

# 1,1'-Di(hydrazinocarbonylmethyl)- 2,2'-biimidazole monohydrate and 1,1'-di[2-(hydrazinocarbonyl)ethyl]- 2,2'-biimidazole

W. Mark Barnett,<sup>a</sup> Russell G. Baughman,<sup>b\*</sup> Paula M. Secondo<sup>c</sup> and Charles J. Hermansen<sup>d</sup>

<sup>a</sup>GEM Gravure Company Inc., West Hanover, MA 02339, USA, <sup>b</sup>Division of Science, Truman State University, Kirksville, MO 63501, USA, <sup>c</sup>Department of Chemistry, Western Connecticut State University, Danbury, CT 06810, USA, and <sup>d</sup>Department of Chemistry, Northern State University, Aberdeen, SD 57401, USA  
Correspondence e-mail: baughman@truman.edu

Received 4 July 2002

Accepted 24 July 2002

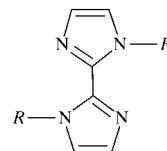
Online 21 August 2002

The crystal structures of the title compounds, alternatively called 2,2'-(2,2'-biimidazole-1,1'-diyl)diacetohydrazide monohydrate, C<sub>10</sub>H<sub>14</sub>N<sub>8</sub>O<sub>2</sub>·H<sub>2</sub>O, (I), and 3,3'-(2,2'-biimidazole-1,1'-diyl)dipropionohydrazide, C<sub>12</sub>H<sub>18</sub>N<sub>8</sub>O<sub>2</sub>, (II), respectively, have been determined. The molecules consist of half-molecule asymmetric units related by a twofold rotation in (I) and by a center of inversion in (II). The imidazole rings of both molecules crystallize in a nearly coplanar fashion [dihedral angles of 5.91 (3) and 0.0 (1)° for (I) and (II), respectively]. Both planar hydrazinocarbonylalkyl substituents are essentially planar and assume the *E* orientation.

## Comment

Compounds containing the 2,2'-biimidazole moiety have been the focus of several investigations due to their biological activity as cardiotonics (Matthews *et al.*, 1990), antiprotozoals (Melloni *et al.*, 1975), and enzyme active-site models (Overberger & Vorchheimer, 1963; Kirchner & Krebs, 1987). In addition to its physiological activity, the aromatic biheterocyclic structure has also been incorporated into a variety of polymer systems (Chi & Collier, 1988; Lui *et al.*, 1988; Elmer & Collier, 1993; Lister & Collier, 1993; Barnett, 1997) in a series of attempts to imbue polymers with thermal stability, conductivity and metal-ion binding selectivity. Recently, a new class of 2,2'-biimidazole compounds, *viz.* the 1,1'-diester derivatives (Barnett, 1997; Barnett *et al.*, 1996, 1997, 1999; Secondo *et al.*, 1996), has been developed. Ready acylation of primary amines or hydrazine with these diesters proceeds with excellent yields. The hydrazide macromolecules 1,1'-di(hydrazinocarbonylmethyl)-2,2'-biimidazole monohydrate, (I), and 1,1'-di[2-(hydrazinocarbonyl)ethyl]-2,2'-biimidazole, (II),

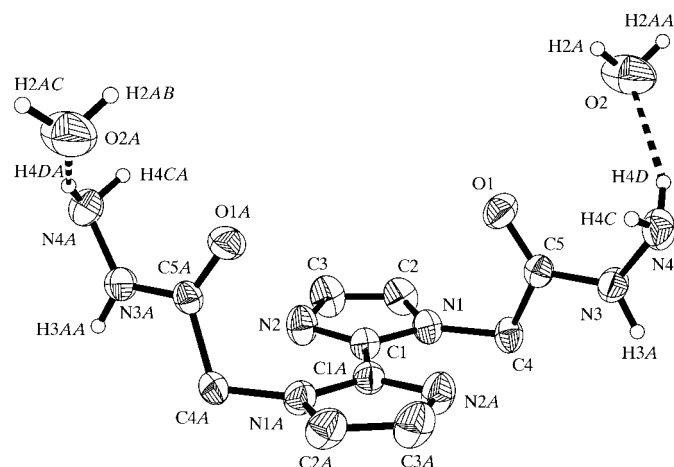
illustrated in the *Scheme* below, were prepared as monomers for subsequent polymer syntheses.



