(Sheldrick, 1990); program(s) used to refine structures: *SHELXTL* (Siemens, 1996*a*); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Financial support for this research and the award of a research scholarship to SGC from the National University of Singapore are gratefully acknowledged.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1085). Services for accessing these data are described at the back of the journal.

References

Boyer, P. L., Currens, J. J., McMahon, J. B., Boyd, M. R. & Hughes, S. H. (1993). *J. Virol.* **67**, 2412–2420.
Cao, S.-G., Chong, K.-L., Vittal, J. J., Sim, K.-Y. & Goh, S.-H. (1998). *Nat. Prod. Lett.* **11**, 233–236.
Cao, S.-G., Sim, K.-Y., Pereira, J. & Goh, S.-H. (1998). *Phytochemistry*, **47**, 1051-1055.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Fuller, R. W., Bokesch, H. R., Gustafson, K. R., McKee, T. C., Cardellina, J. H. II, McMahon, J. B., Cragg, G. M., Soerjarto, D. D. & Boyd, M. R. (1994). *Bioorg. Med. Chem. Lett.* **4**, 1961–1964.
Galinis, D. L., Fuller, R. W., McKee, T. C., Cardellina, J. H. II, Gulakowski, R. J., McMahon, J. B. & Boyd, M. R. (1996). *J. Med. Chem.* **39**, 4507–4510.
Gustafson, K. R., Bokesch, H. R., Fuller, R. W., McKee, T. C., Cardelina, J. H. II, Kadushin, M. R., Soejarto, D. D. & Boyd, M. R. (1994). *Tetrahedron Lett.* **35**, 5821–5824.
Kashman, Y., Gustafson, K. R., Fuller, R. W., Cardellina, J. H. II, McMahon, J. B., Currens, M. J., Buckheit, R. W. Jr, Hughes, S. H., Cragg, G. M. & Boyd, M. R. (1992). *J. Med. Chem.* **35**, 2735–2743.
McKee, T. C., Cardellina, J. H. II, Dreyer, G. B. & Boyd, M. R. (1995). *J. Nat. Prod.* **58**, 916–920.
McKee, T. C., Fuller, R. W., Covington, C. D., Cardellina, J. H. II, Gulakowski, R. J., Krepps, B. L., McMahon, J. B. & Boyd, M. R. (1996). *J. Nat. Prod.* **59**, 754–758.
Pengparp, T., Serit, M., Hughes, S. H., Soerjarto, D. D. & Pettuto, J. M. (1996). *J. Nat. Prod.* **59**, 839–842.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1996). *SADABS. Program for Empirical Absorption Correction*. University of Göttingen, Germany.
Siemens (1996*a*). *SHELXTL Reference Manual*. Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Siemens (1996*b*). *SMART* and *SAINT Software Reference Manuals*. Version 4.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Acta Cryst. (1998). C**54**, 1540–1542

Thiosemicarbazid-1-ium Dihydrogenphosphate

ALICJA WAŚKOWSKA

Institute of Low Temperature and Structure Research, Polish Academy of Sciences, Okólna str. 2, 50-50 Wrocław, Poland. E-mail: waskowsk@int.pan.wroc.pl

(*Received 27 March 1998; accepted 27 April 1998*)

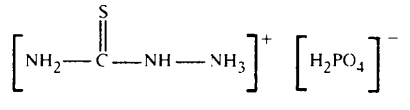
Abstract

Thiosemicarbazid-1-ium dihydrogenphosphate, $CH_6N_3S^+.H_2PO_4^-$, unlike the semicarbazide complex compounds, does not exhibit temperature-dependent ferroelectric properties. X-ray structure determination at room temperature has shown that the crystal is centrosymmetric (space group *C*2/*c*) and thermal mobility of the structural units is relatively low. This allowed the refinement of all H-atom parameters without any space constraints. The $H_2PO_4^-$ anions, with a distorted tetrahedral configuration, are hydrogen bonded to the thiosemicarbazidium cations. The average observed U_{iso} value for the H atoms (0.045 Å^2) suggests that the protons are well fixed at their sites, and the extensive three-dimensional system of moderately short hydrogen bonds forms a structure in which dynamic disorder by hydrogen 'jumping' is not pronounced.

