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Interaction of Fullerenes with the Concave Surfaces of Perchloroazatriquinacene

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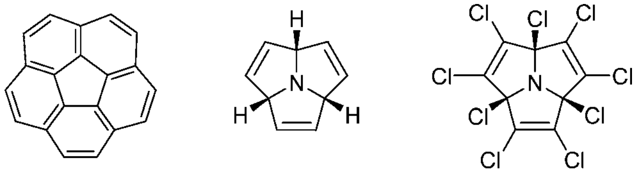
ABSTRACT

Crystal structures of the one-to-one co-crystals of C_{60}·perchloroazatriquinacene and C_{70}·perchloroazatriquinacene show that the rigid, chalice-like azatriquinacene packs between completely ordered fullerene molecules with multiple, close Cl···fullerene contacts.

The supramolecular chemistry of fullerenes is replete with examples of complexes involving conformationally mobile macrocyclic hosts which can accommodate C_{60} and/or C_{70}. Such hosts include calix[5]-,[1a] [6]-,[1b] and -[8]arenes,[1c] hexahomotrioxacalix[3]arenes,[1d] cyclodextrins,[1e] crown ethers,[1f] and cyclotriveratrylenes.[1g] Complexation of fullerenes with entirely rigid hemispherical molecules is unknown in the crystallographic literature, although a number of structures of C_{60} with planar porphyrins[2a,b] and rigid, saddle-shaped dibenzotetraaza[14]annulenes[2c] have been described. Corannulene (**1**, Chart 1), whose carbon framework represents a fragment of the C_{60} cage, is an obvious candidate for true "ball and socket" complementarity between a rigid concave molecule and C_{60}. Because the bowl depth of **1** (0.87 Å)[3] is substantially less than that of the same fragment in the C_{60} sphere (1.5 Å), the radius of curvature for its inner surface (r = 4.8 Å) turns out to be a good match for that of the exterior surface of C_{60} (r = 5.0 Å). However, the low barrier for bowl-to-bowl interconversion of corannulene in solution (ca. 10 kcal mol^{-1}) may complicate matters.[4] Indeed, the complexation of C_{60} by derivatives of **1** has been studied, and 1:1 association constants of ≤500 M^{-1} in toluene were observed.[5]

Chart 1. Concave Molecules



1 **2** **3**

Our interest in the rigid, bowl-shaped, tricyclic 10-azatriquinacene molecule (**2**)[6] led us to consider possible

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(1) Examples: (a) Haino, T.; Yanase, M.; Fukazawa, Y. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 259−260. (b) Atwood, J. L.; Barbour, L. J.; Raston, C. L.; Sudria, I. B. N. *Angew. Chem., Int. Ed.* **1998**, *37*, 981−983. (c) Atwood, J. L.; Koutsantonis, G. A.; Raston, C. L. *Nature* **1994**, *368*, 229−231. (d) Atwood, J. L.; Barbour, L. J.; Nichols, P. J.; Raston, C. L.; Sandoval, C. A. *Chem.—Eur. J.* **1999**, *5*, 990−996. (e) Andersson, T.; Nilsson, K.; Sundahl, M.; Westman, G.; Wennerström, O. *J. Chem. Soc., Chem. Commun.* **1992**, 604−606. (f) Diederich, F.; Effing, J.; Jonas, U.; Jullien, L.; Plesnivy, T.; Ringsdorf, H.; Thilgen, C.; Weinstein, D. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1599−1602. (g) Steed, J. W.; Junk, P. C.; Atwood, J. L.; Barnes, M. J.; Raston, C. L.; Burkhalter R. S. *J. Am. Chem. Soc.* **1994**, *116*, 10346−10347.

(2) Examples: (a) Olmstead, M. M.; Costa, D. A.; Maitra, K.; Noll, B. C.; Phillips, S. L.; Van Calcar, P. M.; Balch, A. L. *J. Am. Chem. Soc.* **1999**, *121*, 7090−7097. (b) Boyd, P. D. W.; Reed, C. A. *Acc. Chem. Res.* **2005**, *38*, 235−242. (c) Soldatov, D. V.; Diamente, P. R.; Ratcliffe, C. I.; Ripmeester, J. A. *Inorg. Chem.* **2001**, *40*, 5660−5667.

