

ions to provide reasonable coordination distances. In view of the close-packed nature of the observed structure this may not be an energetically favoured process, in which case the ion would probably prefer to lie closer to either the triad of MePh carbonyl O atoms or to the triad of HyIv carbonyl O atoms and there would then be no good reason for choosing the inside rather than the outside of the cavity. At the moment there does not seem to be any experimental evidence for a significant covalent contribution to the $M^+ \cdots O$ bond which might cause the ion to prefer to be outside the cavity.

Finally, we note that the crystal structure conformation of uncomplexed Bv crystallized from *n*-heptane is similar to that proposed by spectroscopic studies for Bv in polar solvents. The predominant environment of the molecule in the crystal is non-polar, with only 1 to 2 molecules of water for each Bv molecule. The structure described would seem to be a likely candidate for the uncomplexed molecule within biological membranes.

I thank Dr Larry Steinrauf for suggesting the problem and providing the material, the Indiana University Medical Centre for support over the period during which the crystals were grown, the Leeds University Computing Laboratory for facilities, Dr Bernard Sheldrick for help with data collection, and the MRC and SRC for supporting the crystallographic studies.

References

- DICKERSON, R. E. & GEIS, I. (1969). In *The Structure and Action of Proteins*. New York: Harper & Row.
- DORSCHNER, E. & LARDY, H. (1968). *Antimicrobial Agents Ann.* pp. 11–19.
- ESTRADA-O, S., GOMEZ-LOUERO, C. & MONTAL, M. (1972). *Bioenergetics*, **3**, 417–428.
- GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–376.
- HAMILL, R. L., HIGGINS, C. E., BOAZ, H. E. & GORMAN, M. (1969). *Tetrahedron Lett.* pp. 4255–4258.
- HAMILTON, J. A., STEINRAUF, L. K. & BRADEN, B. (1975). *Biochem. Biophys. Res. Commun.* **64**, 151–156.
- IUPAC-IUB COMMISSION ON BIOCHEMICAL NOMENCLATURE (1970). *J. Mol. Biol.* **52**, 1–17.
- IVANOV, V. T., EVSTRATOV, A. V., SUMSKAYA, L. V., MELNIK, E. I., CHUMBURIDZE, T. S., PORTNOVA, S. L., BALASHOVA, T. A. & OVCHINNIKOV, YU. A. (1973). *FEBS Lett.* **36**, 65–71.
- KITAIGORODSKY, A. I. (1965). *Acta Cryst.* **18**, 585–590.
- MUELLER, P. & RUDIN, D. O. (1967). *Biochem. Biophys. Res. Commun.* **26**, 398–404.
- OVCHINNIKOV, YU. A., IVANOV, V. T., EVSTRATOV, A. V., MIKHALEVA, I. I., BYSTROV, V. F., PORTNOVA, S. L., BALASHOVA, T. A., MESHCHERYAKOVA, E. N. & TULCHINSKY, V. M. (1974). *Int. J. Peptide Protein Res.* **6**, 465–498.
- OVCHINNIKOV, YU. A., IVANOV, V. T. & MIKHALEVA, I. I. (1971). *Tetrahedron Lett.* 159–162.
- POPOV, E. M., PLETNEV, B. Z., EVSTRATOV, A. V., IVANOV, V. T. & OVCHINNIKOV, YU. A. (1970). *Khim. Prir. Soedin.* **5**, 616–622.
- PRINCE, R. C., CROFTS, A. R. & STEINRAUF, L. K. (1974). *Biochem. Biophys. Res. Commun.* **59**, 697–703.
- ROESKE, R. W., ISAAC, S., KING, T. E. & STEINRAUF, L. K. (1974). *Biochem. Biophys. Res. Commun.* **57**, 554–561.
- STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. & HALL, S. R. (1972). The X-RAY system – version of June 1972, Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland.
- YAFUSO, M., FREEMAN, A. R., STEINRAUF, L. K. & ROESKE, R. W. (1974). *Fed. Proc. Abstr.* **33**, 1258.

