Stereoselective Syntheses, Structures and Properties of Extremely Distorted Chiral Nanographenes Embedding Hextuple Helicenes

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Myriam Roy,[a c] Veronika Berezhnaia,[a] Marco Villa,[a] Nicolas Vanthuyne,[b] Michel Giorgi,[d] Jean-Valère Naubron,[d] Salomé Poyer,[e] Valérie Monnier,[d] Laurence Charles,[e] Yannick Carissan,[b] Denis Hagebaum-Reignier,[b] Jean Rodriguez,[b] Marc Gingras,*[a] Yoann Coquerel*[b]

Abstract: We report a mo ecu ar des gn and concept us ng π system e ongat on and ster c effects from he cenes surround ng a tr pheny ene core toward stab e ch ra po ycyc c aromat c hydrocarbons (PAHs) w th a max ma π d stort on to tack e the r aromat c ty, supramo ecu ar and mo ecu ar propert es. The se ect ve syntheses, and the structura , conformat ona and ch ropt ca propert es of two d astereomer c arge mu t he cenes of formu a $C_{90}H_{48}$ hav ng a tr pheny ene core and embedd ng three [5]he cene un ts on the r nner edges and three [7]he cene un ts at the r per phery are reported based on d astereose ect ve and, when app cab e, enant ospec f c (!) Yamamoto type cyc otr mer zat ons of racem c or enant opure 9,10 d bromo[7]he cene. Both mo ecu es have an extreme y d storted tr pheny ene core, and one of them exh b ts the argest tors on ang e recorded so far for a benzene r ng (tw st = 36.9°). The ana ys s of aromat c ty d str but on n these mode mo ecu es us ng magnet c cr ter a revea ed a non aromat c character of the r tr pheny ene cores and prov des a new ook at aromat c ty n three d mens ona PAHs. One d astereomer can comp ex up to three s ver(I) ons n the bay reg on (cav t es) of ts per phera [7]he cene un ts, open ng the door to ch ra cat on c meta nanographene hybr ds.

Introduction

Two d mens ona po ycyc c aromat c hydrocarbons (PAHs) are d verse n s zes and shapes, start ng from sma naphtha ene or tr pheny ene un ts to graphene sheets and/or f akes hav ng both d mens ons arger than 100 nm. Large PAHs can exh b t except ona e ectron c and phys ca propert es governed by the r s ze and the nature of the r per phery. Thus, cons derab e efforts are current y underway to synthes ze we def ned arge 2D PAHs such as graphene nanor bbons and nanographenes by organ c synthes s (bottom up approach) n so ut on or on a surface and to nvest gate the r propert es and app cat ons.[1] Because PAHs are somewhat f ex b e and stretchab e mo ecu es, t a ows the des gn of curved PAHs such as bow s, sadd es, co ed r bbons, prope ers and c rcu ar be ts w th def ned mo ecu ar ch ra ty.[2] The atter property s of a great nterest n fe, chem ca , and phys ca sc ences as we as techno ogy, because t a ows an add t ona tun ng of mo ecu ar propert es and funct ons for many app cat ons.[3] Large ch ra PAHs have thus become mo ecu es of utmost nterest as three d mens ona ch ra nanographenes, and sma curved PAHs are now often sought as bu d ng b ocks for the r construct on n the racem c ser es.[4] In that d rect on, mu t he cenes have emerged as a c ass of prom s ng we def ned arge ch ra PAHs.[5] Mu t he cenes can ex st as severa d astereomers, each ex st ng as a pa r of enant omers (except n the cases of some ach ra *meso* d astereomers), that can more or ess rap d y nterconvert depend ng on the tors ona energy and f ex b ty of the mo ecu es. The proper accumu at on of he ca stra n n mu t he cenes can produce except ona y d storted mo ecu es show ng some benzene un ts suffer ng from an extreme tors on ang e. For nstance, record tors ons of 35.3° and 35.7° were recent y measured n a D_2 symmetr c quadrup e he cene[6] and a C_2 symmetr c hextup e he cene,[7] respect ve y. A fru tfu approach to racem c tr p e he cenes and h gher order congeners was based on cyc otr mer zat on react ons to forge a d storted tr pheny ene core.[7 8] Us ng th s approach, we report here n the d astereose ect ve and, when app cab e, enant ospec f c syntheses of two arge and extreme y d storted d astereomer c hextup e he cenes of formu a $C_{90}H_{48}$. The conformat ona behav or, the structure, the ch ropt ca propert es and the tors on nduced def c ent oca aromat c ty n these mo ecu es are d scussed n deta , together w th the exp orat on of the comp exat on ab ty toward s ver(I) ons for one of them.