(I) R = -CH<sub>2</sub>CONHNH<sub>2</sub>·H<sub>2</sub>O

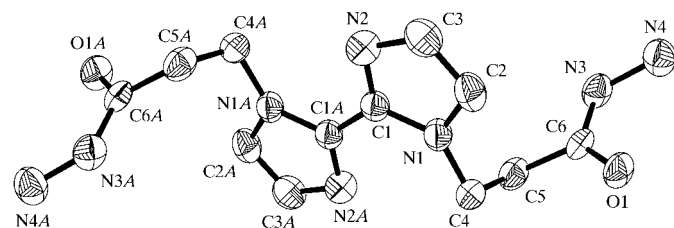
(II) R = -CH<sub>2</sub>CH<sub>2</sub>CONHNH<sub>2</sub>

As with similar unconjugated disubstituted biimidazole derivatives, the imidazole rings of (I) and (II) are coplanar, with r.m.s. deviations of 0.003 and 0.001 Å, respectively. The N1/C1/N2/C3/C2 planes and their associated symmetry partners, as shown in Figs. 1 and 2, are essentially coplanar, as they exhibit dihedral angles of 5.91 (3) and 0.0 (1)° in (I) and (II), respectively. Previously reported derivatives (Barnett, 1997; Barnett *et al.*, 1999; Secondo *et al.*, 1996) have torsion angles along the ring-bridging C atoms of less than 1°, while the dihedral angle for the ring planes of unsubstituted 2,2'-biimidazole has been reported to be 4.6° (Cromer *et al.*, 1987). Thus, biimidazoles (I) and (II) represent the greatest disparity between imidazole-plane torsion angles for similar derivatives.



**Figure 1**

View of (I), showing the labeling of the non-H and selected H atoms. Displacement ellipsoids are shown at the 50% probability level and H atoms are drawn as small spheres of arbitrary radii.



**Figure 2**

View of (II), showing the labeling of the non-H atoms. Displacement ellipsoids are shown at 50% probability levels.

The N1/C4/C5 least-squares plane of (I) forms a dihedral angle of 76.7 (2)° with respect to the adjacent imidazole ring, while the same angle in (II) is 84.9 (1)° (*cf.* Figs. 1 and 2). Both dihedral angles are comparable to those observed in analogous compounds. Each hydrazinocarbonylalkyl (*R*) group adopts a zigzag conformation and is essentially planar, as the r.m.s. deviations for the non-H atoms (including N1) are 0.092 and 0.550 Å for (I) and (II), respectively. Fig. 1 shows the hydrogen bonding to the water molecules entrained in the crystal lattice of (I). The remaining bond lengths and angles do not differ significantly from 1,1'-disubstituted biimidazole structures reported previously. Selected distances and angles, together with hydrogen-bonding parameters, for (I) and (II) are given in Tables 1–4.

Extensive hydrogen-bonding networks exist in (I) and (II), as both compounds take advantage of the presence of various amine and amide H atoms and a carbonyl O atom. These are supplemented in (I) by the presence of a water of hydration. In the crystal, an intra-asymmetric unit hydrogen bond exists between atoms H4D and O2 (dashed lines in Fig. 1), while inter-asymmetric unit hydrogen bonds are present between H2A and N4, and H3A and O1, as well as between H4C and N2 (*cf.* Table 2). Thus, the presence of water in the crystal is an important contributor to the overall packing of this biimidazole derivative. In contrast, no strong intramolecular hydrogen bond is present in (II), although a number of intermolecular bonds, similar to those in (I), do exist (*cf.* Table 4). While both compounds were crystallized from water, only (I) draws on the hydrogen-bonding potential of the water in crystal formation.

## Experimental

The title compounds were prepared by reacting 1,1'-di(methoxycarbonylmethyl)-2,2'-biimidazole (0.25 g, 0.898 mmol) or 1,1'-di[2-(ethoxycarbonyl)ethyl]-2,2'-biimidazole (0.25 g, 0.748 mmol) with 64% hydrazine (10 ml, 200 mmol) in a 25 ml round-bottomed flask with stirring. The mixtures were stirred for a minimum of 3 d, after which time the white powdery products were filtered off, washed with water, and crystallized by slow cooling from hot aqueous solutions. Yields were ~60 and 78% for (I) and (II), respectively. The crystal of (I) was sealed with mother liquor in a capillary to minimize possible gain or loss of water.

**Table 1**

Selected geometric parameters (Å, °) for (I).

O1–C5	1.222 (4)	N3–N4	1.410 (4)
N1–C4	1.455 (3)	C1–C1 <sup>i</sup>	1.453 (5)
N3–C5	1.331 (4)	C4–C5	1.521 (4)
C1–N1–C4	129.2 (2)	O1–C5–N3	124.0 (3)
C2–N1–C4	123.7 (3)	O1–C5–C4	122.4 (2)
C5–N3–N4	123.6 (3)	N3–C5–C4	113.5 (3)
N2–C1–C1 <sup>i</sup>	125.3 (3)	H4D–O2–H2A	102
N1–C1–C1 <sup>i</sup>	123.6 (3)	H4D–O2–H2A <sup>ii</sup>	122
N1–C4–C5	110.8 (2)		

Symmetry codes: (i) 1 – x, 1 – y, z; (ii) 1 – x, –y, z.