Acta Cryst. (1976). **B32**, 3171

The Crystal and Molecular Structure of 2,4-Dinitrophenol

BY TATSUIKI KAGAWA, RYOICHI KAWAI, SETSUO KASHINO AND MASAO HAISA

Department of Chemistry, Faculty of Science, Okayama University, Tsushima, Okayama 700, Japan

(Received 31 March 1976; accepted 30 April 1976)

The crystal structure of 2,4-dinitrophenol has been determined from visually estimated Cu $K\alpha$ X-ray data. The crystals are orthorhombic, space group $P2_12_12_1$, with $a = 6.106$ (6), $b = 23.24$ (2), $c = 5.168$ (5) Å and $Z = 4$. The structure was solved by the Patterson method and refined by block-diagonal least-squares calculations to $R = 0.076$ for 768 non-zero reflexions. The molecules related by an a translation are stacked to form a column. The columns are held together by an interaction between the phenolic and nitro groups [$O \cdots H$ 2.23 Å] of the molecules related by a twofold screw axis along the c axis, to form a sheet parallel to (010). The sheets are stacked along the b axis by van der Waals interactions. The molecule is nearly planar and the *o*-quinonoid nature of the benzene ring is remarkable. The phenolic C–O bond length 1.331 (7) Å is appreciably shortened. The geometry of the intramolecular hydrogen bonding between the phenolic and *o*-nitro groups is similar to that of the other *o*-nitrophenols [$O \cdots O$ 2.593 (7) Å, $O-H \cdots O$ 130 (6)°, $H \cdots O$ 1.89 (7) Å].

Introduction

As part of a programme of studies on the crystal and molecular structures of substituted phenols (Kawai,

Kashino & Haisa, 1976), the structure of 2,4-dinitrophenol, the prototype of ‘uncouplers’ of oxidative phosphorylation (White, Handler & Smith, 1973), has been studied by X-ray analysis. The main object of

this work is to study the geometry of intramolecular hydrogen bonding in *o*-nitrophenols, especially those having low acidity (pK_a) values (Andersen & Andersen, 1975), and the molecular stacking and overlapping in the crystals.

Experimental

2,4-Dinitrophenol crystallizes from an ethanol solution as yellow plates parallel to (010), elongated along [100] and bounded by {100} and {001}.

Crystal data

2,4-Dinitrophenol, $C_6H_4N_2O_5$, M.W. 184.1; m.p. 112–113°C; orthorhombic, $a=6.106$ (6), $b=23.24$ (2), $c=5.168$ (5) Å, $V=733$ (1) Å³, $D_x=1.667$ for $Z=4$, $D_m=1.67$ g cm⁻³ (by flotation in aqueous KI solution); $\mu(\text{Cu } K\alpha)=8.1$ cm⁻¹, $F(000)=376$; systematic absences $h00$, $h=\text{odd}$; $0k0$, $k=\text{odd}$; $00l$, $l=\text{odd}$; space group $P2_12_12_1$.

Crystals with dimensions $0.6 \times 0.2 \times 0.5$ and $0.3 \times 0.2 \times 0.3$ mm in glass capillaries were used to obtain Weissenberg photographs for the layers $0kl$ to $4kl$ and $hk0$ to $hk4$ respectively. Intensities were visually estimated and corrected for Lorentz and polarization factors and for spot shape. A total of 768 independent reflexions (75.4% of the total accessible in the Cu sphere) were placed on an absolute scale by means of a Wilson plot ($B=5.1$ Å²).

Structure determination and refinement

Trial coordinates for the non-H atoms were obtained from a sharpened Patterson map. Block-diagonal least-squares refinements with isotropic and then anisotropic thermal parameters reduced R from 0.32 to 0.10. At this stage, a difference Fourier map revealed all the H atoms. All the positional parameters in the final cycles of refinement were included along with anisotropic thermal parameters for the non-H atoms

and isotropic ones for the H atoms. The weighting scheme adopted was $w=1.0$ for $0 < |F_o| \leq 5.0$, and $w=(5.0/|F_o|)^2$ for $|F_o| > 5.0$. The final R value was 0.076 for 768 non-zero reflexions.*

The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). The computation was carried out on an NEAC 2200-500 computer at the Okayama University Computer Center. The programs used were *HBL5-5* and *DAPH* (Ashida, 1973).

