₁₆. The top route via 4 failed because this compound was found to be too
 unstable for sublimation.

99 **On-surface synthesis and structural characterisation:** Precursor 7 was sublimed by fast heating 100 from a Si wafer¹⁰ onto a Cu(111) single crystal surface partially covered with bilayer NaCl, 101 denoted as NaCl(2ML)/Cu(111), at a sample temperature of about T = 10 K. On-surface synthesis 102 (Fig. 3a) and characterisation by STM and AFM with CO tip functionalisation^{34,35} were 103 performed at T = 5 K. We found intact molecules of 7 on the NaCl(2ML)/Cu(111) surface, as

- shown in Fig. 3b. The Br atoms appear as bright (repulsive) dots in the AFM image²¹, whereas
- 105 the CO masking groups are dark features¹⁰. The triple bonds show up as bright features, due to
- bond-order related contrast obtained with CO tip functionalisation^{10,37,36}; for additional data on 7
- 107 see Fig. S5).

- 108 Voltage pulses, applied from the tip above the molecules, were used to unmask individual molecules of precursor 7 by successively increasing the voltage. Debromination occurred at V =109 110 1.3–3.2 V, resulting in 8 (Fig. 3c; see Fig. S6 for additional data). The CO masking groups dissociated at V = 1.5 - 3.3 V. Intermediate 9 was observed after dissociating the first pair of CO 111 112 masking groups (Fig. 3d; see Fig. S7 for additional data). Removal of a second pair of CO molecules gave the final product C_{16} (Fig. 3e, Figs. S8, S9). Previously, gas-phase C_{16} has been 113 formed from a molecular precursor^{37,38}, and studied in its anionic^{38–40} and cationic^{18,41} forms, but 114 this is the first time C₁₆ has been generated in a condensed phase or structurally characterised. 115 The yield for the on-surface synthesis of C_{16} was about 30%; in unsuccessful attempts, the ring 116 opened to form linear polyynic chains (see Fig. S10) or the molecule was picked up by the tip. 117
- 118 We observed C₁₆ in two different forms on the NaCl surface (Fig. 3f,g) that we assign to neutral C₁₆⁰ and negatively charged C₁₆⁻, respectively (see also Fig. 4, Figs. S11, S12 and Tables 119 S1, S2). Whereas C₁₆⁰ appears circular, C₁₆⁻ adopts a distorted oval geometry on defect-free 120 NaCl. We observed a variety of adsorption sites for C_{16}^0 on the NaCl surface (Fig. S13), 121 indicating a weak interaction with the substrate. In contrast, C_{16} showed a systematic preference 122 for adsorption above a bridge site (see Figs. S14, S15). To investigate the interaction of C_{16}^{0} and 123 C_{16} with the NaCl surface, we performed DFT calculations with periodic boundary conditions. 124 The calculated lowest-energy adsorption sites of C_{16}^{0} and C_{16}^{-} on NaCl are shown in Fig. 3h,i 125 126 respectively. For the neutral charge state, we calculated an adsorption energy of 0.65 eV, which is similar to the value of 0.67 eV previously calculated for C₁₈ on NaCl (ref. 42) that was predicted 127 to diffuse readily across the surface. The calculated relaxed adsorption geometry of C₁₆⁻ on NaCl 128 is oval shaped, with the molecule centred on a bridge site (Fig. 3i), in agreement with its 129 experimentally observed site and shape (Fig. 3g, Fig. S14 and Table S1). This adsorption 130 geometry can be attributed to electrostatic interactions of the C₁₆⁻ anion with the Na cations and 131 Cl anions, resulting in a significantly stronger adsorption energy (1.44 eV), compared to the 132 neutral molecule. 133
- The C₁₆ molecules frequently moved on the surface during imaging with AFM and STM, 134 indicating a small diffusion barrier and making it challenging to characterise them. To that end, 135 the molecule was often moved close to a 3rd layer NaCl island, that provides a more stable 136 adsorption site, facilitating detailed characterisation. Fig. 3j-m show C₁₆ adsorbed in a bay of a 137 3rd layer island imaged with AFM at different tip heights. Kelvin probe force spectroscopy 138 (KPFS) confirmed that the molecule in Fig. 3f and j-m is charge neutral (Tables S2, S3 and Fig. 139 S16). The bright contrast obtained by CO-tip AFM above the triple bonds for larger tip heights 140 (Fig. 3j,k) evolves to the shape of an octagon with corners at the positions of triple bonds at 141

decreased tip heights (Fig. 31, m). The results indicate BLA¹⁰, i.e., a polyynic structure of neutral

