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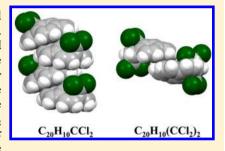


Addition of Dihalocarbenes to a π -Bowl: First Structural Study

Cristina Dubceac, [†] Alexander S. Filatov, [†] Alexander V. Zabula, [‡] and Marina A. Petrukhina*, [†]

Supporting Information

ABSTRACT: The products of 1,2-cycloaddition of dihalocarbene to the bowl-shaped corannulene $(C_{20}H_{10}, 1)$ have been isolated in the solid state and fully characterized. The first X-ray diffraction analysis of mono- and bis-adducts, C₂₀H₁₀CCl₂ (2) and $C_{20}H_{10}(CCl_2)_2$ (3), has been accomplished to reveal structural changes of the corannulene framework upon addition of dichlorocarbene groups as well as to show variations in the solid state packing of the functionalized polar bowls. For the monoadduct 2, the C_s symmetric molecular structure with the hub attachment of the CCl₂ group to a bowl was confirmed. In the solid state, the polar C₂₀H₁₀CCl₂ molecules form one-dimensional (1D) columns based on strong concave—convex $\pi \cdots \pi$ interactions (ca. 3.36-3.37 Å). The resulting polar 1D stacks in 2 are all oriented in the



same direction to form polar crystals. The addition of the second dichlorocarbene group in $C_{20}H_{10}(CCl_2)_2$ caused the drastic reduction of the dipole moment from 3.7 D in 2 to 2.0 D in 3, which was also accompanied by a change of the solid state packing pattern. For the bis-adduct 3, two different polymorphs were obtained under different crystallization conditions, solution (3a) vs gas-phase deposition (3b). Both crystal structures are based on bimolecular aggregation of $C_{20}H_{10}(CCl_2)_2$ molecules held by C-H.··Cl interactions (2.988 Å for 3a and 2.891 Å for 3b). The resulting dimers show different packing in the solid state structures of 3a and 3b.

1. INTRODUCTION

Bowl-shaped polyaromatic hydrocarbons that serve as prototypes of fullerene surfaces (and thus often referred to as buckybowls, fullerene fragments or π -bowls) constitute an important and unique class of curved carbon-rich compounds.1 Buckybowls exhibit a range of special properties stemming from their curvature such as bowl-to-bowl inversion, different preferences of concave and convex π -faces toward metal binding,³ enhanced $\pi \cdots \pi$ interactions with curved aromatic surfaces,4 and molecular curvature trade-off effects with complementary partners.⁵ They also show interesting redox properties and can acquire multiple electrons in stepwise reduction reactions to afford sets of curved carbanions.⁶ Because of their unique properties, this class of nonplanar polyarenes has been rapidly expanding over the last decades.⁷ The known examples of carbon bowls now range in size from the smallest fragments of C₆₀-fullerene such as corannulene templates for carbon nanotubes.

The studies of solid state packing of carbon-rich and curved polyarenes attract considerable attention as a key for understanding their properties. 11 For example, anisotropy in conductivity demonstrated by the Hirao group in 2009 for sumanene 12 and more recently by Lentz and co-workers for the 1,2-trifluoromethylated corannulene derivative 13 is associated with the aligned stacking of polar bowl-shaped molecules in the single-crystalline state. Our first in-depth analysis of solid state packing trends for π -bowls of different size and curvatures

reported in 2010 helped to identify other prospective candidates for such interesting anisotropic effects. 4 Overall, the role of rim functionalization of π -bowls on the resulting structures, which are responsible for their specific properties, has been noted. A variety of different functional groups has been added to the bowl periphery which significantly altered physical properties of the resulting products, such as solubility, redox, and self-assembly properties. In contrast, the interior bowl surface derivatization methods have been less developed. 18 We have recently accomplished the X-ray structural characterization of a family of hub-alkylated corannulene cations and showed the effect of the surface group size on the overall solid state packing. 19 Herein, we report the isolation and full characterization of the solid products of 1,2cycloaddition of the reactive dichlorocarbene to corannulene $(C_{20}H_{10}, 1, Scheme 1)$. We accomplished the first X-ray crystallographic study of mono- and bis-adducts, C₂₀H₁₀CCl₂ (2) and $C_{20}H_{10}(CCl_2)_2$ (3), that revealed unique molecular geometry and interesting solid state packing trends for the dichlorocarbene functionalized bowl-shaped corannulene molecules.