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31888 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

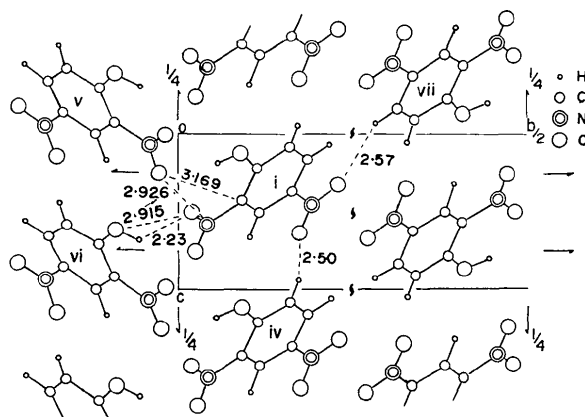


Fig. 1. Projection of the crystal structure viewed down the a axis. Broken lines show intermolecular contacts. Symmetry code: (i) x, y, z ; (ii) $1+x, y, z$; (iii) $x, y, 1+z$; (iv) $1+x, y, 1+z$; (v) $\frac{1}{2}-x, -y, -\frac{1}{2}+z$; (vi) $-\frac{1}{2}-x, -y, \frac{1}{2}+z$; (vii) $\frac{1}{2}+x, \frac{1}{2}-y, -z$.

Table 1. Final atomic parameters

Positional and thermal parameters for the non-H atoms are $\times 10^4$ with their e.s.d.'s in parentheses. Positional parameters for the H atoms are $\times 10^3$. The β_{ij} 's are defined by: $\exp(-h^2\beta_{11} - k^2\beta_{22} - l^2\beta_{33} - hk\beta_{12} - hl\beta_{13} - kl\beta_{23})$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O(1)	-1777 (6)	914 (2)	1291 (9)	295 (11)	19.9 (0.7)	568 (18)	-28 (5)	-132 (29)	13 (6)
O(2)	-1194 (8)	186 (2)	5032 (10)	464 (16)	28.6 (0.9)	634 (22)	-102 (7)	-0 (35)	57 (8)
O(3)	1509 (8)	264 (2)	7621 (8)	464 (15)	22.0 (0.7)	442 (16)	10 (6)	-3 (30)	55 (6)
O(4)	6880 (8)	1741 (2)	6494 (10)	414 (14)	35.6 (1.1)	511 (19)	-57 (7)	-493 (33)	53 (8)
O(5)	6737 (7)	2306 (2)	3245 (9)	347 (12)	21.8 (0.7)	521 (17)	-63 (5)	-1 (28)	15 (6)
N(1)	492 (8)	425 (2)	5773 (8)	352 (14)	16.8 (0.9)	384 (16)	-17 (5)	78 (29)	12 (6)
N(2)	6000 (7)	1913 (2)	4561 (8)	235 (11)	20.0 (0.8)	387 (16)	-22 (5)	-14 (26)	-10 (6)
C(1)	105 (9)	1127 (2)	2168 (10)	245 (13)	18.0 (0.9)	345 (18)	-1 (6)	2 (28)	-22 (7)
C(2)	1271 (8)	911 (2)	4296 (9)	268 (14)	14.6 (0.7)	310 (16)	-12 (6)	101 (28)	-5 (6)
C(3)	3231 (8)	1168 (2)	5074 (9)	257 (12)	15.7 (0.7)	308 (16)	-1 (6)	-20 (28)	4 (6)
C(4)	3972 (8)	1636 (2)	3728 (10)	220 (12)	15.8 (0.7)	334 (16)	-5 (5)	21 (28)	-10 (6)
C(5)	2856 (9)	1856 (2)	1627 (10)	303 (15)	15.9 (0.8)	331 (18)	-3 (6)	-65 (30)	10 (7)
C(6)	948 (9)	1603 (2)	859 (10)	280 (14)	18.0 (0.8)	354 (19)	9 (6)	-125 (31)	2 (7)
	x	y	z	B_{iso} (Å ²)	x	y	z	B_{iso} (Å ²)	
H(1)	-213 (12)	55 (3)	196 (14)	4.3 (1.6)	H(3)	340 (11)	219 (3)	71 (13)	3.7 (1.4)
H(2)	397 (9)	103 (2)	682 (11)	2.4 (1.2)	H(4)	13 (9)	172 (2)	-57 (10)	2.0 (1.2)