Comment

Different complexes of semicarbazide with, for example, copper(II) and zinc chlorides (Nardelli *et al.*, 1963), and the salts with hydrobromide (Boldrini, 1971), hydrochloride (Nardelli *et al.*, 1965) and nitric acid (Wawrzak *et al.*, 1981), have attracted considerable attention due to their interesting physical properties connected with ferroelectric phase transitions. In this family of compounds, the phase transitions are related to the high molecular polarizability of inorganic and organic sublattices. In particular, it is interesting to study the role of inorganic anions in orienting the organic unit in a way which promotes a non-centrosymmetric molecular arrangement (Datta *et al.*, 1994; Herbert, 1978). Certain characteristics of the phase transitions in these compounds are also connected with the dynamics of the protons in the hydrogen bonds, which in the present structure can be formed easily between the N···O and O···O atoms. In our search for ferroelectric materials, a new compound of thiosemicarbazide with phosphoric acid, thiosemicarbazid-1-ium dihydrogenphosphate (TSCDHP), has been synthesized. Measurement of the dielectric constant and thermal analysis by differential scanning calorimetry did not indicate, however, any temperature-

Acta Crystallographica Section C
ISSN 0108-2701 © 1998



$$[NH_2-\overset{\overset{S}{\|}}{C}-NH-NH_3]^+\ [H_2PO_4]^-$$

TSCDHP

dependent non-linear features. Therefore, no para- to ferroelectric phase transition takes place. The present structure determination was undertaken as an attempt to explain the distinctive feature of TSCDHP, *i.e.* the absence of a Curie point compared with the semicarbazide ferroelectrics. In the asymmetric unit, one of the acidic protons joins the thiosemicarbazide molecule to form the semicarbazidium cation, $[H_2NCSNHNH_3]^+$, the latter being hydrogen bonded to the dihydrogenphosphate anion (Fig. 1). The bond distances in the cation are comparable with the values found in other similar structures, while the $H_2PO_4^-$ anion shows a slightly distorted tetrahedral configuration (Table 2). Besides electrostatic forces, there is also a system of hydrogen bonding which stabilizes the structure.

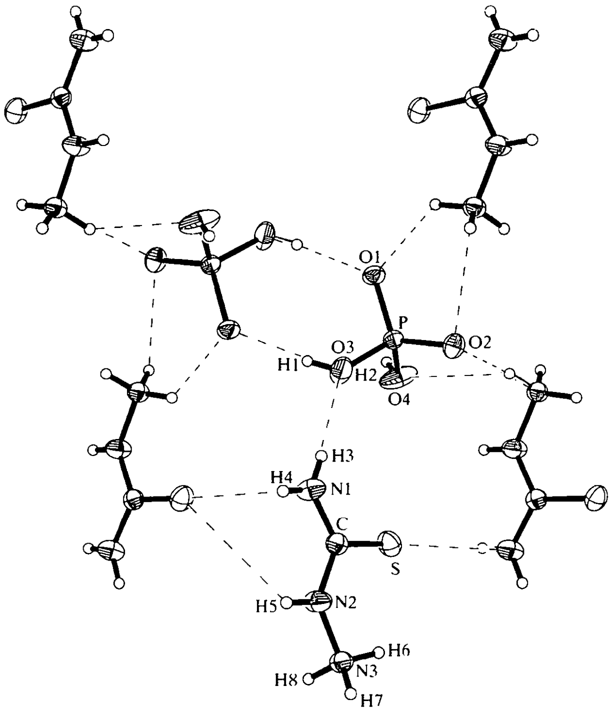


Fig. 1. The molecular structure of TSCDHP, showing the intermolecular hydrogen bonding and the atom-numbering scheme. Non-H atoms have been plotted as displacement ellipsoids at the 50% probability level.

