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# 1,4-Bis(benzimidazol-2-yl)benzene dimethylformamide disolvate

De-Hong Wu\* and Ling Hu

Ordered Matter Science Research Center, College of Chemistry and Chemical Engineering, Southeast University, Nanjing 210096, People's Republic of China  
Correspondence e-mail: wudh1971@sohu.com

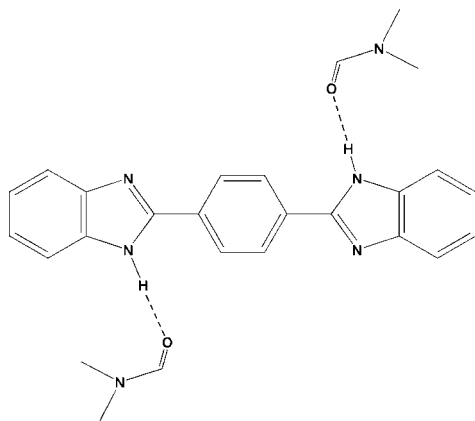
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Key indicators: single-crystal X-ray study;  $T = 291$  K; mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å;  $R$  factor = 0.057;  $wR$  factor = 0.158; data-to-parameter ratio = 17.7.

The aromatic molecule of the title compound,  $\text{C}_{20}\text{H}_{14}\text{N}_4 \cdot 2\text{C}_3\text{H}_7\text{NO}$ , occupies a special position on an inversion center. The benzimidazole unit (planar to within 0.008 Å) forms a dihedral angle of  $9.1(2)^\circ$  with the central benzene ring. The benzimidazole H atom participates in a hydrogen bond with the dimethylformamide solvent molecule, thus giving rise to the title 1:2 aggregate. These aggregates are further linked in the crystal structure by aromatic  $\pi$ - $\pi$  stacking interactions [centroid-centroid distance =  $6.356(2)$  Å].

## Related literature

For background literature concerning benzimidazole compounds, see: Zarrinmayeh *et al.* (1998); Gallagher *et al.* (2001); Howarth & Hanlon (2001). For the unsolvated structure, see: Bei *et al.* (2000); Dudd *et al.* (2003).



## Experimental

### Crystal data

$\text{C}_{20}\text{H}_{14}\text{N}_4 \cdot 2\text{C}_3\text{H}_7\text{NO}$   
 $M_r = 456.54$   
Monoclinic,  $P2_1/n$   
 $a = 6.3556(13)$  Å  
 $b = 20.931(2)$  Å  
 $c = 9.0097(18)$  Å  
 $\beta = 98.26(2)^\circ$   
 $V = 1186.1(4)$  Å<sup>3</sup>  
 $Z = 2$   
Mo  $K\alpha$  radiation  
 $\mu = 0.08$  mm<sup>-1</sup>  
 $T = 291$  K  
 $0.32 \times 0.26 \times 0.24$  mm

### Data collection

Rigaku Mercury2 diffractometer  
Absorption correction: multi-scan  
(*CrystalClear*; Rigaku, 2005)  
 $T_{\min} = 0.970$ ,  $T_{\max} = 0.990$   
12310 measured reflections  
2723 independent reflections  
1718 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.054$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.057$   
 $wR(F^2) = 0.158$   
 $S = 1.00$   
2723 reflections  
154 parameters  
H-atom parameters constrained  
 $\Delta\rho_{\max} = 0.24$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.21$  e Å<sup>-3</sup>

**Table 1**

Hydrogen-bond geometry (Å, °).

| $D-H \cdots A$                            | $D-H$ | $H \cdots A$ | $D \cdots A$ | $D-H \cdots A$ |
|---|-------|--------------|--------------|----------------|
| $\text{N2}-\text{H2A} \cdots \text{O1}^i$ | 0.86  | 1.95         | 2.787(3)     | 165            |

Symmetry code: (i)  $-x + 2, -y + 1, -z + 1$ .

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: YA2086).

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## supporting information

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## 1,4-Bis(benzimidazol-2-yl)benzene dimethylformamide disolvate

De-Hong Wu and Ling Hu

### S1. Comment

Benzimidazole systems continue to attract considerable attention in chemical synthesis, structural science and applied medicinal research (Zarrinmayeh *et al.*, 1998; Gallagher *et al.*, 2001; Howarth & Hanlon, 2001). Here we report the crystal structure of the title compound, 1,4-bis(2-benzimidazolyl)benzene bis(dimethylformamide) solvate.

