O2—C2—C3	136.1 (3)	O7—C7—C6	131.2 (3)
C1—C2—C3	93.0 (2)	C8—C7—C6	92.5 (2)
O3—C3—C2	136.9 (3)	O8—C8—C7	138.1 (3)
O3—C3—C4	135.2 (3)	O8—C8—C9	131.9 (3)
C2—C3—C4	87.9 (2)	C7—C8—C9	90.0 (2)
O4—C4—C1	136.8 (3)	O9—C9—C8	133.1 (3)
O4—C4—C3	134.5 (3)	O9—C9—C6	137.8 (3)
C1—C4—C3	88.7 (2)	C8—C9—C6	89.1 (2)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···O8^{i}	1.04 (3)	1.46 (3)	2.488 (3)	167 (3)
O7—H7···O1	1.06 (3)	1.41 (3)	2.462 (3)	174 (3)
N1—H1*A*···O2^{ii}	0.86 (3)	2.29 (3)	2.934 (4)	132 (3)
N1—H1*B*···O1^{ii}	0.89 (3)	2.29 (3)	3.009 (4)	138 (3)
N3—H3*B*···O6^{iii}	0.85 (3)	2.06 (3)	2.903 (4)	170 (3)
N3—H3*A*···O3^{iv}	0.87 (3)	2.02 (3)	2.873 (4)	168 (3)
N2—H2*A*···O4^{iv}	0.89 (3)	2.08 (3)	2.960 (4)	170 (3)
N2—H2*B*···O9^{v}	0.86 (3)	2.01 (3)	2.871 (4)	172 (3)
N5—H5*B*···O9^{v}	0.86 (4)	2.19 (4)	2.994 (5)	154 (3)
N6—H6*B*···O8^{v}	0.89 (4)	1.99 (3)	2.865 (4)	169 (3)
N6—H6*A*···O4^{vi}	0.88 (3)	2.09 (4)	2.929 (4)	160 (3)
N4—H4*B*···O7^{vii}	0.88 (4)	2.14 (4)	2.927 (4)	148 (3)
N4—H4*A*···O6^{vii}	0.90 (3)	2.23 (4)	2.997 (4)	142 (3)
N5—H5*A*···O3^{viii}	0.91 (3)	2.06 (3)	2.959 (4)	170 (3)

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

The title complex was characterized by elemental analysis and spectroscopic methods. The solid-state IR spectrum (KBr pellets) confirms that only one hydroxyl group is 'free' and that the guanidine molecule is protonated. The strong peaks at 3475 and 3184 cm^{-1}, and the other bands around 3000 cm^{-1} show the existence of a network of strong hydrogen bonds. The melting point of guanidinium hydrogen squarate is over 580 K with decomposition. The structure was solved by direct methods (*SHELXS*86; Sheldrick, 1990) and successive difference Fourier syntheses. Refinement applied full-matrix least-squares methods (*SHELXL*93; Sheldrick, 1993). All H atoms were taken from difference Fourier maps and refined with restrained O—H and N—H distances (*SADI* 0.03), and U_{iso} constrained to be $1.5U_{eq}$ of the carrier atom. The crystal was slightly longer than the beam diameter, which may lead to small systematic errors in *U* values.

Data collection: *R*3*m*/*V* software. Cell refinement: *R*3*m*/*V* software. Data reduction: *R*3*m*/*V* software. Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1991). Software used to prepare material for publication: *SHELXL*93 and *PARST*95 (Nardelli, 1995).

