

Acta Cryst. (1998). **C54**, 1018–1019

2,5-Diamino-3,6-dichloropyrazine

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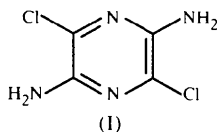
(Received 24 November 1997; accepted 19 January 1998)

Abstract

The synthesis and crystal structure of 2,5-diamino-3,6-dichloropyrazine, C₄H₄Cl₂N₄, are described. The centrosymmetric molecule has an exocyclic C—N distance of 1.362 (3) Å and a nearly planar amine group [the angles at nitrogen sum to 351 (2)°]. Within the crystal, the molecules form a ribbon through two centrosymmetric pairs of N—H···N hydrogen-bond interactions, where the N···N distance is 3.110 (3) Å.

Comment

Both 2,3-diamino-5,6-dichloro- and 2,6-diamino-3,5-dichloropyrazine have been known for many years; they are formed by the reaction of aqueous ammonia with tetrachloropyrazine (Palmidessi & Luini, 1966). The 2,5-isomer is not produced. The parent 2,5-diaminopyrazine is known, but its preparation is lengthy (Sharefkin & Spoerri, 1951). We report herein the synthesis and structural details of 2,5-diamino-3,6-dichloropyrazine, (I).



The entire molecule, which is located on a center of symmetry, is planar within 0.015 (3) Å. The bond distances and angles are all within four e.s.d.'s of the corresponding values found for 2-amino-3-chloropyrazine (Morrow & Huddle, 1972), including the exocyclic C—N distance of 1.362 (3) Å and the relative planarity of the amine N atom [the sum of the angles at N1 is 351 (2)°]. Interestingly, there are no N—H···Cl hydrogen bonds; the only hydrogen bond is N1—H1···N2' with an H···N separation of 2.21 (2) Å and an N—H···N angle of 168 (2)° (N2' = N2 at $z - 1$). The hydrogen bonding links the molecules together in chains, parallel to the crystallographic *c* axis, as opposed to the three-dimensional hydrogen-bonding

arrangements of 2-amino-3-chloropyrazine (Morrow & Huddle, 1972) or *para*-phenylenediamine (Povet'eva & Zvonkova, 1975).

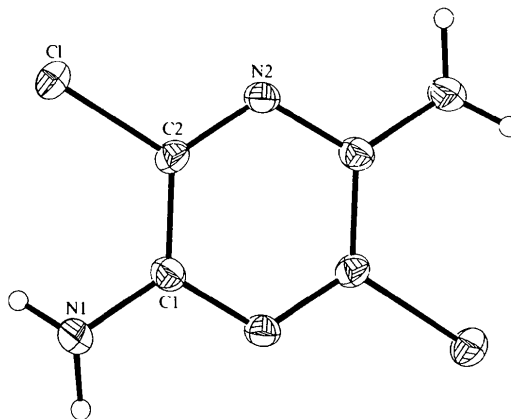


Fig. 1. ORTEP (Johnson, 1976) plot of C₄H₄Cl₂N₄ with the atomic labeling scheme. The ellipsoids are drawn at the 30% probability level. The H atoms have artificially small displacement parameters for clarity.

Experimental

The title compound was prepared by treating tetrachloropyrazine (Allison *et al.*, 1966) with two equivalents of potassium phthalimide in dimethylformamide at 323 K for 16 h. The reaction was quenched with water to precipitate the intermediate diphtalimide. The latter was hydrolyzed by aqueous hydrazine to give 2,5-diamino-3,6-dichloropyrazine, which was recrystallized from ethanol as yellow flakes (sublimation point 453 K). Crystals suitable for X-ray work were grown by sublimation *in vacuo*.

Crystal data

C₄H₄Cl₂N₄
M_r = 179.01
 Monoclinic
*P*2₁/*n*
a = 3.7582 (4) Å
b = 14.5505 (15) Å
c = 6.2451 (6) Å
 β = 101.162 (8)°
V = 335.05 (6) Å³
Z = 2
D_x = 1.774 Mg m⁻³
D_m not measured

Mo *K*α radiation
 λ = 0.7107 Å
 Cell parameters from 25 reflections
 θ = 12–15°
 μ = 0.89 mm⁻¹
T = 293 K
 Block
 0.42 × 0.32 × 0.26 mm
 Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
 $\theta/2\theta$ scan
 Absorption correction: analytical (ABSORB; Gabe *et al.*, 1989)
 T_{\min} = 0.754, T_{\max} = 0.813
 1617 measured reflections
 765 independent reflections

765 reflections with $I_{\text{net}} > 0$
 R_{int} = 0.026
 θ_{max} = 27.40°
 h = -4 → 4
 k = -18 → 18
 l = 0 → 8
 3 standard reflections
 frequency: 60 min
 intensity decay: 2.0%

