Self-Recognition in the Crystal Chemistry of *N*,*N*′-Bis(3-hydroxyphenyl)isophthalamide

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The synthesis, characterization, and crystal chemistry of *N*,*N*′-bis(3-hydroxyphenyl)-isophthalamide is described. Through a combination of single-crystal X-ray diffraction, molecular orbital, and crystal packing calculations, the important intermolecular interactions have been determined. The structure contains examples of the more important nonbonded contacts including O−H···O hydrogen bonding, C−H···O special hydrogen bonds, $\pi-\pi$ stacking, N−H···π and aromatic edge-to-face interactions. The two pendent amidophenolic units of the molecule adopt different conformations, one *syn* and one *anti*. In the solid state these conformations exclusively recognize each other forming *syn*−*syn* and *anti*−*anti* hydrogen-bonded pairings. There are no examples of *syn*−*anti* hydrogen-bonding pairs. The structure consists of columns that are made up of *anti*−*anti* hydrogen-bonded pairs held together by $\pi-\pi$ stacking interactions. These columns are linked by the *syn*−*syn* hydrogen-bonding pairs. Lattice energy calculations suggest that the *anti*−*anti*, *syn*−*syn*, and $\pi-\pi$ interactions are equally important in the formation of the solid-state structure.

Introduction

An organic crystal is an example of a near-perfect supramolecular assembly. The result of a crystallization process is the gathering together of millions of molecules into a unique ordered arrangement. This gathering is repeatable under the same crystallization conditions. The solid-state arrangements, adopted by organic materials, are the result of an "intermolecular synthesis"[1] which is due to the interactions between atoms which constitute the molecular framework. Solid-state structures are essentially the consequence of molecular recognition on a grand scale.[1−6] Polymorphism, the adoption of different solid-state arrangements by the same molecular system, is due to the recognition of a slightly different subtle balance of these interactions.

The design of synthetic receptors, within preorganized assemblies, is a fast-growing area of supramolecular chemistry, the aim being to use intermolecular forces to encapsulate small organic guest molecules to function as sensors or in catalysis performing specific chemical reactions.[7,8] Structures similar to that reported here have been shown to act as models for the active site of ribonuclease A.[9]

Crucial to the design of supramolecular assemblies using specific intermolecular interactions is the understanding of the relative importance of different interaction types. Topological analysis has been used to describe different classical hydrogen-bonding patterns found in molecular materials.[3] More recently, work has focused on the role of weaker intermolecular interactions in solid-state structures formed by single molecules[10] and cocrystals.[11]

In this paper we report the synthesis, characterization, and crystal chemistry of *N*,*N*′-bis(3-hydroxyphenyl)isophthalamide (**1**, Figure 1). Through a combination of single-crystal X-ray diffraction, molecular orbital and crystal packing calculations the important intermolecular interactions have been determined. This structure contains fragments which can constitute a number of the more important nonbonded contacts. These include hydrogen bonding, special C−H···O hydrogen bonds, $\pi-\pi$ stacking, and aromatic edge-to-face interactions. Understanding the relative importance of these interaction types forms the basis for an ongoing study of host−guest interactions in the solid state. This uses **1** and related molecules as "host" structures to encapsulate smaller organic systems, such as urea and barbital, as "guests"[12] in a manner similar to that described earlier in this journal.[6] The process involves the design of host structures with the ideal spatial and bonding complementarity to bind the guest structures with multiple hydrogen-bonding sites to maximize the

