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Molecular Tectonics. Selective Exchange of Cations in Porous Anionic Hydrogen-Bonded Networks Built from Derivatives of Tetraphenylborate

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Abstract: Tetraphenylmethanes with multiple hydrogen-bonding sites are known to associate to form robust porous supramolecular networks. Analogous anionic networks can be built from the corresponding tetraphenylborates. Crystallization of the tetraphenylphosphonium salt of tetraphenylborate **2** produces an anionic network in which 74% of the volume is available for including cations and neutral guests. Other salts of anion **2** with diverse cations crystallize consistently to form the same network, whereas a neutral analogue of anion **2**, tetraphenylmethane **1**, produces an uncharged network that is far less open. Cations can be exchanged in single crystals of salts of tetraphenylborate **2** with retention of crystallinity and with selectivities similar to those observed in typical zeolites. Together, these observations provide new strategies for making ordered molecular materials by design, and they reveal that constructing such materials from charged subunits offers special advantages.

Introduction

Learning how to predict the structures and properties of molecular crystals is a major challenge in modern science.[1] This challenge is creating a surge of excitement in the field of crystal engineering,[2] an area of rich opportunity where much new knowledge awaits discovery and exploitation. Reaching the goal of making crystalline molecular materials by design will require sustained effort and creative use of tools drawn from many separate disciplines, including crystallography, statistics, theory, and synthesis.

In this effort, systematic comparisons of how related molecules crystallize will continue to be a particularly valuable source of deeper understanding. From such comparisons has emerged the notion that certain functional groups in molecules can play a dominant role in crystallization, by taking part in attractive intermolecular interactions according to reliable patterns. When multiple sticky groups are incorporated in properly designed molecules, their interactions can be considered to determine the resulting structures. Molecules of this type have been called tectons, from the Greek word for builder,[3] and the term molecular tectonics has been used to refer to the art and science of constructing ordered molecular materials from tectonic subunits.[4,5]

When tectons can form multiple interactions that are strong and directional, such as hydrogen bonds, crystallization normally generates open networks.[6–15] Volume unfilled by the networks themselves is then occupied by included guests or by independent interpenetrating networks.[16,17] Systematic studies of derivatives of tetraphenylmethane have provided particularly strong support for these generalizations.[9–11] For example, crystallization of tetraphenylmethane **1** from HCOOH/dioxane is directed
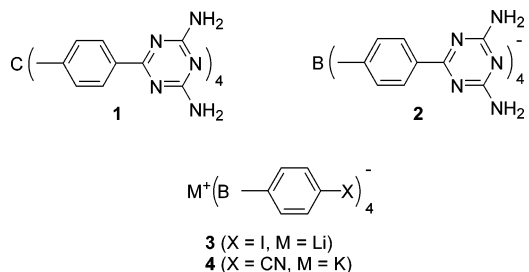
by hydrogen bonding of its diaminotriazine groups according to established motifs,[6–9] thereby producing a robust three-

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dimensional network in which each tecton forms a total of 16 hydrogen bonds with eight neighbors. About 45% of the volume is available for including guests, which lie in parallel channels and can be exchanged in single crystals or even partly removed without loss of crystallinity.

