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1,1'-Diketone and 1,1'-dinitrile Derivatives of 2,2'-biimidazole

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1,1′-Diketone and 1,1′-Dinitrile Derivatives of 2,2′-Biimidazole

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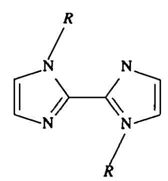
Abstract

The crystal structures of 2,2′-biimidazole-1,1′-diacetone, $C_{12}H_{14}N_4O_2$, and 2,2′-biimidazole-1,1′-diacetonitrile, $C_{10}H_8N_6$, have been determined. Both molecules crystallize with coplanar rings having substituents in a *trans* disposition with a center of inversion located midway between the bridging C atoms.

Comment

Derivatives containing the 2,2′-biimidazole moiety have been incorporated in the synthesis of various organic polymers (Liu, Kokorudz & Collier, 1988; Elmer & Collier, 1993) and macrocyclic complexes (Kandil & Collier, 1988; Lehn & Regnouf de Vains, 1989). The crystal structure determinations of 1,1′-di(2-propanone)-2,2′-biimidazole, (I), and 1,1′-di(cyaomethyl)-2,2′-biimidazole, (II), were undertaken to elucidate better the stereochemical reactivity of the molecules and to model the conformation of such macrocyclic and polymeric systems.



(I) $R = —CH_2COCH_3$
(II) $R = —CH_2CN$

In both structures, which lie about inversion centers, the biimidazole ring atoms (C1, C2, C3, N1, N2 and their inversion-related partners) exhibit an essentially coplanar conformation, as expected in an aromatic system. The two ten-atom least-squares planes have standard deviations and maximum values of 0.0018 and 0.0048, and 0.00042 and 0.0014 Å for (I) and (II), respectively. The C5 atoms are out of this plane by 1.312 (4) and 1.235 (3) Å and the values of the C1—N1—C4—C5 torsion angles are −70.5 (3) and −75.2 (2)° for (I) and (II), respectively. Although both (I) and (II) adopt a *trans* orientation in the solid state, ongoing investigations have demonstrated that both molecules assume a *cis* configuration when chelating a metal center through the N atoms. Bond lengths and angles lie within 1σ of observed ranges for 2,2′-biimidazole (Cromer, Ryan & Storm, 1987) and its related dinitro derivatives (Bryan *et al.*, 1995; Cromer & Storm, 1990).

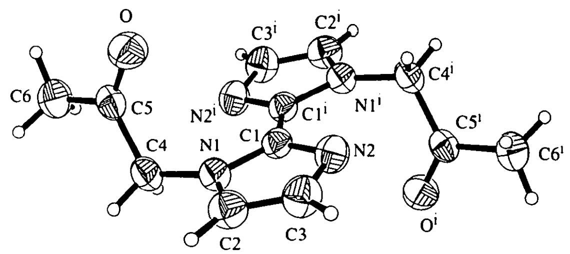


Fig. 1. View of (I) showing the labeling of the non-H atoms [symmetry code: (i) −*x*, 1 − *y*, 1 − *z*]. Displacement ellipsoids are shown at 50% probability levels; H atoms are drawn as small spheres of arbitrary radii.

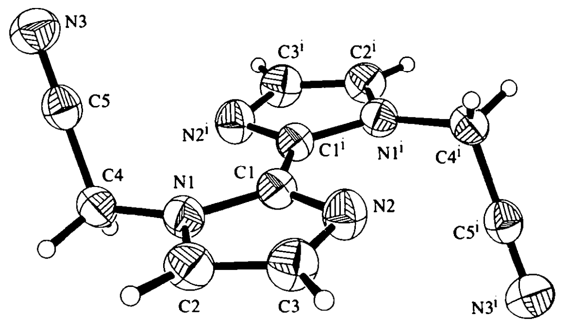


Fig. 2. View of (II) showing the labeling of the non-H atoms [symmetry code: (i) 1 − *x*, −*y*, 1 − *z*]. Displacement ellipsoids are shown at 50% probability levels; H atoms are drawn as small spheres of arbitrary radii.

Experimental

The preparation of (I) and (II) has been described by Barnett, Secondo & Collier (1996). Crystals were grown by slow evaporation from acetone and warm methanol for compounds (I) and (II), respectively.