2. EXPERIMENTAL SECTION

Materials and Methods. The adducts C₂₀H₁₀CCl₂ (2) and $C_{20}H_{10}(CCl_2)_2$ (3) were synthesized using procedures reported in the

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Scheme 1. Chemical Drawing of 1, 2, and 3

literature. ^{18b} Corannulene was prepared as previously described²⁰ and sublimed at 175 °C prior to use. Tetrabutylammonium hydrogen sulfate (98.0%, TCI), sodium hydroxide (97.0%, Fluka), and sodium sulfate (99.0%, Sigma-Aldrich) were used as received. Chloroform (99.8%), pentane (99.5%), and hexanes (99.5%) were purchased from Pharmco and used without further purification. Rh₂(O₂CCF₃)₄, used as a transport agent, was prepared based on literature procedures. ²¹ Sublimation-deposition procedures were performed in evacuated (less than 10⁻² Torr) and sealed glass ampules (ca. 8 cm long with an o.d. of 1.1 cm), which were placed in electric furnaces having a small temperature gradient along the length of the tube. ¹H NMR spectra were measured on a Bruker AC-400 instrument at 400 MHz. CDCl₃ was used as solvent, and the residual solvent peak was taken as an internal standard (¹H NMR: CDCl₃ 7.26 ppm). Infrared spectra were obtained on a PerkinElmer Spectrum One FT-IR spectrometer.

Crystallization of C₂₀H₁₀CCl₂ (2). Colorless needles of **2** suitable for single crystal X-ray diffraction analysis were obtained by sublimation/deposition technique at 95 °C in 2 days. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.78 (s, 2H), 7.66 (d, 2H, $J_{\rm H,H}$ = 8.6 Hz), 7.16 (d, 2H, $J_{\rm H,H}$ = 8.6 Hz), 6.80 (d, 2H, $J_{\rm H,H}$ = 9.1 Hz), 5.88 (d, 2H, $J_{\rm H,H}$ = 9.1 Hz). IR (cm⁻¹): 3029(w), 2160(w), 2029(w), 1660(w), 1626(w), 1435(m), 1408(w), 1312(m), 1228(m), 1189(w), 1134(m), 1072(w), 1024(w), 950(w), 835(s), 821(s), 760(w), 747(m), 658(s), 603(w), 592(w), 575(w), 546(s).

Crystallization of C₂₀**H**₁₀(**CCl**₂)₂ (**3**). Colorless blocks of **3a** were grown from a chloroform solution layered with hexanes by slow evaporation of solvents at 15 °C over 4 weeks. Colorless blocks of **3b** were obtained by sublimation/deposition technique of a 1.5:1 mixture of Rh₂(O₂CCF₃)₄ and C₂₀H₁₀(CCl₂)₂ at 105 °C in 3 days. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.69 (d, 1H, $J_{\rm H,H}$ = 8.8 Hz), 7.63 (d, 1H, $J_{\rm H,H}$ = 8.6 Hz), 7.62 (d, 1H, $J_{\rm H,H}$ = 8.6 Hz), 7.60 (d, 1H, $J_{\rm H,H}$ = 8.8 Hz), 7.16 (d, 1H, $J_{\rm H,H}$ = 6.6 Hz), 7.14 (d, 1H, $J_{\rm H,H}$ = 6.6 Hz), 6.87 (d, 1H, $J_{\rm H,H}$ = 9.6 Hz), 6.07 (d, 1H, $J_{\rm H,H}$ = 9.6 Hz), 3.07 (d, 1H, $J_{\rm H,H}$ = 10.1 Hz), 2.95 (d, 1H, $J_{\rm H,H}$ = 10.1 Hz). IR (cm⁻¹): 3029(w), 2959(m), 2902(w), 1434(m), 1410(w), 1395(w), 1314(m), 1259(s), 1084(s), 1013(s), 862(w), 833(s), 793(s), 747(m), 693(w), 658(s), 576(w), 545(m), 536(m).