The 1,4-bis(2-benzimidazolyl)benzene molecule occupies a special position on the inversion center, and benzimidazole moiety (planar within 0.0078 Å) forms dihedral angle of 9.1 (2)° with the plane of the central benzene ring (Fig. 1). This shows that 1,4-(2-benzimidazolyl)benzene molecule in the structure of the title compound deviates from planarity to a much lesser degree than in the unsolvated structure, wherein the corresponding dihedral angle is equal to 31.0° (Bei *et al.*, 2000; Dudd *et al.*, 2003).

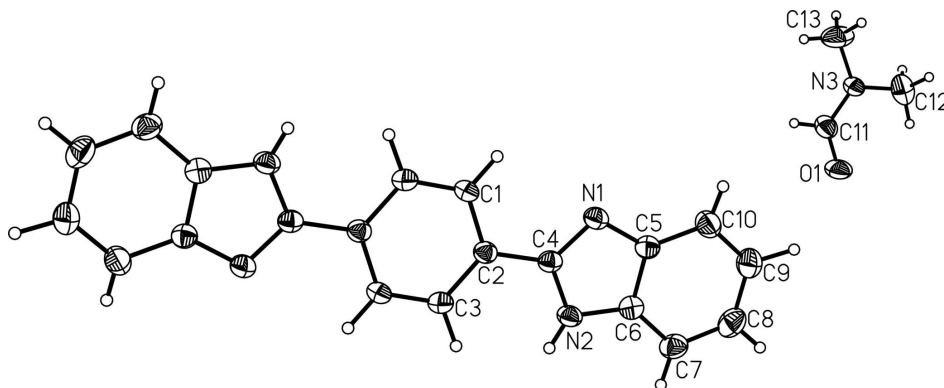
The only 'active' hydrogen atom H2 participates in the H-bond with the carbonyl atom of the dimethylformamide molecule (H2...O1 1.95 Å, N2—H2...O1 165.1°) thus giving rise to the 1,4-bis(2-benzimidazolyl)benzene:DMFA (1:2) complexes, which are further linked in crystal through the  $\pi$ — $\pi$  stacking interactions.

### S2. Experimental

The title compound was synthesized by refluxing terephthalaldehyde (0.53 g, 4 mmol) and benzene-1,2-diamine (0.86 g, 8 mmol) in absolute methanol (50 ml) for 8 h. After cooling to room temperature, the yellow solid thus formed was isolated and dried under vacuum (1.13 g, yield 80 %). Single crystals suitable for X-ray structure analysis were obtained by the slow evaporation of a dimethylformamide solution in air.

### S3. Refinement

H atoms were placed in calculated positions (N—H = 0.86 Å; C—H = 0.93 Å and 0.96 Å for  $C_{sp^2}$  and  $C_{sp^3}$  atoms, respectively), assigned fixed  $U_{iso}$  values [ $U_{iso} = 1.2U_{eq}(C_{sp^2}/N)$  and  $1.5U_{eq}(C_{sp^3})$ ] and allowed to ride.

**Figure 1**

The structure of 1,4-bis(2-benzimidazolyl)benzene and dimethylformamide molecules in the crystal of the title compound, showing the atomic numbering scheme and 30% probability displacement ellipsoids. Unlabelled atoms are related to the labelled atoms by the  $(1 - x, -y, 1 - z)$  symmetry transformation.

### 1,4-Bis(benzimidazol-2-yl)benzene dimethylformamide disolvate

#### Crystal data

$C_{20}H_{14}N_4 \cdot 2C_3H_7NO$

$M_r = 456.54$

Monoclinic,  $P2_1/n$

Hall symbol:  $-P\ 2_1n$

$a = 6.3556$  (13) Å

$b = 20.931$  (2) Å

$c = 9.0097$  (18) Å

$\beta = 98.26$  (2)°

$V = 1186.1$  (4) Å<sup>3</sup>

$Z = 2$

$F(000) = 484$

$D_x = 1.278$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 9216 reflections