Results and discussion

Crystal structure

The final atomic parameters with their estimated standard deviations are listed in Table 1. The crystal structure viewed down the *a* axis is illustrated in Fig. 1. The molecules related by an *a* translation are stacked by a dipole-dipole interaction between the phenolic and nitro groups as shown in Fig. 2, to form a column along the *a* axis. The molecular overlapping is less than in 2-nitro-4-chlorophenol (Kawai, Kashino & Haisa, 1976). The columns are held together by an interaction between the atoms O(2) and H(1^{vi}) of the molecules related by a twofold screw axis along the *c* axis to form a sheet parallel to (010). The O(2)···H(1^{vi}) distance is 2.23 Å but the angle O(2)···H(1^{vi})-O(1^{vi}) is 129°, so that the interaction cannot be described as a bifurcated hydrogen bond. Such a situation has been discussed for α -glycine (Jönsson & Kvik, 1972). The contact is closer than the similar contact in 2-nitro-4-chlorophenol [O···H(O2^{iv}) 2.45 Å, O(1)···H(O2^{iv})-O(2^{iv}) 124°, O(1)···O(2^{iv}) 3.029 Å], hence the higher melting point.

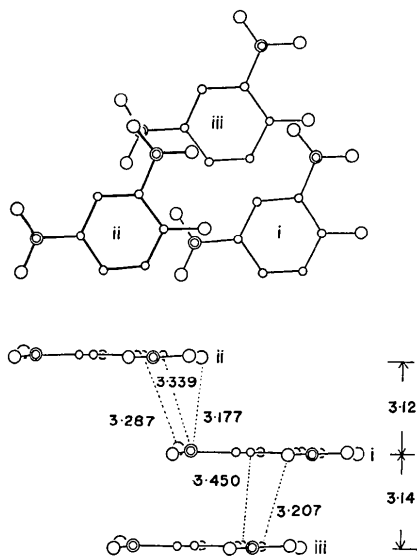


Fig. 2. The molecular overlapping and stacking, together with inter-ring spacing (Å) and intermolecular distances (Å). The symmetry code is given in the legend of Fig. 1.

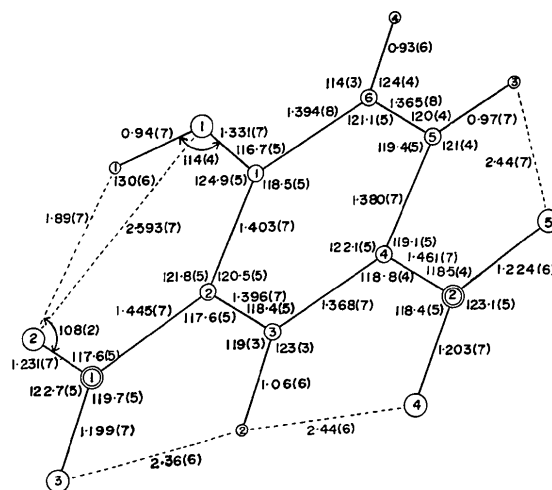


Fig. 3. Bond lengths (Å) and bond angles (°), with their e.s.d.'s in parentheses.

Table 2. The least-squares planes and displacements (Å) of the atoms from the planes

X, *Y* and *Z* refer to the crystallographic axes in Å. Atoms with an asterisk were used for the calculation of the plane.