In many ways, such porous molecular networks are strikingly similar to zeolites, and they may find analogous applications in separation, catalysis, and other areas of technology. However, zeolitic networks are anionic, whereas porous molecular networks that have been studied so far have rarely carried a net charge.[15,18] We have now synthesized tetraphenylborate **2**, which is a charged analogue of tetraphenylmethane **1**, and we have
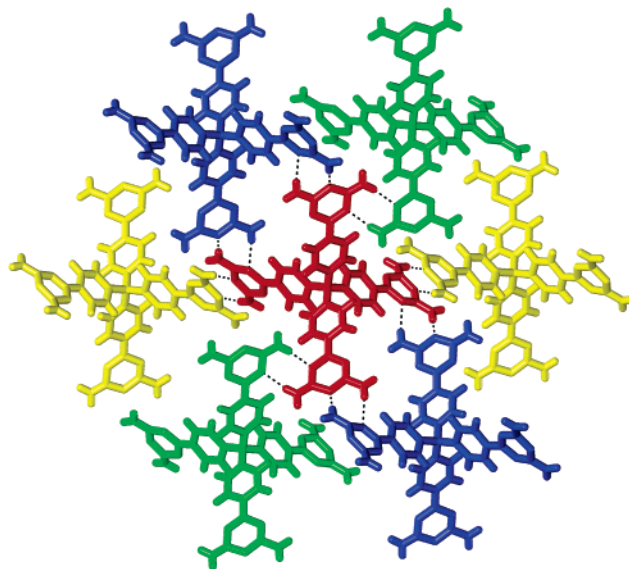
(13) For other recent studies of crystal engineering using molecules designed to associate by hydrogen bonding, see: Uemura, K.; Kitagawa, S.; Fukui, K.; Saito, K. *J. Am. Chem. Soc.* **2004**, *126*, 3817. Sada, K.; Inoue, K.; Tanaka, T.; Tanaka, A.; Epergyes, A.; Nagahama, S.; Matsumoto, A.; Miyata, M. *J. Am. Chem. Soc.* **2004**, *126*, 1764. Maspoch, D.; Domingo, N.; Ruiz-Molina, D.; Wurst, K.; Tejada, J.; Rovira, C.; Veciana, J. *J. Am. Chem. Soc.* **2004**, *126*, 730. Baudron, S. A.; Avarvari, N.; Canadell, E.; Auban-Senzier, P.; Batail, P. *Chem. Eur. J.* **2004**, *10*, 4498. Angeloni, A.; Crawford, P. C.; Orpen, A. G.; Podesta, T. J.; Shore, B. J. *Chem. Eur. J.* **2004**, *10*, 3783. Murata, T.; Morita, Y.; Fukui, K.; Sato, K.; Shiomi, D.; Takui, T.; Maesato, M.; Yamochi, H.; Saito, G.; Nakasuji, K. *Angew. Chem., Int. Ed.* **2004**, *43*, 6343. Soldatov, D. V.; Moudrakovski, I. L.; Ripmeester, J. A. *Angew. Chem., Int. Ed.* **2004**, *43*, 6308. Du, Y.; Creighton, C. J.; Tounge, B. A.; Reitz, A. B. *Org. Lett.* **2004**, *6*, 309. Bhogala, B. R.; Vangala, V. R.; Smith, P. S.; Howard, J. A. K.; Desiraju, G. R. *Cryst. Growth Des.* **2004**, *4*, 647. Balasubramaniam, V.; Wong, L. G. J.; Vittal, J. J.; Valiyaveettil, S. *Cryst. Growth Des.* **2004**, *4*, 553. Dale, S. H.; Elsegood, M. R. J.; Coombs, A. E. L. *CrystEngComm* **2004**, *6*, 328. Vinodu, M.; Goldberg, I. *CrystEngComm* **2004**, *6*, 215. Aakeröy, C. B.; Desper, J.; Helfrich, B. A. *CrystEngComm* **2004**, *6*, 19. Alshahateet, S. F.; Nakano, K.; Bishop, R.; Craig, D. C.; Harris, K. D. M.; Scudder, M. L. *CrystEngComm* **2004**, *6*, 5. Brown, R. J.; Camarasa, G.; Griffiths, J.-P.; Day, P.; Wallis, J. D. *Tetrahedron Lett.* **2004**, *45*, 5103. Pedireddi, V. R.; SeethaLekshmi, N. *Tetrahedron Lett.* **2004**, *45*, 1903. Martin, S. M.; Yonezawa, J.; Horner, M. J.; Macosko, C. W.; Ward, M. D. *Chem. Mater.* **2004**, *16*, 3045. Kumar, D. K.; Jose, D. A.; Dastidar, P.; Das, A. *Chem. Mater.* **2004**, *16*, 2332. Barton, O. G.; Schmidtmann, M.; Müller, A.; Mattay, J. *New J. Chem.* **2004**, *28*, 1335. Shimizu, L. S.; Hughes, A. D.; Smith, M. D.; Davis, M. J.; Zhang, B. P.; zur Loye, H.-C.; Shimizu, K. D. *J. Am. Chem. Soc.* **2003**, *125*, 14972. Ouyang, X.; Fowler, F. W.; Lauher, J. W. *J. Am. Chem. Soc.* **2003**, *125*, 12400. Kobayashi, K.; Sato, A.; Sakamoto, S.; Yamaguchi, K. *J. Am. Chem. Soc.* **2003**, *125*, 3035. Rakotondradany, F.; Whitehead, M. A.; Lebuis, A.-M.; Sleiman, H. F. *Chem. Eur. J.* **2003**, *9*, 4771. Jagadish, B.; Carducci, M. D.; Bosshard, C.; Günter, P.; Margolis, J. I.; Williams, L. J.; Mash, E. A. *Cryst. Growth Des.* **2003**, *3*, 811. Bhogala, B. R.; Nangia, A. *Cryst. Growth Des.* **2003**, *3*, 547. Olenik, B.; Smolka, T.; Boese, R.; Sustmann, R. *Cryst. Growth Des.* **2003**, *3*, 183. Kitamura, M.; Nakano, K. *Cryst. Growth Des.* **2003**, *3*, 25. Ma, B.-Q.; Coppens, P. *Chem. Commun.* **2003**, 2290. Yagai, S.; Karatsu, T.; Kitamura, A. *Chem. Commun.* **2003**, 1844. Walsh, R. D. B.; Bradner, M. W.; Fleischman, S.; Morales, L. A.; Moulton, B.; Rodríguez-Hornedo, R.; Zaworotko, M. J. *Chem. Commun.* **2003**, 186. Blay, G.; Fernández, I.; Pedro, J. R.; Ruiz-García, R.; Muñoz, M. C.; Cano, J.; Carrasco, R. *Eur. J. Org. Chem.* **2003**, 1627. Braga, D.; Polito, M.; Bracaccini, M.; D'Addario, D.; Tagliavini, E.; Sturba, L. *Organometallics* **2003**, *22*, 2142. Hosseini, M. W. *Coord. Chem. Rev.* **2003**, *240*, 157. Roesky, H. W.; Andruh, M. *Coord. Chem. Rev.* **2003**, *236*, 91. Ermer, O.; Kusch, A.; Röbke, C. *Helv. Chim. Acta* **2003**, *86*, 922. Arora, K. K.; Pedireddi, V. R. *J. Org. Chem.* **2003**, *68*, 9177. Wen, J.-F.; Hong, W.; Yuan, K.; Mak, T. C. W.; Wong, H. N. C. *J. Org. Chem.* **2003**, *68*, 8918. Moon, K.; Chen, W.-Z.; Ren, T.; Kaifer, A. E. *CrystEngComm* **2003**, *5*, 451. Burke, N. J.; Burrows, A. D.; Mahon, M. F.; Pritchard, L. S. *CrystEngComm* **2003**, *5*, 355. Pérez, C.; Rodríguez, M. L.; Foces-Foces, C.; Pérez-Hernández, N.; Pérez, R.; Martín, J. D. *Org. Lett.* **2003**, *5*, 641. Shan, N.; Bond, A. D.; Jones, W. *New J. Chem.* **2003**, *27*, 365. Kobayashi, N.; Naito, T.; Inabe, T. *Bull. Chem. Soc. Jpn.* **2003**, *76*, 1351.
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(17) An updated list of examples of interpenetration is available on the web site of Dr. Stuart R. Batten at Monash University (www.chem.monash.edu.au).
(18) For a review of ionic self-assembly, see: Faul, C. F. J.; Antonietti, M. *Adv. Mater.* **2003**, *15*, 673.

Figure 1. View of the structure of crystals of tetraphenylborate **2**·PPh$_4$$^+$ grown from DMSO/toluene, showing a central tecton (red) surrounded by its six hydrogen-bonded neighbors (yellow, green, and blue). Hydrogen bonds appear as broken lines, and all guests are omitted for clarity. The four diaminotriazine groups of the central tecton form a total of 16 hydrogen bonds according to all three standard motifs **I**−**III**. Two of the neighbors (yellow) each form two hydrogen bonds with the central tecton according to motif **I**, and two other neighbors (green) each form two hydrogen bonds according to motif **III**. Two diaminotriazine groups of each of the remaining two neighbors (blue) interact simultaneously with two arms of the central tecton according to motif **II**.

found that its salts crystallize to generate an anionic hydrogen-bonded network with special properties of porosity and selective ion exchange. Moreover, the behavior of tecton **2** suggests new strategies of potentially general value for creating molecular crystals by design.

