

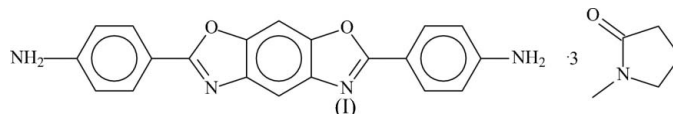
Hui Zhao,<sup>a</sup> Li-Ping Sun<sup>a</sup> and  
Seik Weng Ng<sup>b\*</sup><sup>a</sup>College of Chemistry and Materials Science,  
Heilongjiang University, Harbin 150080,  
People's Republic of China, and <sup>b</sup>Department of  
Chemistry, University of Malaya, Kuala Lumpur  
50603, Malaysia

Correspondence e-mail: seikweng@um.edu.my

## Key indicators

Single-crystal X-ray study  
 $T = 295$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.004$  Å  
 $R$  factor = 0.066  
 $wR$  factor = 0.184  
Data-to-parameter ratio = 17.2For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.2,6-Bis(4-aminophenyl)benzo[1,2-*d*:5,4-*d'*]-  
dioxazole 1-methylpyrrolidin-2-one trisolvateThe title compound,  $\text{C}_{20}\text{H}_{14}\text{N}_4\text{O}_2 \cdot 3\text{C}_5\text{H}_9\text{NO}$ , crystallizes with  
three molecules of 1-methyl-2-pyrrolidinone. The amino  
groups at each end of the fused-ring heterocycle each interact  
with two of the solvent molecules.

## Comment

2,6-Bis(4-aminophenyl)benzo(1,2-*d*:5,4-*d'*)dioxazole, which  
can be used for the synthesis of thermally stable polyhetero-  
cycles, has been known for a long time (Evstaf'ev *et al.*, 1970;  
Preston *et al.*, 1968). A recent study described its synthesis  
from 1,2,3-trichlorobenzene and its purification (Chen *et al.*,  
2003). We have used another method to synthesize this  
monomer, but our choice of solvent for recrystallization led to  
the isolation of the compound as a trisolvate, (I) (Fig. 1). The  
compound has the two aminophenyl substituents of the  
benzodioxazole group coplanar with the fused-ring system.  
Bond dimensions are similar to those found in the only other  
report on this class of 2,6-bis(phenyl)benzo(1,2-*d*:5,4-*d'*)-  
dioxazole derivatives, *viz.* the parent unsubstituted compound  
itself (Fratini, 1978). The amino groups interact with two of  
the three solvent molecules through  $\text{N}-\text{H} \cdots \text{O}$  hydrogen  
bonds (Table 1). The third solvent molecule makes no signif-  
icant contacts. The bond dimensions of the three methyl-  
pyrrolidinone solvent molecules compare well with those  
found in the parent compound itself, whose structure was  
determined at low temperature (Müller *et al.*, 1996).

## Experimental

Equimolar quantities of 4,6-diamino-1,3-benzenediol (14.0 g,  
0.1 mol) and 4-aminobenzoic acid (13.7 g, 0.1 mol) were dissolved in  
polyphosphoric acid (50 ml). The mixture was heated at 423 K for  
five h. The cool solution yielded a pale-yellow powder that was  
purified by recrystallization from 1-methylpyrrolidone. The recryst-  
tallization process took about a month, and yellow prisms were  
obtained. Analysis calculated for  $\text{C}_{35}\text{H}_{41}\text{N}_7\text{O}_5$ : C 65.71, H 6.46, N  
15.33%; found: C 65.74, H 6.48, N 15.35%.

## Crystal data

 $\text{C}_{20}\text{H}_{14}\text{N}_4\text{O}_2 \cdot 3\text{C}_5\text{H}_9\text{NO}$   
 $M_r = 639.75$   
Triclinic,  $P\bar{1}$   
 $a = 7.586$  (2) Å  
 $b = 12.525$  (2) Å  
 $c = 17.627$  (2) Å  
 $\alpha = 94.92$  (1)°  
 $\beta = 92.88$  (2)°  
 $\gamma = 99.19$  (1)°  
 $V = 1643.8$  (6) Å<sup>3</sup> $Z = 2$   
 $D_x = 1.293$  Mg m<sup>-3</sup>  
Mo  $K\alpha$  radiation  
Cell parameters from 14761  
reflections  
 $\theta = 3.0$ – $27.4$ °  
 $\mu = 0.09$  mm<sup>-1</sup>  
 $T = 295$  (2) K  
Prism, yellow  
 $0.39 \times 0.27 \times 0.20$  mm

