ORGANIC COMPOUNDS

Acta Cryst. (1995). C**51**, 2300–2301

4,4′-Dinitro-2,2′-biimidazole Dimethylformamide Solvate

CLINTON D. BRYAN, SYRONA SCOTT, A. WALLACE CORDES AND SUSAN L. FOLKERT

Department of Chemistry and Biochemistry, University of Arkansas, Fayetteville, AR 72701, USA

COLIN HESTER AND HARVEST COLLIER

Department of Chemistry, University of Missouri-Rolla, Rolla, MO 65401, USA

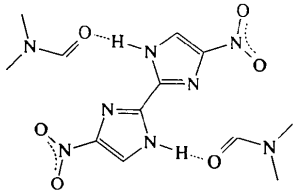
(*Received* 5 *October* 1994; *accepted* 29 *March* 1995)

Abstract

The title molecules, $C_6H_4N_6O_4.2C_3H_7NO$, lie on a center of inversion. One N atom of the ring is hydrogen bonded to the O atom of the dimethylformamide (DMF) solvate molecule [N—H···O = 2.699 (4) Å]. The nitro group is tilted by 4.11 (18)° with respect to the imidazole ring.

Comment

Derivatives of 2,2′-biimidazole have been incorporated into the backbone of organic polymers (Lister & Collier, 1993; Elmer & Collier, 1993) and were found to effectively bind transition metal ions. The structure determination of the title compound, (I), was undertaken to better model the conformation of such polymers.



(I)

The asymmetric unit consists of one-half of $C_6H_4N_6O_4$ and one DMF molecule. The imidazole ring atoms (C1, C2, C3, N1 and N2) are essentially coplanar (χ^2 = 2.772), with a maximum deviation from the mean plane of −0.005 Å by atom C2. The nitro group (N3, O1 and O2) is twisted out of the ring plane by 4.11 (18)°. The DMF molecule is hydrogen bonded through its carbonyl O atom to the H atom on the pyridial-type N atom of the imidazole ring [N1—H1···O3 = 2.699 (4) Å]. Molecular parameters are comparable to those of 2,2′-biimidazole (Cromer, Ryan & Storm, 1987), 4,4′,5,5′-tetranitro-2,2′-biimidazole (Cromer & Storm, 1990*a*) and its diammonium salt (Cromer & Storm, 1990*b*).

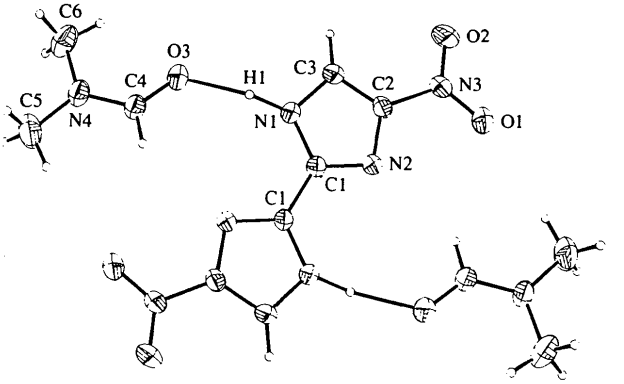


Fig. 1. An *ORTEP*II (Johnson, 1976) drawing of the title molecule with 30% probability ellipsoids and showing the atom-numbering scheme.

Experimental

The preparation of 4,4′-dinitro-2,2′-biimidazole has been described by Melloni, Dradi, Logemann, de Carneri & Trane (1972). Crystals were grown by slow evaporation of a dimethylformamide solution.

Crystal data

$C_6H_4N_6O_4.2C_3H_7NO$
M_r = 370.32
Monoclinic
$P2_1/n$
a = 6.336 (4) Å
b = 7.986 (5) Å
c = 17.602 (9) Å
β = 92.88 (6)°
V = 889.5 (9) Å^3
Z = 2
D_x = 1.383 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.7107 Å
Cell parameters from 25 reflections
θ = 7.50–9.50°
μ = 0.11 mm^{-1}
T = 293 K
Block
0.68 × 0.40 × 0.16 mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
T_{min} = 0.939, T_{max} = 0.999
2106 measured reflections
1931 independent reflections
823 observed reflections [$I > 3\sigma(I)$]
R_{int} = 0.013
θ_{max} = 26.90°
$h = -8 \rightarrow 8$
$k = 0 \rightarrow 10$
$l = 0 \rightarrow 22$
3 standard reflections
frequency: 60 min
intensity decay: 0.7%

Refinement

Refinement on F
R = 0.051
wR = 0.067
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.20 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 e Å^{-3}

S = 1.07	Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)
823 reflections	
118 parameters	
H-atom parameters not refined	
$w = 1/[\sigma^2(F) + 0.0025F^2]$	