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(1) Desiraju, G. R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2311.
(2) Dunitz, J. D. *Pure Appl. Chem.* **1991**, *63*, 177.
(3) Etter, M. C. *J. Phys. Chem.* **1991**, *95*, 4601.
(4) Aakeröy, C. B.; Seddon, K. R. *Chem. Soc. Rev.* **1993**, *22*, 397.
(5) MacDonald, J. C.; Whitesides, G. M. *Chem. Rev.* **1994**, *94*, 2383.
(6) Fan, E.; Vicent, C.; Geib, S. J.; Hamilton, A. D. *Chem. Mater.* **1994**, *6*, 1113.
(7) Webb, T. H.; Wilcox, C. S. *Chem. Soc. Rev.* **1993**, 383.
(8) Lehn, J. M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1304.
(9) Kato, T.; Takeuchi, T.; Karube, I. *J. Chem. Soc. Chem. Commun.* **1996**, 953.
(10) Desiraju, G. R. *Acc. Chem. Res.*, **1991**, *24*, 290.
(11) Pedireddi, V. R.; Jones, W.; Chorlton, A. P.; Docherty, R. *J. Chem. Soc., Chem. Commun.* **1996**, 987. Pedireddi, V. R.; Jones, W. ; Chorlton, A. P.; Docherty, R. *J. Chem. Soc., Chem. Commun.* **1996**, 997.
(12) Murray, C. M. Ph.D. Thesis, The Queen's University of Belfast, 1997.

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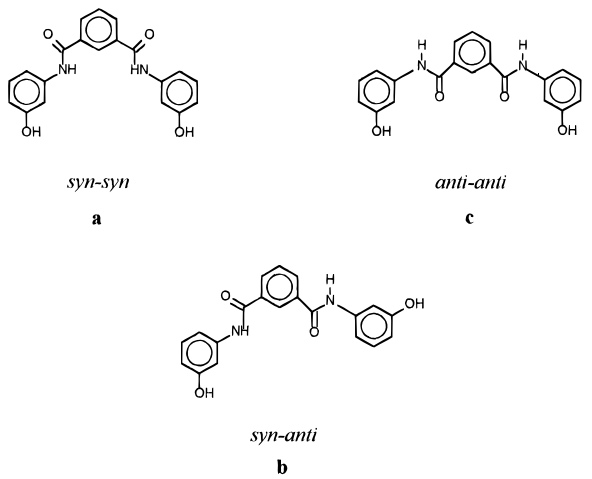

Figure 1. Possible conformations for **1**. The crystal structure has conformation **b**.

interaction between the host and the guest. The host structure **1** demonstrates a preference for self-recognition potentially precluding the inclusion of guests.

Experimental Section

General Methods of Preparation. The product **1** was formed as the result of the condensation reaction between isophthaloyl chloride and 3-aminophenol in 93.9% yield. Isophthaloyl dichloride (3.995 g, 0.02 mol) was dissolved in acetonitrile (50 mL) and this was added to an excess of 3-aminophenol (4.609 g, 0.042 mol) also dissolved in acetonitrile. Although the product started to precipitate out almost immediately the mixture was refluxed at 70−80 °C for 1.5 h to ensure the reaction was complete. The precipitate was then filtered with suction and dried. An attempt was made to crystallize from ethanol, but this yielded a microcrystalline product. Subsequent vapor diffusion, using ethanol and hexane, within a sealed environment for 6 weeks yielded light-brown single crystals.

Found: C, 68.23; H, 4.33; N, 8.01. $C_{20}H_{16}N_2O_4$ requires C, 68.95; H, 4.63; N, 8.04%. δ_c (250 MHz, $(CD_3)_2SO$) 108.52, 111.97, 112.16, 127.95, 129.53, 130.26, 131.60, 136.22, 141.10, 158.54, 166.02; δ_H (400 MHz, $(CD_3)_2SO$) 6.5−8.5 (12 H, M, Ar), 9.5 (2 H, broad NH), and 10.35 (2H, s, OH); m/z = 348 (EI).

Crystal Structure Determination. *Data Collection and Processing.* The crystal selected for analysis was 0.68 × 0.27 × 0.18 mm in size. Data were collected on a Siemens P4 four circle diffractometer with Mo Kα (graphite monochromated λ = 0.7107 Å) radiation at 120 K. Crystal stability was checked every 100 reflections and showed no significant variation (±1%). Cell parameters were determined from 35 accurately centered reflections in the 2θ range 10−28°, and 4092 observations were collected over the range $4 \leqslant 2\theta \leqslant 50°$ for $0 \leqslant h \leqslant 5$, $-15 \leqslant k \leqslant 15$, and $-20 \leqslant l \leqslant 20$. Lorentz and polarization corrections were applied. 3581 independent reflections were used in the refinement. Crystal data are listed in Table 1.