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: JZ1154). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Adams, J. M. (1978). *Acta Cryst.* B**34**, 1218–1220.
Angelova, O., Petrova, R., Radomirska, V. & Kolev, Ts. (1996). *Acta Cryst.* C**52**, 2218–2220.
Angelova, O., Velikova, V., Kolev, Ts. & Radomirska, V. (1996). *Acta Cryst.* C**52**, 3252–3256.
Brach, I., Roziere, J., Anselment, B. & Peters, K. (1987). *Acta Cryst.* C**43**, 458–460.
Bull, R. J., Ladd, M. F. C., Povey, D. C. & Shirley, R. (1973). *Cryst. Struct. Commun.* **2**, 625–628.
Greenhill, J. & Lue, P. (1993). *Prog. Med. Chem.* **30**, 203–326.
Katrusiak, A. & Szafranski, M. (1994). *Acta Cryst.* C**50**, 1161–1163.
Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.
Semmingsen, D. (1976). *Acta Chem. Scand. Ser. A*, **30**, 808–812.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1991). *SHELXTL-Plus*. Release 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Wang, Y. & Stucky, G. D. (1974). *J. Chem. Soc. Perkin Trans.* 2, pp. 925–928.
West, R. (1980). Editor. *Oxocarbons*. New York: Academic Press.

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α-Formylphenylacetonitrile in the Solid State at 220 K

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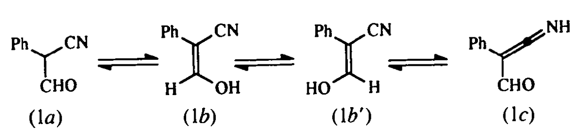
Abstract

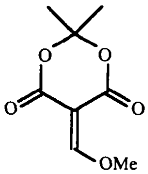
The title compound, 3-hydroxy-2-phenylpropenonitrile (α-hydroxymethylene-α-phenylacetonitrile), C_9H_7NO, exists in the solid state as the *Z*-enol tautomer, forming one-dimensional chains *via* hydrogen bonding between the enol OH group and the nitrile N atom.

Comment

The title compound, (1), which is a useful intermediate in heterocyclic synthesis, can, in principle, exist in three tautomeric forms (see scheme below), one of which can occur as *Z* and *E* isomers [(1*b*) and (1*b*′), respectively]. In solution, (1) is present as a 1:1 mixture of (1*b*) and (1*b*′) (Kirsch, Mieloszynski, Paquer & Andrieu, 1983), and the present study was undertaken in order to establish whether this persists in the solid state.



In the solid state, (1) exists solely as the *Z*-enol form α-hydroxymethylene-α-phenylacetonitrile [(1*b*); Fig. 1]. The formation of the enol forms in solution was ascribed to their stabilization by hydrogen bonding, and packing in the crystal structure of (1*b*) is dominated by hydrogen bonding between the cyano and hydroxyl groups of neighbouring molecules leading to the formation of chains disposed about the crystallographic 2_1 axes. Further stabilization through π resonance from the hydroxyl group *via* the C=C bond to the cyano group also plays an essential role in the formation of the enol forms, since analogues of (1*a*) which lack a π-active group α to the carbonyl do not significantly adopt the enol form.



(2)

For example, only 2.9% of phenylacetone is typically present as the enol tautomer (Gero, 1954). The bond lengths within the enol unit in (1*b*) (Table 1) are consistent with this delocalization, although the shortening of the C—O and lengthening of the C=C bond lengths relative to typical values are not as pronounced as in (2), which has two electron-withdrawing groups (Blake, Hunter & McNab, 1989). The cyano–enol unit is planar [maximum deviation 0.029 (2) Å for the C13 atom] and is twisted by 19.98 (7)° relative to the plane of the phenyl ring.