Results and Discussion

Syntheses and conformational properties. It was env s oned that the ch ra three b ade prope er shaped hextup e he cene D_3 **2** of formu a $C_{90}H_{48}$ cou d be prepared by a Yamamoto type cyc otr mer zat on of 9,10 d bromo[7]he cene **1** (F gure 1a). Th s

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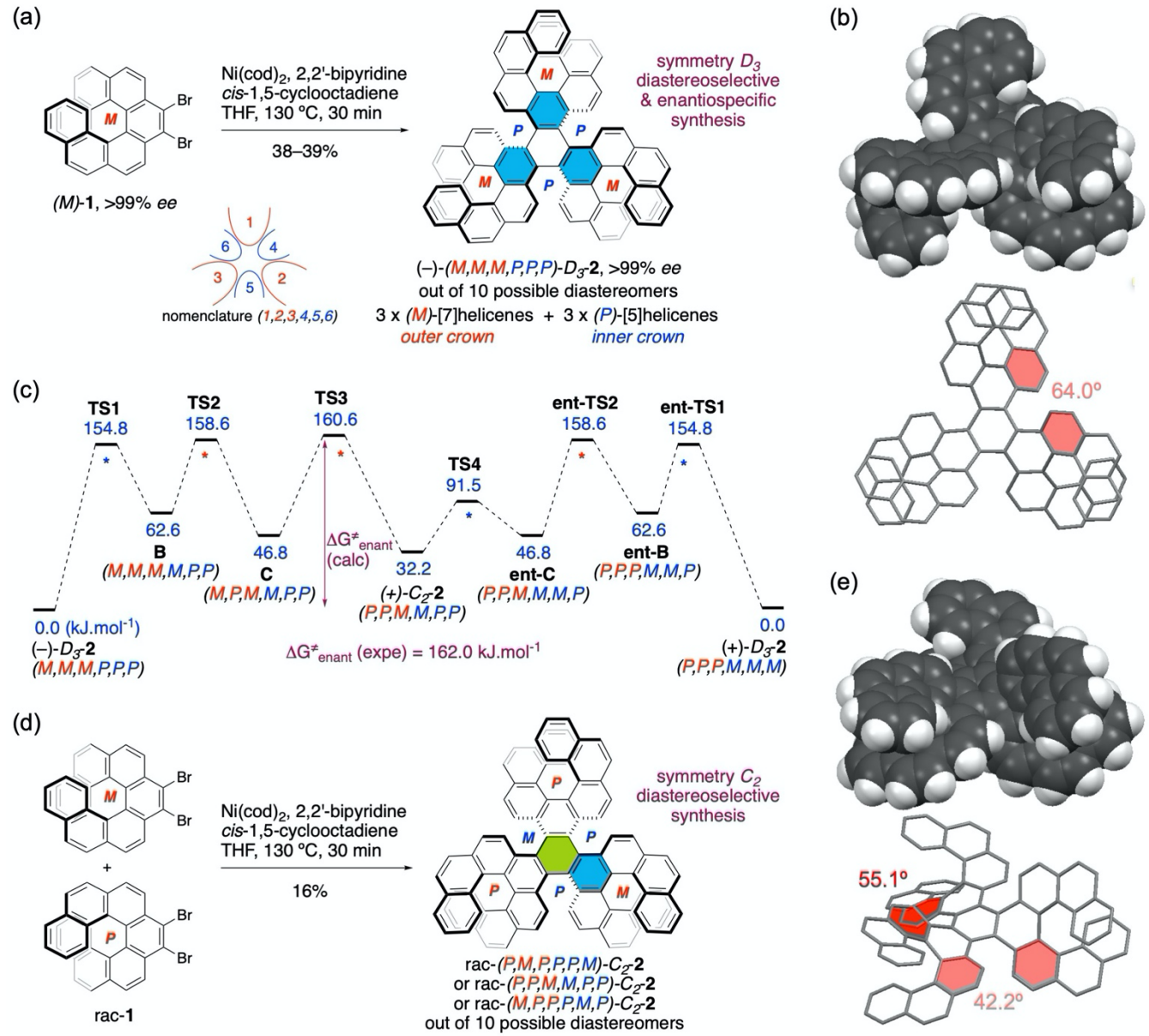

Figure 1. Syntheses and some properties of the hextuple helicenes ( )-*D*3-**2** and rac-*C*2-**2** (a) Yamamoto-type cyclotrimerization of (*M*)-9 10-dibromo[7]helicene [*(M)*-**1**] leading to ( )-*D*3-**2** (b) Three-dimensional representations of ( )-*D*3-**2** obtained from single-crystal X-ray diffraction analysis remarkable interplanar angles are highlighted in red (c) Simplified plausible enantiomerization pathway of *D*3-**2** obtained by DFT calculations [B3LYP/6-31G(d) in the gas phase] energies are free Gibbs energies and are expressed in kJ·mol 1 see the Supporting nformation for details (d) Yamamoto-type cyclotrimerization of racemic 9 10-dibromo[7]helicene (rac-**1**) leading to rac-*C*2-**2** (e) Three-dimensional representations of rac-*C*2-**2** obtained from single-crystal X-ray diffraction analysis remarkable interplanar angles are highlighted in red