Results and Discussion

Synthesis, Crystallization, and Structure of the Tetraphenylphosphonium Salt of Tetraphenylborate 2. Salts of anionic tecton **2** were made in the following way. Monolithiation of 1,4-diiodobenzene (BuLi, 1 equiv, −10 °C), followed by the addition of BF$_3$·O(C$_2$H$_5$)$_2$ (0.2 equiv, 25 °C), provided lithium tetrakis(4-iodophenyl)borate (**3**) in 85% yield. Subsequent Pd-catalyzed cyanation (KCN, Pd(OOCCH$_3$)$_2$)[19] gave an 85% yield of potassium tetrakis(4-cyanophenyl)borate (**4**). Intermediate **4** was then converted in 87% yield into the sodium salt of anionic tecton **2** by reaction with dicyandiamide under standard conditions,[20] and the tetraphenylphosphonium salt and other salts were prepared in quantitative yield from the sodium salt by cation exchange.

Colorless single crystals of tecton **2**·PPh$_4$$^+$ suitable for X-ray diffraction could be grown from DMSO/toluene. The crystals proved to belong to the monoclinic space group *P*2/*n* and to correspond to an inclusion compound of approximate composition **2**·PPh$_4$$^+$·5DMSO.[21] Views of the structure appear in Figures

(19) Takagi, K.; Okamoto, T.; Sakakibara, Y.; Ohno, A.; Oka, S.; Hayama, N. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 3177.
(20) Simons, J. K.; Saxton, M. R. *Organic Syntheses*; Wiley: New York, 1963; Collect. Vol. IV, p 78.
(21) The composition was estimated by ^{1}H NMR spectroscopy of dissolved samples. The amount of any H$_2$O included could not be determined accurately.
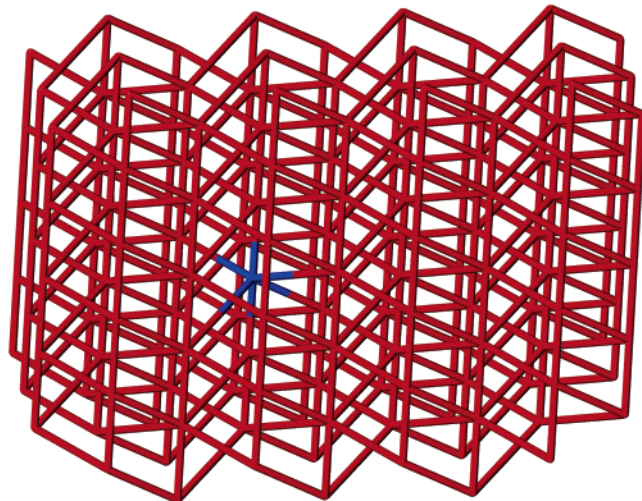
Figure 2. Representation of the structure of crystals of anionic tecton **2·PPh₄⁺** grown from DMSO/toluene showing the three-dimensional 6-connected network defined by joining the central boron atom of each tecton with the centers of the set of six neighbors shown in Figure 1. For clarification, one boron center and its six connections are highlighted in blue.

1–4. Anionic tecton **2** and its neutral analogue **1** have the same hydrogen-bonding sites, oriented tetrahedrally by cores with nearly identical molecular structures, so the emerging rules of molecular tectonics suggest that the resulting networks should share key features and perhaps even be isostructural. In fact, the networks show extensive homology, and both are porous, three-dimensional, and connected by multiple hydrogen bonds, as planned. Moreover, each tecton in both networks participates in a total of 16 hydrogen bonds, and in neither network is interpenetration observed. It is noteworthy that ionic repulsion and the need to incorporate counterions do not conspire to prevent tecton **2** from self-associating in the normal manner to form a porous hydrogen-bonded three-dimensional network similar in many ways to the one formed by neutral analogue **1**.

Despite these fundamental similarities, however, the architectures of the two networks differ in important details. In particular, each tecton **1** in the neutral network has eight hydrogen-bonded neighbors (Figure 5), whereas each tecton **2** in the anionic network has only six (Figure 1). The C···C distance between the central carbon atom of each neutral tecton **1** and those of its hydrogen-bonded neighbors is 14.91 Å, whereas the corresponding average B···B distance in crystals of anionic tecton **2·PPh₄⁺** is 15.64 Å. Reducing the number of neighbors and increasing their separation, as observed in crystals of tecton **2**, presumably decreases overall ionic repulsion and creates space for the inclusion of counterions. This suggests that modifying tectons by introducing charge may be a generally effective strategy for making molecular networks less compact and more porous.

Even when the charge/volume ratio of ions is small, as it is in the salt **2·PPh₄⁺**, the structural consequences of incorporating charge may be profound. Indeed, crystals of the closely related salt BPh₄⁻PPh₄⁺, which lacks hydrogen-bonding sites, are not isostructural with those of neutral analogues MPh₄, where M = C, Si, Ge, Sn, Pb, and Os.[22] In crystals of the isostructural

(22) Lloyd, M. A.; Brock, C. P. *Acta Crystallogr.* **1997**, *B53*, 773.

series of neutral compounds MPh₄, each molecule has 14 neighbors in van der Waals contact. Each ion in crystals of the salt BPh₄⁻PPh₄⁺ also has 14 neighbors, but only four have the same charge, thereby confirming the importance of ionic repulsion as a structural determinant in molecular crystal engineering. For similar reasons, neutral tectons and their charged analogues are unlikely to crystallize isostructurally; however, the disadvantage of losing a degree of structural predictability is offset by gaining significantly higher porosity, at least in the case of tecton **2**.

