

minimize the steric repulsion with the equatorial N-donors. A similar value for the Co—C distance [2.052 (2) Å] was found in {H₂OC[Co(DO)(DOH)pn]-CH₂Ph}⁺ (Zangrando, Parker, Bresciani Pahor, Thomas, Marzilli & Randaccio, 1987).

In both structures (I) and (II) the py ligand, planar within ±0.009 and ±0.006 Å, respectively, has the orientation usually found in pyCo(DH)₂R compounds, *i.e.* nearly perpendicular to the equatorial coordination plane and bisecting the oxime bridges. A very short O...C(py) van der Waals distance of 3.06 Å was observed in (I).

We thank Professor L. G. Marzilli, Emory University, Atlanta (USA), for kindly supplying the crystals and MPI (Rome) for financial support.

References

- BRESCIANI PAHOR, N., FORCOLIN, M., MARZILLI, L. G., RANDACCIO, L., SUMMERS, M. F. & TOSCANO, P. J. (1985). *Coord. Chem. Rev.* **63**, 1–125.
- CLEARFIELD, A., GOPAL, R., KLINE, R. J., SIPAKI, M. & URBAN, L. O. (1978). *J. Coord. Chem.* **8**, 5–13.
- HALPERN, J. (1985). *Science*, **227**, 869–875.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
- MARZILLI, L. G., BAYO, F., SUMMERS, M. F., THOMAS, L. B., ZANGRANDO, E., BRESCIANI PAHOR, N., MARI, M. & RANDACCIO, L. (1987). *J. Am. Chem. Soc.* **109**, 6045–6052.
- MARZILLI, L. G., TOSCANO, P. J., RANDACCIO, L., BRESCIANI PAHOR, N. & CALLIGARIS, M. (1979). *J. Am. Chem. Soc.* **101**, 6754–6756.
- PALENIK, G. J., SULLIVAN, D. A. & NAJK, D. V. (1976). *J. Am. Chem. Soc.* **98**, 1177–1182.
- RANDACCIO, L., BRESCIANI PAHOR, N., TOSCANO, P. J. & MARZILLI, L. G. (1981). *J. Am. Chem. Soc.* **103**, 6347–6351.
- SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
- ZANGRANDO, E., BRESCIANI PAHOR, N., RANDACCIO, L., CHARLAND, J. & MARZILLI, L. G. (1986). *Organometallics*, **5**, 1938–1944.
- ZANGRANDO, E., PARKER, W. O. JR., BRESCIANI PAHOR, N., THOMAS, B. L., MARZILLI, L. G. & RANDACCIO, L. (1987). *Gazz. Chim. Ital.* **117**, 307–316.

Acta Cryst. (1988). **C44**, 2055–2057

Structure of 2-Carboxyanilinium Dihydrogenmonoarsenate

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(Received 16 March 1988; accepted 4 July 1988)

Abstract. C₇H₈NO₂⁺.H₂AsO₄⁻, *M_r* = 279.08, monoclinic, *P*2₁/*c*, *a* = 9.867 (2), *b* = 10.827 (3), *c* = 9.305 (2) Å, β = 100.19 (5)°, *V* = 978.4 (8) Å³, *Z* = 4, *D_x* = 1.894 Mg m⁻³, λ(Ag *K*α) = 0.5608 Å, μ = 1.951 mm⁻¹, *F*(000) = 560, *T* = 295 K, final *R* = 0.025 for 3230 unique reflexions. Planes of H₂AsO₄⁻ tetrahedra alternate with sheets of C₇H₈NO₂⁺ cations in a centrosymmetrical framework. The two-dimensional network of H₂AsO₄⁻ is held together through hydrogen bonds.

Introduction. The reactions between ethanolic solutions of anthranilic acid, 3-aminobenzoic acid or 4-aminobenzoic acid and monophosphoric or monoarsenic acid water solutions yield compounds corresponding to the formulas C₇H₅O₂(NH₂).H₃XO₄ or C₇H₅O₂(NH₂).H₃XO₄.H₂O (*X* = P, As). Crystals obtained with phosphoric acid are air sensitive, while the corresponding arsenic salts are stable under normal conditions. The monoarsenates of the three amino-

benzoic acid isomers have been crystallized. The present paper and the following one (Tordjman, Masse & Guitel, 1988) describe the structures of the two forms C₇H₈NO₂⁺.H₂AsO₄⁻ and C₇H₈NO₂⁺.H₂AsO₄⁻.H₂O.

Experimental. An ethanolic solution of anthranilic acid was mixed with an aqueous solution of H₃AsO₄ in a stoichiometric ratio. The final solution was concentrated at 343 K and slowly evaporated at room temperature.