new ch ra PAH embeds three homoch ra [7]he cene un ts on ts outer she and three homoch ra [5]he cene un ts of oppos te conf gurat on on ts nner edges. [7]He cene tse f has a h gh barr er to enant omer zat on (178.8 kJ·mo $^{-1}$)[9] prec ud ng ts nvers on of conf gurat on at a s gn f cant rate under the projected react on cond t ons (ca. 130 °C). It was assumed that the barr ers to nvers on of conf gurat on of the var ous [7]he cene conta n ng spec es nvo ved n the p anned n cke (0) med ated cyc otr mer zat on wou d be too h gh for the synthes s to re y on a thermodynam c contro as n prev ous stud es.[7 8] Thus, t shou d be poss b e to perform the synthes s from enant opure *(P)* or *(M)* **1** to obta n the correspond ng enant opure hextup e he cene *D*3 **2** n an enant ospec f c manner. Indeed, the n cke (0) med ated cyc otr mer zat on of *(M)* **1** afforded ( ) (*M M M P P P*) *D*3 **2** n a 38% y e d (F gure 1a). The same react on performed w th *(P)* **1** gave (+) (*P P P M M M*) *D*3 **2** n a 39% y e d (not dep cted). Both enant omers of *D*3 **2** were thus d rect y obta ned as enant opure hextup e he cenes, as conf rmed by ana yt ca chromatography on a ch ra stat onary phase. The structure and abso ute conf gurat on of ( ) (*M M M P P P*) *D*3 **2** were unamb guous y

conf rmed by s ng e crysta X ray d ffract on methods (F gure 1b) and c rcu ar d chro sm spectroscop es (see Support ng Informat on). On a stereochem ca po nt of v ew, ten d astereomers of **2** are poss b e: two of C_1 symmetry, s x of C_2 symmetry and two of D_3 symmetry. The r re at ve free G bbs energ es were ca cu ated by DFT methods from 0.0 kJ·mo^{-1} for D_3 **2**, the thermodynam c d astereomer, up to 108.3 kJ·mo^{-1} for a C_2 symmetr c metastab e d astereomer. A p aus b e enant omer zat on pathway for D_3 **2** was computed w th a barr er to enant omer zat on ca cu ated at 160.6 kJ·mo^{-1} (F gure 1c), n agreement w th a va ue exper menta y determ ned at 162.0 kJ·mo^{-1} correspond ng to a racem zat on ha f fe $t_{1/2}$ = 43 m on years at 25 ºC or 1.3 years at 130 ºC. Notab y, the barr er to enant omer zat on of D_3 **2** s ower than for the parent [7]he cene, an odd ty for D_n symmetr c mu t he cenes n genera .[5] Amus ng y, hextup e he cene D_3 **2** s the second tr ske on shaped nanographene reported w th n a short per od of t me.[4e] The enant ospec f c synthes s of both enant omers of D_3 **2** from e ther *(P)* and *(M)* **1** conf rmed our hypothes s that no s gn f cant nvers on of conf gurat on of [7]he cene un ts can occur at a s gn f cant rate n the var ous synthet c ntermed ates nvo ved n ts synthes s. Th s trans ated n a un que opportun ty to synthes ze d astereose ect ve y a d astereomer of D_3 **2** from racem c **1**, th s t me m x ng he c t es of the [7]he cene un ts at the outer she of the mo ecu e. Accord ng y, the n cke (0) med ated cyc otr mer zat on of rac **1** a owed the format on of both the racem c (*P M P P P M*) C_2 **2** and D_3 **2** d astereomers n a 13.8:1 rat o and the so at on of (*P M P P P M*) C_2 **2** n a 16% y e d (F gure 1d); note that hextup e he cene rac (*P M P P P M*) C_2 **2** can a so be denom nated rac (*P P M M P P*) C_2 **2** or rac (*M P P P M P*) C_2 **2** accord ng to the proposed nomenc ature. The structure and re at ve conf gurat ons of rac C_2 **2** were ascerta ned by s ng e crysta X ray d ffract on ana ys s (F gure 1e). The free G bbs energy of d astereomer C_2 **2** was ca cu ated at +32.2 kJ·mo^{-1} re at ve to D_3 **2**, and d astereomer C_2 **2** s an ntermed ate n the computed enant omer zat on pathway for D_3 **2** (F gure 1c). The enant omers of d astereomer C_2 **2** were separated by ch ra HPLC techn ques and were fu y character zed by ch ropt ca methods, nc ud ng the attr but on of the r abso ute conf gurat ons (see the Support ng Informat on).