As shown in Figure 1, the four diaminotriazine groups of each anionic tecton **2** interact with eight diaminotriazine groups provided by six neighboring tectons according to all three normal hydrogen-bonding motifs **I–III**.[6–9] Figure 5 reveals that the
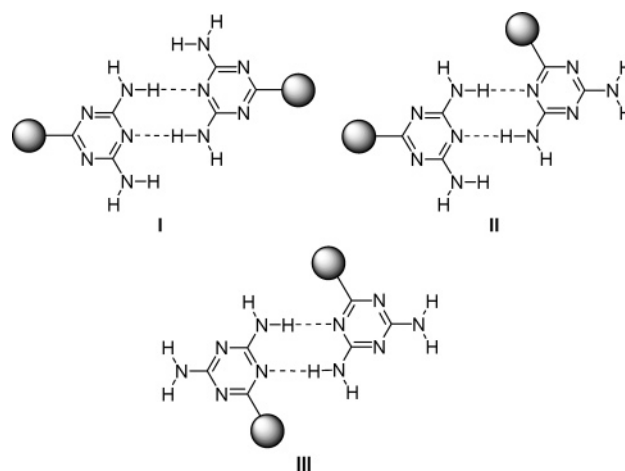
four diaminotriazine groups of each neutral tecton **1** form hydrogen bonds of type **II** only, using eight diaminotriazine groups provided by eight neighbors. Lines joining the central boron atom of each anionic tecton **2** with the centers of its hydrogen-bonded neighbors define the complex three-dimensional 6-connected network shown in Figure 2. In crystals of salt **2·PPh₄⁺**, the C–B–C angles at the core of each anionic tecton vary from 100° to 113°, whereas the central C–C–C angles in crystals of neutral analogue **1** lie in a narrower range (107°–111°). This shows that deviations from an ideal tetrahedral geometry are more pronounced in the network derived from tetraphenylborate **2**, possibly because it is inherently more difficult to optimize hydrogen bonding, ionic interactions, and molecular packing at the same.

The anionic network produced by crystallization of tecton **2·PPh₄⁺** is exceptionally porous. Only 26% of the volume of the crystals is occupied by the ordered tectons themselves,[23,24] and the remaining 74% is available for including cations and guests, which are disordered. The observed porosity is greater than that of all other networks built from small molecules, with

(23) The percentage of volume accessible to cations and guests was estimated by the PLATON program.[24] PLATON calculates the accessible volume by allowing a spherical probe of variable radius to roll over the internal van der Waals surface of the crystal structure. PLATON uses a default value of 1.20 Å for the radius of the probe, which is an appropriate model for small guests such as water. The van der Waals radii used to define surfaces for these calculations are as follows: C: 1.70 Å, H: 1.20 Å, N: 1.55 Å, and B: 1.63 Å. If V is the volume of the unit cell and V_g is the guest-accessible volume as calculated by PLATON, then the porosity P in % is given by $100V_g/V$.

(24) Spek, A. L. *PLATON, A Multipurpose Crystallographic Tool*; Utrecht University: Utrecht, The Netherlands, 2001. van der Sluis, P.; Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, 194.
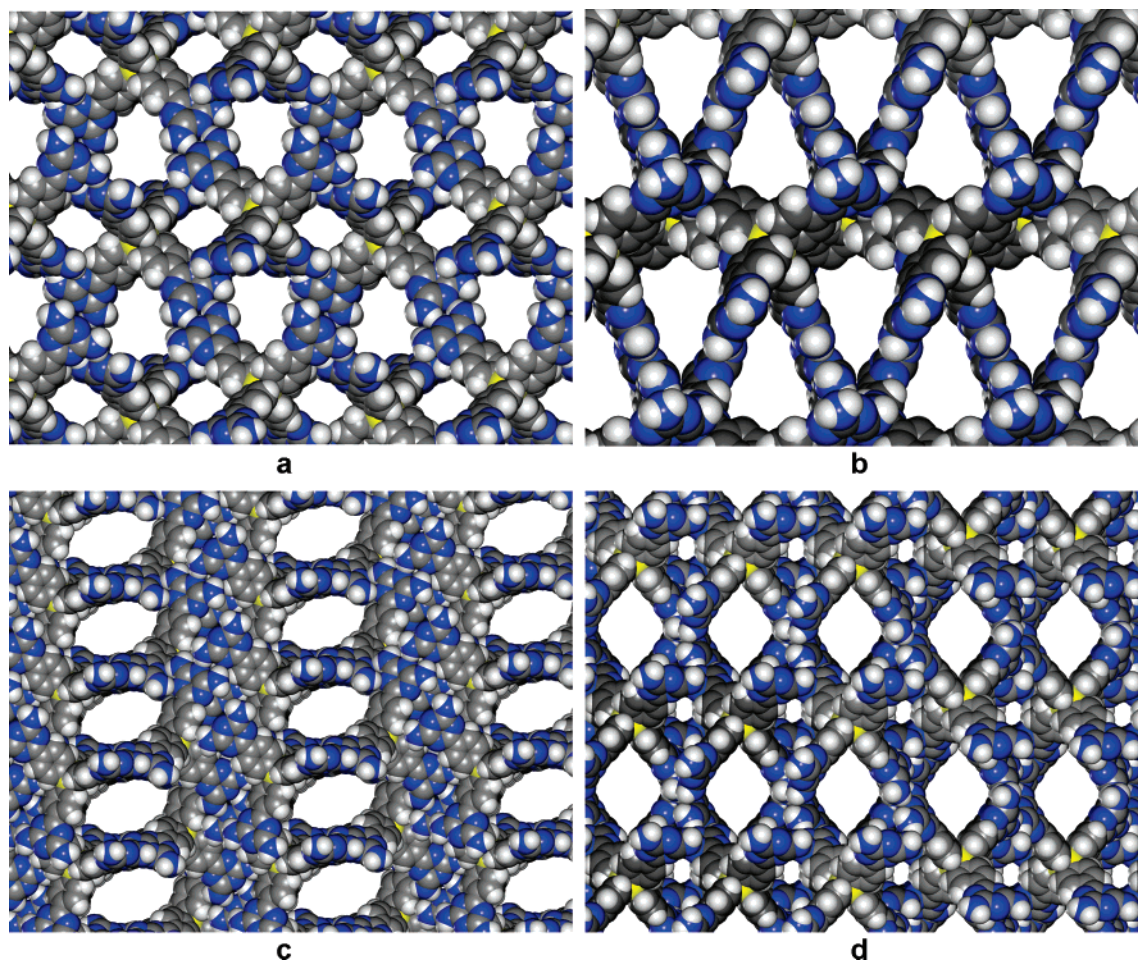
Figure 3. Porosity of the network constructed from anionic tecton **2**·PPh$_4^+$, viewed along the *a* axis (Figure 3a), the *c* axis (Figure 3b), the *ab* diagonal (Figure 3c), and the *ac* diagonal (Figure 3d). All views show a 3 × 2 × 4 array of unit cells, with guests omitted and atoms represented by spheres of van der Waals radii to reveal the cross sections of the channels. Atoms of hydrogen appear in light gray, atoms of boron in yellow, atoms of carbon in dark gray, and atoms of nitrogen in blue.
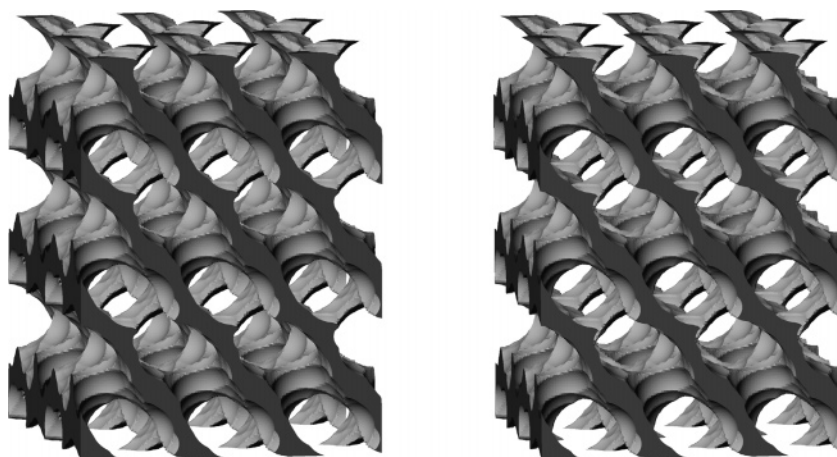