X-ray Data Collection and Structure Refinement. Single crystal X-ray diffraction experiments were collected at 100 K for 2, 3a, and 3b on a Bruker AXS diffractometer equipped with a SMART CCD detector with a Mo-target X-ray tube ($\lambda=0.71073$ Å) using the SMART software package. Cell refinement and data reduction were performed using SAINT. Data were corrected for absorption effects using the empirical methods SADABS. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL software package (Version 6.14). All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were constrained to the parent carbon atoms using a riding model. Crystallographic data and X-ray experimental conditions for 2, 3a, and 3b are listed in Table S1 in Supporting Information. Selected geometric parameters of functionalized π -bowls are given in Tables 1 and 2. The CCDC reference numbers 1029023, 1029024, and

1029025 contain the supplementary crystallographic data for 2, 3a, and 3b, respectively.

Table 1. Selected Bond Length Distances of the Cyclopropane Rings in 2, 3a, and 3b (Å)

	2	3a	3b
C1-C2	1.494(3)	1.495(3)	1.503(2)
C1-C3	1.537(3)	1.520(3)	1.523(2)
C2-C3	1.573(3)	1.525(3)	1.533(2)
C4-C22		1.496(3)	1.489(2)
C5-C22		1.517(3)	1.514(2)
C4-C5		1.547(3)	1.551(2)

Table 2. Selected Bond Length Distances for 2, 3a, and 3b (Å)

	2	3a	3b
C2-C18	1.476(3)	1.483(3)	1.486(2)
C2-C21	1.473(3)	1.475(3)	1.479(2)
C18-C19	1.409(3)	1.400(3)	1.410(2)
C19-C20	1.426(3)	1.420(3)	1.424(2)
C20-C21	1.403(3)	1.398(3)	1.401(2)
bowl depth ^a	1.068(3)	1.003(3)	1.024(2)

^aThe shortest distance between the centroid of the five interior carbon atoms and the mean plane of the 10 carbon atoms on the bowl exterior.

3. RESULTS AND DISCUSSION

The products of 1,2-cycloaddition of dichlorocarbene to corannulene, namely, mono- and bis-adducts (Scheme 1), have been identified by in situ NMR investigation back in 1999. 18 However, no crystalline products have been isolated since then, and thus structural data revealing geometric perturbations of the corannulene framework upon addition of dichlorocarbene groups as well as crystal packing of the functionalized polar bowls remained unavailable. Therefore, in this work we focused on the isolation of the cyclopropanated corannulenes in the single-crystalline form and adapted the synthetic procedure reported by Preda and Scott. 18b

Adducts 2 and 3 were prepared by mixing corannulene and chloroform in the presence of tetrabutylammonium sulfate and a 50% (w/v) solution of NaOH.^{18b} As it was previously established, the phase-transfer generated dichlorocarbene first adds to one of the radial C=C bonds of corannulene, and then the reactive olefinic bonds in 2 begin to compete with corannulene for the carbene, leading to the formation of the

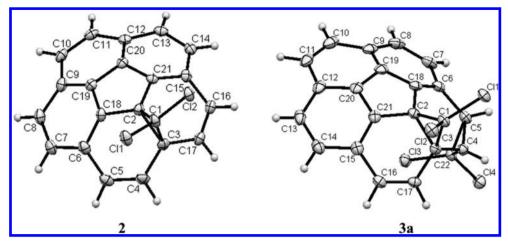
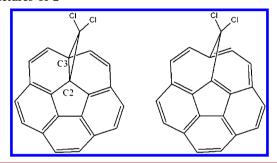


Figure 1. ORTEP representations of $C_{20}H_{10}CCl_2$ (2) and $C_{20}H_{10}(CCl_2)_2$ (3a). Atoms are represented by thermal ellipsoids at the 40% probability level. H atoms are shown as spheres of arbitrary radii.