$\theta = 3.0$ – $27.7$ °

$\mu = 0.08$  mm<sup>-1</sup>

$T = 291$  K

Block, yellow

$0.32 \times 0.26 \times 0.24$  mm

#### Data collection

Rigaku Mercury2  
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 13.6612 pixels mm<sup>-1</sup>

CCD profile fitting scans

Absorption correction: multi-scan

(*CrystalClear*; Rigaku, 2005)

$T_{\min} = 0.970$ ,  $T_{\max} = 0.990$

12310 measured reflections

2723 independent reflections

1718 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.054$

$\theta_{\max} = 27.5$ °,  $\theta_{\min} = 3.0$ °

$h = -8 \rightarrow 8$

$k = -27 \rightarrow 27$

$l = -11 \rightarrow 11$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.057$

$wR(F^2) = 0.158$

$S = 1.00$

2723 reflections

154 parameters

0 restraints

Primary atom site location: structure-invariant  
direct methods

Secondary atom site location: difference Fourier  
map

Hydrogen site location: inferred from  
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0615P)^2 + 0.4757P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.24$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.21$  e Å<sup>-3</sup>

*Special details*

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted R-factor wR and goodness of fit S are based on  $F^2$ , conventional R-factors R are based on F, with F set to zero for negative  $F^2$ . The threshold expression of  $F^2 > 2\sigma(F^2)$  is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on  $F^2$  are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

|      | x          | y            | z            | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|------|------------|--------------|--------------|----------------------------------|
| C1   | 0.4424 (3) | 0.03145 (10) | 0.6222 (2)   | 0.0442 (5)                       |
| H1A  | 0.4027     | 0.0527       | 0.7045       | 0.053*                           |
| C2   | 0.6334 (3) | 0.04722 (9)  | 0.5722 (2)   | 0.0394 (5)                       |
| C3   | 0.6877 (3) | 0.01491 (10) | 0.4482 (2)   | 0.0454 (5)                       |
| H3A  | 0.8140     | 0.0249       | 0.4126       | 0.054*                           |
| C4   | 0.7705 (3) | 0.09548 (9)  | 0.6530 (2)   | 0.0396 (5)                       |
| C5   | 0.9076 (3) | 0.16201 (10) | 0.8206 (2)   | 0.0431 (5)                       |
| C6   | 1.0397 (3) | 0.16157 (9)  | 0.7099 (2)   | 0.0425 (5)                       |
| C7   | 1.2235 (4) | 0.19770 (11) | 0.7212 (3)   | 0.0563 (6)                       |
| H7A  | 1.3119     | 0.1966       | 0.6474       | 0.068*                           |
| C8   | 1.2694 (4) | 0.23526 (12) | 0.8464 (3)   | 0.0655 (7)                       |
| H8A  | 1.3914     | 0.2604       | 0.8575       | 0.079*                           |
| C9   | 1.1379 (4) | 0.23673 (12) | 0.9574 (3)   | 0.0638 (7)                       |
| H9A  | 1.1734     | 0.2630       | 1.0404       | 0.077*                           |
| C10  | 0.9577 (4) | 0.20035 (11) | 0.9471 (3)   | 0.0578 (6)                       |
| H10A | 0.8713     | 0.2012       | 1.0221       | 0.069*                           |
| C11  | 0.7511 (4) | 0.87860 (14) | 0.7174 (3)   | 0.0663 (7)                       |
| H11A | 0.6668     | 0.8486       | 0.6607       | 0.080*                           |
| C12  | 0.7988 (5) | 0.95068 (16) | 0.9240 (3)   | 0.0905 (10)                      |
| H12A | 0.9305     | 0.9584       | 0.8865       | 0.136*                           |
| H12B | 0.8277     | 0.9357       | 1.0255       | 0.136*                           |
| H12C | 0.7187     | 0.9897       | 0.9210       | 0.136*                           |
| C13  | 0.4746 (5) | 0.88579 (18) | 0.8728 (4)   | 0.0984 (11)                      |
| H13A | 0.4093     | 0.8540       | 0.8042       | 0.148*                           |
| H13B | 0.3850     | 0.9229       | 0.8681       | 0.148*                           |
| H13C | 0.4937     | 0.8689       | 0.9728       | 0.148*                           |
| N1   | 0.7398 (3) | 0.12012 (9)  | 0.78322 (19) | 0.0470 (5)                       |
| N2   | 0.9489 (3) | 0.11884 (8)  | 0.60413 (19) | 0.0442 (4)                       |
| H2A  | 0.9957     | 0.1087       | 0.5223       | 0.053*                           |
| N3   | 0.6781 (3) | 0.90317 (9)  | 0.8324 (2)   | 0.0526 (5)                       |
| O1   | 0.9230 (3) | 0.89199 (11) | 0.6780 (2)   | 0.0845 (6)                       |

