Acentric Extended Solids by Self Assembly of 4,4′-Bipyrazolyls**

Ishtvan Boldog, Eduard B. Rusanov,
Alexander N. Chernega, Joachim Sieler, and
Konstantin V. Domasevitch*

Design of solid-state structure and therefore functionality by using the principles of crystal engineering represents a new and growing area of chemistry which offers intriguing possibilities for the development of novel functional materials.[1] Solids that adopt noncentrosymmetric structures are predisposed to exhibit a range of useful bulk physical properties, including second-order nonlinear optical (NLO), piezoelectric, and pyroelectric effects.[2] Elaboration of such materials that combine acentric structure with chemical and thermal stability presents a significant challenge.[2, 3] A particularly promising tool in the control of overall polarity is supramolecular retro-synthesis, that is, to design the molecular building blocks (tectons), their size, and conformations and thus to program at the molecular level the pathways of self-assembly processes for the formation of a certain desired inherently polar topology. For instance, diamondoid[1, 4] and helical[5] architectures were recently investigated and represent the most common and obvious types of acentric arrays.

Novel insights into the development of strategies for designing polar solids without the need for chiral building blocks may be offered by a number of three-connected topologies, particularly due to the lack of inversion symmetry in three-connected units. An especially attractive target in this context is a family of three-dimensional (3D) three-connected decagonal nets,[6] three types of which are exemplified by the structures of hydrogen peroxide, $ThSi_2$, and B_2O_3 (Figure 1).[7] The (10,3)-*b* and (10,3)-*c* topologies can be viewed as a system of zigzag polymeric chains,[6] and they appear to be realistic models for the assembly of molecular species capable of generating two noncoplanar zigzag chains by self-complementary donor–acceptor interactions. The corresponding tecton is a tetrafunctional molecule containing two pairs of coplanar self-complementary binding sites that are rotated with respect to one another (e.g., hydrogen-bond donors and acceptors).[8]

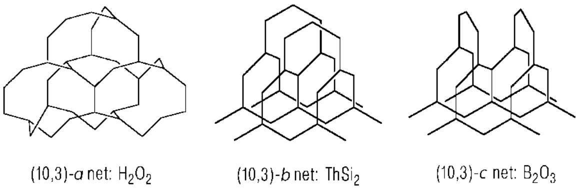
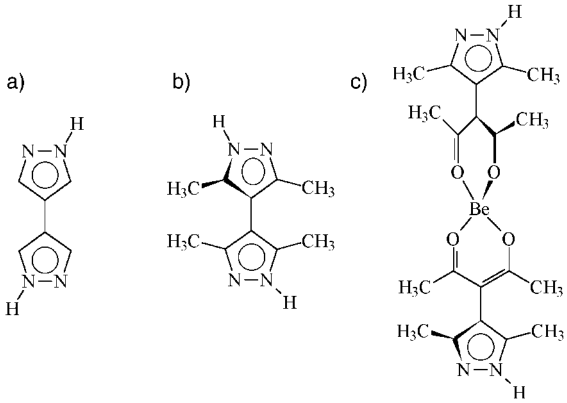


Figure 1. Three-connected decagonal nets.

As a suitable molecular system for the design of (10,3) topologies we examined 4,4′-bipyrazolyls (Scheme 1). They have a set of effective self-complementary hydrogen-bond donor (NH) and acceptor (N) sites for the formation of hydrogen bonds, and the desired orientation of these binding sites can be controlled by varying the substituents in the 3,3′- and 5,5′-positions.[9] Tetramethyl-substituted 4,4′-bipyrazolyl (4,4′-Me_4bpz, Figure 2) exists in at least two polymorphic forms,[10] both of which are acentric, and the entities may be best described in terms of 3D nets. The points of such nets in both structures are single pyrazolyl rings. Each point is three-coordinate and is linked to two of its three closest neighbors by hydrogen bonding, and to the third by the 4,4′ carbon–carbon bond within the 4,4′-Me_4bpz molecule. Hence two-thirds of the links in the resulting net are N–H···N hydrogen bonds, and one-third carbon–carbon bonds. The shortest circuits of these nets include ten points, and in accordance with Wells their topological symbol is (10,3).[6] Two of the present nets correspond to $ThSi_2$ (10,3)-*b* (monoclinic α-form **2**) and B_2O_3 (10,3)-*c* topologies (hexagonal β-form **3**) and differ in the angle of rotation of successive sets of zigzag chains in the structure: 79° and 60°, respectively (Scheme 2).



