the single crystal diffractometer and auxiliary equipment (Project P1-092)

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HA1145). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). C**52**, 705–707

Ethyl 2-[(*E*)-5-Chloro-2-hydroxy-4-nitrophenylazo]-3-(*E*)-amino-2-butenoate

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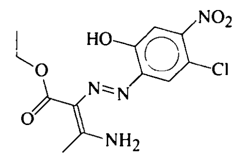
Abstract

The title molecule, $C_{12}H_{13}ClN_4O_5$, has two intramolecular hydrogen bonds (O1—H11···N3 and N4—H42···N2) and π-electron delocalization in the azoenamine group. Adjacent molecules in the crystal are linked through N—H···O hydrogen bonds and this results in an infinite chain structure.

Comment

Enaminones are compounds with interesting structural characteristics, such as distinct geometric forms (Eberlin, Takahata & Kascheres, 1990) and tautomerism between oxo, imino and enol forms (Naringrekar & Stella, 1990).

An *ORTEP* (Johnson, 1965) drawing of the title compound, (I), is presented in Fig. 1. The molecule has the oxo tautomeric form and the *E,s-Z* geometric form. The compound has two intramolecular hydrogen bonds, namely O1—H11···N3 [O1—H11 0.92 (6), O1···N3 2.568 (6) Å, O1—H11···N3 129 (5)°] and N4—H42···N2 [N4—H42 0.94 (6), N4···N2 2.584 (7) Å, N4—H42···N2 126 (5)°]. The hydrogen bond between atoms N4 and N2 may be responsible for the presence of the *E,s-Z* configuration in the compound.



(I)

The crystal packing involves N4—H41 ··O4^{i} intermolecular hydrogen bonds [N4—H41 0.92 (6), N4···O4^{i} 2.910 (7) Å, N4—H41···O4^{i} 169 (5)°; symmetry code: (i) $x, \frac{3}{2}-y, -\frac{1}{2}+z$], resulting in an infinite chain structure in the *c* direction. A stereoscopic view of the crystal packing is presented in Fig. 2.

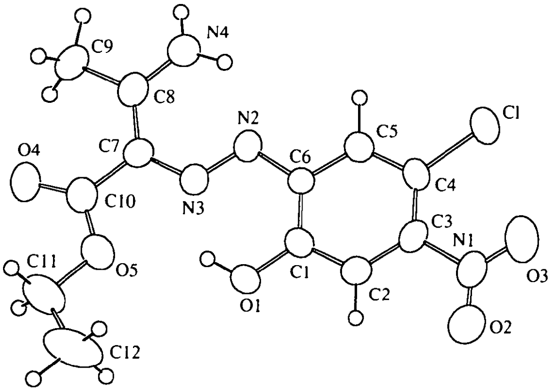


Fig. 1. View of the title compound (displacement ellipsoids are shown at 50% probability levels and H atoms as small circles of arbitrary radii) including the atom numbering.

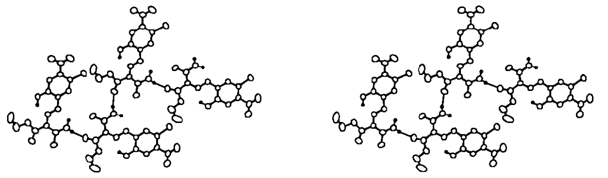


Fig. 2. Stereoscopic view of the crystal packing showing the intermolecular hydrogen bonding.

The π-electron delocalization is another interesting feature of enamines (Schwotzer & Philipsborn, 1977). The title compound exhibits delocalization in the azoenamine group. This can be inferred from a shortening of the C7—C10 [1.451 (9) Å] and C8—N4 [1.314 (9) Å] single bonds, and a lengthening of the N2═N3 [1.300 (7) Å] and C7═C8 [1.422 (8) Å] double bonds.

Experimental

Crystals of the title compound were obtained by slow evaporation of a saturated chloroform solution.

Crystal data

$C_{12}H_{13}ClN_4O_5$
$M_r = 328.71$
Monoclinic
$P2_1/c$
$a = 9.238\ (2)$ Å
$b = 14.388\ (3)$ Å
$c = 11.763\ (2)$ Å
$\beta = 109.40\ (2)°$
$V = 1474.8\ (5)$ Å^3
$Z = 4$
$D_x = 1.480$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 11–19°$
$\mu = 0.284$ mm^{-1}
$T = 298$ K
Prismatic
0.5 × 0.3 × 0.3 mm
Red

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2089 measured reflections
2089 independent reflections
1062 observed reflections [$F > 6\sigma(F)$]

$\theta_{\max} = 26.29°$
$h = -11 \rightarrow 10$
$k = 0 \rightarrow 17$
$l = 0 \rightarrow 14$
3 standard reflections
frequency: 120 min
intensity decay: 2.3%