Structural and chiroptical studies. The structura features of hextup e he cenes D_3 **2** and C_2 **2** were carefu y exam ned (F gure 2). The four benzene un ts from the tr pheny ene core of D_3 **2** show a marked a ternat on of bond engths from 1.404 Å to 1.465 Å (mean va ues because of the crysta ograph c C_2 symmetry of D_3 **2**), to be compared to 1.393 Å n benzene,1.420 Å n graphene, and 1.338 Å and 1.454 Å n 1,3 butad ene,[10a b] and may be regarded as the r Keku é structures, .e. 1,3,5 cyc ohexatr enes. The centra r ng n D_3 **2** ex sts n a cha r conformat on and the three surround ng r ngs adopt severe y tw sted conformat ons w th a mean tors on ang e of 32.4º (F gure 2a). Eva uat on of the photophys ca propert es of D_3 **2** nd cated a max ma absorpt on at 417 nm (ε = 90000 M^{-1}cm^{-1}) and max ma em ss on at 538 nm (quantum y e d = 5.7%). The opt ca rotat on of (*M M M P P P*) D_3 **2** was measured at $[\alpha]_D^{25}$ = 300 (c = 0.0325, CHC$_3$), wh ch s an unexpected y sma abso ute va ue when compared to the arge opt ca rotat on va ues of so ated (*P*) [5]he cene ($[\alpha]_D^{25}$ = +1670) and (*M*) [7]he cene ($[\alpha]_D^{25}$ = 5900). S m ar y, the e ectron c and v brat ona c rcu ar d chro sm spectra of D_3 **2** were found of ow ntens ty (see the Support ng Informat on). It was reasoned that the strong contr but on to the ch ropt ca propert es of the three moderate y stretched homoch ra (*M*) [7]he cene un ts at the outer she n (*M M M P P P*) D_3 **2** (mean nterp anar ang e of the two term na r ngs = 39.7º vs 32.3º n [7]he cene tse f[11a b]) s somehow compensated by a strong contr but on of oppos te ntens ty of the three severe y stretched homoch ra (*P*) [5]he cene un ts at ts edges (mean nterp anar ang e of the two term na r ngs = 64.0º vs 46.0º n [5]he cene tse f[11c]). The structura ana ys s of C_2 **2** a so revea ed a pronounced bond engths a ternat on of the four benzene un ts from ts tr pheny ene core, w th bond engths

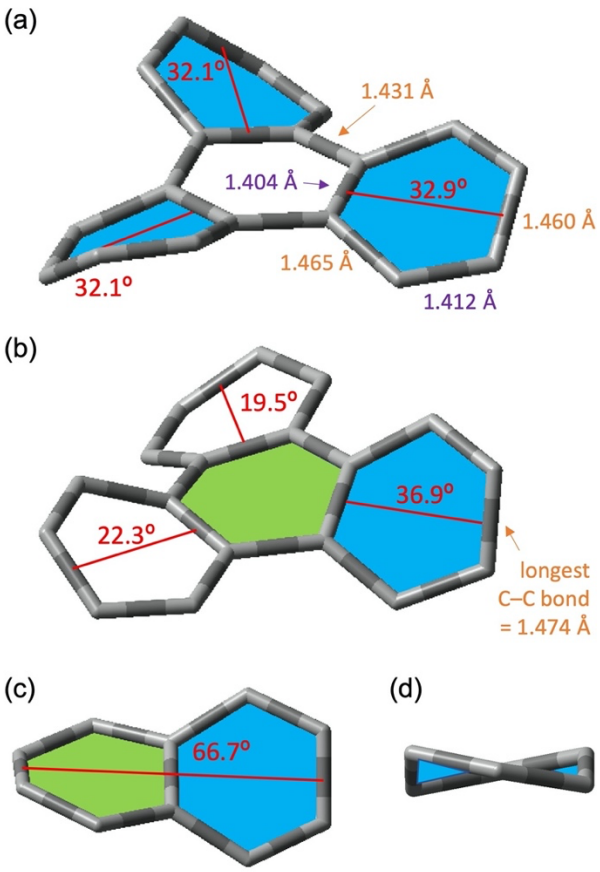

Figure 2. Some structural features of D_3-**2** and C_2-**2** (a) The triphenylene core in D_3-**2** including remarkable torsion angles and bond lengths (mean values) The solid-state conformation of D_3-**2** has crystallographic C_2-symmetry justifying for the non-equivalent torsions in all the three blue-colored rings (b) The triphenylene core in C_2-**2** including remarkable torsion angles and bond length The solid-state conformation of C_2-**2** has no crystallographic symmetry justifying for the non-equivalent torsions in the two white-colored rings (c) The naphthalene unit along the molecular C_2 axis in C_2-**2** showing a very high end-to-end torsion (d) Profile view of the most twisted benzene ring in C_2-**2**

genera y comparab e w th those n D_3 **2**. However, the ongest nteratom c d stance n C_2 **2** s the C C bond crossed by the C_2 ax s n the per phery of the tr pheny ene core has a ength of 1.474 Å (F gure 2b), comparab e w th the one of the C(sp^2) C(sp^2) s ng e bond n some b pheny s.[10c] The C_2 **2** d astereomer was found s gn f cant y more d storted than somer D_3 **2**, w th a max ma tors on ang e cu m nat ng at 36.9º (!) for the per phera r ng of the tr pheny ene core on the C_2 ax s, estab sh ng the current record of tors on for a "benzene" r ng (F gures 2b,d). A so, the naphtha ene un t a gned w th the C_2 ax s n C_2 **2** exh b ts a very h gh end to end tors on of 66.7º (F gure 2c, current record = 69.5º[6]). The opt ca rotat on of (*P M P P P M*) C_2 **2** was measured at $[\alpha]_D^{25}$ = +705 (c = 0.0337, CH_2C_2) and ts e ectron c c rcu ar d chro sm spectrum showed a re at ve y ow ntens ty (see Support ng Informat on), ch ropt ca features comparab e w th those of d astereomer D_3 **2**. The h gh y d storted structures of D_3 **2** and C_2 **2** m t the format on of ntermo ecu ar π π nteract ons, thus a ow ng enhanced so ub ty n organ c so vents. Th s s we ustrated by the crysta pack ng of (*M M M P P P*) D_3 **2** that shows few nteract ons between the nd v dua mo ecu es that stack to form supra he ces of *(P)* conf gurat on w th n the crysta , creat ng arge ch ra CDC$_3$ so vent channe s organ zed a ong the a and b crysta ograph c axes (F gure 3).