In the diffraction pattern of thiosemicarbazide hydrochloride, a marked diffuse X-ray scattering was observed, indicating either molecular vibrations or small molecular displacements, or a combination of both phenomena (Rocaries & Boldrini, 1972). No such effects were observed in TSCDHP. An important distinction between the ferroelectric semicarbazides and TSCDHP is in the well determined locations of all the atoms, including the protons. A combination of the interactions between the ions and the extensive network of hydrogen bonds (Table 3) prevents the disordering problems which are characteristic of the ferroelectric semicarbazides.

Experimental

The title compound was crystallized from an aqueous solution of thiosemicarbazide (Merck), with a molar excess of phosphoric acid. The solution was allowed to evaporate at room temperature.

Crystal data

$CH_6N_3S^+.H_2PO_4^-$
M_r = 189.13
Monoclinic
$C2/c$
a = 19.799 (4) Å
b = 8.914 (2) Å
c = 8.411 (2) Å
β = 107.75 (1)°
V = 1413.8 (5) Å^3
Z = 8
D_x = 1.777 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 36 reflections
θ = 8–28°
μ = 0.649 mm^{-1}
T = 293 (2) K
Parallelepiped
0.32 × 0.24 × 0.24 mm
Colourless

Data collection

Kuma KM-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
5607 measured reflections
3054 independent reflections
2144 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.036

$\theta_{\rm max}$ = 35.07°
$h = -30 \rightarrow 30$
$k = 0 \rightarrow 14$
$l = -12 \rightarrow 13$
2 standard reflections every 50 reflections intensity decay: 1.14%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.093
S = 1.049
3047 reflections
124 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0566P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max}$ = 0.001

$\Delta\rho_{\rm max}$ = 0.574 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.636 e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.167 (5)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
P	0.04323 (2)	0.77741 (4)	0.01872 (4)	0.01978 (11)
S	−0.22456 (2)	0.70829 (4)	−0.22840 (5)	0.02855 (11)
O1	−0.03173 (5)	0.82253 (12)	−0.07940 (12)	0.0233 (2)
O2	0.05036 (6)	0.63582 (12)	0.11793 (13)	0.0261 (2)
O3	0.07857 (7)	0.90704 (14)	0.1418 (2)	0.0473 (4)

O4	0.08850 (7)	0.7579 (2)	−0.1035 (2)	0.0450 (4)
N1	−0.29212 (7)	0.5195 (2)	−0.0857 (2)	0.0309 (3)
N2	−0.17380 (7)	0.5343 (2)	0.0374 (2)	0.0283 (3)
N3	−0.10575 (6)	0.58840 (14)	0.0473 (2)	0.0229 (2)
C	−0.23129 (7)	0.57975 (15)	−0.0869 (2)	0.0211 (2)

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

P—O2	1.496 (1)	S—C	1.686 (2)
P—O1	1.516 (1)	N1—C	1.322 (2)
P—O4	1.566 (1)	N2—C	1.352 (2)
P—O3	1.567 (1)	N2—N3	1.409 (2)
O2—P—O1	115.96 (6)	O4—P—O3	106.61 (10)
O2—P—O4	107.28 (7)	C—N2—N3	120.51 (12)
O1—P—O4	109.47 (7)	N1—C—N2	115.25 (13)
O2—P—O3	107.85 (8)	N1—C—S	123.36 (11)
O1—P—O3	109.26 (6)	N2—C—S	121.36 (10)

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H3···O3^{i}	0.82 (3)	2.12 (3)	2.943 (2)	176 (3)
N3—H6···O1	0.99 (3)	2.18 (3)	2.931 (2)	131 (2)
N3—H7···O2^{ii}	0.99 (2)	1.74 (2)	2.725 (2)	170 (2)
N3—H8···O2^{iii}	0.93 (2)	1.92 (3)	2.839 (2)	170 (2)
O3—H1···O1^{iv}	0.76 (3)	1.83 (3)	2.578 (2)	166 (3)
O4—H2···O1^{v}	0.78 (3)	1.84 (3)	2.623 (2)	172 (3)
N1—H4···S^{vi}	0.82 (3)	2.80 (3)	3.535 (2)	152 (3)
N2—H5···S^{vi}	0.87 (2)	2.44 (2)	3.282 (1)	161 (2)

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

The structure was solved by direct methods (*SHELXS*86; Sheldrick, 1990*a*) and refined by full-matrix least-squares techniques. All H atoms were located from difference maps and refined isotropically without any distance constraints.