Compound (I)

Crystal data

$C_{12}H_{14}N_4O_2$	Mo $K\alpha$ radiation
$M_r = 246.3$	$\lambda = 0.71073$ Å

Monoclinic
$P2_1/n$
$a = 8.1649\,(9)$ Å
$b = 8.6999\,(13)$ Å
$c = 8.9848\,(11)$ Å
$\beta = 110.744\,(9)°$
$V = 596.85\,(13)$ Å^3
$Z = 2$
$D_x = 1.370$ Mg m^{-3}
D_m not measured

Cell parameters from 50 reflections
$\theta = 6.61–20.65°$
$\mu = 0.097$ mm^{-1}
$T = 288\,(2)$ K
Block cut from prism
$0.50 \times 0.35 \times 0.25$ mm
Colorless

Data collection

Siemens *P*3 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
1842 measured reflections
1053 independent reflections
895 observed reflections $[I > 2\sigma(I)]$
$R_{int} = 0.0117$

$\theta_{max} = 25.05°$
$h = -2 \rightarrow 9$
$k = -2 \rightarrow 10$
$l = -10 \rightarrow 10$
3 standard reflections monitored every 50 reflections intensity decay: average of 1.5% in σ(I)'s

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0435$
$wR(F^2) = 0.1401$
$S = 1.146$
1047 reflections
82 parameters
H atoms riding, C—H 0.96 Å
$w = 1/[\sigma^2(F_o^2) + (0.0692P)^2 + 0.2406P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.268$ e Å^{-3}
$\Delta\rho_{min} = -0.210$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (I)*

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	*y*	*z*	U_{eq}
O	−0.0384 (2)	0.1411 (2)	0.6075 (2)	0.0565 (5)
N1	0.0224 (2)	0.3281 (2)	0.3837 (2)	0.0397 (5)
N2	0.2191 (2)	0.5125 (2)	0.4845 (2)	0.0455 (5)
C1	0.0606 (3)	0.4619 (2)	0.4688 (2)	0.0365 (5)
C2	0.1659 (3)	0.2938 (3)	0.3451 (3)	0.0483 (6)
C3	0.2838 (3)	0.4070 (3)	0.4066 (3)	0.0510 (6)
C4	−0.1351 (3)	0.2357 (3)	0.3418 (2)	0.0436 (5)
C5	−0.1571 (3)	0.1534 (2)	0.4804 (2)	0.0403 (5)
C6	−0.3326 (3)	0.0849 (3)	0.4484 (3)	0.0580 (7)

Table 2. *Selected geometric parameters (Å, °) for (I)*

O—C5	1.213 (2)	N2—C3	1.369 (3)
N1—C1	1.367 (3)	C1—C1^i	1.459 (4)
N1—C2	1.368 (3)	C2—C3	1.351 (3)
N1—C4	1.449 (3)	C4—C5	1.501 (3)
N2—C1	1.326 (3)	C5—C6	1.483 (3)
C1—N1—C2	106.3 (2)	C3—C2—N1	106.7 (2)
C1—N1—C4	128.6 (2)	C2—C3—N2	110.5 (2)
C2—N1—C4	125.1 (2)	N1—C4—C5	113.9 (2)
C1—N2—C3	105.1 (2)	O—C5—C6	122.8 (2)
N2—C1—N1	111.3 (2)	O—C5—C4	122.2 (2)
N2—C1—C1^i	125.3 (2)	C6—C5—C4	115.0 (2)
N1—C1—C1^i	123.4 (2)		

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

Compound (II)

Crystal data

$C_{10}H_8N_6$
$M_r = 212.2$
Monoclinic
$P2_1/c$
$a = 7.1044\,(9)$ Å
$b = 5.2590\,(5)$ Å
$c = 13.421\,(2)$ Å
$\beta = 99.646\,(10)°$
$V = 494.35\,(10)$ Å^3
$Z = 2$
$D_x = 1.426$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 50 reflections
$\theta = 6.00–21.39°$
$\mu = 0.096$ mm^{-1}
$T = 288\,(2)$ K
Block cut from prism
$0.56 \times 0.38 \times 0.31$ mm
Colorless

Data collection

Siemens *P*3 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
1792 measured reflections
877 independent reflections
772 observed reflections $[I > 2\sigma(I)]$
$R_{int} = 0.0201$

$\theta_{max} = 25.07°$
$h = 0 \rightarrow 8$
$k = -6 \rightarrow 6$
$l = -15 \rightarrow 15$
3 standard reflections monitored every 50 reflections intensity decay: average of 0.88% in σ(I)'s

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0367$
$wR(F^2) = 0.1034$
$S = 1.058$
869 reflections
73 parameters
H atoms riding, C—H 0.96 Å
$w = 1/[\sigma^2(F_o^2) + (0.0557P)^2 + 0.1297P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.200$ e Å^{-3}
$\Delta\rho_{min} = -0.215$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (II)*