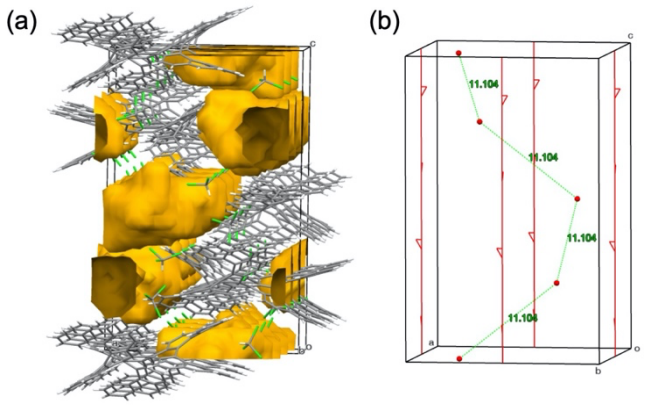

Figure 3. (a) Crystal packing of (*M,M,M,P,P,P*)-D_3-**2** and representation of the solvent channels along the b axis The content of the channels is a mix of explicitly determined *d*1-chloroform molecules and the calculated mask of solvent (yellow voids) (b) Representation of the *(P)*-configured supra-helix (pitch = crystallographic c vector = 27 2785 Å) in the crystal packing of (*M,M,M,P,P,P*)-D_3-**2** side view along the c axis the four-fold 4_3 screw axis is in red the centroids of the central rings of each molecule are represented as red dots and the distances between them (Å) are noted in green

Evaluation of aromaticity. The hextup e he cenes D_3 **2** and C_2 **2** susta n unprecedented d stort on for stab e PAHs, po nt ng out for unusua def c enc es n oca aromat c ty. Aromat c ty s an extreme y usefu and popu ar concept n chem stry a though there s no s ng e quant tat ve def n t on of t, and t s not d rect y measurab e exper menta y.[12] App cat on of the qua tat ve C ar's ru e[13] to D_3 **2** (or C_2 **2**, stereochem stry s not accounted for n C ar's structures) pred cts an a ternat on of oca aromat c ty w th 13 separated π sextets n the C ar's structure conta n ng the argest number of d sjo nt aromat c π sextets (F gure 4d), and n ne d sjo nt π sextets n the comp ementary C ar's structure. However, the C ar's ru e s str ct y va d for p anar po ycyc c aromat c systems. Structura [14] energet c [15] e ectron dens ty based,[16] and magnet c based nd ces[17] have been deve oped to character ze and to quant fy aromat c ty as a property of mo ecu es. However, these nd ces were a so deve oped for p anar systems and the r transpos t on to three d mens ona systems can ead to errat c resu ts. For nstance, t was ear er recogn zed that the popu ar structura based nd ces as HOMA (Harmon c Osc ator Mode of Aromat c ty) and energet c based nd ces as TRE (Topo og ca Resonance Energy), as we as some e ectron dens ty based methods, do not perform we for co ed systems as [n]he cenes and can ead to d screpanc es.[18] Indeed, we exper enced d ff cu t es w th the HOMA dur ng our ear y work (see Support ng Informat on). Actua y, on y magnet c based methods appear app cab e to severe y tw sted aromat cs. When an externa magnet c f e d s app ed to a mo ecu e, strong nduced e ectrons currents are created at aromat c (d atrop c currents) and ant aromat c (paratrop c currents) r ngs. The ACID (An sotropy of the Induced Current Dens ty) method[19] a ows the v sua zat on of an sosurface on wh ch the nduced current dens ty vectors are p otted, show ng d atrop c (c ockw se, aromat c) and paratrop c (counterc ockw se, ant aromat c) currents. However, the method s sens t ve to the or entat on of the app ed externa magnet c f e d, norma y perpend cu ar to the mo ecu ar p ane, wh ch can be prob emat c w th h gh y d storted PAHs such as D_3 **2** and C_2 **2**. The NICS (Nuc eus Independent Chem ca Sh fts) ndex re es on the computat on of the oca magnet c env ronment at any des red po nt n space, often referred to as a ghost atom, and s expressed n ppm.[20] NICS(0) va ues refer to ghost atoms p aced at the center of each cyc e, w th arge negat ve NICS(0) prob ng nduced d atrop c r ng currents attr buted to aromat c ty. For nstance, benzene has a NICS(0) ca cu ated at 8.6 ppm at the eve of theory emp oyed here n. A though the comb nat on of both methods a ows for a qua tat ve and quant tat ve descr pt on of the nduced e ectron currents, t shou d be kept n m nd that the connect on between nduced d atrop c r ng currents and aromat c ty s not stra ghtforward.[12b 17]