*Atomic displacement parameters ( $\text{\AA}^2$ )*

|    | $U^{11}$    | $U^{22}$    | $U^{33}$    | $U^{12}$    | $U^{13}$   | $U^{23}$    |
|----|-------------|-------------|-------------|-------------|------------|-------------|
| C1 | 0.0431 (11) | 0.0534 (13) | 0.0382 (11) | 0.0016 (10) | 0.0135 (9) | -0.0061 (9) |

|     |             |             |             |              |              |              |
|-----|-------------|-------------|-------------|--------------|--------------|--------------|
| C2  | 0.0390 (11) | 0.0442 (11) | 0.0355 (10) | 0.0044 (9)   | 0.0071 (8)   | 0.0028 (8)   |
| C3  | 0.0397 (11) | 0.0537 (12) | 0.0451 (12) | -0.0003 (10) | 0.0144 (9)   | -0.0011 (10) |
| C4  | 0.0386 (11) | 0.0425 (11) | 0.0385 (10) | 0.0033 (9)   | 0.0088 (9)   | 0.0043 (9)   |
| C5  | 0.0431 (11) | 0.0414 (11) | 0.0457 (12) | 0.0015 (9)   | 0.0088 (9)   | 0.0011 (9)   |
| C6  | 0.0441 (11) | 0.0398 (11) | 0.0440 (11) | 0.0015 (9)   | 0.0080 (9)   | 0.0061 (9)   |
| C7  | 0.0494 (13) | 0.0570 (14) | 0.0655 (15) | -0.0081 (11) | 0.0183 (11)  | 0.0020 (12)  |
| C8  | 0.0543 (15) | 0.0584 (15) | 0.0827 (19) | -0.0146 (12) | 0.0066 (13)  | -0.0018 (13) |
| C9  | 0.0672 (16) | 0.0582 (15) | 0.0649 (16) | -0.0106 (13) | 0.0052 (13)  | -0.0125 (12) |
| C10 | 0.0635 (15) | 0.0580 (14) | 0.0537 (14) | -0.0070 (12) | 0.0146 (12)  | -0.0107 (11) |
| C11 | 0.0706 (17) | 0.0797 (18) | 0.0501 (14) | 0.0029 (14)  | 0.0129 (13)  | -0.0001 (13) |
| C12 | 0.112 (3)   | 0.085 (2)   | 0.0701 (19) | 0.0047 (19)  | -0.0020 (18) | -0.0122 (16) |
| C13 | 0.078 (2)   | 0.126 (3)   | 0.101 (2)   | -0.001 (2)   | 0.0443 (19)  | 0.023 (2)    |
| N1  | 0.0467 (10) | 0.0530 (10) | 0.0439 (10) | -0.0042 (8)  | 0.0158 (8)   | -0.0052 (8)  |
| N2  | 0.0454 (10) | 0.0488 (10) | 0.0414 (9)  | -0.0018 (8)  | 0.0166 (8)   | -0.0012 (8)  |
| N3  | 0.0540 (11) | 0.0625 (12) | 0.0438 (10) | 0.0004 (9)   | 0.0153 (9)   | 0.0007 (9)   |
| O1  | 0.0695 (12) | 0.1293 (18) | 0.0613 (12) | 0.0077 (12)  | 0.0318 (10)  | 0.0092 (11)  |