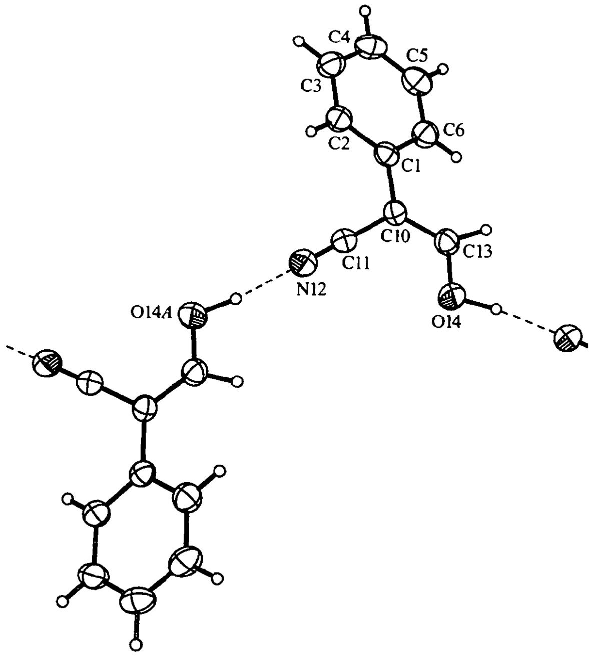


Fig. 1. The formation of hydrogen bonds in the crystal structure of (1*b*). The O14 and O14*A* atoms are related by the operation $(1-x, -\frac{1}{2}+y, \frac{1}{2}-z)$. The N12···O14*A* distance is 2.737 (3) Å and H14*A*···N12 is 1.72 (3) Å. Displacement ellipsoids enclose 50% probability surfaces.

Experimental

Compound (1) was prepared according to the literature procedure of Anderson, Casey, Greene, Lafferty & Reiff (1964) and recrystallized from ethyl acetate.

Crystal data

C_9H_7NO
$M_r = 145.16$
Monoclinic
$P2_1/c$
$a = 8.648\ (4)$ Å
$b = 11.561\ (8)$ Å
$c = 8.189\ (4)$ Å
$\beta = 114.43\ (4)°$
$V = 745.4\ (7)$ Å^3
$Z = 4$
$D_x = 1.293$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 14 reflections
$\theta = 20–30°$
$\mu = 0.693$ mm^{-1}
$T = 220.0\ (2)$ K
Tablet
0.35 × 0.23 × 0.12 mm
Colourless

Data collection

Stoe Stadi-4 diffractometer equipped with an Oxford Cryosystems variable temperature device (Cosier & Glazer, 1986)
ω–θ scans [width $(1.32 + 0.15\tan\theta)°$]
Absorption correction: none
2078 measured reflections
1097 independent reflections

910 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.0196$
$\theta_{\rm max} = 60.01°$
$h = -3 \rightarrow 9$
$k = -12 \rightarrow 12$
$l = -9 \rightarrow 9$
3 standard reflections frequency: 120 min intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.0359$
$wR(F^2) = 0.0976$
$S = 1.045$
1097 reflections
109 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0566P)^2 + 0.1377P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.16$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.13$ e Å^{-3}
Extinction correction: *SHELXTL/PC*
Extinction coefficient: 0.0095 (15)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

C1—C10	1.483 (2)	C11—N12	1.145 (2)
C10—C13	1.336 (2)	C13—O14	1.330 (2)
C10—C11	1.429 (2)		
C13—C10—C11	117.1 (2)	N12—C11—C10	179.4 (2)
C13—C10—C1	124.87 (15)	O14—C13—C10	122.1 (2)
C11—C10—C1	118.05 (14)		

Atoms H2–H6 were placed in calculated positions, while atoms H13 and H14 were located in a difference map. The low value of $\theta_{\rm max}$ is a consequence of the mechanical restrictions arising from the use of the low-temperature device.

Data collection: *DIF*4 (Stoe & Cie, 1990*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1990*b*). Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1995). Program(s) used to refine structure: *SHELXTL/PC*. Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXTL/PC*.

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: BM1136). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Anderson, E. L., Casey, J. E., Greene, L. C., Lafferty, J. J. & Reiff, H. E. (1964). *J. Med. Chem.* **7**, 259–268.
Blake, A. J., Hunter, G. A. & McNab, H. (1989). *J. Chem. Res.* (*S*), pp. 118–119; *J. Chem. Res.* (*M*), pp. 0921–0943.
Cosier, J. & Glazer, A. M. (1986). *J. Appl. Cryst.* **19**, 105–108.
Gero, A. (1954). *J. Org. Chem.* **19**, 1960–1970.
Kirsch, G., Mieloszynski, J. L., Paquer, D. & Andrieu, C. G. (1983). *Recl. Trav. Chim. Pays-Bas*, **102**, 489–495.
Sheldrick, G. M. (1995). *SHELXTL/PC*. Version 5.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Stoe & Cie (1990*a*). *DIF4. Diffractometer Control Program*. Version 7.09/DOS. Stoe & Cie, Darmstadt, Germany.
Stoe & Cie (1990*b*). *REDU4. Data Reduction Program*. Version 7.03/DOS. Stoe & Cie, Darmstadt, Germany.

