Pergamon

Tetrahedron Letters, Vol. 38, No. 35, pp. 6281-6284, 1997
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0040-4039/97 $17.00 + 0.00

PII: S0040-4039(97)01408-1

Crystal Engineering Based on Nitro Derivatives of 10-Hydroxy-10,9-borazarophenanthrene

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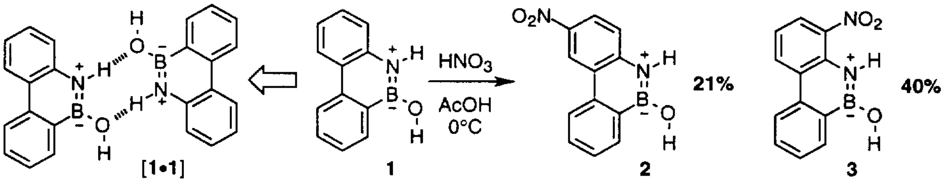
Abstract: The steric and molecular recognition properties of the nitro group control the molecular packing of 10-hydroxy-10,9-borazarophenanthrene derivatives facilitating the formation of stepped hydrogen bonded molecular tapes of 8-nitro-10-hydroxy-10,9-borazarophenanthrene and cyclic homodimers of 6-nitro-10-hydroxy-10,9-borazarophenanthrene. © 1997 Elsevier Science Ltd.

The design of specific molecular packing arrangements – so called crystal engineering[1] – is heavily dependent on a thorough understanding of intermolecular interactions. In many cases, this exploits the controlled aggregation of molecules using conventional hydrogen bonding motifs.[2] Recently, we reported[3] a new self-complementary hydrogen bonding motif (Scheme 1), based on a borazaroaromatic compound, namely 10-hydroxy-10,9-borazarophenanthrene **1**. The crystal structure of **1** demonstrates its capacity to form cyclic hydrogen-bonded homodimers [**1•1**] (Scheme 1) which are structurally similar to those formed by carboxylic acids and 2-pyridones. Here, we report the opportunity to control the crystal packing and molecular recognition patterns observed in this system simply by the addition of a single functional group which can influence the system through specific molecular recognition and/or steric effects.



Scheme 1

The nitro group was chosen for these studies on the basis of the following design criteria: it can be introduced into the borazaroaromatic skeleton readily – **1** undergoes electrophilic substitution at the 6- and 8-positions (Scheme 1), it is strongly electron withdrawing and it can participate in hydrogen bonds under appropriate conditions. In principle, the 6-substituted compound **2** could, in the solid state, form cyclic homodimers – denoted [**2•2**] – which are analogous to [**1•1**]. However, we would not expect the 8-substituted compound **3** to form cyclic homodimers analogous to [**1•1**] as a consequence of the steric congestion introduced by the presence of the nitro group directly adjacent to the heteroaromatic ring. The expectation that **2** should form the self-complementary [**2•2**] homodimer and the steric effect of the nitro group inhibiting the formation of the self-complementary [**3•3**] homodimer are further supported by semiempirical SCF-MO calculations. AM1 calculations demonstrate that in the case of **2**, there is no significant perturbation of the cyclic homodimer structure [**2•2**] in comparison with the parent structure [**1•1**]. However, in the case of the cyclic homodimer [3•3] there is significant lengthening of the N–H···O hydrogen bonds and the two molecules of 3 are no longer coplanar. In order to test these hypotheses, 6-nitro-10-hydroxy-10,9-borazarophenanthrene 2 and 8-nitro-10-hydroxy-10,9-borazaro phenanthrene 3 were prepared[4] by nitration of 1.

The crystal structure[5] of 2 (Figure 1) contains cyclic [2•2] homodimers of the type shown in Scheme 1 (N···O distance 3.062(3) Å, N–H···O angle[6] 170.2°). These dimers are linked by additional NO···H–O interactions (O···O distance 2.810(3) Å, O–H···O angle 148.8°) between the nitro group in the 6-position and the free hydroxyl proton of a molecule in an adjacent homodimer. This interaction creates infinite chains of hydrogen-bonded self-complementary homodimers, the principal axes of which lie in the crystallographic *ac* plane. Within these tapes, adjacent dimers are inclined at approximately 45° with respect to each other and are arranged in π-stacked columns (mean plane separation 3.40 Å).