The NICS ana ys s of D_3 **2** (F gure 4a) a owed dent fy ng three groups of r ngs w th d st nct oca aromat c ty:) the A and B r ngs of the tr pheny ene core have NICS(0) va ues compr sed between 0.6 and +0.8 ppm account ng for poor y d rect ona nduced r ng currents nd cat ng a non aromat c character of these two r ngs;) the C and D r ngs have def c ent nduced d atrop c r ng currents w th NICS(0) va ues ca cu ated around 5.3 ppm po nt ng out for marked def c ent oca aromat c ty; and) the term na E r ngs w th NICS(0) va ues of 9.6 ppm denot ng fu aromat c ty. The over est mat on of NICS n the term na r ngs of [7]he cene s documented and s due to the magnet c coup ng w th the ne ghbor ng r ng p aced be ow or above.[17a] Notab y, for each [5]he cene and [7]he cene subun t n D_3 **2** an overa ower aromat c ty than for the parent so ated [5]he cene and [7]he cene was computed (see graphs n F gure 4a). A so, the d str but on of oca aromat c ty n the [7]he cene un ts n D_3 **2** d ffers s gn f cant y from the one of so ated [7]he cene w th the centra r ng B be ng non aromat c n D_3 **2**. In order to d fferent ate tors ona effects

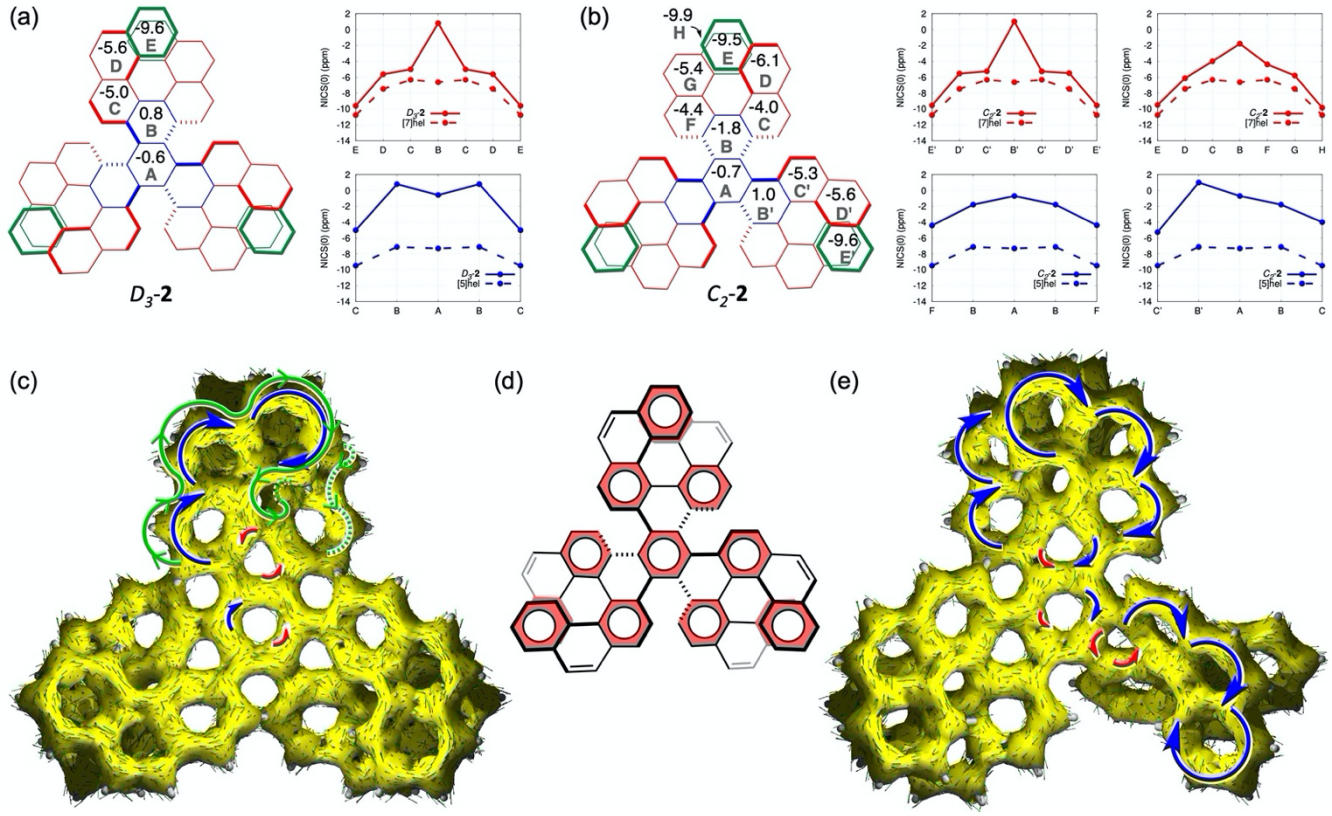

Figure 4. Aromaticity analysis in D_3-**2** and C_2-**2** (a) N CS(0) values for all non-equivalent rings in D_3-**2** The graphs show the N CS(0) values for the [7]helicene and [5]helicene units in D_3-**2** (solid red and blue lines respectively) and isolated [7]helicene and [5]helicene (dashed lines) (b) N CS(0) values for all non-equivalent rings in C_2-**2** The graphs show the N CS(0) values for the [7]helicene and [5]helicene units in C_2-**2** (solid red and blue lines respectively) and isolated [7]helicene and [5]helicene (dashed lines) (c) AC D plot of D_3-**2** the magnetic field is applied along the +z axis perpendicular to the view plane pointing to the observer diatropic currents are highlighted with blue and green arrows and paratropic currents are highlighted with red arrows (d) Clar's perspective of D_3-**2** showing 13 separated π-sextets the Clar's perspective of C_2-**2** would be identical (e) AC D plot of C_2-**2** the magnetic field is applied along the +z axis perpendicular to the view plane pointing to the observer diatropic currents are highlighted with blue arrows and paratropic currents are highlighted with red arrows