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N-Methylbenzothiazole-2(3*H*)-selone, C_8H_7NSSe

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Abstract

The crystal structure of *N*-methyl-1,3-benzothiazole-2(3*H*)-selone (mbts) has been studied in order to estimate the changes in the molecular geometry of the mbts ligand upon coordination. Hypervalent complexes of mbts with Te^{II} and I^{I} have been studied by us previously. A significant elongation of the Se═C bond [from 1.817 (7) in mbts to 1.85–1.88 Å in the complexes] was found, but there were no significant changes in the other geometric parameters of the ligand. The only other bond-length decrease of note was for SeC—NMe [from 1.35 (1) in mbts to 1.32–1.34 Å in the complexes]. Thus, only the amino group takes part in electron redistribution upon coordination.

Comment

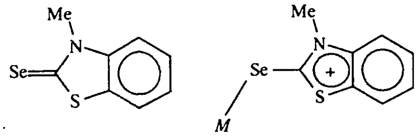
Recently, we have shown (Rudd, Lindeman & Husebye, 1996) that the *trans* influence of chalcogen-containing ligands in hypervalent three-coordinate complexes of Te^{II} can be modified significantly depending on the ability of the rest of the ligand (apart from the coordinating chalcogen atom) to accept/delocalize positive charge, owing to the following resonance:

$$\underset{(a)}{X\text{—Te(Ar)}:Y{=}L} \leftrightarrow \underset{(b)}{X^-:\text{Te(Ar)—}Y^+{=}L} \leftrightarrow \underset{(c)}{X^-:\text{Te(Ar)—}Y\text{—}L^+}$$

(most often, X = a halogen, Ar = phenyl, Y = a chalcogen, L = the organic remainder of the ligand $Y{=}L$ and ':' denotes a lone pair). Moreover, we have demonstrated (Rudd, Lindeman & Husebye, 1997) that the same hypervalent three-center four-electron bonding scheme (Wiebenga, Havinga & Boswijk, 1961; Foss, 1962; Alcock, 1972) can be applied to isoelectronic hypervalent complexes of two-coordinate I^{I}:

$$X\text{—I}:Y{=}L \leftrightarrow X^-:\text{I—}Y^+{=}L \leftrightarrow X^-:\text{I—}Y\text{—}L^+$$

(most often, X = I or Br, Y = S or Se, and L = the organic remainder of the ligand). *N*-Methylbenzothiazole-2(3*H*)-selone (mbts), (1), has just been used as a ligand both in Te^{II} and Se^{II} complexes [(mbts)TePhBr, (2) (Rudd, Lindeman & Husebye, 1996), and $(mbts)_4Se^{2+}$ (Adamo *et al.*, 1996)], and in I^{I} complexes [$(mbts)_2I^+.(I_3)^-$, (3) (Demartin *et al.*, 1993), (mbts)II_3, (4), and (mbts)IBrIBr, (5) (Cristiani *et al.*, 1994)], but the structure of the ligand itself has not yet been studied. Looking at the chemical structure of mbts, we might expect that it is good at delocalizing the positive charge owing to the resulting aromatic structure upon complexation.



(1)

Nevertheless, the effect of the organic remainder of the ligand upon the *trans* influence of Se is rather small. For instance, mbts has a weaker *trans* influence than selenourea (Rudd, Lindeman & Husebye, 1996). In order to examine the reasons for this limited effect, we undertook the X-ray structural investigation of (1).