(3) Hanson, J. C.; Nordman, C. E. *Acta Crystallogr. B.* **1976**, *32*, 1147−1153.

(4) Scott, L. T.; Hashemi, M. M.; Bratcher, M. S. *J. Am. Chem. Soc.* **1992**, *114*, 1920−1921.

10.1021/ol050557p CCC: $30.25

complex formation between the C_{60} and C_{70} fullerenes and derivatives of **2**. Although the acute curvature of **2** itself is not a close match for the contour of C_{60}, the perchloro derivative **3** presents two opposing surfaces in a sort of chalice arrangement: a "top" with six chlorine atoms in a hexagonal plane and a "bottom" with three chlorine atoms forming a tripod. Covalent chlorine forms weak *n*-donor charge-transfer interactions with fullerenes,[7] and this type of association is implicated in the general increase in solubility of C_{60} with degree of chlorination in aliphatic solvents.[8]

The electrostatic potential map of **3** was modeled at the B3LYP/6-31G(d,p) level of theory.[9] As seen in Figure 1, the top surface of **3** shows a ring of moderate electron density in the Cl_6 plane, while the lower Cl_3 plane shows a somewhat greater surface charge. This suggested that the interaction of these chlorinated surfaces with the fullerenes should be favorable.

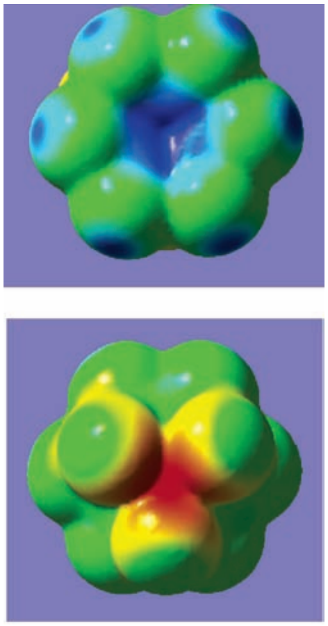

Figure 1. Calculated B3LYP/6-31G(d,p) electrostatic potential surfaces for **3**, with surface energy ranging from −18 (red) to +18 (blue) kcal mol^{-1}.

Large black prisms of the one-to-one adduct, $C_{60}{\cdot}C_9Cl_9N$, were obtained by careful layering of a solution of **3** in chlorobenzene over a solution of C_{60} in carbon disulfide. A view of the solid-state structure of $C_{60}{\cdot}C_9Cl_9N$ as determined by X-ray crystallography is shown in Figure 2.[10] The asymmetric unit contains one fullerene and one molecule of **3**. These units are arranged into columns with alternating molecules of **3** and C_{60}. In these columns there are fullerenes

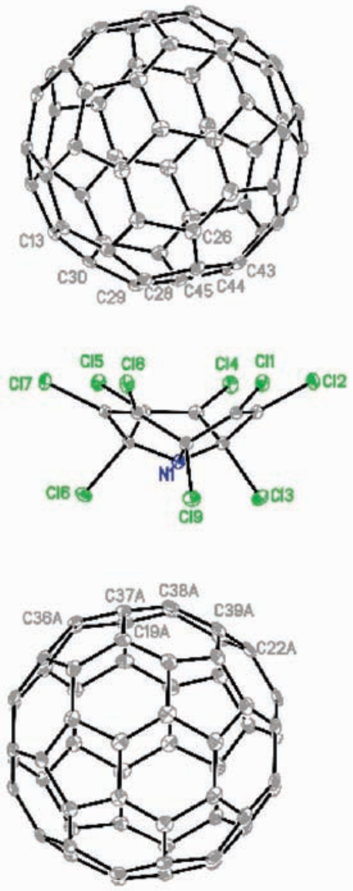

Figure 2. View of the stacking motif between C_{60} and the chlorinated surfaces of **3** in crystalline $C_{60}{\cdot}C_9Cl_9N$ showing 50% thermal contours for all atoms.