Refinement

Refinement on F^2
$R(F) = 0.0447$
$wR(F^2) = 0.0563$
$S = 1.44$
1062 reflections
224 parameters
$w = 1/[\sigma^2(F) + 0.0001F^2]$
$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.203$ e Å^{-3}
$\Delta\rho_{\min} = -0.242$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.3.1)

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

$B_{\rm iso}$ for H atoms; $B_{\rm eq} = (8\pi^2/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ for others.

	x	y	z	$B_{\rm eq}/B_{\rm iso}$
Cl	0.0141 (2)	0.3969 (1)	0.1471 (1)	4.91 (6)
O1	−0.1739 (5)	0.3766 (3)	0.5770 (3)	4.3 (2)
O2	0.0899 (6)	0.1624 (3)	0.4000 (5)	7.8 (2)
O3	0.1472 (5)	0.2312 (3)	0.2630 (4)	6.7 (2)
O4	−0.4765 (4)	0.6527 (3)	0.6830 (3)	4.7 (1)
O5	−0.3624 (4)	0.5147 (3)	0.6916 (3)	4.3 (1)
N1	0.0812 (6)	0.2284 (4)	0.3359 (5)	4.2 (2)
N2	−0.2454 (5)	0.5402 (3)	0.4132 (4)	3.3 (1)
N3	−0.2910 (4)	0.5371 (3)	0.5065 (4)	3.1 (1)
N4	−0.3687 (6)	0.7030 (4)	0.3650 (5)	4.4 (2)
C1	−0.1329 (6)	0.3834 (4)	0.4771 (5)	3.3 (2)
C2	−0.0529 (6)	0.3084 (4)	0.4524 (5)	3.5 (2)
C3	−0.0060 (6)	0.3108 (4)	0.3530 (6)	3.4 (2)
C4	−0.0371 (6)	0.3859 (4)	0.2746 (4)	3.2 (2)
C5	−0.1164 (6)	0.4598 (4)	0.3006 (5)	3.3 (2)
C6	−0.1658 (6)	0.4595 (4)	0.3996 (5)	2.8 (2)
C7	−0.3720 (6)	0.6096 (4)	0.5301 (5)	3.3 (2)
C8	−0.4147 (6)	0.6911 (4)	0.4584 (6)	3.5 (2)
C9	−0.5117 (7)	0.7671 (4)	0.4812 (6)	4.8 (2)
C10	−0.4115 (6)	0.5968 (5)	0.6386 (5)	3.4 (2)
C11	−0.3828 (8)	0.4990 (5)	0.8065 (6)	5.8 (3)
C12	−0.2995 (8)	0.4118 (6)	0.8544 (7)	7.8 (3)
H11	−0.216 (6)	0.429 (4)	0.598 (5)	6.0
H41	−0.405 (7)	0.753 (4)	0.315 (6)	6.0
H42	−0.307 (6)	0.660 (4)	0.342 (5)	6.0

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

C1—O1	1.353 (8)	N2—N3	1.300 (7)
O1—H11	0.92 (6)	N3—C7	1.365 (8)
C1—C2	1.392 (8)	C7—C8	1.422 (8)
C2—C3	1.38 (1)	C8—C9	1.493 (9)
C3—N1	1.484 (8)	C8—N4	1.314 (9)
N1—O2	1.199 (8)	N4—H41	0.92 (6)
N1—O3	1.207 (9)	N4—H42	0.94 (6)
C3—C4	1.387 (8)	C7—C10	1.451 (9)
C4—Cl	1.723 (6)	C10—O4	1.220 (8)
C4—C5	1.382 (8)	C10—O5	1.342 (8)
C5—C6	1.385 (9)	O5—C11	1.443 (9)
C6—C1	1.392 (8)	C11—C12	1.48 (1)
C6—N2	1.412 (7)		
C6—C1—O1	124.2 (5)	N4—C8—C7	120.0 (6)
C6—C1—C2	119.2 (6)	N4—C8—C9	115.8 (5)
O1—C1—C2	116.5 (5)	C7—C8—C9	124.2 (6)
C1—C2—C3	119.8 (5)	O4—C10—C7	126.6 (6)
N1—C3—C2	115.7 (5)	O4—C10—O5	121.3 (6)
N1—C3—C4	122.3 (6)	C7—C10—O5	112.0 (6)
C2—C3—C4	122.0 (6)	O5—C11—C12	106.0 (6)
Cl—C4—C3	126.4 (5)	O2—N1—O3	122.0 (6)
Cl—C4—C5	116.2 (4)	O2—N1—C3	118.3 (6)
C3—C4—C5	117.4 (6)	O3—N1—C3	119.6 (5)
C6—C5—C4	122.1 (5)	C6—N2—N3	113.2 (4)
N2—C6—C1	125.5 (5)	N2—N3—C7	119.9 (5)
N2—C6—C5	115.0 (5)	H41—N4—H42	117 (6)
C1—C6—C5	119.5 (5)	H41—N4—C8	119 (5)
C10—C7—N3	113.4 (5)	H42—N4—C8	123 (4)
C10—C7—C8	121.7 (6)	C1—O1—H11	116 (4)
N3—C7—C8	124.9 (6)	C10—O5—C11	116.3 (5)

The H11, H41 and H42 atoms, which contribute to the hydrogen bonds, were located in the difference Fourier synthesis and their coordinates were refined. All other H atoms were refined as riding.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *SDP* (Frenz, 1978). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELX*76 (Sheldrick, 1976). Molecular graphics: *ORTEP* (Johnson, 1965).