**Table 2**

Hydrogen-bonding geometry (Å, °) for (I).

D–H...A	D–H	H...A	D...A	D–H...A
O2–H2A...N4 <sup>i</sup>	0.850 (5)	2.27 (2)	3.080 (3)	161 (4)
N3–H3A...O1 <sup>ii</sup>	0.90	1.93	2.830 (3)	176
N4–H4C...N2 <sup>iii</sup>	0.90	2.41	3.260 (4)	157
N4–H4D...O2	0.90	2.30	3.165 (4)	161

Symmetry codes: (i)  $\frac{1}{2} + y, 1 - x, z - \frac{1}{4}$ ; (ii)  $1 - y, x - \frac{1}{2}, \frac{1}{4} + z$ ; (iii)  $\frac{3}{2} - y, x, z - \frac{1}{4}$ .

## Compound (I)

### Crystal data

C<sub>10</sub>H<sub>14</sub>N<sub>8</sub>O<sub>2</sub>·H<sub>2</sub>O  
*M<sub>r</sub>* = 296.29  
 Tetragonal, *I*4<sub>1</sub>  
*a* = 9.7451 (3) Å  
*c* = 14.1764 (6) Å  
*V* = 1346.30 (8) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 1.462 Mg m<sup>-3</sup>  
 Mo *K*α radiation

Cell parameters from 100 reflections  
 $\theta$  = 6.4–19.7°  
 $\mu$  = 0.11 mm<sup>-1</sup>  
*T* = 293 (2) K  
 Block cut from larger crystal, colorless  
 0.59 × 0.50 × 0.45 mm

### Data collection

Bruker *P4* diffractometer  
 $\theta/2\theta$  scans  
 939 measured reflections  
 620 independent reflections  
 562 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.015  
 $\theta_{\max}$  = 25.0°

*h* = –11 → 1  
*k* = –1 → 11  
*l* = –16 → 1  
 3 standard reflections every 100 reflections  
 intensity decay: average in σ(*I*)'s of 1.7%

### Refinement

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.032  
*wR*(*F*<sup>2</sup>) = 0.077  
*S* = 1.14  
 620 reflections  
 99 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0380P)^2 + 0.5103P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.14 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.16 \text{ e \AA}^{-3}$

## Compound (II)

### Crystal data

C<sub>12</sub>H<sub>18</sub>N<sub>8</sub>O<sub>2</sub>  
*M<sub>r</sub>* = 306.33  
 Monoclinic, *P*2<sub>1</sub>/*c*  
*a* = 10.0505 (5) Å  
*b* = 4.9326 (2) Å  
*c* = 15.4663 (7) Å  
 $\beta$  = 106.904 (3)°  
*V* = 733.61 (6) Å<sup>3</sup>  
*Z* = 2

*D<sub>x</sub>* = 1.387 Mg m<sup>-3</sup>  
 Mo *K*α radiation  
 Cell parameters from 100 reflections  
 $\theta$  = 7.7–19.7°  
 $\mu$  = 0.10 mm<sup>-1</sup>  
*T* = 293 (2) K  
 Rectangular block, colorless  
 0.50 × 0.36 × 0.30 mm

### Data collection

Bruker *P4* diffractometer  
 $\theta/2\theta$  scans  
 1899 measured reflections  
 1287 independent reflections  
 1078 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.026  
 $\theta_{\max}$  = 25.0°

*h* = –11 → 1  
*k* = –5 → 1  
*l* = –17 → 18  
 3 standard reflections every 100 reflections  
 intensity decay: average in σ(*I*)'s of 1.7%

**Table 3**  
Selected geometric parameters (Å, °) for (II).

O1—C6	1.233 (2)	C1—C1 <sup>i</sup>	1.458 (3)
N1—C4	1.464 (2)	C4—C5	1.518 (3)
N3—C6	1.328 (2)	C5—C6	1.509 (2)
N3—N4	1.417 (2)		
C1—N1—C4	129.90 (15)	N1—C4—C5	112.03 (14)
C2—N1—C4	123.6 (2)	C6—C5—C4	112.07 (15)
C6—N3—N4	123.37 (15)	O1—C6—N3	122.2 (2)
N2—C1—C1 <sup>i</sup>	125.1 (2)	O1—C6—C5	121.3 (2)
N1—C1—C1 <sup>i</sup>	123.9 (2)	N3—C6—C5	116.58 (15)

