C3	−0.0515 (4)	0.6706 (3)	0.22626 (9)	0.0172 (5)
C4	−0.2326 (4)	0.7744 (3)	0.23723 (9)	0.0154 (5)
C5	−0.3234 (4)	0.8731 (3)	0.19891 (9)	0.0171 (5)
C6	−0.2405 (4)	0.8648 (3)	0.15238 (9)	0.0171 (5)
C7	0.1977 (4)	0.9331 (3)	0.06816 (10)	0.0189 (5)
C8	0.2104 (4)	0.5727 (3)	0.07349 (10)	0.0195 (5)
C9	−0.1867 (4)	0.7432 (3)	0.03677 (9)	0.0183 (5)
C10	−0.2044 (4)	0.6942 (3)	0.32375 (9)	0.0225 (5)
C11	−0.5154 (4)	0.8768 (3)	0.29290 (10)	0.0226 (6)

Table 5. *Selected geometric parameters* (Å, °) *for* (II)

P1—C1	1.784 (2)	C1—C6	1.400 (3)
P1—C8	1.785 (2)	C1—C2	1.401 (3)
P1—C9	1.788 (2)	C2—C3	1.388 (3)
P1—C7	1.793 (2)	C3—C4	1.413 (3)
N1—C4	1.373 (3)	C4—C5	1.415 (3)
N1—C11	1.456 (3)	C5—C6	1.379 (3)
N1—C10	1.457 (3)		
C1—P1—C8	110.1 (1)	C6—C1—P1	120.5 (2)
C1—P1—C9	110.1 (1)	C2—C1—P1	121.8 (2)
C8—P1—C9	109.6 (1)	C3—C2—C1	121.6 (2)
C1—P1—C7	110.7 (1)	C2—C3—C4	120.6 (2)
C8—P1—C7	108.6 (1)	N1—C4—C3	121.3 (2)
C9—P1—C7	107.8 (1)	N1—C4—C5	121.1 (2)
C4—N1—C11	120.4 (2)	C3—C4—C5	117.6 (2)
C4—N1—C10	120.3 (2)	C6—C5—C4	120.9 (2)
C11—N1—C10	119.3 (2)	C5—C6—C1	121.6 (2)
C6—C1—C2	117.7 (2)		

Table 6. H···I *distances* (Å) *in* (II)

I1···H7*A*	3.163 (3)	I1···H8*B*^{ii}	3.163 (3)
I1···H8*A*	3.235 (3)	I1···H9*C*^{ii}	3.178 (2)
I1···H6^{i}	3.105 (2)	I1···H11*A*^{iii}	3.164 (3)
I1···H7*C*^{i}	3.107 (3)		

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

For both (I) and (II), all H atoms were located by a difference synthesis but positioned geometrically and refined with free isotropic displacement parameters using a riding model. The two independent molecules of (I) differ significantly in the torsion angle of their trimethylphosphonium group [C8—P1—C1—C2 10.9 (5) and C18—P2—C11—C12 23.7 (5)°, respectively; see Fig. 1]. The Flack (1983) absolute-structure parameter converged to χ = 0.18 (3) and, therefore, the absolute structure cannot be determined successfully. Origin constraints were generated automatically by the program of Flack & Schwarzenbach (1988).

For both compounds, data collection: *DIF*4 (Stoe & Cie, 1988*a*); cell refinement: *DIF*4; data reduction: *REDU*4 (Stoe & Cie, 1988*b*); program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1985); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *SHELXTL/PC XP* (Sheldrick, 1990); software used to prepare material for publication: *SHELXL*93 *CIFTAB*.

This project is supported by the Deutsche Forschungsgemeinschaft, the State of Hesse, the Fonds der Chemischen Industrie and the A. Messer Foundation.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: JZ1022). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Cambridge Structural Database (1992). Version 4.6. Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, England.
Cotton, F. A. & Najjar, C. (1981). *Inorg. Chem.* **20**, 1866–1869.
Domenicano, A. (1989). *Methods Stereochem. Anal.* **10**, 281–324.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Flack, H. D. & Schwarzenbach, D. (1988). *Acta Cryst.* A**44**, 499–506.
Kaim, W. & Bock, H. (1978). *Chem. Ber.* **111**, 3843–3856.
Michaelis, A. (1876). *Liebigs Ann. Chem.* **181**, 265–363.
Pauling, L. (1960). *The Nature of the Chemical Bond*, 3rd ed., pp. 242–247. Ithaca: Cornell Univ. Press.
Schiemenz, G. P. (1964). *Tetrahedron Lett.* **38**, 2729–2735.
Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures.* Univ. of Göttingen, Germany.
Sheldrick, G. M. (1990). *SHELXTL/PC User's Manual.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* Univ. of Göttingen, Germany.
Stoe & Cie (1988*a*). *DIF4. Diffractometer Control Program.* Version 6.2. Stoe & Cie, Darmstadt, Germany.
Stoe & Cie (1988*b*). *REDU4. Data Reduction Program.* Version 6.2. Stoe & Cie, Darmstadt, Germany.
Trippett, S. & Walker, D. M. (1961). *J. Chem. Soc.* (*London*), pp. 2130–2133.