Scheme 1. Bipyrazolyl species used in the present study: a) 4,4′-bipyrazolyl (4,4′-bpz (**1**)); b) 3,3′,5,5′-tetramethyl-4,4′-bipyrazolyl (4,4′-Me_4bpz; α-form: **2**, β-form: **3**); 3(4,4′-Me_4bpz)·H_2O·Solv: **4** (solv = acetone: **4a**, ethyl acetate: **4b**, THF: **4c**); c) bis[3-(3,5-dimethylpyrazol-4-yl)pentane-2,4-dionate]beryllium (Be(acacpz)$_2$; Be(acacpz)$_2$·2CH_3OH: **5**).

The characteristic parameter of the structure that determines the above-mentioned angles of rotations and is responsible for such dramatic topological changes is clearly the interplanar angle φ of the bipyrazolyl molecule. These values for two polymorphs (α: 75.6°, β: 56.2°) almost exactly correspond to the observed geometry of the whole nets and satisfy the demands of their topology (90° and 60°). This solid-state manifestation of conformational flexibility of the tecton

---

[*] Dr. K. V. Domasevitch, I. Boldog
Inorganic Chemistry Department, Kiev University
Volodimirska Street 64, Kiev 01033 (Ukraine)
Fax: (+380) 44-2962467
E-mail: dk@anorgchemie.univ.kiev.ua
Dr. E. B. Rusanov, Dr. A. N. Chernega
Institute of Organic Chemistry
Murmanskaya Street 5, Kiev-94, 02094 (Ukraine)
Prof. Dr. J. Sieler
Institut für Anorganische Chemie, Universität Leipzig
Linnéstrasse 3, 04103 Leipzig (Germany)

[**] The authors gratefully acknowledge support from the Deutsche Forschungsgemeinschaft and the Sächsisches Staatsministerium für Wissenschaft und Kunst.

Supporting information for this article is available on the WWW under http://www.angewandte.com or from the author.

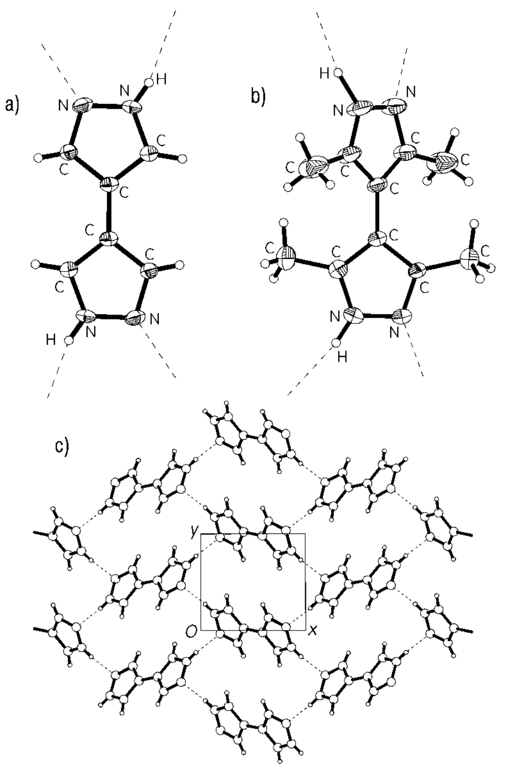
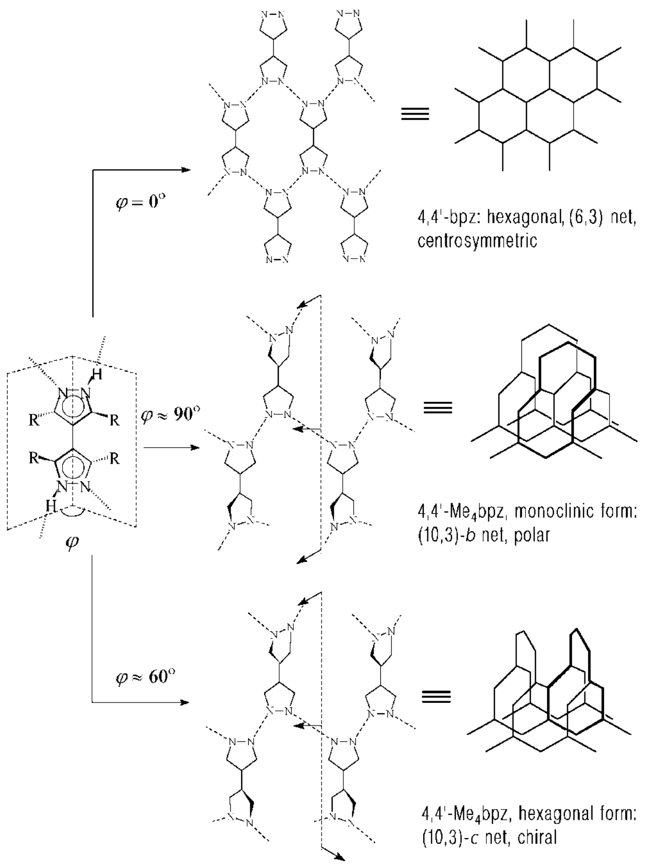