Structure Solution and Refinement. The structure was solved by direct methods, and non-hydrogen atoms were refined with allowance for anisotropic vibrations. All hydrogen atom positions were initially located from a difference Fourier map but were included in the refinement using the riding model with temperature factors, B_{iso}, fixed at 1.2 U_{ij}(eq) for the attached atom. The XSCANS,[13] SHELXTL PC,[14] and SHELXL-93[15] software packages were used for data collection, reduction and structure solution and refinement. The final R factor was $R_1 = 0.060$ for 2427 data with $F > 4\sigma|F_o|$.

(13) XSCANS, Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1994.
(14) Sheldrick, G. M. SHELXTL PC, Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1990.
(15) Sheldrick, G. M. SHELXL-93, University of Göttingen, 1993.

Table 1. Crystallographic Data for 1

formula	$C_{20}H_{16}N_2O_4$
M	348.35
temp (K)	123
crystal size (mm)	0.68 × 0.27 × 0.18
crystal system	triclinic
space group	$P\bar{1}$
Z	2
a, Å	3.993(1)
b, Å	12.368(3)
c, Å	16.049(4)
α, deg	82.56
β, deg	86.82
γ, deg	86.96
U, Å^3	783.9(3)
range h	0 → 5
range k	−15 → 15
range l	−20 → 20
D_c, g cm^{-3}	1.476
F (000)	364
μ (Mo Kα)	0.104
ω scans: 2θ range	4.5−55
independent reflections	3581
parameters refined	235
residual density e/Å^3	0.317, −0.365
S	1.063
$wR2$ (all data)	0.2014
$R1$ (2427 data, $F > 4\sigma(F_o)$)	0.0597

Table 2. Atomic Fractional Coordinates and Esd's [×10^4] for 1

atom	x	y	z
C(1)	−2143(8)	3289(2)	9976(2)
C(2)	−2311(8)	2555(2)	10708(2)
C(3)	−621(8)	1534(2)	10746(2)
C(4)	1232(8)	1251(2)	10048(2)
C(5)	1370(8)	1961(2)	9307(2)
C(6)	−328(8)	2978(2)	9276(2)
C(7)	−1142(8)	4691(2)	8258(2)
C(8)	−74(8)	5161(2)	7380(2)
C(9)	790(8)	4523(2)	6741(2)
C(10)	1883(8)	5001(2)	5952(2)
C(11)	2100(8)	6125(2)	5787(2)
C(12)	1264(7)	6771(2)	6429(2)
C(13)	142(7)	6290(2)	7217(2)
C(14)	1620(8)	7987(2)	6223(2)
C(15)	2776(8)	10398(2)	6181(2)
C(16)	3596(8)	11472(2)	6242(2)
C(17)	5357(8)	11717(2)	6907(2)
C(18)	6315(8)	10890(3)	7527(2)
C(19)	5486(7)	9823(2)	7494(2)
C(20)	3724(7)	9579(2)	6815(2)
N(1)	22(7)	3648(2)	8490(2)
N(2)	2931(6)	8472(2)	6829(2)
O(1)	−4111(6)	2794(2)	11416(1)
O(2)	−2934(6)	5205(2)	8733(1)
O(3)	851(6)	8466(2)	5535(1)
O(4)	2633(6)	12314(2)	5654(1)

Results and Discussion

Molecular Structures. The crystal structure of **1** was solved using direct methods as described in the Experimental Section. The basic crystallographic data are summarized in Table 1, and atomic coordinates are given in Table 2. The molecular conformation is shown in Figure 2. The atoms of each amidophenolic moiety are coplanar, but each of the planes is twisted relative to the central aromatic ring. Figure 2 also shows the differences in the conformation of the two pendent amidophenolic groups with C13−C8−C7−N1 *anti* and C13−C12−C14−N2 *syn*. The twists between the central benzene ring and the respective carbonyls are 26° (*anti*) and 39° (*syn*).