Data collection: *KM*-4 *Software* (Kuma, 1998). Cell refinement: *KM*-4 *Software*. Data reduction: *KM*-4 *Software*. Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1990*b*). Software used to prepare material for publication: *SHELXL*93.

The author is grateful to Professor Z. Czapla (Wrocław University, Institute of Experimental Physics) for the crystal sample.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1366). Services for accessing these data are described at the back of the journal.

References

Boldrini, P. (1971). *Acta Cryst.* B**27**, 860–861.

Datta, M., Podder, A. & Dattagupta, J. K. (1994). *Acta Cryst.* C**50**, 1132–1135.

Herbert, H. (1978). *Acta Cryst.* B**34**, 611–615.

Kuma (1998). *KM*-4 *Software*. Version 8b. Kuma Diffraction, Wroclaw, Poland.

Nardelli, M., Fava, G., Boldrini, P. & Giraldi, G. (1963). *Acta Cryst.* **16**, A-70.

Nardelli, M., Fava, G. & Giraldi, G. (1965). *Acta Cryst.* **19**, 1038–1042.

Rocaries, J.-R. & Boldrini, P. (1972). *Appl. Phys. Lett.* **20**, 49–51.

Sheldrick, G. M. (1990*a*). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1990*b*). *SHELXTL-Plus*. 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.

Wawrzak, Z., Grochulski, P., Karniewicz, J., Gałdecki, Z. & Główka, M. (1981). *Ferroelectrics*, **34**, 157–159.

Acta Cryst. (1998). C**54**, 1542–1544

13*H*-Dibenzo[*a*,*g*]fluoren-13-one

DAVID G. MORRIS,[a] KARL S. RYDER[b] AND R. ALAN HOWIE[b]

[a]*Department of Chemistry, Joseph Black Building, University of Glasgow, Glasgow G12 8QQ, Scotland, and* [b]*Department of Chemistry, Meston Walk, University of Aberdeen, Old Aberdeen AB24 3UE, Scotland. E-mail: d.morris@chem.gla.ac.uk*

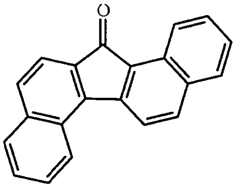
(*Received 21 January 1998; accepted 28 April 1998*)

Abstract

The crystal structure determination of 13*H*-dibenzo[*a*,*g*]fluoren-13-one, $C_{21}H_{12}O$, has shown the molecule to be distorted from planarity as a consequence of the repulsive interaction between an $O_{carbonyl}$ lone pair and the juxtaposed proton. These results substantiate an earlier indication of this interaction, suggested by a conspicuously low-field absorption in the ^1H NMR spectrum of this compound.

Comment

We report the crystal structure of the title compound, (I) (CAS Registry No. [63041-47-4]). This compound was of interest since its ^1H NMR spectrum (Harvey *et al.*, 1992) showed, in addition to a cluster of absorptions corresponding to seven protons in the range $\delta = 7.37$–7.76, single-proton absorptions at δ values of 7.78, 7.91, 8.07, 8.41 and 8.92 p.p.m. The lowest field absorption is assigned to H4 (Fig. 1) on account of its proximity to a lone pair on an O atom. This raises the question of whether the approach of H4 to the $O_{carbonyl}$ lone pair is sufficiently close to make the molecule 'buckle' to any extent and thereby become non-planar.



(I)

In this context, the structure determination of (I) shows two interesting features. Firstly, the C atoms of the six-membered rings at each end of the molecule show small but significant displacements from the plane defined by atoms C21, C1 and C2, which comprises the carbonyl C atom and the adjacent C atoms of the five-membered ring [displacement values: C4 −0.116 (7), C5 −0.238 (9), C6 −0.305 (8), C7 −0.248 (8), C15 0.15 (2), C16 0.07 (2), C17 0.018 (12) and C18 0.023 (9) Å].