Figure 2. Molecular structures of planar tecton 4,4′-bpz (a) and angular tecton 4,4′-Me_4bpz (b); flat 2D hexagonal net by self assembly of 4,4′-bpz (c).



Scheme 2. Pathways for the self assembly of bipyrazolyls and nature of the supramolecular isomerism of 4,4′-Me_4bpz. Decagonal circuits of the resulting 3D nets are represented by bold lines.

agrees with a theoretical study:[13] the optimal conformation of the 4,4′-Me_4bpz molecule has $\varphi = 87.5°$, but in the broad range of $\varphi \approx 50-90°$, the relative energies of the conformers are very similar (75°: $\Delta E = 0.92$ kJ mol^{-1}; 60°: 3.89; 45°: 11.02; 30°: 27.17).

It seems likely that the desired topology of the 3D array, as well as the properties of the crystal in the context of inducing bulk polarity, can be designed at the molecular level by varying the angle φ of the molecular unit. Nonplanar species with corresponding interplanar angles of up to about 60° will tend to induce the chiral (10,3)-*c* net, while more highly substituted units and an interplanar angle near the maximum value of 90° will produce the (10,3)-*b* net. Related planar species with $\varphi \approx 0°$ associate into a flat hexagonal net, that is, the centrosymmetric motif for self assembly of unsubstituted planar 4,4′-bpz tecton **1** (Figure 2).[14]

Both the nets **2** and **3** are characterized by a helical motif of the aligned links. However, the (10,3)-*b* topology (Scheme 2) has an equal number of helices of opposite chirality, and the resulting network is achiral. In contrast, the (10,3)-*c* topology generates helices of the same chirality and hence is inherently chiral.[6] The helical motif of the β-polymorph **3**, with a pitch of 26.35 Å, is shown in Figure 3.

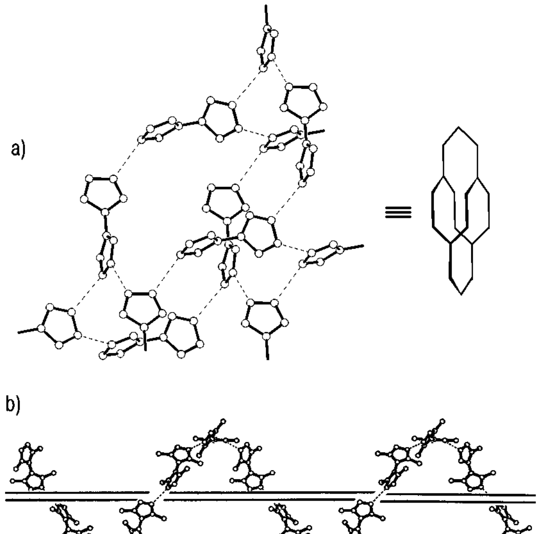


Figure 3. a) "Pseudoadamantoid" unit of the (10,3)-*b* net in the structure of the monoclinic polymorph and b) helicate motif in the structure of the hexagonal polymorph of 4,4′-Me_4bpz.