Scheme 2. "Closed" (Left) and "Open" (Right) Molecular Structures of 2



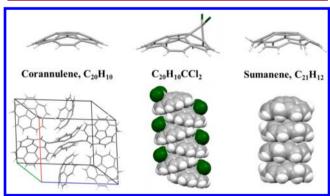


Figure 2. Molecular structures and crystal packing of corannulene (1), $C_{20}H_{10}CCl_2$ (2), and sumanene.

bis-adduct 3.¹⁸ As a result, the concentration of 2 remains low, while the amount of 3 increases with time. After approximately 5 h, the crude product contains ca. 93% of corannulene, 6% of 2, and 1% of 3 (based on ¹H NMR signal integration ratios). Even after 46 h of reaction time, a significant amount of corannulene remains unreacted, and the crude product consists of 15% corannulene, 4% of 2, and 81% of 3. Column chromatography has been used for separation of the mixture and isolation of 2 and 3.

Compounds 2 and 3 are light yellow air-stable solids, soluble in chloroform, dichloromethane, acetone, and diethyl ether and slightly soluble in pentane. To access crystalline materials for X-ray diffraction studies we employed gas-phase sublimation/deposition procedures 24 as well as solution crystal growth

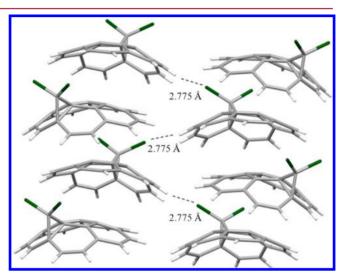


Figure 3. Intermolecular $C-H\cdots Cl$ interactions between the polar stacks of 2.

techniques. The monoadduct 2 was found to crystallize as almost colorless needles in low yield from the gas-phase at 95 °C. For the bis-adduct 3, two different types of crystals were obtained depending on the crystallization procedure used. First, colorless blocks (3a) were grown in good yield from a chloroform solution layered with hexanes by slow evaporation of solvents at 15 °C. Second, smaller blocks (3b) were obtained in low yield from the gas-phase sublimation of a 1.5:1 mixture of $Rh_2(O_2CCF_3)_4$ with $C_{20}H_{10}(CCl_2)_2$ at 105 °C. In the latter reaction, Rh₂(O₂CCF₃)₄ acted as a transporting agent by coordinating 3 through weak intermolecular interactions in the vapor phase and releasing it in the cold zone of the ampule where 3b deposits. Indeed, next to the colorless crystals of 3b the deposition of very small green crystals of Rh₂(O₂CCF₃)₄^{21b} was also observed. It can be mentioned here that the electrophilic Rh₂(O₂CCF₃)₄ unit is known to form adducts with corannulene and other bowls in the solid state based on $Rh \cdot \cdot \cdot \pi$ interactions, ^{24,25} but the steric bulkiness of 3 coupled with its electrophilicity seems to prevent such binding in this case.