Figure 4. Stereoscopic representation of interconnected channels within the network constructed from anionic tecton **2**·PPh$_4^+$. The image shows a 3 × 3 × 2 array of unit cells viewed along the *c* axis. The outsides of the channels appear in light gray, and dark gray is used to show where the channels are cut by the boundaries of the array. The surface of the channels is defined by the possible loci of the center of a sphere of diameter 5 Å as it rolls over the surface of the ordered network.[27]

only a single exception.[10] Moreover, the porosity exceeds the percentage of volume occupied by water and other guests in all but the most highly hydrated crystals of proteins,[25] even though tecton **2** has a simple shape that can in principle be packed efficiently, whereas proteins have complex topologies that disfavor close packing.

Cations and guests included in the anionic network built from tecton **2** occupy large interconnected channels (Figures 3 and

(25) Rangarajan, S. E.; Tocilj, A.; Li, Y.; Iannuzzi, P.; Matte, A.; Cygler, M. *Acta Crystallogr.* **2003**, *D59*, 2348. Quillen, M. L.; Matthews, B. W. *Acta Crystallogr.* **2000**, *D56*, 791. Andersson, K. M.; Hovmöller, S. *Acta Crystallogr.* **2000**, *D56*, 789.
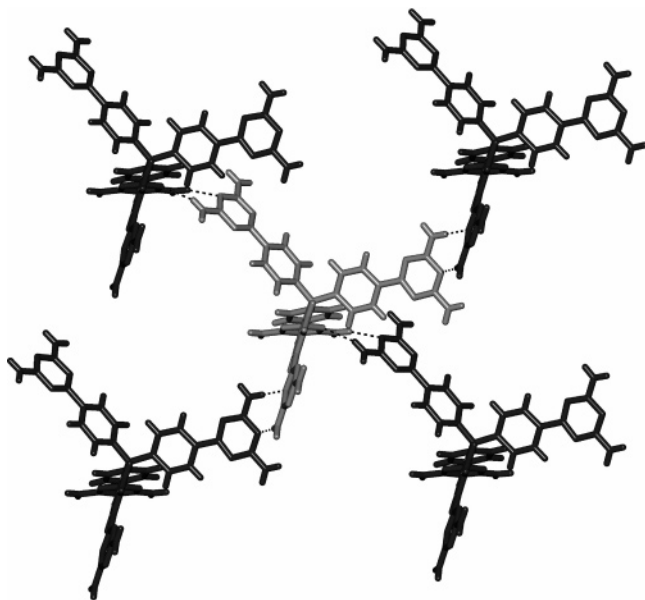
Figure 5. View of the structure of crystals of tetraphenylmethane **1** grown from HCOOH/dioxane, showing a central tecton (light gray) surrounded by four hydrogen-bonded neighbors (dark gray).[9] Four other symmetry-equivalent neighbors are omitted for clarity. Hydrogen bonds appear as broken lines, and guests are not shown. The four diaminotriazine groups of the central tecton form a total of 16 hydrogen bonds, all of type **II**.

4). The most impressive channels are aligned with the *c* axis and have triangular cross sections measuring approximately 8 × 12 Å² at the narrowest points (Figure 3b).[26] The channels themselves are represented by the surface shown in Figure 4.[27] Those in crystals of neutral tecton **1** are separate and parallel, but those in crystals of anionic analogue **2** are highly interconnected. In principle, guests that diffuse inside crystals of tecton **2** can reach any point within the channels by many redundant paths, which should facilitate diffusion when channels are blocked or other defects are present.[28]

Crystallization and Structure of Other Salts of Tetraphenylborate 2. Tectons **1** and **2** incorporate multiple sticky sites that have reliable patterns of association, oriented tetrahedrally by attachment to rigid cores with well-defined structures. Such compounds are valuable tools for probing the generality of polymorphism in molecular crystals and for testing the widespread notion that the number of polymorphic forms of any compound is limited only by the effort needed to find them.[29,30] In contrast, the particular structural features of tectons are designed to disfavor crystallization in many polymorphic forms; instead, tectons are programmed to form one particular network, or a restricted number of related alternatives, even under markedly different conditions of crystallization.

(26) The dimensions of a channel in a particular direction correspond to those of an imaginary cylinder that could be passed through the hypothetical open network in the given direction in contact with the van der Waals surface. Such values are inherently conservative because (1) they measure the cross section at the narrowest constriction and (2) they systematically underestimate the sizes of channels that are not uniform and linear.
(27) Representations of channels were generated by the Cavities option in the program ATOMS (*ATOMS*, Version 5.1; Shape Software: 521 Hidden Valley Road, Kingsport, TN 37663; www.shapesoftware.com).
(28) For a discussion of pathways for diffusion in microporous materials, see: Venuto, P. B. *Microporous Mater.* **1994**, *2*, 297.
(29) Bernstein, J. *Polymorphism in Molecular Crystals*; Oxford University Press: New York, 2002.
(30) McCrone, W. C. In *Physics and Chemistry of the Organic Solid State*; Fox, D., Labes, M. M., Weissberger, A., Eds.; Wiley-Interscience: New York, 1965; Vol. 2, pp 725−767.