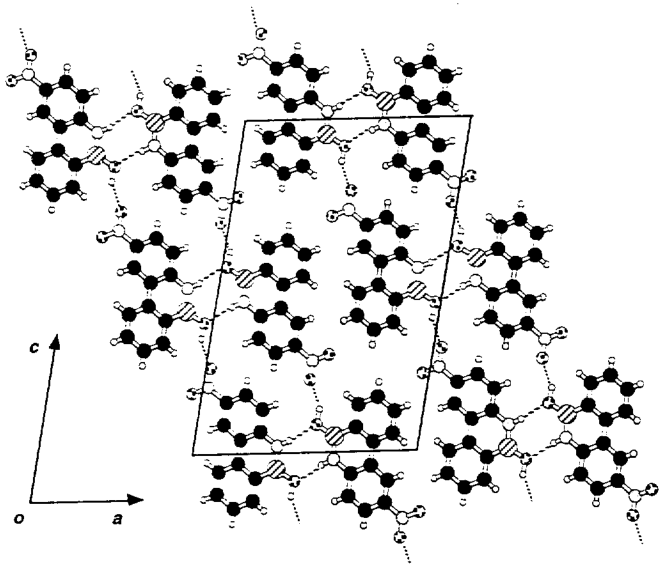


Figure 1 Ball and stick representation of the crystal structure of 2 viewed along the crystallographic *b* axis. Hydrogen bonds between molecules of 2 are shown as dashed lines. The projection of the unit cell is represented by the solid lines.

In complete contrast, the crystal structure[7] of 3 (Figure 2) has infinite hydrogen-bonded molecular tapes, the principal axes of which lie in the crystallographic *bc* plane. These tapes are related by translation in the *bc* plane and are stacked along the *a* axis. Within each molecule of 3 in this structure, the N–H group forms an intramolecular hydrogen bond to the adjacent nitro group. In order to facilitate hydrogen bonding between the molecules of 3 within the tape, the O–H bond is oriented *syn* with respect to the N–H bond – this is the higher energy conformation for the isolated molecule. This hydroxyl proton forms a short hydrogen bond to one of the oxygens of the nitro group in the adjacent molecule of 3 in the tape (O···O distance 2.922(3) Å, O···H–O angle 154.8°). In addition, the hydroxyl proton makes a second, longer contact (O···O distance 3.326(3) Å, O···H–O angle 149.6°) to the other oxygen of the same nitro group. The nitro oxygen to hydroxyl oxygen (O···O) distances observed in this structure are similar to the O···O distances found[8] in crystal structures containing short NO_2···H–O contacts. The component molecules of each tape do not lie in the same plane, but exist in a stepped array (Figure 2b) which involves the slight torsion (dihedral angle 9°) of the O–H bond away from coplanarity with the rest of the borazarophenanthrene skeleton.

(a)

(b)

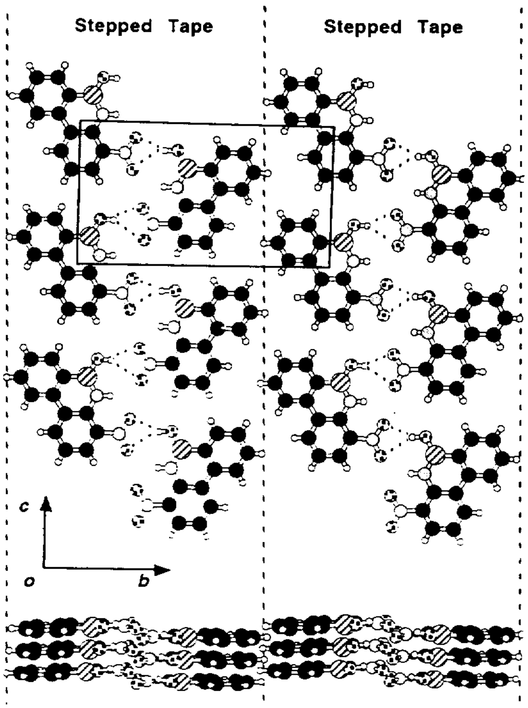


Figure 2 (a) Ball and stick representation of the crystal structure of 3 viewed along the crystallographic *a* axis. Hydrogen bonds between molecules of 3 are shown as dashed lines (b) Ball and stick representation of the crystal structure of 3 viewed approximately parallel to the crystallographic *c* axis illustrating the stepped nature of the continuous hydrogen-bonded molecular tapes. The projection of the unit cell is represented by the solid lines.

It was our expectation that the electronic effect of the nitro substituent of **2** would influence the geometry of the hydrogen bonding in the cyclic homodimer. However, the hydrogen bond distances and angles in the homodimers [**1•1**] and [**2•2**] are, in fact, very similar (N···O distances 3.050(3) Å and 3.062(3) Å; N–H···O angles 176.3° and 170.2°, respectively). It is thought[9] that electrostatic interactions provide a significant contribution to the binding energy and geometry of hydrogen bonds. A comparison of the calculated electrostatic potential surfaces (HF/6-31G(d.p)) of **1**, **2** and **3** shows that although there is an increase in the electrostatic potential around both the nitrogen atom and the hydrogen atom of the N–H group (*i.e.* the molecular surface in this locale is more positive), there is also an increase in the value associated with the oxygen atom (*i.e.* the molecular surface is less negative). These calculations suggest that, at a qualitative level, the changes in the electrostatic potential surface of **2**, as compared to **1**, should have little overall effect on the structure of the homodimer.