Calculations were performed to investigate the conformational preference of the molecular structure. Us-

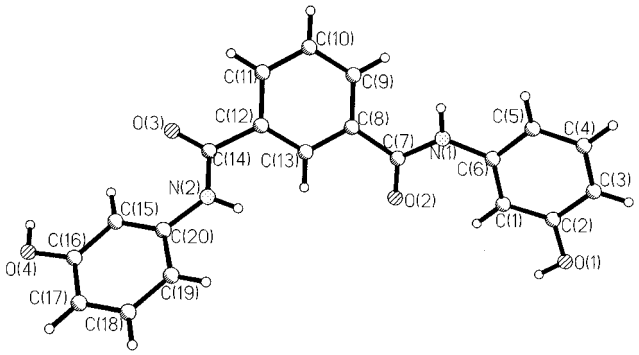

Figure 2. Labeled view of molecule **1**.

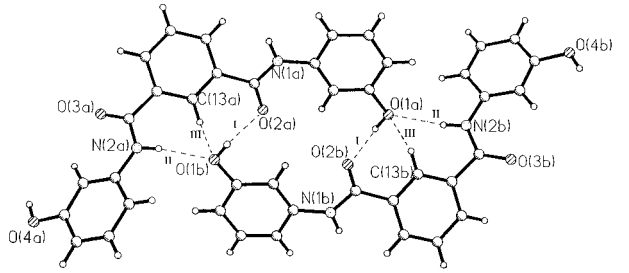

Figure 3. View of the *anti*−*anti* interactions, with the hydrogen bonds O−H···O (I), N−H···O (II), and C−H···O close contact (III). This is essentially a view down the *a*-axis, i.e., down a column.

Table 3. Calculated Heats of Formation of Conformations 1a−c (As Shown in Figure 1)

motif		$-H_f$, kcal/mol
syn−syn	**1a**	−69.96
syn−anti	**1b**	−72.25
anti−anti	**1c**	−67.13

ing MOPAC (v. 6.0)[16] the structures of the *syn*−*syn*, *syn*−*anti*, *anti*−*anti* conformations (Figure 1a−c) were optimized at the AM1 level.[17] The default minimization criteria were employed along with the MMOK keyword, which applies the molecular mechanics correction needed to reproduce the structural features of the amide linkage. The heats of formation for the various conformers are given in Table 3.

The calculated preference for the *syn*−*anti* conformation (by about 2.3 kcal/mol) agrees with that observed in the crystal structure. This is probably due to the repulsions experienced in the *syn*−*syn* conformer between the two amide hydrogens and by the two carbonyls in the *anti*−*anti* arrangement. In the calculated *syn*−*anti* conformation the twist angles between the carbonyls and the central benzene ring are 40°.

Crystal Packing and Interatomic Contacts. Each molecule is involved in two centrosymmetric hydrogen-bonded pairings formed between carbonyl and phenolic O−H groups. The first is formed between two units in the *anti* conformation with an O−H···O distance of 1.793 Å (I in Figure 3). The second, formed by O−H···O interactions at 1.786 Å (IV in Figure 4), takes place between two *syn* units. Detailed descriptions of these hydrogen-bond geometries are given in Table 4. In addition the *anti*−*anti* pair is supplemented by further

(16) MOPAC (v. 6.0), Quantum Chemistry Program Exchange Program No. 455. Creative Arts Building 181, Indiana University, Bloomington, IN 47405

(17) Dewar, M. J. S.; Zoebisch, E. G.; Healy E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

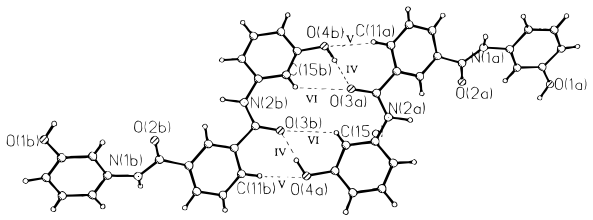

Figure 4. View of the *syn*−*syn* interactions.