Scheme 1
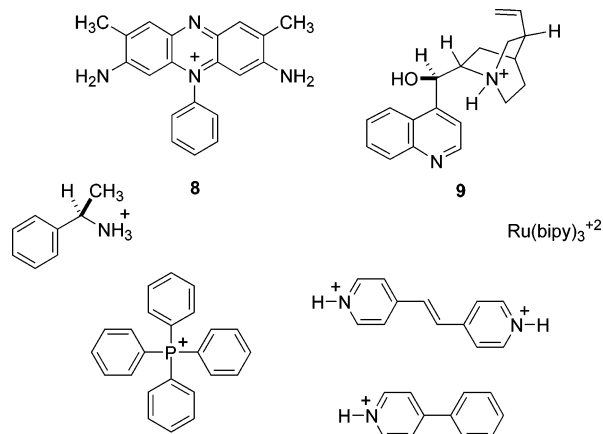
Anionic tecton **2** provides a special opportunity to test these hypotheses. Many tectons that have been studied so far are polar and rigid molecules, with low solubility in most solvents. As a result, conditions for crystallization can normally be varied only within narrow limits. In attempts to crystallize tecton **1**, for example, HCOOH can be replaced by similar polar solvents, or precipitants other than dioxane can be used. For these reasons, the notion that tectons resist polymorphism cannot normally be tested rigorously by crystallizing them under widely different conditions. In contrast, the hypothesis that anionic tecton **2** favors a particular network can easily be subjected to a demanding test, simply by crystallizing salts with many different cations.

Inducing salts of tecton **2** to form single crystals suitable for X-ray diffraction was difficult, but eventually we obtained structural data for salts with the diverse group of mono- and dications shown in Scheme 1. In all seven cases, crystallization from DMSO/toluene or DMF/toluene produces the same anionic network, and the unit cell parameters are closely similar (6%) to those of the PPh₄⁺ salt. Again, the included cations and guests are disordered. We were also able to crystallize the Li⁺, Na⁺, K⁺, and [CH₃(CH₂)₃]₄N⁺ salts of tecton **2** from DMSO/toluene. In this group of salts, the unit cells appear to be different from those of salts of the cations shown in Scheme 1; however, the quality of the crystals was poor, and we could not collect full sets of data suitable for complete determination of the structures.

Salts of tetraphenylborate **2** with different cations are distinctly different compounds. Moreover, the size and structural complexity of some of the cations in Scheme 1 rival those of anionic tecton **2** itself. For these reasons, the consistent preference for the formation of the same hydrogen-bonded network is a significant observation. It validates the notion that tecton **2** and other compounds with oriented arrays of sticky sites are programmed to form specific molecular networks and to disfavor alternatives, in agreement with the emerging principles of molecular tectonics.[14]

Exchange of Ions in Single Crystals of Salts of Tetraphenylborate 2. The strategy of using ionic tectons to build porous charged networks offers unique advantages and may help solve long-standing problems in the chemistry of inclusion compounds. For example, including a specific desired guest in a neutral network is often difficult, but networks and guests can be made to have stronger mutual affinity by giving them opposite charges. The diversity of the cations shown in Scheme 1 is consistent with the notion that ionic attraction provides an

additional driving force for inclusion in molecular crystals, thereby ensuring that guests with an impressively wide range of sizes and shapes can be induced to enter, at least within geometric limits imposed by the channels.

In crystalline salts of anionic tecton **2**, the cations and guests are disordered, potentially mobile, and located in large interconnected channels that in principle provide multiple paths of escape. Furthermore, the structure is maintained by an extensive network of hydrogen bonds, with each tecton held in place by 16 hydrogen bonds. Although the resulting network is robust, it is not strong enough to resist decomposition when crystals are removed from their mother liquors for extended periods or when volatile guests are removed under vacuum. Nevertheless, single crystals show high structural integrity, and they undergo exchange of cations without loss of crystallinity. For example, red single crystals of the salt of tecton **2** with phenazinium cation **8**, with approximate dimensions 0.5 mm × 0.5 mm × 0.5 mm, were exposed to a solution of excess $PPh_4^+Br^-$ in DMSO/toluene for 24 h at 25 °C. Complete exchange of cations ($\geq$98%) occurred under these conditions to give single crystals of the colorless salt $\mathbf{2} \cdot PPh_4^+$.[31] The recovered crystals (1) remained transparent and morphologically unchanged, (2) continued to diffract and to exhibit uniform extinction between crossed polarizers, and (3) showed unit cell parameters similar to those of the starting salt ($\pm$2%). Similar single-crystal to single-crystal exchanges could be carried out with other pairs of cations selected from the group in Scheme 1, as well as with many other cations that do not exceed geometric limits imposed by the channels.

Of particular interest are exchanges that replace a larger cation by a smaller cation. Such exchanges liberate space within the crystals that can then be occupied by additional neutral guests. Reducing the volume of the cation allows the network to use more of its high porosity (74%) to include neutral guests, with less space needed for the counterions that maintain overall electroneutrality. For this reason, it is proper to claim that ionic tecton **2** forms one of the most porous molecular networks observed so far, even though counterions are a necessary component of the structure and must occupy part of the available volume. It is also noteworthy that the exchange of cations is a predictable source of single crystals of new salts of tecton **2** with the specific structure shown in Figures 1−4, even when direct crystallization of the new salt is impossible or favors a different structure. For example, single crystals of the $[CH_3(CH_2)_3]_4N^+$ salt can be prepared by exchange, starting from single crystals of the salts shown in Scheme 1, but direct crystallization of the $[CH_3(CH_2)_3]_4N^+$ salt from DMSO/toluene gives crystals that belong to a different space group. Such examples demonstrate that (1) structural reorganization of the network is slower than the exchange of cations, which presumably involves simple diffusion, and (2) exchange does not require substantial movement of the individual tectons, which is expected to permit recrystallization and lead to the formation of alternative structures.[32]

As in zeolites, the exchange of cations in the anionic network built from tecton **2** shows useful selectivity. This was established
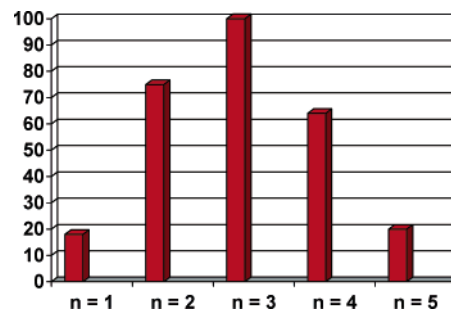
(31) The extent of exchange was estimated by ^1H NMR spectroscopy of dissolved samples.
(32) For an analysis of potential mechanisms of ion exchange in porous charged networks, see: Khlobystov, A. N.; Champness, N. R.; Roberts, C. J.; Tendler, S. J. B.; Thompson, C.; Schröder, M. *CrystEngComm* **2002**, *4*, 426.