RefinementRefinement on F^2 $R(F) = 0.033$ $wR(F^2) = 0.063$ $S = 1.08$

757 reflections

54 parameters

All H atoms refined

 $w = 1/[\sigma^2(F) + 0.0025F^2]$ $(\Delta/\sigma)_{\max} < 0.001$ $\Delta\rho_{\max} = 0.26 \text{ e } \text{Å}^{-3}$ $\Delta\rho_{\min} = -0.25 \text{ e } \text{Å}^{-3}$

Extinction correction: none

Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Palmidessi, G. & Luini, F. (1966). *Farmaco Ed. Sci.* **21**, 811–817.
 Povet'eva, Z. P. & Zvonkova, Z. V. (1975). *Kristallografiya*, **20**, 69–73.
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Table 1. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

U_{iso} for H atoms, $U_{\text{eq}} = (1/3)\sum_i \sum_j U^{ij} a^i a^j$ for C and N atoms.

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}/U_{\text{eq}}$
C1	0.67959 (15)	0.81283 (3)	0.06751 (10)	0.0378 (3)
N1	0.8140 (7)	0.89041 (14)	-0.3591 (4)	0.0475 (14)
N2	0.9522 (5)	0.97172 (11)	0.2038 (3)	0.0303 (10)
C1	0.8998 (6)	0.94546 (13)	-0.1801 (4)	0.0305 (12)
C2	0.8597 (6)	0.91998 (12)	0.0281 (4)	0.0286 (11)
H1	0.819 (6)	0.9172 (13)	-0.491 (4)	0.052 (8)
H2	0.658 (6)	0.8492 (13)	-0.354 (4)	0.057 (9)

Table 2. Selected geometric parameters (Å , $^\circ$)

C1—C2	1.7361 (19)	N2—C1'	1.347 (3)
N1—C1	1.362 (3)	N2—C2	1.321 (3)
N1—H1	0.91 (2)	C1'—N2	1.347 (3)
N1—H2	0.84 (2)	C1—C2	1.388 (3)
C1—N1—H1	116.4 (13)	N1—C1—C2	124.07 (19)
C1—N1—H2	116.4 (16)	N2'—C1—C2	117.63 (19)
H1—N1—H2	118 (2)	C1—C2—N2	116.18 (15)
C1'—N2—C2	117.80 (17)	C1—C2—C1	119.25 (16)
N1—C1—N2'	118.2 (2)	N2—C2—C1	124.57 (17)

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

The structure was solved using direct methods. The H atoms were found on a difference map and were refined isotropically.

Data collection: *CAD-4-PC Software* (Enraf–Nonius, 1994). Cell refinement: *CAD-4-PC Software*. Data reduction: *DATRD2* in *NRCVAX* (Gabe *et al.*, 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*.

Financial support at Guelph was provided by the Natural Science Foundation Engineering Research Council of Canada (NSERC) and at Arkansas by the National Science Foundation, USA (EPSCOR program). TMB acknowledges a DOE Fellowship.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1107). Services for accessing these data are described at the back of the journal.

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1,5,7,11-Tetraoxaspiro[5.5]undecane, 3,9-Dimethylidene-1,5,7,11-tetraoxaspiro[5.5]undecane and 1,5-Dioxo-7,11-dithiaspiro[5.5]undecane

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(Received 15 August 1997; accepted 6 January 1998)

Abstract

In all three title compounds, $\text{C}_7\text{H}_{12}\text{O}_4$, (1), $\text{C}_9\text{H}_{12}\text{O}_4$, (2), and $\text{C}_7\text{H}_{12}\text{O}_2\text{S}_2$, (3), the spiro C—O distances are substantially shorter than the non-spiro C—O distances as a result of the anomeric effect. In contrast, the spiro C—S distances of compound (3) are similar to the non-spiro C—S distances. In all three compounds, steric repulsions between the lone pairs on the O or S atoms and the axial H atoms of the opposite ring result in a distorted geometry around the spiro-C atoms.

Comment

Bicyclic spiro-orthocarbonates (SOCs) and spiro-thio-orthocarbonates (STOCs) have been extensively studied, particularly in the area of polymer chemistry, the depth of work leading to the publication of a monograph (Sadhir & Luck, 1992). As O-heteroatom SOC's have demonstrated more potential for polymerization than their S- and N-heteroatom counterparts, these compounds have been studied in greater detail. Very little attention has been given to mixed-heteroatom systems, which appears to be due mainly to the lack of appropriate synthetic procedures. Our recent work (Bromley *et al.*, 1998) has developed a synthetic route to O/S-hybrid