## Data collection

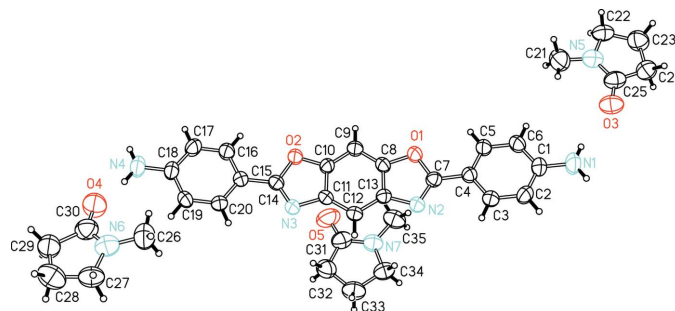
Rigaku R-AXIS RAPID IP  
diffractometer  
 $\omega$  scans  
Absorption correction: multi-scan  
(*ABSCOR*; Higashi, 1995)  
 $T_{\min} = 0.654$ ,  $T_{\max} = 0.983$   
15592 measured reflections

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.066$   
 $wR(F^2) = 0.184$   
 $S = 1.02$   
7333 reflections  
427 parameters  
H-atom parameters constrained

7333 independent reflections  
4014 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.038$   
 $\theta_{\text{max}} = 27.4^\circ$   
 $h = -9 \rightarrow 9$   
 $k = -16 \rightarrow 16$   
 $l = -22 \rightarrow 22$

$w = 1/[\sigma^2(F_o^2) + (0.0898P)^2 + 0.1894P]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 0.50 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.19 \text{ e } \text{\AA}^{-3}$



**Figure 1**  
*ORTEP* (Johnson, 1976) plot of (I). Displacement ellipsoids are drawn at the 70% probability level, and H atoms are drawn as spheres of arbitrary radii.

**Table 1**

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N1-H1n1\cdots O3$	0.86	2.25	3.092 (3)	166
$N1-H1n2\cdots O4^i$	0.86	2.21	3.060 (3)	172
$N4-H4n1\cdots O3^{ii}$	0.86	2.34	3.122 (3)	152
$N4-H4n2\cdots O4$	0.86	2.37	3.130 (3)	148

Symmetry codes: (i)  $x, y + 1, z + 1$ ; (ii)  $x, y - 1, z - 1$ .

The C-bound H atoms were placed at calculated positions ( $C-H_{\text{aromatic}} = 0.93 \text{ \AA}$ ,  $C-H_{\text{methylene}} = 0.97 \text{ \AA}$  and  $C-H_{\text{methyl}} = 0.96 \text{ \AA}$ ), and were included in the refinement in the riding-model approximation, with  $U_{\text{iso}}(\text{H})$  set to  $1.2U_{\text{eq}}(\text{C})$  for the aromatic and methylene C atoms, and to  $1.5U_{\text{eq}}(\text{C})$  for the methyl groups. The methyl groups were rotated to fit the electron density. The N-bound H atoms were treated similarly [ $N-H = 0.86 \text{ \AA}$  and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ ].

Data collection: *RAPID-AUTO* (Rigaku Corporation, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSK, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

We thank the National Natural Science Foundation of China (grant No. 20101003), the Scientific Fund for Remarkable Teachers of Heilongjiang Province (grant No. 1054 G036) and the University of Malaya for supporting this study.

## References

- Chen, X.-Q., Huang, Y.-D. & Li, D. W. (2003). *Chin. J. Org. Chem.* **23**, 1306–1308; *Wuhan Univ. J. Nat. Sci.* **8**, 1143–1146.  
Evstaf'ev, V. P., Braz, G. I. & Yakubovich, A. Ya. (1970). *Khim. Geterotsikl. Soed.* pp. 739–743. (In Russian.)  
Fratini, A. V. (1978). *Rep. AFSR, AFOSR-77-3276*. [From *Gov. Rep. Announce. Index US*, (1979), **79**, 119.]  
Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.  
Johnson, C. K. (1976). *ORTEP*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.  
Müller, G., Lutz, M. & Harder, S. (1996). *Acta Cryst.* **B52**, 1014–1022.  
Preston, J., De Winter, W. & Hofferbert, W. L. (1968). *J. Heterocycl. Chem.* **5**, 269–273.  
Rigaku Corporation (1998). *RAPID-AUTO*. Rigaku Corporation, Tokyo, Japan.  
Rigaku/MSK (2002). *CrystalStructure*. Rigaku/MSK Inc., 9009 New Trails Drive, The Woodlands, TX 77381-5209, USA.  
Sheldrick, G. M. (1997). *SHELXL97* and *SHELXS97*. University of Göttingen, Germany.