Structural Description. A colorless needle of $C_{20}H_{20}CCl_2$ (2) was analyzed at -173 °C and found to belong to the rhombohedral crystal symmetry. Adduct 2 crystallizes in the

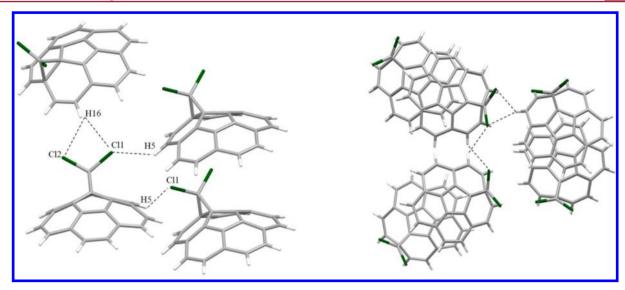


Figure 4. Side view (left) and top view (right) of the intermolecular C-H···Cl interactions in the 3D network of 2.

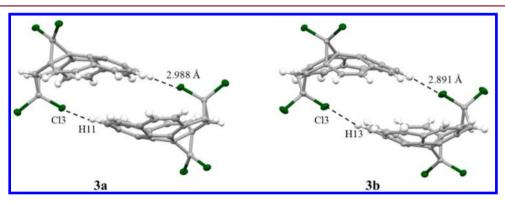


Figure 5. Bimolecular aggregation of $C_{20}H_{10}(CCl_2)_2$ in 3a (left) and 3b (right).

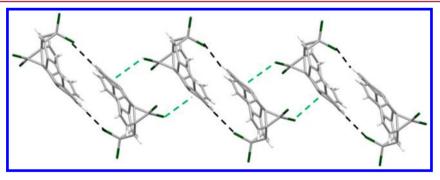


Figure 6. Fragment of a 2D network in the structure of 3a formed via intermolecular $C-Cl\cdots\pi$ interactions (green dashed line) and $C-H\cdots Cl$ interactions (black dashed line).

R3c space group (Z=18) and contains one crystallographically independent molecule in the asymmetric unit. The X-ray diffraction analysis of **2** shows its C_s -symmetric molecular structure, similar to the symmetry of the alkylated corannulene cations $[C_{20}H_{10}R]^+$ ($R=CH_xCl_{3-x}$ (where x=0-3), CH_2CH_2Cl , CH_2CH_2Br).¹⁹

The X-ray diffraction study revealed that the bis-adduct isolated from solution (3a) crystallizes in the centrosymmetric triclinic space group $P\overline{1}$ (Z=2). The asymmetric unit contains one crystallographically independent molecule of the chiral $C_{20}H_{10}(CCl_2)_2$ bowl. The bis-adduct has *anti* stereochemistry (Figure 1), thus avoiding the steric hindrance that would be encountered in the *syn* isomer. The crystalline compound 3a is

a racemic mixture of two enantiomeric forms. Both enantiomers are packed in the unit cell with the ratio of 1:1. The bis-adduct isolated from the gas-phase (3b) at elevated temperature crystallizes in the centrosymmetric monoclinic space group $P2_1/n$ (Z=4). There are four molecules of $C_{20}H_{10}(CCl_2)_2$ in the unit cell with a 1:1 enantiomeric ratio.

The bond lengths of the cyclopropane rings of the mono- (2) and bis-adducts (3a and 3b) (Table 1) are within the range of the literature values for 1,1-dichlorocyclopropanes. The bond lengths for the two C–C bonds to which the chlorine atoms are attached were reported to be in between 1.45 and 1.54 Å, the base C–C bond was found to be longer (1.50 –1.55 Å). For both mono- and bis-adducts, the C1–

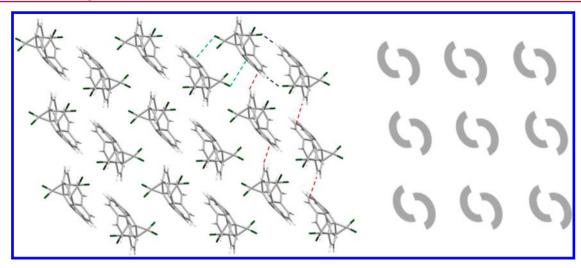


Figure 7. Fragment of a 2D network in the structure of 3a formed via intermolecular $C-Cl\cdots\pi$ interactions (green dashed line), $C-H\cdots Cl$ interactions (black dashed line), and $C-H\cdots\pi$ interactions (red dashed line) (left) along with the schematic representation of the same fragment (right).