Crystals appeared as large tabular monoclinic prisms up to 5 mm long. Crystal size used for data collection: 0.48 × 0.48 × 0.30 mm. Density not measured. Enraf-Nonius CAD-4 diffractometer, graphite monochromator. Extinction rules: *h*0*l*, *l* = 2*n*, 0*k*0, *k* = 2*n*. 21 reflexions (11 < θ < 14°) used for refining unit-cell dimensions. ω scan. 4962 non-zero unique reflexions collected (3 < θ < 27.5°). ±*h*,*k*,*l*, *h*_{max} = 16, *k*_{max} = 17, *l*_{max} = 15. Scan width 1.20°, scan speed from 0.02 to 0.06° s⁻¹, total background measuring time: 10 to 27 s.

Orientation reference reflexions: $\bar{3}45$ and $\bar{3}45$, intensity reference reflexions: 345 and 066, no variation. Lorentz and polarization corrections, no absorption correction. Structure solved by direct methods (*MULTAN77*; Main, Lessinger, Germain, Declercq & Woolfson, 1977), Patterson and successive Fourier syntheses. H atoms located from difference Fourier map. Anisotropic full-matrix least-squares refinement (on *F*), isotropic for H atoms. Unit weights. Final refinement cycles with 3230 reflexions corresponding to $I > 4\sigma_I$. Final $R = 0.025$ ($wR = 0.029$). Max. $\Delta/\sigma = 0.04$. Max. peak height in the final difference Fourier synthesis $0.62 \text{ e } \text{\AA}^{-3}$. No extinction correction. $R = 0.04$ for the

Table 1. Final atomic coordinates, B_{eq} for non-H atoms and B_{iso} for H atoms

$$B_{eq} = \frac{4}{3} \sum_i \beta_i a_i^2$$

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{eq}, B_{iso}(\text{\AA}^2)$
As	0.94607 (2)	0.18888 (2)	1.00391 (2)	1.472 (2)
O(1)	0.8510 (2)	0.2875 (2)	0.3349 (2)	2.45 (3)
O(2)	0.8494 (2)	0.0839 (1)	1.0807 (2)	2.04 (2)
O(3)	0.1026 (1)	0.1351 (1)	-0.0016 (2)	1.94 (2)
O(4)	0.9436 (2)	0.3200 (1)	1.0961 (1)	1.95 (2)
O(5)	0.2777 (2)	0.1557 (2)	0.2459 (2)	3.02 (3)
O(6)	0.1036 (2)	0.0890 (2)	0.3479 (2)	2.60 (3)
C(1)	0.3249 (2)	0.3875 (2)	-0.0040 (2)	1.89 (3)
C(2)	0.2946 (2)	0.4449 (2)	0.1212 (2)	1.77 (3)
C(3)	0.3924 (2)	0.4547 (2)	0.2463 (2)	2.41 (4)
C(4)	0.5222 (2)	0.4037 (3)	0.2508 (3)	2.80 (4)
C(5)	0.5526 (2)	0.3442 (3)	0.1297 (3)	2.98 (4)
C(6)	0.4556 (2)	0.3376 (2)	0.0034 (3)	2.65 (4)
C(7)	0.2230 (2)	0.1178 (2)	0.3577 (2)	1.94 (3)
N	0.8417 (2)	-0.0031 (2)	0.3775 (2)	1.84 (3)
H(1)	0.906 (4)	0.308 (4)	0.255 (4)	6 (1)
H(2)	0.135 (4)	0.517 (3)	0.450 (4)	5.2 (9)
H(3)	0.630 (3)	-0.003 (3)	0.172 (4)	3.7 (7)
H(4)	0.596 (3)	0.404 (3)	0.337 (3)	2.7 (6)
H(5)	0.637 (3)	0.312 (3)	0.135 (3)	4.1 (7)
H(6)	0.484 (4)	0.192 (3)	0.421 (4)	5.1 (8)
H(7)	0.858 (3)	0.049 (3)	0.456 (3)	2.2 (5)
H(8)	0.087 (3)	0.438 (3)	0.105 (3)	3.5 (7)
H(9)	0.849 (4)	0.031 (3)	0.293 (4)	4.2 (8)
H(10)	0.218 (4)	0.144 (4)	0.172 (4)	6 (1)

Table 2. Main interatomic distances (\AA) and bond angles ($^\circ$)

AsO ₄ tetrahedron				
As	O(1)	O(2)	O(3)	O(4)
O(1)	1.702 (1)	2.680 (2)	2.801 (2)	2.704 (2)
O(2)	103.15 (7)	1.719 (2)	2.796 (2)	2.716 (2)
O(3)	112.82 (7)	111.65 (7)	1.660 (2)	2.793 (2)
O(4)	107.02 (7)	106.90 (7)	114.50 (7)	1.661 (1)