Figure 6. Selective exchange of tetraalkylammonium cations $[CH_3(CH_2)_n]_4N^+$ in single crystals of tetraphenylborate **2**, showing relative preferences as a function of chain length.

by exposing single crystals of the (R)-α-methylbenzylammonium salt of tecton **2** to solutions in DMF/toluene containing excess amounts of competing pairs of tetraalkylammonium bromides, present in equal amounts. The following relative preferences for $[CH_3(CH_2)_n]_4N^+$ were observed at equilibrium at 25 °C: 0.18, 0.75, 1.0, 0.64, and 0.20 for $n = 1-5$, respectively (Figure 6). Similar degrees of selectivity have been observed for the inclusion of alkylammonium cations in natural zeolites and synthetic analogues, including chabazite, faujasite, and Linde A.[33] However, the largest cations accommodated in the anionic network derived from tecton **2** are much too big to enter classical natural and synthetic zeolites. These observations underscore the high degree of porosity that can be attained in molecular networks, and they show that the performance of such molecular materials can equal or even surpass that of classical inorganic analogues. Preference for the inclusion of $[CH_3(CH_2)_3]_4N^+$ in networks built from tecton **2** appears to reflect various competing factors, including the size of the cation, the interaction of its substituents with the walls of the channels, the ability of the cation to approach the anionic boron centers of the network, and the entropically favorable effect of replacing a small cation with a large one, which presumably frees neutral guests from inside the network and places them in a more disordered state in the surrounding solution.

Conclusions

Our study of crystals formed by salts of tetraphenylborate **2** is significant because it subjects the emerging principles of molecular tectonics to critical tests.[14] In addition, the results provide new insights that can be used to guide future attempts to engineer crystalline materials with predictable properties. The simple expedient of replacing carbon by boron in the core of tetraphenylmethane **1** creates anionic tecton **2** and logically transforms the robust porous hydrogen-bonded network built from tecton **1** into an anionic analogue with closely similar structural features. The resulting charged network is among the most porous ever observed in molecular crystals, in part because ionic repulsion disfavors close packing. Crystallization of salts of tecton **2** with diverse cations consistently yields the same network, supporting the hypothesis that compounds with oriented arrays of sticky sites are intrinsically disposed to form specific molecular networks and to disfavor polymorphs. Cations can be exchanged in single crystals of salts of tecton **2** with retention of crystallinity and with selectivities similar to those observed in typical zeolites. Such exchanges can produce new

(33) Breck, D. W. *Zeolite Molecular Sieves*; Wiley-Interscience: New York, 1974, Chapter 7.

salts in a predictable crystalline form, even when direct crystallization proves impossible or favors a different structure. Together, these observations underscore the potential of molecular tectonics as a strategy for making new ordered molecular materials by design, and they reveal that constructing such materials from charged tectons has special benefits.

Experimental Section

Ether was dried by distillation from the sodium ketyl of benzophenone. All other reagents were commercial products that were used without further purification.

Lithium Tetrakis(4-iodophenyl)borate (3). A solution of 1,4-diiodobenzene (10.0 g, 30.3 mmol) in ether (300 mL) was stirred at $-10\,°C$ under N_2 and treated dropwise with a solution of butyllithium (12.1 mL, 2.5 M in hexane, 30 mmol). The resulting mixture was kept at $-10\,°C$ for 10 min, and $BF_3·O(C_2H_5)_2$ (0.796 g, 5.61 mmol) was then added. The temperature was allowed to rise to 25 °C, and after 18 h, the mixture was filtered to remove a solid. The solid was washed with ether (200 mL), and the desired product was extracted with acetone (20 mL). Acetone was removed from the filtered extracts by evaporation under reduced pressure, leaving a residue of lithium tetrakis(4-iodophenyl)borate (**3**) as a colorless solid (3.95 g, 4.76 mmol, 85%). An analytically pure sample was prepared by recrystallization from CH_2Cl_2: mp 289−290 °C; ^1H NMR (300 MHz, DMSO-d_6) δ 6.87 (m, 8H), 7.29 (d, 8H, $^3J = 8.0$ Hz); ^{11}B NMR (96.0 MHz, DMSO-d_6) δ −6.35; ^{13}C NMR (100.6 MHz, DMSO-d_6) δ 88.5, 134.5, 137.9, 161.1 (q, $^1J_{C-B} = 49$ Hz); HRMS (FAB, 3-nitrobenzyl alcohol) calcd for $C_{24}H_{16}^{11}BI_4$ m/e 822.7524, found 822.7503. Anal. Calcd for $C_{24}H_{16}BI_4Li$: C, 34.74; H, 1.94. Found: C, 34.80; H, 1.76.

Potassium Tetrakis(4-cyanophenyl)borate (4). A mixture of lithium tetrakis(4-iodophenyl)borate (**3**; 4.50 g, 5.42 mmol), KCN (3.90 g, 59.9 mmol), KOH (0.054 g, 0.96 mmol), and Pd(OOCCH$_3$)$_2$ (0.018 g, 0.080 mmol) in tetramethylurea (9 mL) was heated at reflux under N_2. After 18 h, volatiles were removed by evaporation under reduced pressure; the residual solid was washed with H_2O, saturated aqueous KCl, and CH_2Cl_2; and the product was then dried in vacuo. This provided potassium tetrakis(4-cyanophenyl)borate (**4**) as a beige solid (2.03 g, 4.43 mmol, 82%). An analytically pure sample was prepared by recrystallization from CH_3CN: mp >300 °C; IR (KBr) 2222 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 7.23 (m, 8H), 7.44 (d, 8H, $^3J = 7.8$ Hz); ^{11}B NMR (96.0 MHz, DMSO-d_6) δ −5.92; ^{13}C NMR (100.6 MHz, DMSO-d_6) δ 105.6, 120.2, 129.7, 135.6, 167.6 (q, $^1J_{C-B} = 49$ Hz); HRMS (FAB, 3-nitrobenzyl alcohol) calcd for $C_{28}H_{16}^{11}BN_4$ m/e 419.1468, found 419.1454.