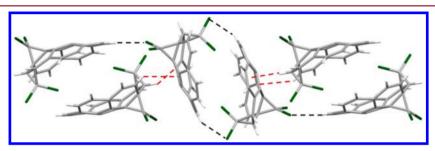


Figure 8. Fragment of a 2D network in the structure of 3b formed via intermolecular $C-H\cdots\pi$ interactions (red dashed line) and $C-H\cdots Cl$ interactions (black dashed line).

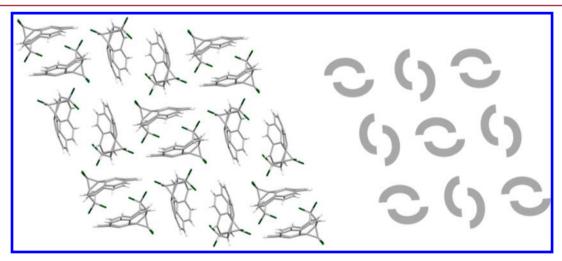


Figure 9. View of a 2D network in 3b (left) along with the schematic representation of the same fragment (right).

C2 and C1–C3 bond distances between the corannulene moiety and the spoke-bound CCl₂ group are 1.494(3) and 1.537(3) Å in **2**, 1.495(3) and 1.520(3) Å in **3a**, and 1.503(2) and 1.523(2) Å in **3b**. For the rim-bound CCl₂ substituent in the bis-adduct, the C4–C22 and C5–C22 bonds are 1.496(3) and 1.517(3) Å for **3a** and 1.489(2) and 1.514(2) Å for **3b**, which is characteristic of typical 1,1-dichlorocyclopropane bond distances. The C2–C3 bond distance is longer in the monoadduct (1.573(3) Å) compared to 1.525(3) and 1.533(2) Å in **3a** and **3b**, respectively. The distances for the C4–C5

bond in the rim cyclopropane rings of the bis-adducts are very close, 1.547(3) Å in 3a and 1.551(2) Å in 3b.

In the structure of the monoadduct (2), the C2–C21 and C2–C18 bond lengths (1.473(3) and 1.476(3) Å) are significantly longer than the conjugated C–C hub bonds in the parent corannulene (average 1.414(2) Å), ²⁸ while the other hub bonds (C20–C21: 1.403(3) Å, C18–C19: 1.409(3) Å, and C19–C20: 1.426(3) Å) remain essentially unchanged relative to those in $\rm C_{20}H_{10}$ (1.412(2)–1.415(2) Å). ²⁸ The corresponding geometric parameters of 3a and 3b follow trends similar to 2 (Table 2).

The distance between the bridge-head carbon atoms, C2 and C3, of 1.573(3) Å in **2** indicates a "closed" structure, rather than an "open" one (Scheme 2). This observation agrees with the results of theoretical calculations based on the AM1 semiempirical level, ²⁹ which predicted that the "closed" structure is more favored energetically.

The C2–C3 spoke bond is most strongly affected by methylation (1.573(3) for 2 vs 1.378(2) Å in $C_{20}H_{10}$), while all the other spoke bond lengths are only slightly elongated (averaged at 1.386(3) Å) when compared to corannulene. Interestingly, in 2 the rim C–C bonds (C7–C8, C10–C11, C13–C14) remain the same (average values of 1.381(3) vs 1.380(2) Å in $C_{20}H_{10}$), while the C4–C5 and C16–C17 rim bonds become considerably shortened (1.359(3) and 1.351(3) Å). The peculiar bond length variation in 2 is a result of cyclopropanation of corannulene at the C2 and C3 sites, which pulls these carbon atoms away from the bowl surface.