143 C₁₆.



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145Fig. 3. On-surface synthesis of C_{16} and structural characterisation. a reaction scheme. b-e, Constant-height, CO-146tip AFM images of precursor 7 (b), intermediates 8, 9 (c, d) and C_{16} (e). Br atoms were dissociated by voltage pulses147applied above the molecule, with V = 1.3-3.2 V. CO masking groups were dissociated with V = 1.5-3.3 V. f-i, AFM148image of C_{16} in neutral (f) and anionic (g) charge state, and calculated lowest-energy adsorption sites of C_{16}^{0} (h) and149 C_{16^-} (i) on NaCl. j-m, C_{16}^{0} adsorbed in a bay of a 3rd layer NaCl island, imaged with AFM at different tip heights. All150molecules are adsorbed on NaCl(2ML)/Cu(111). The tip-height offsets provided in the images refer the STM setpoint151of I = 0.2 pA and V = 0.2 V on bare NaCl(2ML)/Cu(111). Scale bars 0.5 nm.

- 152 *Charge state switching and electronic characterisation:* The charge state of C₁₆ can be
- controllably switched using the applied bias, as shown in Fig. 4. At about V = 0.5 V, the molecule 153 switched from neutral C_{16}^{-0} to the anion C_{16}^{--} , (and at V = -0.3 V in the reverse direction, C_{16}^{--} to 154 C_{16}^{0} , see Figs. S11, S17). The STM images in Fig. 4a, b show C_{16}^{0} and C_{16}^{-} , respectively. The 155 negative charge state leads to a characteristic dark halo (Fig. 4b) and interface state scattering as 156 observed in the difference image Fig. 4c (ref. 43), see also Fig. S11 for images with enhanced 157 contrast. The assignments of these charge states are corroborated by KPFS, see Fig. S17. AFM 158 data for C_{16}^{0} and C_{16}^{-} are shown in Fig. 4d, e with corresponding Laplace filtered data in Fig. 4g, 159 h, respectively. In this case, the structural distortion of C_{16}^{0} and C_{16}^{-} is similar, which we assign 160 to the influence of the 3rd layer NaCl island. 161



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Fig. 4. Charge-state switching and electronic characterisation. a, b, Constant-current STM images of C₁₆ in neutral and negative charge state, respectively (V = 50 mV, I = 0.2 pA). c, Difference of panels b and a. d, e, Constant-height AFM images of C₁₆⁰ and C₁₆⁻, respectively. f, Const.-current STM (I = 0.4 pA and V = +1.2 V) mapping the ionic resonance of C₁₆⁻ to C₁₆²⁻. g-i, Same data as d-f after applying a Laplace filter. The molecule was adsorbed on NaCl(2ML)/Cu(111), near a 3rd layer island. All scale bars 0.5 nm. k, l, Optimised geometries (ω B97XD/def2-TZVP) of C₁₆⁰ and C₁₆⁻, respectively, with bond lengths and bond angles indicated. m, Simulated isosurface at 0.2 a.u. (1.4 e/Å³) of the LUMO of C₁₆⁻.

The more stable adsorption at the third layer island allowed us to image the molecule at increased bias voltages without inducing movement of the molecule. At about 1.2 V, we observe the onset of an electronic resonance by scanning tunnelling spectroscopy (STS; see Fig. S17). The STM image at 1.2 V shown in Fig. 4f (Laplace filtered data in Fig. 4i), reveals the orbital density corresponding to that resonance¹¹. As the molecule is already in the anionic charge state at V > 0.5 V, we assign this resonance to the transition from anionic C₁₆⁻, to the dianionic charge state C₁₆²⁻, giving us insight into the electronic structure of C₁₆.