from through space and conjugat on effects n the NICS(0) ca cu at ons of the tr pheny ene cores of both D_3 **2** and C_2 **2**, the NICS(0) were a so computed for the v rtua tr pheny ene mo ecu es hav ng the d storted geometr es D_3 **2** and C_2 **2** (see the Support ng Informat on). Compar son w th the NICS(0) of tr pheny ene tse f showed an augmentat on of ca. +2 ppm for the d storted r ngs when compared to the r p anar counterparts, show ng that tors ona effects have a s gn f cant contr but on to the unusua NICS(0) va ue computed for D_3 **2** and C_2 **2**. The ACID p ot of D_3 **2** (F gure 4c) conf rmed the NICS ana ys s: the externa E r ngs d sp ay c ear and strong d atrop c r ng currents cons stent w th fu aromat c ty, the C and D r ngs exh b t dom nant d atrop c r ng currents but of ower ntens ty, wh e the A and B r ngs show compet ng sma d atrop c and paratrop c currents nd cat ng weak e ectron c de oca zat on and a non aromat c character. The tr pheny ene core n D_3 **2** s probab y the east aromat c known tr pheny ene un t, wh ch corre ates w th ts unprecedented tors on. More g oba y, a strong d atrop c macrocyc c r ng current s c ear y v s b e at the per phery of the who e mo ecu ar arch tecture show ng g oba e ectron c de oca zat on, wh ch s certa n y compensat ng for the severe d stort ons of the π systems and contr but ng to the thermodynam c stab ty. The ana ys s of oca aromat c ty n d astereomer C_2 **2** revea ed comparab e features to the one of D_3 **2** w th however a more comp ex s tuat on due to the ower symmetry of the mo ecu e (F gures 4b,e). Notab y, the two homoch ra [7]he cene un ts (those not crossed by the C_2 ax s) and the tr pheny ene core have d fferent NICS(0) va ues. The ACID p ot of C_2 **2** conf rmed qua tat ve y ts overa d str but on of oca aromat c ty. A together, the mu t he cenes D_3 **2** and C_2 **2** are PAHs whose oca aromat c ty s subjected to var at ons of arge amp tudes from ent re y aromat c at the edges to non aromat c at the cores, corre at ng the d str but on of d stort on n the mo ecu es.

Complexation properties of multi-helicene D_3-2. [7]He cene tse f was ear er demonstrated to behave as a ch ra mo ecu ar tweezer for s ver(I) ons, the meta c cat on be ng sandw ched between the two outermost bonds of the he cene (C3 C4).[21] It was hypothes zed that hextup e he cene D_3 **2** embedd ng three dent ca and moderate y stretched [7]he cene un ts on ts outer she cou d behave as a mono, b s or tr p e tweezer capab e of comp ex ng up to three s ver(I) ons to form some or g na ch ra cat on c meta nanographene hybr ds (F gure 5). The b nd ng energ es for the terat ve comp exat on of one, two

and three s ver(I) ons ns de the bay reg on of three [7]he cene un ts n D_3 **2** were eva uated by DFT ca cu at ons and compared to the one of Ag^+ w th [7]he cene[21] (see the Support ng Informat on). Th s mode study nd cated a s ght y better

Figure 5. Computationally optimized structures of the most stable mono bis and triscationic Ag^+ complexes of D_3-**2** (DFT wB97XD/Def2TZVP//wB97XD/Def2SVP gas phase) Left $[Ag\subset D_3\text{-}\mathbf{2}]^+$ middle $[2Ag\subset D_3\text{-}\mathbf{2}]^{2+}$ right $[3Ag^+\subset D_3\text{-}\mathbf{2}]^{3+}$