Symmetry code: (i)  $1 - x, 1 - y, 2 - z$ .**Table 4**  
Hydrogen-bonding geometry (Å, °) for (II).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N4—H4C...N2 <sup>i</sup>	0.90	2.47	3.367 (2)	174
N4—H4D...N4 <sup>ii</sup>	0.90	2.40	3.213 (2)	151
N3—H3A...O1 <sup>iii</sup>	0.90	2.03	2.923 (2)	176
C3—H3...O1 <sup>iv</sup>	0.96	2.56	3.441 (2)	152
C4—H4A...N2 <sup>v</sup>	0.96	2.32	2.960 (2)	123
C4—H4B...O1	0.96	2.55	2.900 (2)	102
C5—H5B...O1 <sup>vi</sup>	0.96	2.54	3.471 (2)	162

Symmetry codes: (i)  $1 - x, \frac{1}{2} + y, \frac{3}{2} - z$ ; (ii)  $2 - x, \frac{1}{2} + y, \frac{3}{2} - z$ ; (iii)  $x, y - 1, z$ ; (iv)  $1 - x, y - \frac{1}{2}, \frac{3}{2} - z$ ; (v)  $1 - x, 1 - y, 2 - z$ ; (vi)  $2 - x, 2 - y, 2 - z$ .

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.040$   
 $wR(F^2) = 0.101$   
 $S = 1.08$   
 1283 reflections  
 100 parameters  
 H atoms refined by a mixture of  
 constrained and independent  
 refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0496P)^2 + 0.2482P]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.18 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.19 \text{ e } \text{Å}^{-3}$

For (I), the water H atom, H2A, was first located in a difference map, then refined to produce an O2—H2A distance of 0.85 Å and an H2A—O2—H2A' angle of 105°. For both structures, all other H atoms were refined as riding, with C—H bond lengths constrained to 0.96 Å and N—H to 0.90 Å.

For both compounds, data collection: *P3/P4-PC Diffractometer Program* (Siemens, 1991); cell refinement: *P3/P4-PC Diffractometer Program*; data reduction: *XDISK* (Siemens, 1991); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990a); program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993); molecular graphics: *SHELXTL/PC* (Sheldrick, 1990b); software used to prepare material for publication: *SHELXTL/PC* and *SHELXL93*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1568). Services for accessing these data are described at the back of the journal.

### References

- Barnett, W. (1997). Unpublished doctoral dissertation, University of Missouri—Rolla, Rolla, MO, USA.
- Barnett, W. M., Collier, H. L., Baughman, R. G. & Vizuete, W. G. (1999). *J. Chem. Crystallogr.* **29**, 765–768.
- Barnett, W. M., Lin, G., Collier, H. L. & Baughman, R. G. (1997). *J. Chem. Crystallogr.* **27**, 423–427.
- Barnett, W. M., Secondo, P. M. & Collier, H. L. (1996). *J. Heterocycl. Chem.* **33**, 1363–1365.
- Chi, W. & Collier, H. (1988). *J. Macromol. Sci. Chem.* **25**, 1543–1555.
- Cromer, D., Ryan, R. & Storm, C. (1987). *Acta Cryst.* **C43**, 1435–1437.
- Elmer, R. A. & Collier, H. L. (1993). *Macromol. Rep.* **A30**, 1–11.
- Kirchner, C. & Krebs, B. (1987). *Inorg. Chem.* **26**, 3569–3576.
- Lister, R. L. & Collier, H. L. (1993). *Polym. Prepr.* **34**, 360–361.
- Lui, F. J., Kokorudz, J. S. & Collier, H. L. (1988). *J. Polym. Sci. Polym. Chem. Ed.* **26**, 3015–3029.
- Matthews, D. P., McCarthy, J. R., Whitten, J. P., Kastner, P. R., Barney, C. L., Marshall, F. N., Ertel, M. A., Burkhard, T., Shea, P. J. & Kariya, T. (1990). *J. Med. Chem.* **33**, 317–327.
- Melloni, P., Metilli, R., Bassini, D. F., Confalonieri, C., Logemann, W., de Carneri, I. & Trane, F. (1975). *Arzneim. Forsch.* **25**, 9–14.
- Overberger, C. G. & Vorchheimer, N. (1963). *J. Am. Chem. Soc.* **85**, 951–955.
- Secondo, P. M., Barnett, W. M., Collier, H. L. & Baughman, R. G. (1996). *Acta Cryst.* **C52**, 2636–2638.
- Sheldrick, G. M. (1990a). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1990b). *SHELXTL/PC*. Version 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (1993). *SHELXL93*. University of Göttingen, Germany.
- Siemens (1991). *P3/P4-PC Diffractometer Program* (Version 4.23) and *XDISK* (Version 4.20.2PC). Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.