NH ₃ C ₆ H ₄ COOH group			
C(1)–C(2)	1.398 (3)	C(6)–C(1)–C(2)	117.8 (2)
C(2)–C(3)	1.379 (3)	C(1)–C(2)–C(3)	121.1 (2)
C(3)–C(4)	1.389 (3)	C(2)–C(3)–C(4)	119.9 (2)
C(4)–C(5)	1.377 (4)	C(3)–C(4)–C(5)	119.7 (2)
C(5)–C(6)	1.380 (3)	C(4)–C(5)–C(6)	120.2 (2)
C(6)–C(1)	1.389 (3)	C(5)–C(6)–C(1)	121.3 (2)
C(3)–H(3)	0.95 (3)	C(2)–C(3)–H(3)	119 (2)
		C(4)–C(3)–H(3)	121 (2)
C(4)–H(4)	0.99 (3)	C(3)–C(4)–H(4)	125 (2)
		C(5)–C(4)–H(4)	116 (2)
C(5)–H(5)	0.89 (3)	C(4)–C(5)–H(5)	118 (2)
		C(6)–C(5)–H(5)	122 (2)
C(6)–H(6)	0.92 (4)	C(5)–C(6)–H(6)	117 (2)
		C(1)–C(6)–H(6)	121 (2)
C(7)–C(1)	1.487 (3)	C(1)–C(7)–O(5)	112.7 (2)
C(7)–O(5)	1.320 (3)	C(1)–C(7)–O(6)	123.9 (2)
C(7)–O(6)	1.206 (3)	O(5)–C(7)–O(6)	123.4 (2)
O(5)–O(6)	2.225 (2)	C(2)–C(1)–C(7)	121.7 (2)
		C(6)–C(1)–C(7)	120.5 (2)
C(2)–N	1.460 (3)	C(1)–C(2)–N	120.8 (2)
		C(3)–C(2)–N	118.1 (2)

Hydrogen bonds				
(O,N)–H	H...O	(O,N)–O	(O,N)–H...O	
O(1)–H(1)...O(4)	1.02 (4)	1.59 (4)	2.572 (2)	160 (4)
O(2)–H(2)...O(3)	0.81 (4)	1.75 (4)	2.552 (2)	174 (4)
O(5)–H(10)...O(3)	0.83 (4)	1.81 (4)	2.633 (2)	171 (4)
N–H(7)...O(4)	0.92 (3)	2.01 (3)	2.890 (2)	162 (2)
N–H(8)...O(4)	0.94 (4)	1.90 (3)	2.834 (2)	172 (3)
N–H(9)...O(2)	0.89 (4)	2.06 (4)	2.932 (2)	171 (3)

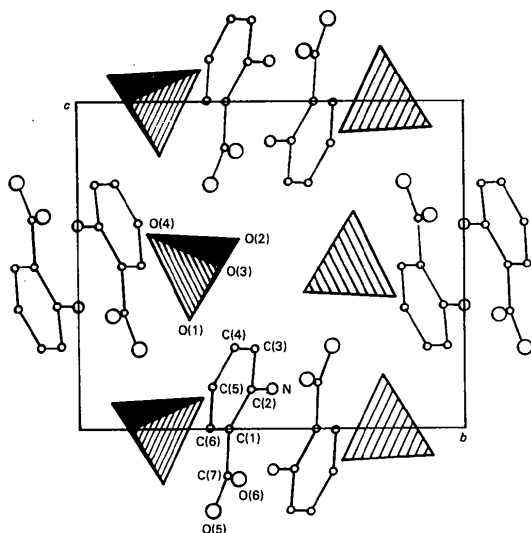


Fig. 1. Projection along the *a* direction of the $\text{C}_7\text{H}_5\text{O}_2\text{NH}_3^+ \cdot \text{H}_2\text{AsO}_4^-$ framework. H atoms are omitted.

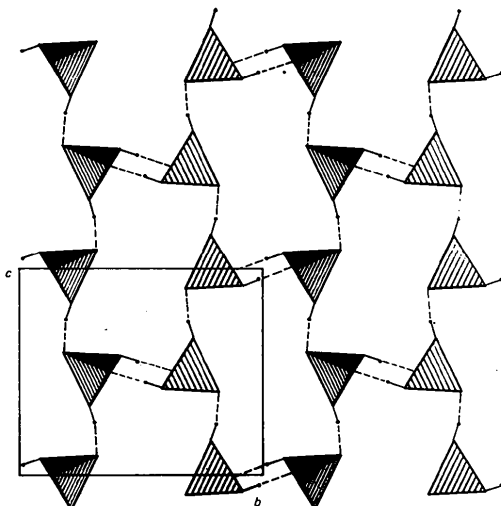


Fig. 2. Layers of H_2AsO_4^- anions developed in the *bc* plane.

complete set of 4220 reflexions.* Scattering factors for neutral atoms and f' , f'' from *International Tables for X-ray Crystallography* (1974). Enraf-Nonius (1977) SDP used for all calculations. Computer: MicroVAX II.