Table 4. Geometric Details of the Hydrogen Bonds in 1

atoms involved	motif	distance/Å: donor··· acceptor	distance/Å: hydrogen··· acceptor	donor−H··· acceptor angle, deg
O1−H···O2[a]	anti−anti (I)	2.67	1.793	161.4
O4−H···O3[b]	syn−syn (IV)	2.72	1.786	175.1
N2−H···O1[c]	anti−anti (II)	3.09	2.22	170.2

[a] $-1-x, 1-y, 2-z$. [b] $-x, 2-y, 1-z$. [c] $-x, 1-y, 2-z$.

Table 5. Geometric Details of the Close Contacts in 1

atoms involved	motif	distance/Å: donor··· acceptor	distance/Å: hydrogen··· acceptor	donor−H··· acceptor angle, deg
C13−H13···O1[c]	anti−anti (III)	3.14	2.57	118.2
C11−H11···O4[d]	syn−syn (V)	3.50	2.67	145.7
C15−H15···O3[b]	syn−syn (VI)	3.30	2.61	129.8

[b] $-x, 2-y, 1-z$. [c] $-x, 1-y, 2-z$. [d] $1-x, 2-y, 1-z$.

N−H···O interactions at 2.22 Å (II, Figure 3) provided by the molecules above and below the hydrogen bonded pair and weaker C−H···O interactions at 2.57 Å (III, Figure 3). The *syn*−*syn* pair also has supporting weak C−H···O interactions at 2.67 Å (V) and at 2.61 Å (VI). These are shown in Figure 4 and geometric details are described in Table 5. It is interesting to note that there are no *syn*−*anti* hydrogen-bonding pairs in the structure. These geometries are combined in Figure 5 which is a view down the *a*-axis.

The *anti*−*anti* hydrogen-bonded pair together with the N−H···O interactions and $\pi-\pi$ stacking combine to produce columns running along the *a*-axis. A view down the column is given in Figure 5 with the hydrogen bonding and close contact interactions highlighted. A side-on view of the column is shown in Figure 6 with the *anti*−*anti* hydrogen bonds perpendicular to the page. The $\pi-\pi$ and N−H···O interactions run up the center and the sides of the column, respectively. The columns are linked to each other through the *syn*−*syn* hydrogen-bonding motif along the *bc*-diagonal. These assemblies of columns are held together through weaker intermolecular bonds such as edge to face aromatic and N−H···π interactions.

The $\pi-\pi$ interaction takes place in the direction of the *a*-axis. The molecules do not sit directly above each other but are slightly offset to maximize electrostatic interactions between the amide linkages. The difference in the *syn* and the *anti* arrangement means that this offset is not uniform and varies across the molecule. The distance between the planes of each of the aromatic rings, along the *a*-axis, varies from 3.8 Å (central benzene) to 3.4 Å (phenolic ring C1−C6) and 3.3 Å (phenolic ring C15−C20). The larger than expected value for the central benzene rings appears to be a consquence of the N−H···O hydrogen-bonding arrangements. There is a C−H···π interaction between H18 and the ring (C15−C20) below at a separation of about 3.2 Å. This interaction is repeated between H15 and

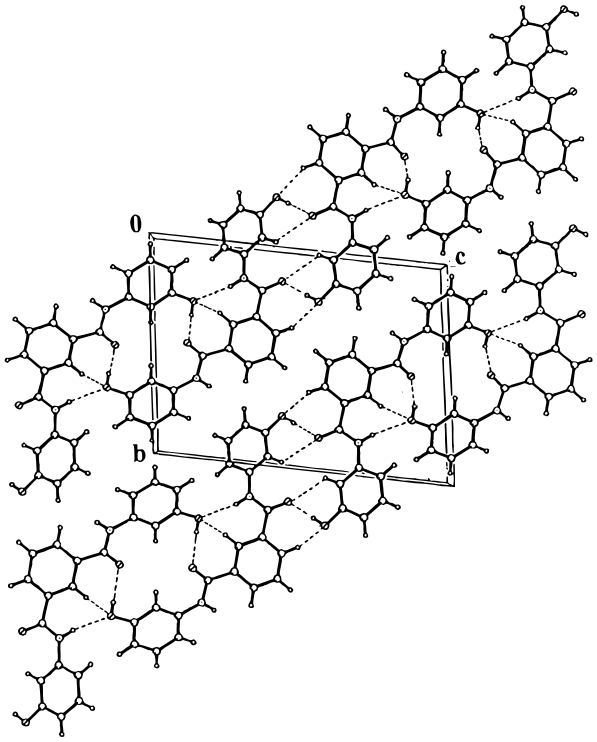

Figure 5. View down the *a*-axis, showing *anti*−*anti* interactions within a column and the *syn*−*syn* interactions between columns.