The different solid state structures of **2** and **3** demonstrate conclusively that (a) the self-complementary recognition motif in hydroxyborazarophenanthrenes – displayed by **1** and **2** – is a viable design element for crystal engineering and (b) the behaviour of this recognition motif can be controlled simply by the appropriate positioning of a single substituent on the borazaroaromatic skeleton.

This research was supported by the University of Birmingham and the Engineering and Physical Sciences Research Council (Quota award to JMAR). Ciba Speciality Chemicals Ltd are thanked for financial support. We thank Mr P. R. Ashton for the mass spectroscopic analyses.

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4. M.J.S. Dewar, V.P. Kubba, *Tetrahedron*, 1959, 7, 213. *Selected spectroscopic data* for **2**: ^{1}H NMR (300 MHz, CD_3COCD_3) 9.21-9.20 (1H, m), 8.57-8.51 (2H, m), 8.30-8.27 (1H, m), 8.23-8.20 (1H, m), 7.84-7.78 (2H, m), 7.60-7.55 (1H, m), 7.51-7.48 (1H, m); ^{13}C NMR (67.5 MHz CD_3COCD_3) 147.9, 140.2, 133.2, 132.3, 128.2, 124.0, 123.6, 122.4, 121.0, 119.8; *m/z* (LSIMS) 240 for $[M^+]$. *Selected spectroscopic data* for **3**: ^{1}H NMR (300 MHz, CD_3COCD_3) 9.90 (1H, s), 8.84-8.81 (1H, m), 8.52-8.49 (1H, m), 8.38-8.35 (1H, m), 8.27-8.24 (1H, m), 8.03 (1H, s), 7.80-7.74 (1H, m), 7.60-7.55 (1H, m), 7.30-7.24 (1H, m); ^{13}C NMR (75 MHz, CD_3COCD_3) 139.8, 138.8, 136.7, 132.8, 132.1, 131.9, 127.9, 126.3, 125.9, 123.5, 119.2; *m/z* (LSIMS) 240 for $[M^+]$.
5. Single crystals of **2** were grown by vapour diffusion of hexane into a solution of **2** in acetone. *Crystal Data* for **2** at 296(2) K: $[C_{12}H_9BN_2O_3]$, M = 240.02 g mol^{-1}, monoclinic space group $P2_1/n$, $a = 13.8520(12)$ Å, $b = 3.7842(4)$ Å, $c = 20.7706(14)$ Å, $\beta = 103.914(2)°$, $V = 1056.8(2)$ Å^3, $Z = 4$, $D_c = 1.509$ g cm^{-3}, $\lambda = 0.71069$ Å, F(000) = 496. A yellow needle-like crystal of dimensions 0.40 mm × 0.03 mm × 0.01 mm was used. Data were measured on a Rigaku R-AXIS II rotating anode diffractometer using graphite-monochromated Mo-Kα radiation and 1721 independent reflections were measured ($3.22° \le 2\theta \le 50.42°$). The structure was solved by direct methods and non-hydrogen atom positions were refined anisotropically by full-matrix least squares to give $R = 0.0704$, $R_w = 0.1588$.
6. The normalisation of X-ray hydrogen bond geometries determined from X-ray diffraction data usually relies on the use of a standard value for the Donor–H distance as derived from neutron diffraction data. As a result of the absence of accurate experimental information on structures related to **1**, **2** and **3** we have used N-H and O-H bond lengths taken from our *ab initio* (HF/6-31G(d,p)) calculations.
7. Single crystals of **3** were grown by vapour diffusion of water into a solution of **3** in acetone. *Crystal Data* for **3** at 296(2) K: $[C_{12}H_9BN_2O_3]$, M = 240.02 g mol^{-1}, monoclinic space group $P2_1/c$, $a = 6.875(2)$ Å, $b = 16.545(3)$ Å, $c = 9.5819(11)$ Å, $\beta = 101.27(2)°$, $V = 1068.9(3)$ Å^3, $Z = 4$, $D_c = 1.491$ g cm^{-3}, $\lambda = 0.71069$ Å, F(000) = 496. An orange needle-like crystal of dimensions 0.50 mm × 0.03 mm × 0.01 mm was used. Data collection and structure solution were carried out as described for **2**: 1598 independent reflections were measured ($4.92° \le 2\theta \le 50.36°$) to give $R = 0.0596$, $R_w = 0.1261$.
8. A search of the Cambridge Structural Database reveals that in structures containing short $NO_2 \cdots H–O$ contacts ($O \cdots H \le 2.8$ Å) the mean O···H distance is 2.34 Å and the mean O···H–O angle is 160°. In these structures, the proton is usually much closer to one of the oxygen atoms of the nitro group than the other – in 4-nitrophenol, for example, the two O···H distances are 1.84 Å and 2.55 Å.
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(Received in UK 16 *June* 1997; *accepted* 11 *July* 1997)