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Roof-Shaped Pyrazaboles as a Structural Motif for Bent-Core Liquid Crystals**

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Bent-core liquid crystals are currently the target of a great deal of research because of the novel molecular arrangements and phenomenology that result from their shape and polarity.[1–4] Indeed, achiral bent-core molecules may generate supramolecular organizations with ferroelectric, antiferroelectric, and/or nonlinear optical properties and superstructural chirality.[5] Moreover, the elusive biaxial nematic phase, a liquid-crystal phase that is highly desirable for its potential display applications, has been described recently and confirmed definitively for a bent-rod molecule derived from 2,5-oxadiazole.[6,7] These discoveries have fueled the development of new compounds and the study of their molecular self-organization. From the point of view of molecular design,[3] bent-core liquid crystals are formed from organic molecules by introducing an "in-plane" angle of between 104 and 135° between two rodlike moieties. For this purpose, an aromatic unit (for example, a *meta*-disubstituted benzene ring, a 2,7-disubstituted naphthalene system, a 2,6-disubstituted pyridine group, or a 1,3-disubstituted five-membered heterocycle) or a rigid or flexible spacer with an odd number of atoms (for example, a carbonyl, methylene, or propylenedioxy group) is commonly used to connect the two rodlike molecules.

Herein, we demonstrate an innovative approach to a bent angle in a liquid-crystal molecule through the use of a nonplanar core derived from a pyrazabole unit appropriately substituted with rodlike moieties. In this way, a "two-point bend" is introduced into the central part of the molecule to give a roof-shaped morphology. The design has the added novelty that the molecule is a coordination compound[8,9] and includes boron atoms. Boron is an unusual element in the field of liquid crystals, but offers interesting possibilities in terms of optical and electronic properties.[10]

Pyrazabole is the heterocycle that results from the dimerization of two pyrazole rings through a double BH_2 bridge connected to the nitrogen atoms,[11] a process that gives a stable six-membered central B_2N_4 ring with a boat conformation.[12,13] We explored the reactivity of the pyrazabole ring and found that 2,6-bis(ethynyl)pyrazabole (**1**), or the deuterated analogue 4,4,8,8-tetradeutero-2,6-bis(ethynyl)pyrazabole (**2**), can be converted into compounds **3** and **4** by a Sonogashira cross-coupling reaction with two equivalents of 4-iodophenyl 4-tetradecyloxybenzoate (Scheme 1) and thus show a similar reactivity to that of ethynylpyrazoles.[14]

We confirmed the bent geometry of these pyrazabole cores by solving the structure of the diacetylenic compound **2** by single-crystal X-ray diffraction.[15] Compound **2** adopts a bent shape as a result of the boat conformation of the central B_2N_4 ring. The bend angle between the mean planes of the two pyrazole (C_3N_2) rings is 134°. Molecules are stacked along the *a* axis. The planes parallel to *ab* are polar, as they are formed by stacks of molecules with the same boat geometry ("all up" or "all down"; Figure 1). Molecules in adjacent *ab* planes are arranged in an antiparallel fashion, which gives rise to a centrosymmetric structure.

Compounds **3** and **4** are liquid crystals with similar thermal behavior. Compound **3**, which is obtained as a crystalline solid at room temperature, forms a viscous phase with low birefringence and an uncharacterized texture denoted as B_x when it is heated for the first time at 99 °C. Further heating leads to a very fluid phase (between 121 and 145 °C), which displays threadlike textures and very intense Brownian motion corresponding to an apparently conventional nematic phase. Chiral monodomains of opposite handedness separated by walls were observed by decrossing the polarizers on the optical microscope (Figure 2). These domain textures are similar to those found for other nematic bent-rod compounds described previously.[16–19]

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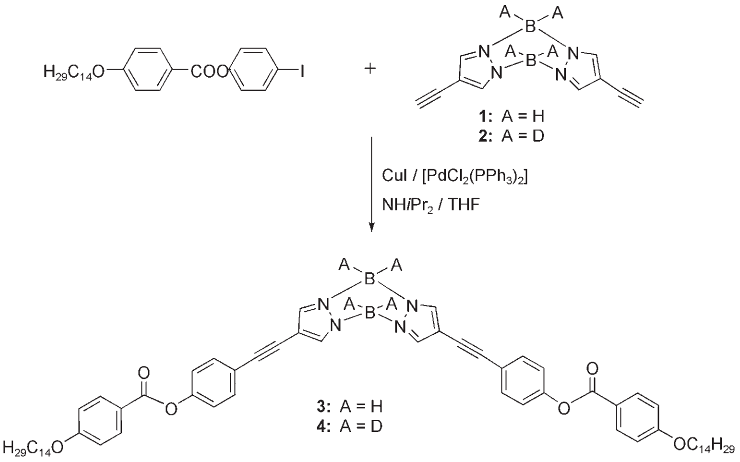
Supporting information for this article, including procedures for the Sonogashira cross-coupling reactions with the pyrazabole derivatives **1** and **2** (synthesis of compounds **3** and **4**) and full characterization data, is available on the WWW under http://www.angewandte.org or from the author.