Sodium Salt of Tetrakis[4-[2-(4,6-diamino-1,3,5-triazinyl)]phenyl]borate (2). A mixture of potassium tetrakis(4-cyanophenyl)borate (**4**; 1.50 g, 3.27 mmol), dicyandiamide (1.36 g, 16.2 mmol), and KOH (0.441 g, 7.86 mmol) in 2-methoxyethanol (9 mL) was heated at reflux under N_2. After 18 h, volatiles were removed by evaporation under reduced pressure, and the residual solid was washed with CH_3OH and dried. The solid was dissolved in boiling deionized H_2O (20 mL), and saturated aqueous NaCl was added. The resulting suspension was filtered, and the solid was washed with deionized H_2O and dried in vacuo. This provided the sodium salt of tetrakis[4-[2-(4,6-diamino-1,3,5-triazinyl)]phenyl]borate (**2**) as a colorless solid (2.21 g, 2.84 mmol, 87%). A purified sample was prepared by recrystallization from H_2O: mp >300 °C; ^1H NMR (300 MHz, DMSO-d_6) δ 6.56 (bs, 16H), 7.28 (m, 8H), 7.90 (d, 8H, $^3J = 7.7$ Hz); ^{11}B NMR (96.0 MHz, DMSO-d_6) δ −5.98; ^{13}C NMR (75.5 MHz, DMSO-d_6) δ 125.4, 130.8, 135.1, 167.3 (2C), 171.4.

Other Salts of Tetrakis[4-[2-(4,6-diamino-1,3,5-triazinyl)]phenyl]borate (2). The sodium salt of tetrakis[4-[2-(4,6-diamino-1,3,5-triazinyl)]phenyl]borate (**2**) was dissolved in boiling deionized H_2O, and the resulting solution was treated with a concentrated aqueous solution containing a large excess of the chloride or bromide salt of the desired

cation. The product was filtered from the resulting suspension, washed with deionized H_2O, and dried in vacuo.

Crystallization of Salts of Tecton 2. In a typical procedure, the salt (∼5 mg) was dissolved in a small amount of DMSO or DMF (∼1 mL), toluene was added dropwise until cloudiness appeared, more DMSO or DMF was added until the cloudiness disappeared, and the resulting solution was kept undisturbed at 25 °C. Crystals appeared within 24 h in the form of complex plates. Alternatively, crystallization could be effected by diffusion of vapors of toluene into solutions of salts of tecton **2** in DMSO or DMF. For analysis by ^1H NMR spectroscopy, the crystals were rinsed with pentane and allowed to dry briefly in a current of air.

Ion Exchange in Single Crystals of Salts of Tecton 2. Single crystals of salts of tecton **2** were obtained by the procedures described above, and the mother liquors were removed by pipet. The crystals were immediately treated with a saturated solution of the chloride or bromide salt of a new cation in a 1:1 mixture of DMSO (or DMF) and toluene, in which the crystals are essentially insoluble. The crystals were kept in contact with this solution at 25 °C until they were analyzed by X-ray crystallography and ^1H NMR spectroscopy.

X-ray Crystallographic Studies. Data were collected using (1) an Enraf-Nonius CAD4 diffractometer with Cu Kα radiation at 205 K or (2) a Bruker SMART 2000 diffractometer with Cu Kα radiation at 223 K. Structures were solved by direct methods using SHELXS-96 or SHELXS-97 and refined with SHELXL-96 or SHELXL-97.[34] All non-hydrogen atoms were refined anisotropically, whereas hydrogen atoms were placed in ideal positions and refined as riding atoms.

Structure of the Salt of Tetraphenylborate 2 with PPh$_4^+$. Crystals of the salt belong to the monoclinic space group $P2/n$ with $a = 13.045(6)$ Å, $b = 17.151(8)$ Å, $c = 24.023(8)$ Å, $β = 92.21(3)°$, $V = 5371(4)$ Å^3, $D_{calcd} = 1.2122$ g/cm^3, and $Z = 2$. Full-matrix least-squares refinements on F^2 led to final residuals $R_f = 0.0546$, $R_w = 0.1391$, and GoF = 0.579 for 5519 reflections with $I > 2σ(I)$.

Structure of the Salt of Tetraphenylborate 2 with Phenazinium Cation 8. Crystals of the salt belong to the monoclinic space group $P2/n$ with $a = 12.845(8)$ Å, $b = 17.134(10)$ Å, $c = 23.896(16)$ Å, $β = 92.11(5)°$, $V = 5256(6)$ Å^3, $D_{calcd} = 1.305$ g/cm^3, and $Z = 2$. Full-matrix least-squares refinements on F^2 led to final residuals $R_f = 0.0480$, $R_w = 0.1084$, and GoF = 0.520 for 5435 reflections with $I > 2σ(I)$.

Structure of the Salt of Tetraphenylborate 2 with Cinchonidinium Cation 9. Crystals of the salt belong to the monoclinic space group $P2/n$ with $a = 12.6010(13)$ Å, $b = 18.1778(17)$ Å, $c = 23.825(2)$ Å, $β = 97.436(5)°$, $V = 5411.4(9)$ Å^3, $D_{calcd} = 0.647$ g/cm^3 (calculated without the contribution of included solvent), and $Z = 2$. Full-matrix least-squares refinements on F^2 led to final residuals $R_f = 0.0668$, $R_w = 0.1703$, and GoF = 0.955 for 6741 reflections with $I > 2σ(I)$.

Supporting Information Available: Further crystallographic details, including ORTEP drawings and tables of crystallographic data, atomic coordinates, anisotropic thermal parameters, and bond lengths and angles for salts of tetraphenylborate **2** with PPh$_4^+$, phenazinium cation **8**, and cinchonidinium cation **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

JA042233M

(34) Sheldrick, G. M. *SHELXS-97, Program for the Solution of Crystal Structures and SHELXL-97, Program for the Refinement of Crystal Structures*; Universität Göttingen: Germany, 1997.