*Geometric parameters (Å, °)*

|                         |             |               |           |
|-------------------------|-------------|---------------|-----------|
| C1—C3 <sup>i</sup>      | 1.370 (3)   | C8—H8A        | 0.9300    |
| C1—C2                   | 1.394 (3)   | C9—C10        | 1.367 (3) |
| C1—H1A                  | 0.9300      | C9—H9A        | 0.9300    |
| C2—C3                   | 1.391 (3)   | C10—H10A      | 0.9300    |
| C2—C4                   | 1.459 (3)   | C11—O1        | 1.229 (3) |
| C3—C1 <sup>i</sup>      | 1.370 (3)   | C11—N3        | 1.300 (3) |
| C3—H3A                  | 0.9300      | C11—H11A      | 0.9300    |
| C4—N1                   | 1.322 (2)   | C12—N3        | 1.441 (3) |
| C4—N2                   | 1.364 (2)   | C12—H12A      | 0.9600    |
| C5—N1                   | 1.384 (3)   | C12—H12B      | 0.9600    |
| C5—C10                  | 1.393 (3)   | C12—H12C      | 0.9600    |
| C5—C6                   | 1.393 (3)   | C13—N3        | 1.440 (3) |
| C6—N2                   | 1.372 (3)   | C13—H13A      | 0.9600    |
| C6—C7                   | 1.383 (3)   | C13—H13B      | 0.9600    |
| C7—C8                   | 1.372 (4)   | C13—H13C      | 0.9600    |
| C7—H7A                  | 0.9300      | N2—H2A        | 0.8600    |
| C8—C9                   | 1.393 (4)   |               |           |
| C3 <sup>i</sup> —C1—C2  | 120.91 (18) | C8—C9—H9A     | 119.3     |
| C3 <sup>i</sup> —C1—H1A | 119.5       | C9—C10—C5     | 117.9 (2) |
| C2—C1—H1A               | 119.5       | C9—C10—H10A   | 121.1     |
| C3—C2—C1                | 118.20 (19) | C5—C10—H10A   | 121.1     |
| C3—C2—C4                | 122.55 (18) | O1—C11—N3     | 125.0 (3) |
| C1—C2—C4                | 119.23 (17) | O1—C11—H11A   | 117.5     |
| C1 <sup>i</sup> —C3—C2  | 120.89 (19) | N3—C11—H11A   | 117.5     |
| C1 <sup>i</sup> —C3—H3A | 119.6       | N3—C12—H12A   | 109.5     |
| C2—C3—H3A               | 119.6       | N3—C12—H12B   | 109.5     |
| N1—C4—N2                | 112.48 (18) | H12A—C12—H12B | 109.5     |
| N1—C4—C2                | 124.01 (18) | N3—C12—H12C   | 109.5     |

|            |             |               |             |
|------------|-------------|---------------|-------------|
| N2—C4—C2   | 123.48 (17) | H12A—C12—H12C | 109.5       |
| N1—C5—C10  | 129.9 (2)   | H12B—C12—H12C | 109.5       |
| N1—C5—C6   | 110.11 (18) | N3—C13—H13A   | 109.5       |
| C10—C5—C6  | 120.0 (2)   | N3—C13—H13B   | 109.5       |
| N2—C6—C7   | 132.4 (2)   | H13A—C13—H13B | 109.5       |
| N2—C6—C5   | 105.38 (17) | N3—C13—H13C   | 109.5       |
| C7—C6—C5   | 122.2 (2)   | H13A—C13—H13C | 109.5       |
| C8—C7—C6   | 116.9 (2)   | H13B—C13—H13C | 109.5       |
| C8—C7—H7A  | 121.6       | C4—N1—C5      | 104.84 (16) |
| C6—C7—H7A  | 121.6       | C4—N2—C6      | 107.19 (16) |
| C7—C8—C9   | 121.6 (2)   | C4—N2—H2A     | 126.4       |
| C7—C8—H8A  | 119.2       | C6—N2—H2A     | 126.4       |
| C9—C8—H8A  | 119.2       | C11—N3—C13    | 122.5 (3)   |
| C10—C9—C8  | 121.5 (2)   | C11—N3—C12    | 120.5 (2)   |
| C10—C9—H9A | 119.3       | C13—N3—C12    | 117.0 (2)   |

Symmetry code: (i)  $-x+1, -y, -z+1$ .

*Hydrogen-bond geometry (Å, °)*

| <i>D—H...A</i>            | <i>D—H</i> | <i>H...A</i> | <i>D...A</i> | <i>D—H...A</i> |
|---------------------------|------------|--------------|--------------|----------------|
| N2—H2A...O1 <sup>ii</sup> | 0.86       | 1.95         | 2.787 (3)    | 165            |

Symmetry code: (ii)  $-x+2, -y+1, -z+1$ .