Acta Cryst. (1995). C**51**, 1844–1846

4-Acetamidocyclohexanone Semicarbazone Dihydrate

Kang-Jing Zhou

Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, People's Republic of China

G. Di Maio, G. Portalone and S. Li

Dipartimento di Chimica, Universita di Roma 'La Sapienza', 00185 Roma, Italy

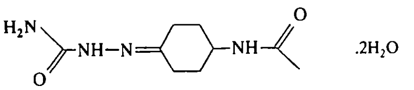
Abstract

The cyclohexane ring of the title molecule, $C_9H_{16}N_4O_2.2H_2O$, adopts a slightly distorted chair conformation. The $NHCONH_2$ group has a conformation in which the C=O bond is *trans* with respect to the N—N bond. The molecules in the crystal are linked by hydrogen bonding involving the $NHCONH_2$ group, the acetamido group and the water molecules.

Comment

This investigation is part of systematic studies of 4-*R*-substituted cyclohexanone semicarbazone derivatives. The X-ray structures of derivatives with *R* = H and *R* = *tert*-butyl (Di Maio, Li, Portalone, Zhou, Marciante

& Spagna, 1993), and R = methyl and R = cyclohexyl (Zhou, Di Maio, Li, Portalone & Migneco, 1993) have been reported. The effects of substitution on the structures of these derivatives were discussed in a previous paper. We now report the X-ray crystallographic results for 4-acetamidocyclohexanone semicarbazone dihydrate (ACSC).



ACSC

A perspective view of the molecule with the atomic numbering scheme is shown in Fig. 1. The six-membered cyclohexanone ring is puckered; it has a slightly distorted chair form flattened at the C=N apex attached to the semicarbazone group. The C(2)—C(1)—C(6) bond angle increases to 114.8 (6)°, while the other internal angles remain close to the corresponding values found in cyclohexane (111.4°; Bastiansen, Fernholt, Seip, Kambara & Kuchitsu, 1973). The bond lengths are similar to the values retrieved from the Cambridge Structural Database (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987) for C_{sp^2}—C_{sp^3} [1.507 (15) Å] and C_{sp^3}—C_{sp^3} [1.535 (16) Å] distances in cyclohexane derivatives. The angle between the planes defined by C(2), C(6) and N(1), and C(2), C(3), C(5) and C(6), A_1, and that between the planes defined by C(3), C(4) and C(5), and C(2), C(3), C(5) and C(6), A_2, have been calculated and were used to compare the puckering of the derivatives. The parameter A_1 of the title compound, 129.0 (3)°, is nearly equal to A_2, 129.1 (5)°, while in the other four derivatives A_1 is much greater than A_2. The possible reason is that there are two kinds of hydrogen bonding present in the ACSC crystal, as described below. In the other four derivatives, the hydrogen bonding only involves the $NHCONH_2$ group of the molecule. The semicarbazone group has a conformation in which the C=O bond is *trans* with respect to the N—N bond. The bond lengths and angles in the acetamido group show no essential differences from those of acetamide (Kitano & Kuchitsu, 1973).

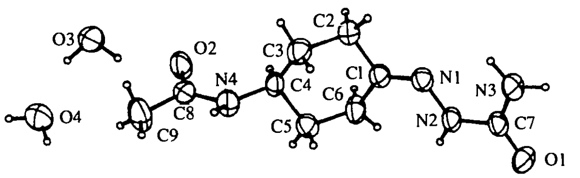


Fig. 1. A perspective drawing of the molecular structure with the atomic numbering scheme. Displacement ellipsoids are plotted at the 50% probability level.

The packing of the molecules in the unit cell is shown in Fig. 2. The molecules are linked by two kinds of hydrogen bonding. For the $NHCONH_2$ group, the N···O distances are 3.103 (7) Å for O(1)···H—N(2) and 2.865 (7) Å for O(1)···H—N(3). At the acetamido group, hydrogen bonds are formed with water molecules. The water atom O(3) is hydrogen bonded to the O(2) atom of the acetamido group, with an O···O distance of 2.756 (7) Å. Water atom O(4) acts as a bridge linking three water O(3) atoms, with an O(4)···H—O(3) O···O distance of 2.734 (8) Å and two O(3)···H—O(4) O···O distances of 2.858 (8) and 2.806 (7) Å.