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

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

	x	y	z	U_{eq}
O1	0.3970 (5)	0.5842 (4)	0.12462 (17)	0.0663 (19)
O2	0.3624 (5)	0.8306 (4)	0.07665 (18)	0.0682 (19)
O3	1.1612 (5)	0.8732 (3)	−0.12086 (17)	0.0651 (18)
N1	0.9182 (5)	0.7181 (4)	−0.02070 (16)	0.0451 (17)
N2	0.7577 (5)	0.5309 (4)	0.04994 (16)	0.0417 (17)
N3	0.4570 (5)	0.6983 (5)	0.08543 (17)	0.0470 (18)
N4	1.4373 (6)	0.8844 (4)	−0.19648 (19)	0.054 (2)
C1	0.9185 (6)	0.5601 (4)	0.0077 (2)	0.038 (2)
C2	0.6497 (6)	0.6778 (5)	0.04699 (19)	0.041 (2)
C3	0.7445 (6)	0.7955 (5)	0.0046 (2)	0.046 (2)
C4	1.3316 (7)	0.8211 (5)	−0.1409 (2)	0.049 (2)
C5	1.6414 (9)	0.8150 (8)	−0.2148 (3)	0.097 (4)
C6	1.3567 (8)	1.0271 (7)	−0.2393 (3)	0.082 (3)

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

O1—N3	1.215 (5)	N3—C2	1.435 (5)
O2—N3	1.221 (5)	N4—C4	1.314 (5)
O3—C4	1.225 (5)	N4—C5	1.458 (6)
N1—C1	1.357 (5)	N4—C6	1.446 (6)
N1—C3	1.357 (5)	C1—C1′	1.446 (7)
N2—C1	1.312 (5)	C2—C3	1.358 (5)
N2—C2	1.358 (5)		
C1—N1—C3	106.8 (3)	N2—C1—C1′	124.8 (3)
C1—N2—C2	103.2 (3)	N2—C2—N3	121.3 (3)
O1—N3—O2	123.7 (3)	N2—C2—C3	112.5 (3)
O1—N3—C2	118.7 (3)	N3—C2—C3	126.2 (3)
O2—N3—C2	117.6 (3)	N1—C3—C2	104.7 (3)
C4—N4—C5	120.7 (4)	O3—C4—N4	125.0 (4)
C4—N4—C6	120.8 (4)	C1—N1—H1	136.4 (8)
C5—N4—C6	118.6 (4)	C3—N1—H1	116.5 (8)
N1—C1—N2	112.8 (3)	C4—O3—H1	125.8 (5)
N1—C1—C1′	122.4 (3)		

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O3	1.047	1.681	2.699 (4)	163.2 (11)

The data crystal was sealed in an epoxy-filled capillary tube. The intensity scans were of width $(1.0 + 0.35\tan\theta)°$, with scan speeds of 4–16° min^{-1}. The total exposure time was 14.6 h. The structure was solved by direct methods. The H atoms were constrained to idealized (C—H = 0.95, N—H = 0.90 Å) positions where the orientation of the methyl groups and the direction of the N—H vector was determined by difference maps. All H atoms were assigned isotropic U values of 0.01 Å^2 plus the value of U of the attached N or C atom.

Data collection: *CAD-4-PC* (Enraf–Nonius, 1993). Cell refinement: *CAD-4-PC*. Data reduction: *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *NRCVAX*. Program(s) used to refine structure: *NRCVAX*. Molecular graphics: *NRCVAX*. Software used to prepare material for publication: *NRCVAX*.

SF acknowledges the support of a SILO Undergraduate Research Fellowship.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: SZ1034). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Cromer, D. T., Ryan, R. R. & Storm, C. B. (1987). *Acta Cryst.* C**43**, 1435–1437.
Cromer, D. T. & Storm, C. B. (1990*a*). *Acta Cryst.* C**46**, 1957–1958.
Cromer, D. T. & Storm, C. B. (1990*b*). *Acta Cryst.* C**46**, 1959–1960.
Elmer, R. & Collier, H. (1993). *Macromol. Rep.* **A30**, 1–11.
Enraf–Nonius (1993). *CAD-4-PC*. Version 1.2. Enraf–Nonius, Delft, The Netherlands.
Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Lister, R. & Collier, H. (1993). *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.* **34**, 360–361.
Melloni, P., Dradi, E., Logemann, W., de Carneri, I. & Trane, F. (1972). *J. Med. Chem.* **15**, 926–930.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Acta Cryst. (1995). C**51**, 2301–2304

(1*S*,8*S*,8a*S*)-(+)-1-(*tert*-Butyldimethylsilyloxy)-8-hydroxy-1,2,3,5,6,7,8,8a-octahydro-5-indolizinone

DUY H. HUA, NADEGE LAGNEAU, JEWN-GIEW PARK AND LINDA A. GOOD

Department of Chemistry, Kansas State University, Manhattan, KS 66506, USA

PAUL D. ROBINSON

Department of Geology, Southern Illinois University, Carbondale, IL 62901, USA

(*Received* 28 *February* 1995; *accepted* 7 *April* 1995)

Abstract

The title compound, $C_{14}H_{27}NO_3Si$, obtained in good yield from a three-step sequence of reactions starting from (4*S*,5*R*)-4-(*tert*-butyldimethylsilyloxy)-3,4-dihydro-5-[(*p*-tolylsulfinyl)methyl]-2*H*-pyrrole, serves as a key intermediate in a study of the total synthesis of (+)-castanospermine. The six-membered lactam ring can be best described as having a distorted envelope conformation.