We thank CNPq for financial support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CR1204). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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The Hemi-Adduct of Bis(diethyldithiocarbamato-*S*,*S*′)tellurium(II) with 4,4′-Bipyridyl

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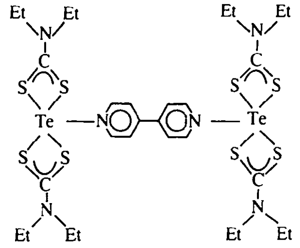
Abstract

In the structure of bis(diethyldithiocarbamato-*S*,*S*′)-tellurium(II)-4,4′-bipyridyl (2/1), $[\mathrm{Te(C_5H_{10}NS_2)_2}].\frac{1}{2}\mathrm{C_{10}H_8N_2}$, the bipyridyl molecule was found to bridge two bis(diethyldithiocarbamato)tellurium moieties centrosymmetrically, *i.e.* μ-(4,4′-bipyridyl-*N*:*N*′)-bis(diethyldithiocarbamato-*S*,*S*′)tellurium. The N atom of the bipyridyl is very weakly coordinated to tellurium and this is the first instance of Te—N coordination observed in a tellurium–dithiocarbamate complex. Each Te atom has an unusual planar-pentagonal arrangement of ligands around it.

Comment

The structure of TeL_2 (L = diethyldithiocarbamate) (Fabiani, Spagna, Vaciago & Zambonelli, 1971) reveals the geometry around the Te atom to be essentially trapezoidal, with the two S atoms from each of the dithiocarbamate groups bonded to the Te atom in a highly anisobidentate manner. In addition, the Te atom exerts a very weak interaction in the same plane with an S atom from a neighbouring TeL_2 moiety leading to a bridged dimer. In order to examine whether other ligands could possibly occupy this fifth coordination site, the reactions of TeL_2 with the nitrogen bases pyridine, 1,10-phenanthroline, 2,2′-bipyridyl and 4,4′-bipyridyl were carried out. We were successful in the isolation of an adduct with 4,4′-bipyridyl only, (I), and its structure is presented here.



(I)

The structure determination of (I) reveals the title compound to be a binuclear species bridged centrosymmetrically by a 4,4′-bipyridyl molecule, as shown in Fig. 1. The dithiocarbamate ligand is bound in an anisobidentate manner, with two short and two long Te—S bonds. The two short bond distances are 2.624 (1) for Te—S(1) and 2.573 (1) Å for Te—S(4), while the two long Te—S(2) and Te—S(3) bonds are 2.826 (1) and 2.720 (1) Å, respectively. The Te—S distances are longer than the sum of the covalent radii of the individual atoms (2.41 Å; Pauling, 1960). The average short Te—S distance of 2.599 Å is longer, while the average long Te—S distance of 2.773 Å is shorter, compared with the average short and long Te—S distances observed in TeL_2 (2.519 and 2.861 Å). Within the chelated dithiocarbamate ligands, the S—Te—S angles are 65.37 (2) and 67.04 (2)°. The angle at Te between the two closest S atoms, S(1) and S(4), is 80.2 (2)°, while that between the two distant S atoms, S(2) and S(3), is 147.4 (2)°. In the adduct, the Te—N bond replaces the weak fifth Te—S bond observed in the structure of TeL_2. The Te—N(3) vector bisects the S(2)—Te—S(3) angle almost equally [angles S(2)—Te—N(3) and S(3)—Te—N(3) are 74.0 (1) and 73.6 (1)°, respectively]. The Te—N distance of 2.700 (2) Å in the title compound is much greater than the sum of the individual covalent radii of Te and N (2.04 Å). This distance is also greater than the Te—N distance observed in the $\mathrm{Te^{II}}$ complex $[\mathrm{Te\{N(SiMe_3)_2\}_2}]$ (2.05 Å; Bjoergvinsson, Roesky, Pauer, Stalke & Sheldrick, 1990) and in many other compounds, where it ranges between 1.98 and 2.10 Å (Johnson, Maclean, Passmore & White, 1989; Bjoergvinsson & Roesky, 1991). A similar weak Te—N interaction is seen in the previously reported

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