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(5) Mizyed, S.; Georghiou, P. E.; Bancu, M.; Cuadra, B.; Rai, A. K.; Cheng, P.; Scott, L. T. *J. Am. Chem. Soc.* **2001**, *123*, 12770−12774.

(6) Mascal, M.; Lera, M.; Blake, A. J. *J. Org. Chem.* **2000**, *65*, 7253−7255 and references therein.

(7) Murthy, C. N.; Geckeler, K. E. *Fullerene Sci. Tech.* **2001**, *9*, 477−486 and references therein.

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(9) Gaussian 03, Revision B.04, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian, Inc., Wallingford CT, 2004.

(10) Crystal data for $C_{60}{\cdot}C_9Cl_9N$: black prism, monoclinic, space group $P2_1/c$, $a = 10.1516(5)$ Å, $b = 15.4731(8)$ Å, $c = 26.0575(13)$ Å, $\beta = 100.362(2)°$, $V = 4026.3(4)$ Å^3, $Z = 4$, $\lambda = 0.710\,73$ Å, $D_c = 1.917$ Mg m^{-3}; $\mu = 0.687$ mm^{-1}; $T = 90(2)$ K; 30228 reflections collected; 8211 independent ($R_{int} = 0.037$) included in the refinement; min/max transmission = 0.77/0.93; Patterson and difference Fourier methods solution (SHELXS-97, Sheldrick, 1990); full-matrix least-squares based on F^2 (SHELXL-97; Sheldrick, 1998); R1 = 0.0547, wR2 = 0.1109 for all data; conventional R1 = 0.0383 computed for 6357 observed data ($>2\sigma(I)$) with no restraints and 538 parameters.

in close contact with both chlorinated surfaces of **3**. No solvent molecule is present in the structure. Unlike the situation in many examples of C_{60} co-crystallized with conformationally mobile macrocyclic hosts where the fullerene is significantly disordered, the C_{60} molecule in $C_{60}{\cdot}C_9Cl_9N$ is fully ordered.

The geometric relationship between the two surfaces of **3** and the C_{60} sphere can be seen by considering views down the C_3 axis of **3** toward the two neighboring C_{60} molecules (Figure 3). The molecule of **3** is positioned such that its C_3 axis passes near the center of the adjacent six-membered ring of the C_{60} molecule in the view shown in Figure 3a. For this contact, the closest C···Cl distance is 3.48 Å. On the opposite surface of **3**, the 3-fold axis passes very nearly through one of the carbon atoms of the neighboring C_{60} molecule as shown in Figure 3b. Here, the closest C···Cl approach is 3.36 Å.

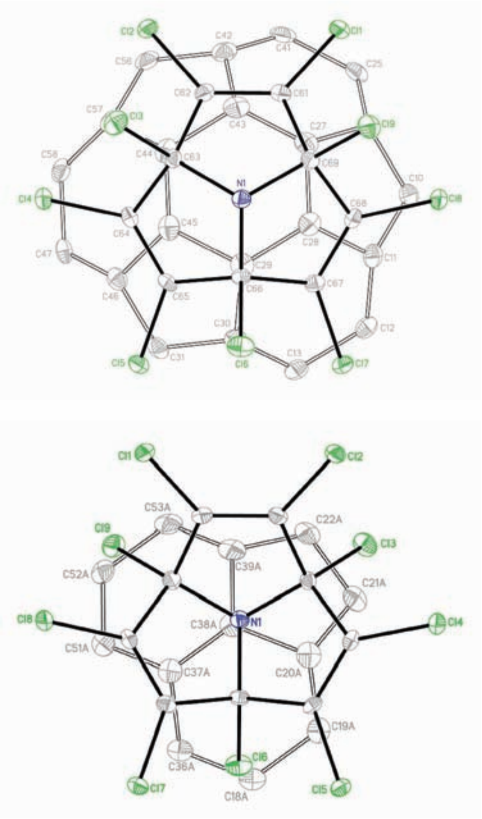

Figure 3. (a) Top: a view of the $C_{60}{\cdot}C_9Cl_9N$ co-crystal showing contact between C_{60} and the Cl_6 plane of **3**. (b) Bottom: a view of the $C_{60}{\cdot}C_9Cl_9N$ co-crystal showing contact between C_{60} and the Cl_3 plane of **3**.