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	*y*	*z*	U_{eq}
N1	0.6420 (2)	0.2278 (2)	0.58988 (9)	0.0341 (3)
N2	0.3271 (2)	0.1772 (3)	0.56128 (9)	0.0402 (4)
N3	0.9958 (2)	−0.2047 (3)	0.66917 (10)	0.0485 (4)
C1	0.4899 (2)	0.0988 (3)	0.53674 (10)	0.0327 (4)
C2	0.5680 (2)	0.3968 (3)	0.65148 (11)	0.0398 (4)
C3	0.3769 (2)	0.3631 (3)	0.63289 (11)	0.0426 (4)
C4	0.8438 (2)	0.2076 (3)	0.58292 (11)	0.0362 (4)
C5	0.9292 (2)	−0.0253 (3)	0.63137 (10)	0.0358 (4)

Table 4. *Selected geometric parameters (Å, °) for (II)*

N1—C1	1.370 (2)	N3—C5	1.136 (2)
N1—C2	1.377 (2)	C1—C1^i	1.456 (3)
N1—C4	1.456 (2)	C2—C3	1.351 (2)
N2—C1	1.321 (2)	C4—C5	1.469 (2)
N2—C3	1.375 (2)		
C1—N1—C2	106.54 (12)	N1—C1—C1^i	123.2 (2)
C1—N1—C4	129.03 (12)	C3—C2—N1	106.13 (13)
C2—N1—C4	124.37 (12)	C2—C3—N2	110.81 (13)
C1—N2—C3	105.22 (12)	N1—C4—C5	111.71 (12)
N2—C1—N1	111.30 (12)	N3—C5—C4	179.65 (13)
N2—C1—C1^i	125.5 (2)		

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

For both compounds, data collection: *P3/P4-PC Diffractometer Program* (Siemens, 1991*a*); cell refinement: *P3/P4-PC Diffractometer Program*; data reduction: *XDISK* (Siemens, 1991*b*); program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990*a*); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *SHELXTL/PC* (Sheldrick, 1990*b*); software used to prepare material for publication: *SHELXTL/PC* and *SHELXL*93.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1166). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Fluorene-9-carboxylic Acid

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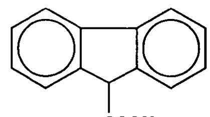
Abstract

In fluorene-9-carboxylic acid, $C_{14}H_{10}O_2$, there are two crystallographically independent sets of molecules each of which exhibits hydrogen bonding of the cyclic dimer type about a center of symmetry. Additionally, one of the sets shows disordering of the carboxyl O atoms. Within the carboxyl groups, however, the carboxyl H atoms were found to be, or modelled as, ordered.

Comment

This study of fluorene-9-carboxylic acid, (I), is the third in a series on hydrogen bonding in fluorene monocarboxylic acids, studies of fluorene-1-carboxylic acid (F1C*A*) and fluorene-4-carboxylic acid (F4C*A*) having been reported previously (Blackburn, Dobson & Gerkin, 1996*a*,*b*).



(I)

The hydrogen bonding is of the cyclic dimer type about a center of symmetry, as shown in Fig 1. The C—O and O—H distances found in the *B* molecule carboxyl group (Table 2) are entirely consistent with an ordered carboxylic H atom; in the disordered carboxyl group of the *A* molecule, the C—O distances and the Fourier difference map, from which the H-atom positions were assigned, strongly suggest the interpretation that these H atoms are also ordered. The dihedral angle between the planes of the disordered carboxyl groups (O1*A*—C14—O2*A* and O1*A**–C14—O2*A**) is 55.8°. The donor–acceptor distances are (as in F1C*A* and F4C*A*) below average for organic O···O hydrogen bonds (2.77 Å; Ceccarelli, Jeffrey & Taylor, 1981).

With respect to interatomic distances in the fluorene core, the two independent molecules reported here exhibit pseudo-mirror symmetry to within smaller deviations than in the cases of F1C*A* and F4C*A*: the r.m.s. deviations within the seven pairs of core distances which would be identical under mirror symmetry are 0.004 (3) and 0.005 (3) Å, respectively, for the *A* and *B* molecules. The one unique core interatomic distance, C11—C12, has values of 1.463 (3) and 1.470 (3) Å for *A* and *B*, respectively; in our report on F4C*A* we surmised that further measurements of this distance would very probably fall in the range from 1.471–1.492 Å.

As in describing F1C*A* and F4C*A*, we have chosen best-fit planes for atoms C1–C4, C10 and C11 and atoms C5–C8, C12 and C13 to define the molecular dihedral angle. The maximum distance of any of these atoms from the best-fit plane including that atom is 0.004 (3) Å for the *A* molecule, 0.006 (3) Å for the *B* molecule; these distances are less than those for F1C*A* or F4C*A*. The resulting molecular dihedral angle is 0.2 (1)° for *A* and 1.2 (1)° for the *B* molecule, values closest to those for fluorene itself at room temperature (Belsky, Zavodnik &