the center of the ring above. No such interaction is observed for the other phenolic unit (C1−C6).

It is perhaps surprising that the NH group in the *anti* arrangement does not take part in hydrogen bonding or indeed have any particular close contacts associated with it. In accordance with Etter's rules[3] the strongest hydrogen-bonding pairs have been matched in this structure. As a consequence of the packing and conformation adopted by this structure only one of the N−H groups is utilized in the hydrogen-bonding patterns. In the absence of any potential hydrogen-bonding partners the *anti* N−H group contents itself with the formation of an N−H···π interaction. This is in agreement with the observations on the structural consequences of assemblies that are deficient in hydrogen-bonding acceptors.[18]

Lattice Energy Calculations and Intermolecular Interactions. To quantify the contributions of the main interactions, the programs HABIT and HABIT 95[19] were used. The lattice energy was calculated using a force-field including hydrogen-bonding potentials,[20] the charges from MOPAC/AM1[16,17] and a summation limit of 50 Å. A description of the methods for calculating the lattice energies of molecular materials, and their validation has been described elsewhere.[21,22] The lattice energy was found to be −51.3 kcal/mol. The contributions along the crystallographic directions of each interaction, and the individual atom contributions are reported in Tables 6 and 7, respectively.

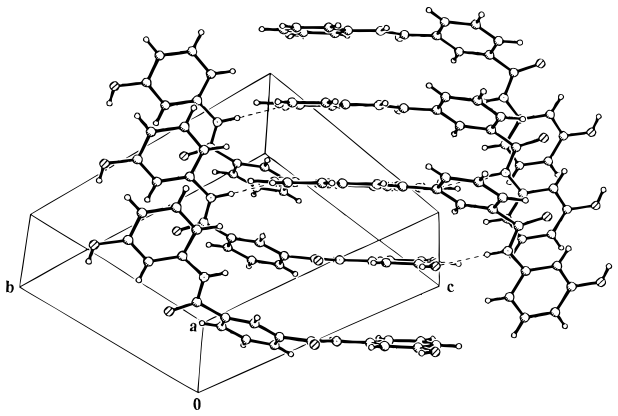

Figure 6. Side view of the column, showing π−π stacking and N−H···O hydrogen bonds.

Table 6. Breakdown of the Interaction Contributions to the Total Lattice Energy[a]

U	*V*	*W*	*Z*	total energy, kcal/mol	description
−1	0	0	1	−8.0	π−π stacking
1	0	0	1	−8.0	π−π stacking
−1	1	2	2	−7.5	C═O···H hydrogen bond (anti−anti)
0	2	1	2	−7.5	C═O···H hydrogen bond (syn−syn)
0	1	2	2	−5.1	N−H···O hydrogen bond
1	2	1	2	−2.2	weak electrostatic interactions

[a] Taken from HABIT based on the atomic coordinates described in the Supporting Information. The central molecule would be *UVW* (0,0,0) and *Z* = 1.

Table 7. Individual Atom Contributions to the Total Lattice Energy

atom name	percentage contribution	atom name	percentage contribution
C7	−0.22	O1	4.27
C14	0.22	H(O1)	5.43
N1	4.70	O2	10.87
H(N1)	−0.99	O3	10.56
N2	4.11	O4	4.11
H(N2)	0.33	H(O4)	5.65

The first four intermolecular interactions listed in Table 6 are within a column. Up and down the columns (i.e., along the *a*-axis) π−π interactions of −8.0 kcal/mol are present. Within each layer of the column the *anti*−*anti* pair plus supplementary interactions are worth −7.5 kcal/mol and the N−H···O hydrogen bonds are worth −5.1 kcal/mol. This gives a total intracolumn energy of −28.6 kcal/mol. The interactions between the columns (through the *syn*−*syn* arrangement) are worth −7.5 kcal/mol.