In addition to the columnar stacking seen in Figure 2, each molecule of **3** in $C_{60}{\cdot}C_9Cl_9N$ is surrounded by six other C_{60} molecules. These C_{60} molecules describe a flattened, pseudo-octrahedral array which is shown in the stereoview in Figure 4. This packing arrangement reveals that there are in fact eight surfaces of **3** which abut neighboring fullerene molecules. Two of these are the unique, polar Cl_6 and Cl_3 planes which describe the "chalice" arrangement. The other six are equatorial features and consist of three equivalent Cl_4 facets and three other equivalent Cl_3 facets, which can be clearly seen by examining Figure 4. Interestingly, the C···Cl distances here are the closest seen in the structure and range from 3.36 to 3.28 Å, which is substantially less than the sum of the van der Waals radii for aromatic carbon and chlorine (3.50 Å).[11]

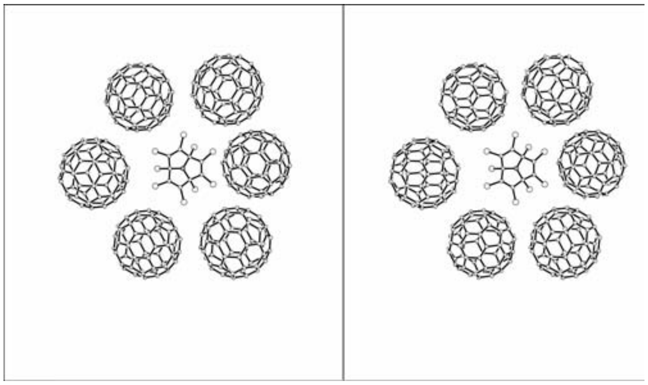

Figure 4. Stereoview showing the packing of six C_{60} molecules around the periphery of **3** in crystalline $C_{60}{\cdot}C_9Cl_9N$.

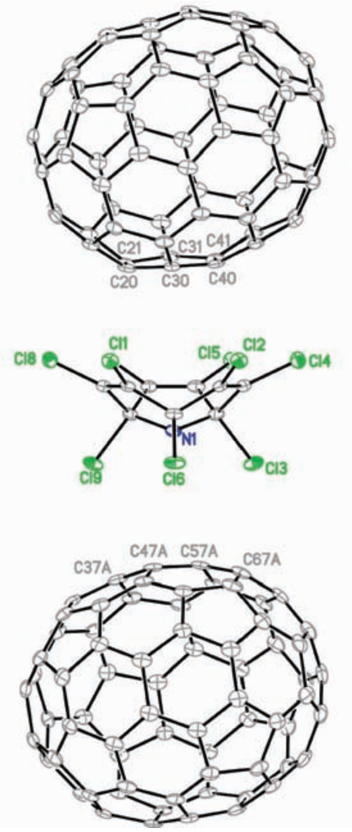

Figure 5. View of the stacking motif between C_{70} and the chlorinated surfaces of **3** in crystalline $C_{70}{\cdot}C_9Cl_9N$ showing 50% thermal contours for all atoms.