stab zat on for $[Ag\subset D_3\ \mathbf{2}]^+$ than for $[Ag\subset$[7]he cene$]^+$, and a so that tr scat on $[3Ag\subset D_3\ \mathbf{2}]^{3+}$ shou d be reasonab y stab e. Exper menta y, a methano /d ch oromethane so ut on of D_3 **2** and $AgNO_3$ (1:1) was ana yzed by e ectrospray on zat on mass spectrometry (ESI MS) us ng very soft cond t ons, drast ca y m t ng the generat on of ons upon co s on n the nterface of the mass spectrometer (*i e* n the gas phase), so that most, f not a , observab es resu t from the e ectrospray of cat on c spec es n t a y present n so ut on. The format on of both the cat on $[Ag\subset D_3\ \mathbf{2}]^+$ and the b scat on $[2Ag\subset D_3\ \mathbf{2}]^{2+}$ n the so ut on cou d be c ear y ev denced. However, perform ng on mob ty separat on (IMS) pr or to mass ana ys s to further enhance the dynam c range of detect on perm tted to ev dence that $[3Ag\subset D_3\ \mathbf{2}]^{3+}$ s a so a stab e comp ex. The re at ve stab ty of the three s ver adducts was eva uated by the 11.2:100:3.8 abundance rat o measured for $[Ag\subset D_3\ \mathbf{2}]^+$ / $[2Ag\subset D_3\ \mathbf{2}]^{2+}$ / $[3Ag\subset D_3\ \mathbf{2}]^{3+}$ by IMS MS, c ear y show ng the b scat on c $[2Ag\subset D_3\ \mathbf{2}]^{2+}$ comp ex as the most stab e one when observed as naked gas phase ons. The actua reasons for th s preference rema n unc ear at th s stage and may nc ude the ex stence of a more compact and better adjusted conformat on for b scat on c $[2Ag\subset D_3\ \mathbf{2}]^{2+}$ than for ts mono and tr scat on c ana ogues as seem ng y nd cated by the exper menta determ nat on of co s on cross sect ons (see Support ng Informat on).

Conclusions

The mo ecu ar des gn and concept us ng π system e ongat on and ster c effects, based on he ca stra ns surround ng a tr pheny ene core w th conf gurat ona y stab e [7]he cenes, has ed to extreme d stort on n some ch ra PAHs. Th s dea was put nto pract ce through a n cke (0) med ated cyc otr mer zat on of enant opure and racem c 9,10 d bromo[7]he cene, wh ch d astereose ect ve y afforded arge ch ra hextup e he cenes of formu a $C_{90}H_{48}$ w th D_3 and C_2 symmetry, respect ve y. The d astereomer w th D_3 symmetry s a three b ade prope er shaped ch ra nanographene that embeds three homoch ra [7]he cene un ts on ts outer she and three homoch ra [5]he cene un ts of oppos te conf gurat on on ts nner edges. Both D_3 symmetr c enant omers were d rect y obta ned as enant opure mater a s by an enant ospec f c Yamamoto type cyc otr mer zat on, a prem ere for arge ch ra PAHs, and a f rst examp e for th s type of cyc otr mer zat on. The structura ana ys s of th s mo ecu e revea ed a h gh y d storted tr pheny ene core w th a marked bond engths a ternat on of the s x membered r ngs. The d astereomer w th C_2 symmetry embeds three [7]he cene un ts of m xed he c ty on ts outer she , and three [5]he cene un ts of m xed he c ty on ts nner edges so that four *(P)* conf gured and two *(M)* conf gured he cenes are present n the mo ecu e. Its structura ana ys s a so en ghtened a pronounced a ternat on of bond engths n ts tr pheny ene core, and more remarkab y extreme tors ons estab sh ng new m ts for benzene (tw st = 36.9º). The ch ropt ca propert es of the two hextup e he cenes were found of re at ve y sma magn tude, poss b y due to a phenomenon of compensat on between the ntertw ned *(P)* and *(M)* conf gured he cenes. Aromat c ty was computat ona y ana yzed n these fasc nat ng mo ecu es us ng severa methods, wh ch was comp cated not on y because the quant f cat on of the concept of aromat c ty s ntr ns ca y d ff cu t, but a so because ex st ng mode s of aromat c ty were deve oped for p anar PAHs. Neverthe ess, magnet c based methods known as NICS and ACID proved to be usefu , though not dea , and they revea ed a non aromat c character of the tr pheny ene cores n both d astereomer c hextup e he cenes, n corre at on to the severe d stort on of the r ngs. An ear y exp orat on of the meta ons av d ty and supramo ecu ar propert es of the D_3 symmetr c d astereomer revea ed ts ab ty to b nd up to three s ver(I) ons n the bay reg ons (cav t es) of three [7]he cene un ts at ts outer she , as eva uated by the comb nat on of DFT s mu at ons w th advanced mass spectrometry methods, open ng the door to the f e d of ch ra cat on c meta nanographene hybr ds. To sum t up, the present study pushes the m ts on the des gn and the synthes s of h gh y d storted ch ra PAHs, where ch ra ty prov des add t ona contro on mo ecu es for modu at ng the r propert es for app cat ons n chem ca and mater a s sc ence. It a so deepens the know edge on the conformat ona , ch ropt ca and supramo ecu ar propert es (so d and so ut on states) of ch ra PAHs and nanographenes, and ra ses quest ons about aromat c ty n these arge d storted mo ecu es.

Experimental Section

Detailed experimental procedures for the syntheses of ( )-D_3-**2** (+)-D_3-**2** and rac-C_2-**2** the resolution of rac-C_2-**2** by HPLC methods the spectroscopic structural chiroptical and photophysical characterization of all compounds the experimental and computational enantiomerization study of D_3-**2** the full-detail analysis of aromaticity in D_3-**2** C_2-**2** and related molecules the full-detail complexation study of silver( ) cations with D_3-**2** and the crystallographic data for ( )-(*M,M,M,P,P,P*)-D_3-**2** (CCDC 1835903) and rac-(*P,M,P,P,P,M*)-C_2-**2** (CCDC 1902495) are included as supporting information for this article

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