In Table 7 the lattice energy has been partitioned onto the individual atoms using the new intermolecular interaction breakdown routines in HABIT95.[19] The main observations are that the OH groups in the *syn* and *anti* amidophenolic groups each contribute about 9.7% to the total lattice energy. The C═O units in both the *syn* (C14═O3) and *anti* (C7═O2) groups each contribute about 10.5%. The most striking result is the difference in the lattice energy contribution of the N−H groups where N2−H, on the *syn* side chain, contributes 4.4% and N1−H, on the *anti* side chain, 3.7%. This difference is a reflection of the roles of the atoms in forming the solid-state structure. The former is in-

(18) Hanton, L. R.; Hunter C. A.; Purvis, D. H. *J. Chem. Soc., Chem. Commun.* **1992**, 1135.
(19) Clydesdale, G.; Docherty R.; Roberts, K. J. *Comput. Phys. Commun.* **1991**, *64*, 311. Clydesdale, G.; Docherty R.; Roberts, K. J. *J. Cryst. Growth*, in press. Clydesdale, G.; Docherty R.; Roberts, K. J. *Crystal Growth of Organic Materials*; Myerson, A. S., Green, D. A., Meenan, P., Eds.; American Chemical Society: Washington, DC, 1996; p 43.
(20) Monamy, F. A.; Carruthers, L. M.; McGuire, R. F. ; Scheraga, H. A. *J. Phys. Chem.* **1974**, *78*, 1595.
(21) Charlton, M. H.; Docherty R.; Hutchings, M. G. *J. Chem. Soc., Perkin Trans. 2* **1995**, 2023.
(22) Gavezzotti, A.; Filippini, G. *J. Phys. Chem.* **1994**, *98*, 4831.

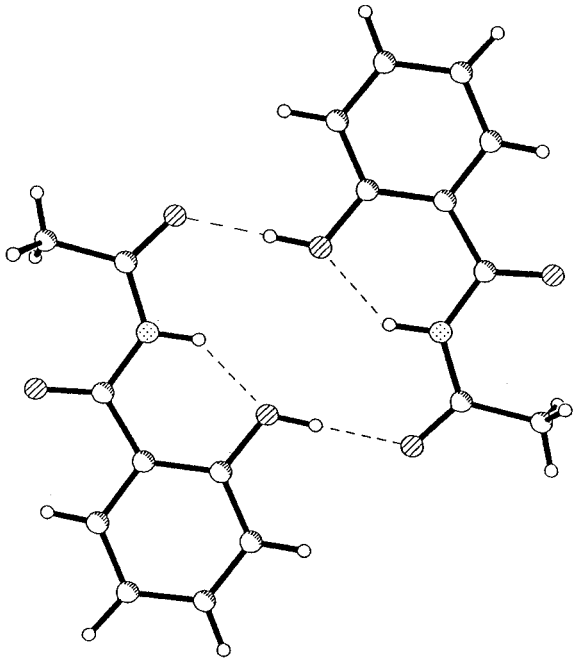

Figure 7. Hydrogen-bonded dimer of *N*-acetylsalicylamide.

volved in hydrogen bonding within the *anti*−*anti* columns whereas the latter only forms an N−H···π interaction.