The 4,4′-Me_4bpz tecton also retains a tendency for helical self assembly in isomorphous compounds of composition 3(4,4′-Me_4bpz) · H_2O · Solv **4** (Table 1).[15] The 3D structures of these hydrogen-bonded adducts can also be clearly derived from the chiral (10,3)-*c* topology. In this idealized case ¾ of the net points are three-connected pyrazolyl cycles, and ¼ are water molecules to which three pyrazolyl cycles are bound. One NH group per three 4,4′-Me_4bpz molecules is not involved in the overall 3D linkage and forms a hydrogen bond with the molecule of solvent (Figure 4). This demon-

Table 1. Crystal data for the bipyrazolyl compounds **1**–**5**.

	1	**2**	**3**	**4a**	**4b**	**4c**	**5**
Formula	$C_6H_6N_4$	$C_{10}H_{14}N_4$	$C_{10}H_{14}N_4$	$C_{33}H_{50}N_{12}O_2$	$C_{34}H_{52}N_{12}O_3$	$C_{34}H_{52}N_{12}O_2$	$C_{22}H_{34}BeN_4O_6$
M_r	134.14	190.25	190.25	646.85	676.88	660.88	459.54
Crystal size [mm]	0.6 × 0.3 × 0.15	0.4 × 0.25 × 0.2	0.4 × 0.3 × 0.3	0.4 × 0.2 × 0.1	0.4 × 0.3 × 0.3	0.3 × 0.2 × 0.1	0.3 × 0.3 × 0.07
Crystal system	monoclinic	monoclinic	hexagonal	orthorhombic	orthorhombic	orthorhombic	tetragonal
Space group	$P2_1/c$	Cc	$P6_5$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P4_12_12$
a [Å]	5.9510(5)	12.544(3)	8.6522(9)	9.751(2)	9.8054(6)	9.754(2)	7.440(1)
b [Å]	5.4548(7)	11.443(2)		13.080(3)	13.0221(8)	13.200(3)	
c [Å]	9.6941(9)	8.301(2)	26.350(5)	30.346(7)	30.307(2)	30.197(6)	44.967(9)
β [°]	96.12(1)	96.81(3)					
V [Å^3]	312.89(6)	1183.1(5)	1708.5(4)	3870(2)	3869.9(4)	3888(1)	2489.1(7)
Z	2	4	6	4	4	4	4
Unique reflections	573	1730	1929	8388	6646	5087	2736
Observed reflections	516	1621	1866	4342	3875	3482	1519
Parameters	59	136	136	424	442	433	151
R, wR_2 (obsd)	0.054, 0.147	0.048, 0.131	0.041, 0.113	0.064, 0.157	0.050, 0.117	0.081, 0.204	0.079, 0.206

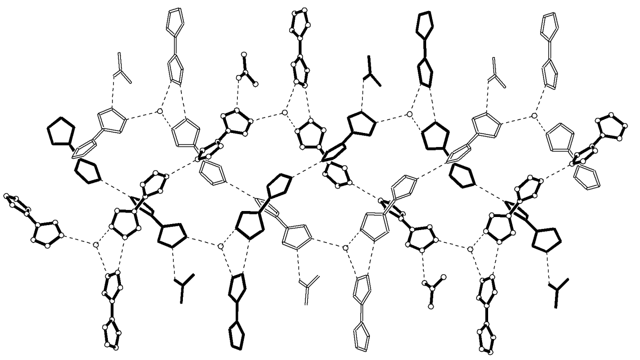


Figure 4. Triple-helicate motif of the structure of **4a**.

strates how molecules of small size may be immobilized in a chiral environment formed by self assembly of bipyrazolyls.