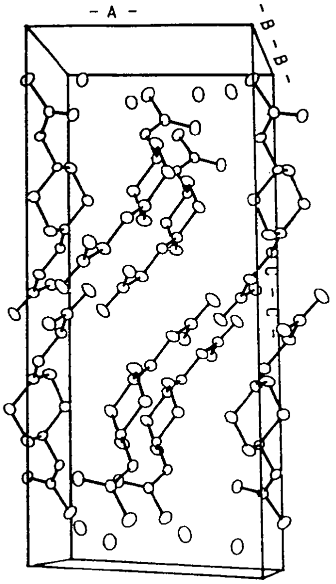


Fig. 2. A molecular packing diagram of the title compound.

Experimental

The title compound was crystallized from a 1:1 mixture of ethanol and $CHCl_3$ by slow evaporation at room temperature.

Crystal data

$C_9H_{16}N_4O_2.2H_2O$
M_r = 248.28
Monoclinic
$P2_1/a$
a = 8.871 (2) Å
b = 7.397 (2) Å
c = 20.393 (4) Å
β = 93.83 (2)°
V = 1335.2 (6) Å^3
Z = 4
D_x = 1.23 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 20 reflections
θ = 5.5–8.5°
μ = 0.091 mm^{-1}
T = 293 K
Plate
0.4 × 0.2 × 0.1 mm
Colorless

Data collection

Rigaku AFC-5R diffractometer
$\omega/2\theta$ scans
Absorption correction: none

$R_{\rm int}$ = 0.038
$\theta_{\rm max}$ = 25°
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 8$
$l = -24 \rightarrow 24$

2732 measured reflections
2356 independent reflections
911 observed reflections
[$I > 3\sigma(I)$]

3 standard reflections
monitored every 250
reflections
intensity decay: <7.5%

Refinement

Refinement on F
$R = 0.064$
$wR = 0.066$
$S = 1.790$
911 reflections
154 parameters
H-atom parameters not refined

$w = 1/[\sigma^2(F_o) + 0.0001(F_o)^2 + 1]$ (Killean & Lawrence, 1969)
$(\Delta/\sigma)_{\max} = 0.29$
$\Delta\rho_{\max} = 0.15$ e Å^{-3}
$\Delta\rho_{\min} = -0.19$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	B_{eq}
O(1)	−0.2627 (6)	0.1020 (7)	0.4918 (3)	4.2 (1)
O(2)	0.1969 (5)	0.8969 (8)	0.8399 (3)	4.7 (1)
O(3)	0.3361 (6)	1.1269 (8)	0.9315 (3)	5.4 (1)
O(4)	0.1504 (6)	1.4142 (9)	0.9514 (3)	6.1 (2)
N(1)	−0.0036 (6)	0.2215 (8)	0.6213 (3)	3.4 (1)
N(2)	−0.1053 (7)	0.2437 (8)	0.5668 (3)	3.6 (1)
N(3)	−0.1113 (7)	−0.0673 (8)	0.5607 (3)	3.9 (1)
N(4)	0.0014 (6)	0.7131 (8)	0.8131 (3)	3.5 (1)
C(1)	0.0484 (8)	0.359 (1)	0.6519 (4)	3.4 (1)
C(2)	0.1550 (9)	0.327 (1)	0.7120 (4)	4.3 (2)
C(3)	0.0922 (9)	0.424 (1)	0.7711 (4)	4.3 (2)
C(4)	0.0638 (7)	0.622 (1)	0.7580 (3)	3.2 (2)
C(5)	−0.0431 (8)	0.646 (1)	0.6974 (4)	3.7 (2)
C(6)	0.015 (1)	0.556 (1)	0.6368 (4)	4.2 (2)
C(7)	−0.1656 (8)	0.090 (1)	0.5367 (3)	3.3 (2)
C(8)	0.0708 (8)	0.839 (1)	0.8508 (4)	3.5 (2)
C(9)	−0.0147 (9)	0.908 (1)	0.9065 (4)	5.5 (2)