Comparison with Other Structures. A search of the Cambridge Crystallographic Database (April, 1996)[23] revealed no data on any host structures similar to **1**, although three cocrystals between *N*,*N*′-bis(6-methylpyrid-2-yl)isophthalamide with biphenyl-3,3′-dicarboxylic acid,[24] pimelic acid,[25] and glutaric acid[25] (refcodes WAPXOA, YALKEB, YALKIF) were found. Two of these structures (WAPXOA, YALKIF) exist in the *syn*−*anti* conformation in the presence of the cocrystallizing entities. The YALKEB structure exists in the *syn*−*syn* conformation, although it is reported that a *syn*−*anti* polymorph has also been observed.[6]

Further searches of the database using a three-dimensional search query based on the hydrogen-bonding motifs in the solid-state structure of **1** found only one hit of interest. The structure of *N*-acetylsalicylamide[26] (ACSLCB10) shows a hydrogen-bonding motif forming O−H···O contacts at a distance of 1.77 Å. This distance is slightly shorter than those found in **1** at 1.786 and 1.793 Å. The donor−acceptor distance at 2.66 Å in *N*-acetylsalicylamide is comparable with the distances found in Table 4. The OHO angle in ACSLCB10 of 170.8° is between the values observed in the *anti*−*anti* and *syn*−*syn* motifs. It should be noted that the dimer structure found in *N*-acetylsalicylamide (see Figure 7) is distinct from that found in **1**. Although they both contain a 16-membered hydrogen-bonded pairing, the motif in *N*-acetylsalicylamide is more compact. The hydroxy substituent is ortho to the amido linkage producing an internal hydrogen bond (N−H···O 1.88 Å) and preventing any C−H···O hydrogen bonds being involved in the dimer arrangements as seen in **1**. The ortho hydroxy substituent (as opposed to meta in **1**) gives an intramolecular donor acceptor (HO···O=C) bite distance of 4.04 Å which is considerably shorter than that in **1** at 4.8 Å. As a consequnce in the *N*-acetylsalicylamide dimer in Figure 7 the hydroxy units point *outward* to the carbonyl units whereas in both *anti*−*anti* and *syn*−*syn* arrangements (Figures 3 and 4) the hydroxy units point *inward* to form the equivalent interactions.

Conclusions

The two pendent amidophenolic units of the structure *N*,*N*′-bis(3-hydroxyphenyl)isophthalamide (**1**) adopt two different conformations, a *syn* and an *anti* arrangement relative to the central benzene fragment. This conformation is the most stable arrangement (by around 2.3 kcal/mol) that can be adopted according to semiempirical molecular orbital calculations at the AM1 level. The calculated gas-phase structure shows good agreement with that seen in the solid.

In the solid state the *syn* and *anti* conformations exclusively recognize each other. The *anti* conformers form hydrogen-bonded centrosymmetric pairs (1.793 Å) which are supplemented by weaker C−H···O interactions. Along the *a*-axis π−π interactions plus N−H···O hydrogen bonds hold these paired species together in columns. The columns are linked by paired *syn*−*syn* hydrogen bonds in a centrosymmetric motif at 1.786 Å with additional C−H···O interactions. There are no examples of *syn*−*anti* hydrogen-bonding pairs.

One of the interesting features in the structure is that not all the potential hydrogen-bonding donors are used. In the absence of any potential hydrogen bonding partners the *anti* N−H group contents itself with the formation of an N−H···π interaction.

Calculations of the lattice energy suggest that the *anti*−*anti*, *syn*−*syn*, and π−π interactions are all worth around −7.5 kcal/mol and can therefore be regarded as equally important in the formation of the solid-state structure.

The current host demonstrates a strong potential for self-recognition. The *syn*−*anti* conformation found in the crystal structure does not favor the inclusion of small guest molecules. Further work is ongoing to prepare selected host structures and to use these to encapsulate small organic molecules.

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Supporting Information Available: Full crystal characterization, atomic coordinates, bond lengths and angles, and anisotropic temperature factors have been deposited as Supporting Information and to the Cambridge Crystallographic Data Centre (5 pages); crystal structure factors (8 pages). Ordering information is given on any current masthead page.

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(23) Allen, F. H.; Kennard, O. *Chem. Design Automation News* **1993**, *8*, 31.
(24) Yang, J.; Fan, E.; Geib S. J.; Hamilton, A. D. *J. Am. Chem. Soc.* **1993**, *115*, 5314.
(25) Geib, S. J.; Vicent, C.; Fan, E.; Hamilton, A. D. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 119.
(26) Vyas, K.; Rao V. M.; Manohar, H. *Acta Crystallogr. C* **1987**, *43*, 1201.