Discussion. The crystal structure determination shows clearly that the atomic arrangement is built up by a stacking of $C_7H_8NO_2^+$ and $H_2AsO_4^-$ units [Figs. 1 and 2; *STRUPLO84* (Fischer, 1985)]. $H_2AsO_4^-$ anions are bonded together by O(1)—H(1)···O(4) and O(2)—H(2)···O(3) hydrogen bonds so as to form layers along the (100) planes. Two types of As—O distances are observed in AsO_4 tetrahedra depending on whether O atoms are hydrogen donors (1.702, 1.719 Å) or acceptors (1.660, 1.661 Å). The two cations are found between these planes of anions. They are bonded to $H_2AsO_4^-$ sheets by hydrogen atoms of the NH_3^+ groups: N—H(8)···O(4), N—H(9)···O(2), N—H(7)···O(4), and carboxylic groups: O(5)—H(10)···O(3). Such a type of two-dimensional $H_2XO_4^-$ ($X = P, As$) network has been pointed out by Adams (1977) in aminoguanidinium dihydrogenmonophosphate. Glycine monophosphate

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51211 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

(Averbuch-Pouchot, Durif & Guitel, 1988) presents layers of $H_2PO_4^-$ connected anions which differ from the previous by the ratio of oxygen donors/oxygen acceptors of H atoms. In the crystal structures of alkali and ammonium dihydrogenmonophosphates two-dimensional or three-dimensional frameworks of $H_2PO_4^-$ connected ions have been found depending on the dimensions of the associated cations. In $R-NH_3^+ \cdot H_2XO_4^-$ ($X = P, As$) organic compounds the steric hindrance of the $R-NH_3^+$ cation has an effect upon the $H_2XO_4^-$ connexion in chains, sheets or three-dimensional networks through the hydrogen bonds. Tables 1 and 2 report the final atomic coordinates and the main interatomic distances.

References

- ADAMS, J. M. (1977). *Acta Cryst.* **B33**, 1513–1515.
 AVERBUCH-POUCHOT, M. T., DURIF, A. & GUITEL, J. C. (1988). *Acta Cryst.* **C44**, 99–102.
 ENRAF-NONIUS (1977). *Structure Determination Package*. Enraf-Nonius, Delft, The Netherlands.
 FISCHER, R. X. (1985). *J. Appl. Cryst.* **18**, 258–262.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
 MAIN, P., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1977). *MULTAN77. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
 TORDJMAN, I., MASSE, R. & GUITEL, J. C. (1988). *Acta Cryst.* **C44**, 2057–2059.

Acta Cryst. (1988). **C44**, 2057–2059

Structure of 4-Carboxyanilinium Dihydrogenmonoarsenate Monohydrate

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(Received 2 May 1988; accepted 4 July 1988)

Abstract. $C_7H_8NO_2^+ \cdot H_2AsO_4^- \cdot H_2O$, $M_r = 297.1$, monoclinic, $P2_1/c$, $a = 14.754$ (14), $b = 8.603$ (4), $c = 8.982$ (9) Å, $\beta = 107.65$ (8)°, $V = 1086.4$ (5) Å³, $Z = 4$, $D_x = 1.816$ Mg m⁻³, $\lambda(Mo K\alpha) = 0.71073$ Å, $\mu = 3.325$ mm⁻¹, $F(000) = 600$, $T = 295$ K, final $R = 0.033$ for 2939 unique reflexions. Two files of $H_2AsO_4^-$ tetrahedra bridged by water molecules form sheets of anions which alternate with sheets of $C_7H_8NO_2^+$ cations.

Introduction. The interactions between amino acids, primary amines and monophosphoric and mono-

arsenic acids have prompted us to develop an interest in chemical reactions between cyclic amines and these acids. The present work is devoted to a detailed structure of the $C_7H_8NO_2^+ \cdot H_2AsO_4^- \cdot H_2O$ compound obtained by reaction of 4-aminobenzoic acid with H_3AsO_4 acid. In the preceding paper (Tordjman, Masse & Guitel, 1988) we described the preparation method of the three monophosphates and monoarsenates of the aminobenzoic acid isomers.

Experimental. Single crystals were easily prepared by slow evaporation at room temperature of an