The bis-adduct 3a has three types of nonequivalent spoke bonds. The C6-C18 (1.356(3) Å) and C15-C21 (1.367(3) Å) are noticeably shorter than the C9-C19 and C12-C20 (both 1.386(3) Å) spoke bonds (vs 1.378(2) Å average in $C_{20}H_{10}$). Moreover, the C2-C3 radial bond in 3a suffers significant elongation (1.525(3) Å) as a result of the cyclopropane formation at that site. The bond most strongly elongated in 3a is the C4-C5 rim bond, which at 1.547(3) Å is much longer than the average rim bond length in C₂₀H₁₀ (1.380(2) Å). Among the remaining rim bonds, the C16-C17 and C10-C11 bonds are significantly shortened (1.343(3) Å and 1.364(4) Å), C7-C8 is slightly elongated (1.386(3) Å), while C13-C14 (1.378(3) Å) remains unchanged when compared to the corresponding bond lengths of the parent corannulene. For both adducts, 2 and 3a, the C-Cl bonds (1.747(2)-1.760(2) Å) are shorter than the C-Cl bonds (1.762(4)-1.792(5) Å) in the alkylated corannulene cations $[C_{20}H_{10}R]^+$ (R = CH_xCl_{3-x} (where x = 0-3), CH_2CH_2Cl , CH_2CH_2Br). The geometrical parameters of **3b** follow the same trends as those in 3a, although they do show an increase in bond lengths that averages to 0.0035 Å and a larger bowl depth (Table 2).

The experimental bowl depth of corannulene is 0.875(2) Å, ²⁸ and, as expected, the addition of CCl₂ substituents to the interior of corannulene framework causes a noticeable increase in bowl curvature for **2**, **3a**, and **3b** (1.068(3), 1.003(3), and 1.024(2) Å, respectively). The bis-adduct **3** shows slightly less curving than **2** due to the additional attachment of a rim substituent, which is known to flatten the corannulene bowl.^{2e} It was reported that the inversion barriers for a wide range of substituted corannulenes are empirically correlated to the bowl depths through a quartic function.^{2e} Thus, curving of the surfaces of **2** and **3** is expected to increase quite significantly the energy barrier for their bowl-to-bowl inversion.

In the solid state, the monoadduct (2) assembles into 1D infinite columns (Figure 2) based on strong concave—convex $\pi \cdots \pi$ stacking interactions (ca. 3.36–3.37 Å) between the polar bowls. Such packing is not found in the crystal structure of the parent corannulene²⁸ with a dipole moment (μ) of 2.10 D, but is generally observed in polyarenes with deeper bowls which have increased strength of concave—convex $\pi \cdots \pi$ interactions. For example, sumanene³⁰ ($C_{21}H_{12}$), cyclopentacorannulene ($C_{22}H_{10}$), hemibuckminsterfullerene ($C_{30}H_{12}$), circumtrindene ($C_{36}H_{12}$), and other bowls with sufficient curvature form aligned stacks through insertion of the convex face of one bowl into the concave surface of the neighboring one. ¹⁴ Notably, this

type of columnar $\pi-\pi$ stacking could be responsible for a possible anisotropy in conductivity of 2 ($\mu=3.70$ D). The sumanene bowls having similar stacking arrangement were measured to have high electron mobility with large anisotropy (9.2 times) along the π -bowl stacking axis. Interestingly, the monoadduct 2 crystallizes in the same trigonal space group, R3c, as sumanene and both exhibit the same needle-like crystal shape. While sumanene has only one-third of the molecule crystallographically independent, in the structure of 2 the entire molecule is crystallographically independent.