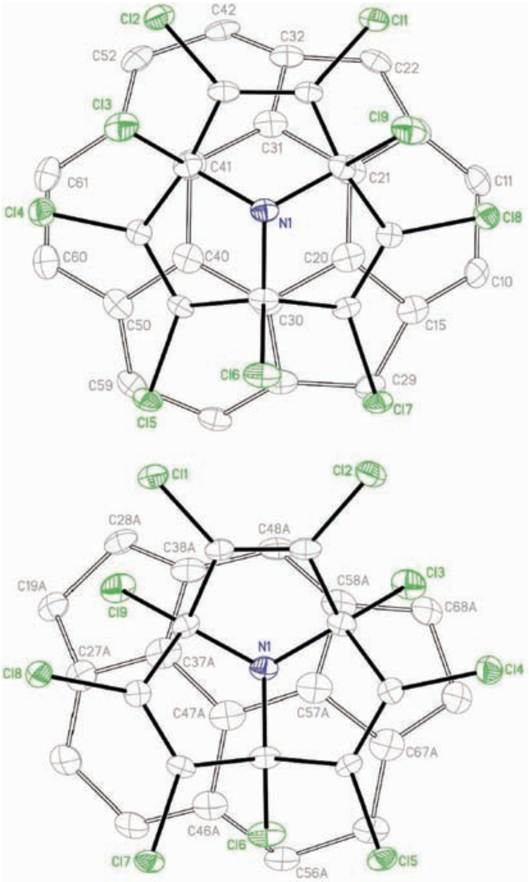

Figure 6. (a) Top: a view of the $C_{70}{\cdot}C_9Cl_9N$ co-crystal showing contact between C_{70} and the Cl_6 plane of **3**. (b) Bottom: a view of the $C_{70}{\cdot}C_9Cl_9N$ co-crystal showing contact between C_{70} and the Cl_3 plane of **3**.

There are in total 17 intermolecular C···Cl contacts to C_{60} that are shorter than 3.5 Å in this structure. We speculate that these close interactions are significantly responsible for absence of fullerene disorder in $C_{60}{\cdot}C_9Cl_9N$.

Large black prisms of a second, one-to-one adduct, $C_{70}{\cdot}C_9Cl_9N$, were obtained by layering of a solution of **3** in chlorobenzene over a solution of C_{70} in carbon disulfide. The structure of $C_{70}{\cdot}C_9Cl_9N$, as determined by X-ray diffraction,[12] also contains columnar stacking of the two components as shown in Figure 5. In this case, it is the flat side of the oblong fullerene that makes contact with the top and bottom surfaces of **3**. Nevertheless, the contacts between these surfaces are analogous to those shown in Figure 3. For example, the 3-fold axis of **3** likewise passes through the center of a hexagon of the adjacent fullerene molecule as shown in Figure 6a. There are in total 20 intermolecular C···Cl contacts to C_{70} in this structure that are shorter than 3.5 Å, the closest being 3.24 Å. Furthermore, there are six additional C_{70} molecules that pack around each molecule of **3** in $C_{70}{\cdot}C_9Cl_9N$ in a pattern very similar to that shown in Figure 4 for $C_{60}{\cdot}C_9Cl_9N$. Again, the interaction of the fullerene with the chlorinated surfaces of **3** leads to the formation of a co-crystalline material in which the C_{70} molecule is fully ordered.

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Supporting Information Available: X-ray crystallographic data for $C_{60}{\cdot}C_9Cl_9N$ and $C_{70}{\cdot}C_9Cl_9N$ (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) Pauling, L. *The Nature of the Chemical Bond*; Cornell University Press: Ithaca, NY, 1960; p 260.

(12) Crystal data for $C_{70}{\cdot}C_9Cl_9N$: black plate, orthorhombic, space group *Pbca*, $a = 16.844(3)$ Å, $b = 19.929(4)$ Å, $c = 26.869(5)$ Å, $V = 9020(3)$ Å^3, $Z = 8$, $\lambda = 0.71073$ Å, $D_c = 1.888$ Mg m^{-3}; $\mu = 0.624$ mm^{-1}; $T = 90(2)$ K; 26087 reflections collected; 9041 independent ($R_{\mathrm{int}} = 0.049$) included in the refinement; min/max transmission = 0.71/0.93; Patterson and difference Fourier methods solution (SHELXS-97, Sheldrick, 1990); full-matrix least-squares based on F^2 (SHELXL-97; Sheldrick, 1998); R1 = 0.051, wR2 = 0.113 for all data; conventional R1 = 0.039 computed for 7151 observed data ($>2\sigma(I)$) with no restraints and 802 parameters.