Fig. 5. Nucleus independent shift. NICS(0)_{zz} plots for **a**, neutral C₁₆ and **b**, C₁₈ (ωB97XD/def2-TZVP).

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Multireference methods and DFT (see Tables S4 and S5 for details) both predict C_{16}^{0} to 179 180 have a |2020> ground state with a polyynic geometry and significant BLA, but no bond-angle alternation (BAA), resulting in D_{8h} symmetry (Fig. 4k). In contrast, C_{16} shows both BLA and 181 BAA (Fig. 4l), i.e., an additional symmetry breaking to C_{8h} . The electronic structure of C_{16}^0 (Fig. 182 1 right and Fig. S18) features a nearly degenerate pair of highest occupied molecular orbitals A" 183 184 (HOMO-1) and A' (HOMO), as well a nearly degenerate pair of lowest unoccupied molecular orbitals B" (LUMO) and B' (LUMO+1); in both pairs, the in-plane orbital has a slightly higher 185 energy than the out-of-plane one. HOMO and LUMO+1 (as well as HOMO-1 and LUMO) are 186 related by rotation, giving rise to a strongly paratropic ring current (25 nA/T). This ring current is 187 reflected by the pattern of shielding and deshielding, visualised using the nucleus independent 188 chemical shift (NICS, Fig. 5a), which is opposite to the pattern for aromatic C₁₈ (Fig. 5b). Single 189 occupation of the B" LUMO in the C₁₆⁻ anion leads to symmetry lowering and BAA. 190

The DFT-predicted LUMO of C_{16} (Fig. 4m, Fig. S19) can be compared to the electronic 191 resonance imaged by STM (Fig. 4f,i), which corresponds to the squared orbital wavefunction^{11,43} 192 and to the addition of a second electron to the singly occupied out-of-plane orbital (B") in C_{16} . 193 Both theory and experiment show high-density lobes above the long bonds of C₁₆⁻, which are 194 located between the bright features of the corresponding AFM images. The symmetry lowering 195 from D_{8h} to C_{8h} in C_{16} , that is the effect of BAA, is reflected in the shape of the orbital lobes and 196 can be observed in both experiment (Fig. 4f,i) and theory (Fig. 4m). AFM data showing BLA, 197 and STM data showing the orbital density for the C_{16}^{-} to C_{16}^{2-} transition, corresponding to 198 addition of an electron to the B" orbital of C16, are all in excellent agreement with the 199 calculations, strongly suggesting the doubly anti-aromatic character of C₁₆⁰, which causes 200 pronounced BLA and a D_{8h} geometry. The two other possible electronic configurations of C_{16} , 201 $|2200\rangle$ and $|1111\rangle$, were calculated by DFT to have nearly identical D_{16h} minima with no BLA 202 and significantly higher energies (2.47 and 1.78 eV, respectively) than the doubly anti-aromatic 203 $|2020\rangle$. Relative ground-state energies of the D_{8h} and D_{16h} minima were also determined using q-204 UCCSD, by simulating quantum circuits with Qiskit⁴⁴. Q-UCCSD predicts that the D_{8h} minimum 205

206	is more stable than the D_{16h} one by 3.38 eV, which is very similar to the result obtained using
207	conventional coupled clusters singles doubles (3.31 eV; see SI for further discussion).

Our experimental results, most importantly the observed BLA for neutral C₁₆, confirm the 208 occupation of both π -systems with 16 electrons (in-plane and out-of-plane), making the molecule 209 doubly anti-aromatic. In addition, NICS and bond current calculations on neutral C₁₆ indicate 210 significant anti-aromaticity in this electronic configuration. The investigation of both C_{16}^{0} and 211 C_{16} provides confidence in the assignment of charge states and insights into the electronic 212 structure of the molecule. The synthesis, stabilisation and characterisation of C_{16} opens the way 213 to create other elusive carbon-rich anti-aromatic molecules by atom manipulation. The high 214 215 reactivity of C₁₆, and other cyclocarbons, renders them promising precursors to novel carbon allotropes¹³. 216

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