Scheme 1. Synthetic pathway to the mesogenic pyrazaboles **3** and **4**.

Figure 1. Structure of an *ab* plane formed by stacks of the bent molecule **2**.

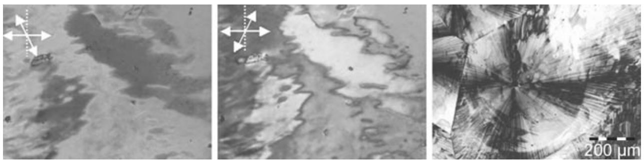


Figure 2. Microphotographs of the nematic phase observed by rotating one polarizer by 20° counterclockwise (left) or clockwise (middle) from the crossed polarizer position; right: microphotograph of the spherulitic texture of the B_x phase.

XRD studies of the mesophase confirmed the nematic nature of the high-temperature phase. Two diffuse reflections were observed in the diffractogram, one at small angles and the other at wide angles. Both reflections appear to be reinforced in some regions, which is an indication of a partial spontaneous orientation of the sample (Figure 3). In particular, the small-angle reflection is also split, and the resulting pattern resembles that described for a biaxial nematic phase of bent-core mesogens,[7,20] although it could also be compatible with the presence of smectic C clusters[18] (cybotactic domains) in an uniaxial nematic phase. The latter possibility appears reasonable, as the low-temperature phase has a lamellar character (see below).

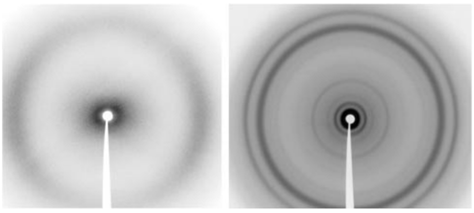


Figure 3. XRD patterns of compound **3**. Left: nematic phase at 124 °C; right: B_x phase at 111 °C.

The dielectric spectrum of the nematic phase is dominated by a relaxation process at 10^7 Hz as a result of reorientation about the molecular long axes (see graphical representation in the Supporting Information). This spectral feature is in accordance with a material with negative dielectric anisotropy. The reorientation frequency is similar to that of other bent-core mesogens[18] and lower than that observed for conventional rodlike nematics.

On cooling, the nematic phase transforms at 116 °C into a phase (B_x) with very low birefringence, which generally has a spherulitic texture with huge (of the order of hundreds of microns) extinction "Maltese crosses" (Figure 2). In the B_x phase the compound is completely transparent to the naked eye and does not change upon further cooling to room temperature. A purple-blue iridescence can also be detected, depending on the thermal history and the viewing angle. The XRD pattern of the low-temperature B_x phase appears to be similar to that described for the B_4 phase of some bent-core liquid crystals.[21] A series of regularly spaced sharp reflections (even sixth-order reflections are observed) in the small-angle region of the diffractogram indicate a very well defined lamellar organization (Figure 3). The B_4 phase has been postulated to be a nontilted lamellar crystal-like phase, as the measured layer spacing is similar to the molecular length. However, in our case, the measured layer spacing obtained by applying the Bragg law is 52.7 Å at 110 °C, and the estimated molecular length, which was calculated with molecular models on the basis of a molecular bend angle of 135°, is 71 Å. Therefore, the layer spacing of the B_x phase is much smaller than the estimated molecular length. The difference between the two values can be explained by interdigitation of the layers or by tilting of the molecules. In the second model, the molecules should be tilted by 41° in an alternating manner (anticlinic mode) to account for the layer spacing and the low birefringence observed. The formation of smectic C clusters in the nematic phase supports the tilted model: The B_x phase could be a tilted analogue of the B_4 phase, the structure of which has not been elucidated completely.[22]

CD spectra of thin films in the B_x phase showed no reflection band in the blue region. Therefore, the blue iridescence of the sample may be related to a light-dispersion phenomenon rather than to a helical structure with a pitch in the blue region. However, the observation of a CD signal in the wavelength region in which the compound exhibits an absorption band indicates a chiral organization of the chromophores (Figure 4). As the molecules are achiral, two possible chiral conglomerates of opposite handedness will exist with equal probability. However, given the intensity of the signal, a sizeable conglomerate is clearly formed. More-comprehensive studies are needed to understand the induced CD effect, as it is possible that extrinsic twisting of the nematic phase could favor the formation of one of the

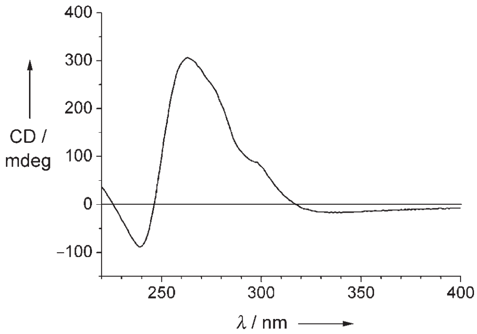


Figure 4. Averaged CD spectrum of the B_x phase.

possible chiral conglomerates preferentially, as reported recently by Choi et al.[23]

In conclusion, innovative bent-core liquid crystals have been obtained from roof-shaped pyrazabole derivatives. Their unusual behavior accounts for a variety of interesting phenomena. In particular, the direct transition from a fluid nematic mesophase, the orientation of which is easy to influence, to a well-structured lamellar phase with a chiral organization is of significance in terms of the macroscopic properties of the liquid crystals.