We were also interested in extending the bipyrazolyl frame into tectons of greater effective length, but which retain the ability for noncentrosymmetric self assembly.[16] The desired angular configuration of hydrogen-bond donor/acceptor sites may exist in extended molecules containing connected planar fragments with an odd number of rotations between them (one rotation for each 4,4′-Me_4bpz core). We propose a flexible approach with species that combine the above features with structural simplicity and chemical accessibility. Beryllium-based β-diketonate **5**[18] (Figure 5) exists as a molecular complex with the expected tetrahedral four-coordinate metal atom,[6b] and the framework of the molecule includes four planes with three successive rotations between them. Two pyrazolyl groups are related by about 77.9°, and this "extended bipyrazolyl" retains the configuration of N/NH binding sites of the 4,4′-Me_4bpz core. Hydrogen-bonded methanol molecules appear to be simply bridging two pyrazolyl cycles: NH···OH···N, so that the overall linkage pattern in the structure is the same as for the α-polymorph of 4,4′-Me_4bpz, **2**, and the compound **5** adopts a chiral structure with a (10,3)-*b* net topology.

Thus, the angular 4,4′-bipyrazolyl moiety may be regarded as a tecton predisposed for self assembly into different variants of (10,3) nets with induced bulk chirality for the resulting solids. Our results provide many possibilities for the rational design of novel polar solids of (10,3) topology and extended helicate arrays by 1) varying the substituents at the 3,3′- and 5,5′-positions of the bipyrazolyl core to tune the desired conformation of the tecton, 2) extension of the bipyrazolyl module without loss of the angular alignment of N/NH binding sites, and 3) elaboration of related systems with varying angular disposition of self-complementary donor/acceptor sites.[8] Our study also contributes to the intriguing problem of polymorphism and supramolecular isomerism[17] and illustrates how relatively slight rotational changes in the molecule may have pronounced chemical significance for the crystal packing. The approach used for the extension of the bipyrazolyl module may be considered as general and can be commonly applied in crystal engineering. We are currently studying self assembly of bipyrazolyls and their use for the rational design of solid-state functionality.[22]

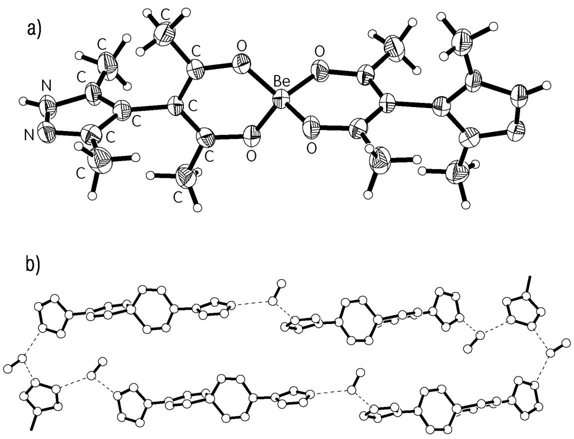


Figure 5. a) "Extended bipyrazolyl" Be(acacpz)$_2$ with angular alignment of pyrazolyl groups. b) The shortest circuits in the structure of **5** including ten pyrazolyl groups.

Experimental Section

1[9a] was prepared in 82% yield by reaction of 1,1,2,2-ethanetetraaldehyde[19] and hydrazine and was crystallized from H_2O/DMF (1/1). Sublimation of 4,4′-Me_4bpz[20] (170 °C, 5 Torr) gave the monoclinic α-form **2** that was also prepared from hot water, while crystallization from acetonitrile provided the hexagonal β-form **3**. Both polymorphs melt above 300 °C; the melts, on cooling, afford the α-form **2**. Crystallization from different solvents at ambient conditions gave the isomorphous adducts (socalled pseudopolymorphs)[21] $3(4,4'\text{-}Me_4bpz)\cdot H_2O\cdot Solv$ (**4**; solv = acetone: **4a**, ethyl acetate: **4b**, THF: **4c**).[15] They easily lose molecules of the solvent at room temperature with disintegration of the structure and formation of poorly hydrated noncrystalline products. The individual hydrate $2(4,4'\text{-}Me_4bpz)\cdot H_2O$ was isolated from wet chloroform: tetragonal, $a = 24.838(1)$, $c = 14.9190(8)$ Å.