Similar to sumanene, ¹² the bowls in all columns in the solid state structure of **2** are oriented in the same direction with respect to each other; therefore **2** can be a good potential candidate for electrically active organic materials. The polar stacks of **2** are aligned along the *c*-axis based on C–H···Cl interactions between the Cl1 of one unit and H5 of another one (Figure 3). The resulting H···Cl distance of 2.775 Å and C–H···Cl angle of 135.99° (Table S2, Supporting Information) corresponds to the expected range for C–H···Cl interactions.³¹

In addition to the H5···Cl1 contact between two adjacent columns, the Cl1 atom is involved in the C–H···Cl interaction with the H16 atom of a different neighboring stack (Figure 4). The Cl2 atom also weakly interacts with the same H16 atom. All the corresponding H···Cl and C···Cl distances and the fairly linear C–H···Cl angles (Table S2, Supporting Information) are consistent with criteria used for C–H···Cl interactions. While Cl1 acts as an acceptor of two C–H···Cl interactions, the Cl2 atom is only involved in one such interaction. Overall, the solid state structure of 2 can be described as a 3D helix held together by π ··· π interactions and extensive intermolecular C–H···Cl contacts.

The two forms of the bis-adduct 3 crystallize in different space groups, triclinic $P\overline{1}$ (3a) vs monoclinic $P2_1/n$ (3b), and their cell volumes normalized by the number of formula units are slightly different (424 and 433 ų per $C_{20}H_{10}(CCl_2)_2$ molecule in 3a and 3b, respectively). As a result of more dense packing, 3a also has higher density (1.628 g/cm³) compared to that of 3b (1.596 g/cm³).

The adducts **2** and **3** exhibit totally different solid state aggregation behaviors. In both crystalline forms, **3a** and **3b**, the bis-adduct does not form the columnar stacking found in the crystals of the monoadduct. The efficient solid state packing of **2** is hampered in **3** by the presence of peripheral CCl₂ groups which prevent close $\pi \cdots \pi$ contacts between the functionalized π -bowls. Instead, the formation of concave—concave bimolecular aggregates can be identified in **3a** and **3b**. These aggregates are based on two C—H····Cl interactions of 2.988 Å in **3a** and of 2.891 Å in **3b** (Figure 5).

However, the extended structures of 3a and 3b are completely different. The solid state packing of 3a reveals that the dimers are packed in a two-dimensional network. In one dimension, the dimers connect through the $C-Cl\cdots\pi$ interactions of 3.347-3.626 Å (Figure 6), which are of similar magnitude to the ones previously reported. 32

Each molecular unit of **3a** is further engaged in C–H··· π interactions responsible for the formation of the extended 2D network (Figure 7). The C–H··· π contacts of 2.653 Å are within the range of those reported in the literature.³³

The dimers of **3b** are also assembled into a 2D network. They are stitched together in one dimension through two C-H···Cl and two C-H··· π interactions (Figure 8). Then the dimers further interact in another direction through the same type of contacts (Figure 9). The C-H11···Cl2 parameters

(2.871 Å and 149.21°) and the C–H17····Cl2 distance of 2.871 Å and 149.21° angle are in agreement with the literature reported values for C–H····Cl interactions. The C–H··· π contacts fall in the range 2.513–2.892 Å, which is typical for interactions of this type. 33

4. CONCLUSIONS

The first X-ray crystallographic characterization of bowl-shaped cyclopropanes, namely, the dichlorocarbene adducts of corannulene, $C_{20}H_{10}CCl_2$ (2) and $C_{20}H_{10}(CCl_2)_2$ (3), revealed the geometric structures of the functionalized bowls and allowed a comparative evaluation of the effects of bulky carbene substituents on the corannulene framework. The addition of the CCl_2 groups to $C_{20}H_{10}$ deepens the bowl, alters the geometrical parameters of the core, and changes the solid state packing. Notably, the monoadduct 2 has a unidirectional orientation of all polar 1D columns in the solid state, indicating potentially interesting electric properties of the crystalline material. A different solid state packing based on bimolecular aggregation of the bis-adduct molecules was revealed in 3, which was crystallized as two different polymorphs under different experimental conditions.

ASSOCIATED CONTENT

S Supporting Information

X-ray crystallographic data in CIF format, table of crystal structure and refinement details, and table of geometrical parameters for hydrogen bonds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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