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[1] M. B. Ros, J. L. Serrano, M. R. de la Fuente, C. L. Folcia, *J. Mater. Chem.* **2005**, *15*, 5093.
[2] H. Takezoe, Y. Takanishi, *Jpn. J. Appl. Phys. Part 1* **2006**, *45*, 597.
[3] R. A. Reddy, C. Tschierske, *J. Mater. Chem.* **2006**, *16*, 907.
[4] G. Pelzl, S. Diele, W. Weissflog, *Adv. Mater.* **1999**, *11*, 707.
[5] D. M. Walba, E. Körblova, R. Shao, J. E. Maclennan, D. R. Link, M. A. Glaser, N. A. Clark, *Science* **2000**, *288*, 2181.
[6] L. A. Madsen, T. J. Dingemans, M. Nakata, E. T. Samulski, *Phys. Rev. Lett.* **2004**, *92*, 145505.
[7] B. R. Acharya, A. Primak, S. Kumar, *Phys. Rev. Lett.* **2004**, *92*, 145506.
[8] J. L. Serrano, *Metallomesogens: Synthesis, Properties, and Applications*, VCH, Weinheim, **1996**.
[9] B. Donnio, D. Guillon, R. Deschenaux, D. W. Bruce in *Comprehensive Coordination Chemistry II*, *Vol. 7* (Eds.: J. A. Mc Cleverty, J. J. Meyer), Elsevier, Oxford, **2003**, p. 357.
[10] K. Ma, M. Scheibitz, S. Scholz, M. Wagner, *J. Organomet. Chem.* **2002**, *652*, 11.
[11] S. Trofimenko, *J. Am. Chem. Soc.* **1966**, *88*, 1842.
[12] E. Hanecker, T. G. Hodgkins, K. Niedenzu, H. Nöth, *Inorg. Chem.* **1985**, *24*, 459.
[13] J. Barberá, R. Giménez, J. L. Serrano, *Chem. Mater.* **2000**, *12*, 481.
[14] S. F. Vasilevsky, E. V. Tretyakov, J. Elguero, *Adv. Heterocycl. Chem.* **2002**, *82*, 1.
[15] Single-crystal X-ray diffraction data were measured on a Xcalibur S diffractometer from Oxford Diffraction Ltd. with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Crystal data for **2**: $C_{10}H_6D_4B_2N_4$, $M_r = 211.86$, monoclinic, $a = 4.2181(12)$, $b = 15.840(7)$, $c = 8.388(4)$ Å, $\beta = 92.17(3)°$, $V = 560.1(4)$ Å^3, $T = 293(2)$ K, space group $P2(1)/m$, $Z = 2$, $\mu(Mo_{K\alpha}) = 0.076\ mm^{-1}$, 7134 reflections measured, 1178 unique ($R_{int} = 0.0388$), all of which were used in the calculations. Final R indices: $R(F) = 0.0369$ (755 reflections with $F^2 \geq 2\sigma(F^2)$), $wR(F^2) = 0.0846$ (all data). CCDC-637338 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
[16] G. Pelzl, A. Eremin, S. Diele, H. Kresse, W. Weissflog, *J. Mater. Chem.* **2002**, *12*, 2591.
[17] M. W. Schröder, S. Diele, G. Pelzl, U. Dunemann, H. Kresse, W. Weissflog, *J. Mater. Chem.* **2003**, *13*, 1877.
[18] W. Weissflog, S. Sokolowski, H. Dehne, B. Das, S. Grande, M. W. Schröder, A. Eremin, S. Diele, G. Pelzl, H. Kresse, *Liq. Cryst.* **2004**, *31*, 923.
[19] V. Görtz, J. W. Goodby, *Chem. Commun.* **2005**, 3262.
[20] V. Prasad, S.-W. Kang, K. A. Suresh, L. Joshi, Q. Wang, S. Kumar, *J. Am. Chem. Soc.* **2005**, *127*, 17224.
[21] J. Thisayukta, H. Takezoe, J. Watanabe, *Jpn. J. Appl. Phys. Part 1* **2001**, *40*, 3277.
[22] D. M. Walba, L. Eshdat, E. Körblova, R. K. Shoemaker, *Cryst. Growth Des.* **2005**, *5*, 2091.
[23] S.-W. Choi, S. Kang, Y. Takanishi, K. Ishikawa, J. Watanabe, H. Takezoe, *Angew. Chem.* **2006**, *118*, 6653; *Angew. Chem. Int. Ed.* **2006**, *45*, 6503.