5: $BeCO_3\cdot 4H_2O$ (0.070 g, 0.5 mmol) was dissolved in 5 mL of hot dilute HCl (2 N), and combined under stirring with a hot solution of Hacacpz (0.388 g, 2.0 mmol)[20] in aqueous ammonia (7 mL, 12 %). The solution was neutralized with HCl, and the resulting precipitate was recrystallized from aqueous methanol to give 0.075 g (30 %) of the complex as colorless plates.

Received: March 26, 2001 [Z16846]

---

[1] R. Robson in *Comprehensive Supramolecular Chemistry*, *Solid-State Supramolecular Chemistry*: *Crystal Engineering*, *Vol. 6* (Eds.: D. D. MacNicol, F. Toda, R. Bishop), Pergamon, Oxford, **1996**, chap. 22, pp. 733–755; M. O'Keeffe, M. Eddaoudi, H. Li, T. Reineke, O. M. Yaghi, *J. Solid State Chem.* **2000**, *152*, 3–20; O. M. Yaghi, H. Li, C. Davis, D. Richardson, T. L. Groy, *Acc. Chem. Res.* **1998**, *31*, 4474–4484; P. J. Hagrman, D. Hagrman, J. Zubieta, *Angew. Chem.* **1999**, *111*, 2798–2848; *Angew. Chem. Int. Ed.* **1999**, *38*, 2638–2684.

[2] F. Agullo-Lopez, J. M. Cabrera, F. Agullo-Rueda, *Electrooptics*: *Phenomena*, *Materials and Applications*, Academic Press, New York, **1994**; J. Zyss, *Molecular Nonlinear Optics*: *Materials*, *Physics and Devices*, Academic Press, New York, **1993**.

[3] G. R. Desiraju, *Crystal Engineering*: *The Design of Organic Solids*, Elsevier, New York, **1989**; J.-M. Lehn, *Supramolecular Chemistry*: *Concepts and Perspectives*, VCH, New York, **1995**; B. Moulton, M. J. Zaworotko in *Crystal Engineering*: *From Molecules and Crystals to Materials* (Eds.: D. Braga, F. Grepioni, A. G. Orpen), Kluwer, Dordrecht, **1999**, pp. 311–330.

[4] M. J. Zaworotko, *Chem. Soc. Rev.* **1994**, *23*, 283–288; O. Ermer, *Angew. Chem.* **1988**, *100*, 856–860; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 829–833.

[5] K. Biradha, C. Seward, M. J. Zaworotko, *Angew. Chem.* **1999**, *111*, 584–587; *Angew. Chem. Int. Ed.* **1999**, *38*, 492–495; W. W. Ellis, M. Schmitz, A. A. Arif, P. J. Stang, *Inorg. Chem.* **2000**, *39*, 2547–2557.

[6] a) A. F. Wells, *Three-Dimensional Nets and Polyhedra*, Wiley-Interscience, New York, **1977**; b) A. F. Wells, *Structural Inorganic Chemistry*, 5th ed., Clarendon, Oxford, **1986**.

[7] Other examples of (10,3) topologies: H. Gudbjartson, K. Biradha, K. M. Poirier, M. J. Zaworotko, *J. Am. Chem. Soc.* **1999**, *121*, 2599–2601; L. Carlucci, G. Ciani, D. M. Prosperio, A. Sironi, *Chem. Commun.* **1996**, 1393–1394; L. Carlucci, G. Ciani, D. M. Prosperio, A. Sironi, *J. Am. Chem. Soc.* **1995**, *117*, 4562–4569; G. B. Gardner, D. Venkataraman, J. S. Moore, S. Lee, *Nature* **1995**, *374*, 792–795; B. F. Abrahams, S. R. Batten, H. Hamit, B. F. Hoskins, R. Robson, *Chem. Commun.* **1996**, 1313–1314.

[8] P. Holy, J. Zavada, I. Cisarova, J. Podlaha, *Angew. Chem.* **1999**, *111*, 393–395; *Angew. Chem. Int. Ed.* **1999**, *38*, 381–383.

[9] Bipyrazolyls also meet important criteria for practical use: good chemical stability, high thermal stability, and melting points of 400 °C or higher. a) S. Trofimenko, *J. Org. Chem.* **1964**, *29*, 3046–3049; b) F. Ramirez, S. B. Bhatia, A. V. Patwardhan, C. P. Smith, *J. Org. Chem.* **1967**, *32*, 3547–3553.