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

O(1)—C(7)	1.218 (8)	C(1)—C(2)	1.516 (9)
O(2)—C(8)	1.231 (8)	C(1)—C(6)	1.513 (9)
N(1)—N(2)	1.391 (7)	C(2)—C(3)	1.54 (1)
N(1)—C(1)	1.264 (8)	C(3)—C(4)	1.51 (1)
N(2)—C(7)	1.383 (8)	C(4)—C(5)	1.517 (9)
N(3)—C(7)	1.339 (8)	C(5)—C(6)	1.53 (1)
N(4)—C(4)	1.454 (8)	C(8)—C(9)	1.51 (1)
N(4)—C(8)	1.332 (9)		
N(2)—N(1)—C(1)	119.7 (5)	C(3)—C(4)—C(5)	110.5 (5)
N(1)—N(2)—C(7)	117.9 (5)	C(4)—C(5)—C(6)	112.6 (6)
C(4)—N(4)—C(8)	126.0 (6)	C(1)—C(6)—C(5)	109.3 (5)
N(1)—C(1)—C(2)	117.2 (6)	O(1)—C(7)—N(2)	120.5 (6)
N(1)—C(1)—C(6)	128.1 (6)	O(1)—C(7)—N(3)	123.9 (6)
C(2)—C(1)—C(6)	114.8 (6)	N(2)—C(7)—N(3)	115.6 (5)
C(1)—C(2)—C(3)	108.9 (6)	O(2)—C(8)—N(4)	122.0 (6)
C(2)—C(3)—C(4)	112.2 (5)	O(2)—C(8)—C(9)	121.9 (6)
N(4)—C(4)—C(3)	112.5 (5)	N(4)—C(8)—C(9)	116.1 (7)
N(4)—C(4)—C(5)	109.1 (5)		

Intensities were corrected for Lorentz and polarization effects. The structure was solved by direct methods using *MITHRIL* (Gilmore, 1984). H atoms were located by difference Fourier synthesis. Full-matrix least-squares refinement was carried out using the *SDP* package (Enraf–Nonius, 1985). Non-H atoms were refined with isotropic displacement factors, then with anisotropic displacement factors. The isotropic displacement factors for H atoms were arbitrarily assigned as $1.3B_{eq}$ of the attached atoms and not refined. The calculations were performed on a VAX11/785 computer.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, intermolecular distances and least-squares-planes data have been deposited with the IUCr (Reference: CR1118). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–S19.
Bastiansen, O., Fernholt, L., Seip, H. M., Kambara, H. & Kuchitsu, K. (1973). *J. Mol. Struct.* **18**, 163–168.
Di Maio, G., Li, S., Portalone, G., Zhou, K.-J., Marciante, C. & Spagna, R. (1993). *Acta Cryst.* C**50**, 635–638.
Enraf–Nonius (1985). *Structure Determination Package*. Enraf–Nonius, Delft, The Netherlands.
Gilmore, C. J. (1984). *J. Appl. Cryst.* **17**, 42–46.
Killean, R. C. G. & Lawrence, J. L. (1969). *Acta Cryst.* B**25**, 1750–1752.
Kitano, M. & Kuchitsu, K. (1973). *Bull. Chem. Soc. Jpn*, **46**, 3048–3051.
Zhou, K.-J., Di Maio, G., Li, S., Portalone, G. & Migneco, M. (1993). *Chin. J. Struct. Chem.* **12**, 43–47.

Acta Cryst. (1995). C**51**, 1846–1849

4-(4-Hydroxy-3,5-dimethylphenylazo)-benzenesulfonic Acid

NOELLE EHLINGER AND MONIQUE PERRIN

Laboratoire de Cristallographie, Université Claude Bernard Lyon I, 43 Boulevard du 11 Novembre 1918, 69622 Villeurbanne CEDEX, France

(*Received* 4 *January* 1995; *accepted* 17 *February* 1995)

Abstract

In the solid state, the title compound, $C_{14}H_{14}N_2O_4S.-H_2O$, exists as two forms: cubes (I) and needles (II). Both kinds of crystal are monohydrates. The dye molecules have the same geometry and are bonded by O—H···O intermolecular hydrogen bonds in both forms: an N^+—H···O^- intermolecular hydrogen bond in (II) and an N^+—H···$(O)_2^-$ bifurcated hydrogen bond in (I).

Comment

There have been many studies on the synthesis and ion-binding properties of chromogenic calixarenes having azo groups (Shinkai, Araki, Shibata, Tsugawa & Manabe, 1989; Nomura, Taniguchi & Tamura, 1989; Nomura, Taniguchi & Otsuji, 1993; Xu & Swagen, 1993; Yeh, Tang, Chen, Liu & Lin, 1994). We are particularly interested in the conformation of azocalixarenes in the solid state and in their interactions with other organic substances (Ehlinger, Lecocq, Perrin & Perrin,

Acta Crystallographica Section C
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