[10] Crystallographic data for **1**–**3** and **5** were recorded at room temperature on an Enraf Nonius CAD4 diffractometer ($Cu_{K\alpha}$ radiation, $\lambda = 1.54178$ Å); the semi-empirical absorption correction was based on ψ-scans. The data for **4a**–**c** were collected at 223 K on a Siemens SMART CCD area-detector diffractometer ($Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å). The structures were solved by direct methods and refined by least-squares techniques in the anisotropic approximation by using SHELXS-86[11] and SHELXL-93.[12] The positions of the CH hydrogen atoms were idealized; NH hydrogen atoms were refined isotropically. In the structure of **5**, the OH hydrogen atoms were disordered and were not included. We were not successful in determining of the absolute structure. Crystal data are presented in Table 1. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-158862 (**1**), CCDC-156288–156292 (**2**–**4**), and CCDC-156294 (**5**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[11] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **1990**, *46*, 467–473.

[12] G. M. Sheldrick, SHELXL-93, Program for Crystal Structure Refinement from Diffraction Data, University of Göttingen, **1993**.

[13] Geometries of $4,4'\text{-}Me_4bpz$ conformers were completely optimized at the RHF/6-31G* level without any restrictions in symmetry and with fixed interplanar angle φ. The calculations were performed with the Gaussian 98 program package: Gaussian 98 (Revision A.3), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **1998**.

[14] Two-dimensional hexagonal nets by self assembly of 9,10-bis-resorcinol anthracene compounds: Y. Aoyama, K. Endo, T. Anzai, Y. Yamaguchi, T. Sawaki, K. Kobayashi, N. Kanehisa, Y. Kai, H. Masuda, *J. Am. Chem. Soc.* **1996**, *118*, 5562–5571; T. Sawaki, Y. Aoyama, *J. Am. Chem. Soc.* **1999**, *121*, 4793–4798.

[15] We have also detected the monoclinic form of **4c**, which is also chiral: space group $C2$, $a = 30.640(7)$, $b = 13.140(3)$, $c = 9.778(2)$ Å, $\beta = 100.34(1)°$.

[16] The possibility of varying the effective size of a tecton is important in the context of crystal engineering of porous solids and control over interpenetration: S. R. Batten, R. Robson, *Angew. Chem.* **1998**, *110*, 1558–1595; *Angew. Chem. Int. Ed.* **1998**, *37*, 1460–1494; R. Robson, *J. Chem. Soc. Dalton Trans.* **2000**, 3735–3744.

[17] "Conformational polymorphism": J. Bernstein in *Organic Solid State Chemistry* (Ed.: G. R. Desiraju), Elsevier, Amsterdam, **1987**, chap. 13; H. G. Brittain, *Polymorphism in Pharmaceutical Solids*, Marcel Dekker, New York, **1999**.

[18] Using metal ions of different charge will provide triangular, square-planar, or tetrahedral "polypyrazolyl tectons" (e.g., $Ga(acacpz)_3$, $Zr(acacpz)_4$). This approach can be easily extended to pyridine derivatives, as corresponding pyridyl-substituted β-diketones and β-dialdehydes are readily available: Z. Arnold, *Collect. Czech. Chem. Commun.* **1963**, *28*, 863–868; L. G. Mackay, H. L. Anderson, J. K. M. Sanders, *J. Chem. Soc. Chem. Commun.* **1992**, 43–44.

[19] Z. Arnold, *Collect. Czech. Chem. Commun.* **1962**, *27*, 2993–2995.

[20] W. L. Mosby, *J. Chem. Soc.* **1957**, 3997–4003.

[21] A. Nangia, G. R. Desiraju, *Chem. Commun.* **1999**, 605–606; V. S. S. Kumar, S. S. Kuduva, G. R. Desiraju, *J. Chem. Soc. Perkin Trans. 2* **1999**, 1069–1073.

[22] Unprecedented metal–organic network engineered with a bipyrazolyl tecton: I. Boldog, E. B. Rusanov, A. N. Chernega, J. Sieler, K. V. Domasevitch, *J. Chem. Soc. Dalton Trans.* **2001**, 893–897.