(I) Benzene ring

$$0.5110X - 0.6073Y - 0.6084Z + 2.2387 = 0$$

C(1)*	-0.001	O(1)	-0.012	N(2)	-0.024
C(2)*	-0.002	O(2)	0.022	H(1)	0.18
C(3)*	0.004	O(3)	-0.059	H(2)	-0.13
C(4)*	-0.003	O(4)	-0.113	H(3)	-0.01
C(5)*	-0.001	O(5)	0.066	H(4)	0.03
C(6)*	0.003	N(1)	-0.022		

(II) 4-Nitro group

$$0.5259X - 0.6563Y - 0.5410Z + 2.2624 = 0$$

O(4)*	0.001	N(2)*	-0.004	C(3)	0.101
O(5)*	0.001	C(4)*	0.001	C(5)	-0.105

(III) 2-Nitro group

$$0.5377X - 0.6113Y - 0.5807Z + 2.1684 = 0$$

O(2)*	0.002	N(1)*	-0.006	C(1)	-0.049
O(3)*	0.002	C(2)*	0.002	C(3)	0.048

(IV) Chelate ring

$$0.5516X - 0.5879Y - 0.5917Z + 2.1651 = 0$$

O(1)*	-0.077	C(1)*	-0.003	C(3)	0.107
O(2)*	-0.030	C(2)*	0.034	C(6)	0.032
N(1)*	-0.015	H(1)*	0.10		

Table 3. The O···O contact (Å), torsion angles τ (°) and bond angles (°) characteristic of the intramolecular hydrogen bonding of *o*-nitrophenols

	(a)	(b)	(c)	(d)	(e)	(f)
O(1)···O(2)	2.546	2.557	2.558	2.587	2.593	2.599
τ [H(1)-O(1)-C(1)-C(2)]	1.9	-4.2	13.6	-5.3	-13.5	-5.7
τ [O(1)-C(1)-C(2)-N(1)]	-2.3	0.9	-1.7	-0.1	-0.4	0.2
τ [C(1)-C(2)-N(1)-O(2)]	3.6	-0.8	-4.6	-0.2	3.2	-8.6
C(2)-C(1)-O(1)	125.0	123.8	124.8	125.5	124.9	125.5
N(1)-C(2)-C(1)	119.7	120.9	120.1	120.6	121.8	120.7

References: (a) π -Molecular compound anthracene-picric acid (Herbstein & Kaftory, 1976). (b) 2,6-Dinitrophenol (Iwasaki, Sato & Aihara, 1976). (c) 2-Chloro-4,6-dinitrophenol (Andersen & Andersen, 1975). (d) 2-Nitro-4-chlorophenol (Kawai, Kashino & Haisa, 1976). (e) 2,4-Dinitrophenol (this work). (f) 2-Bromo-4,6-dinitrophenol (Neustadt & Cagle, 1975).

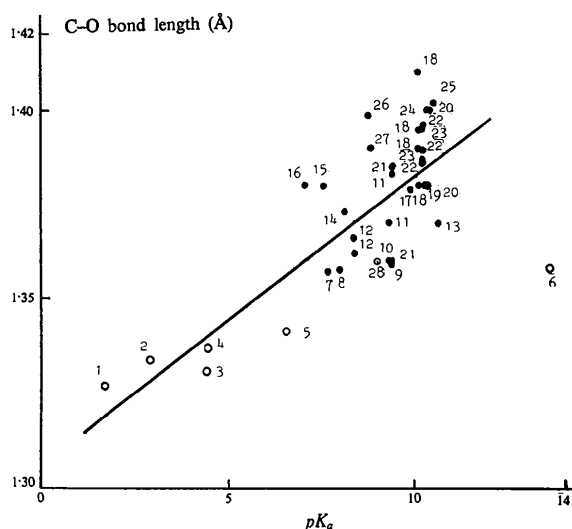


Fig. 4. The phenolic $C(sp^2)$ -O bond lengths vs the pK_a values, based on the complementary data for the Andersen & Andersen plot (solid line). Open circles denote *ortho* substituted phenols having intramolecular hydrogen bonding. References for bond lengths: (1) π -Molecular compound anthracene-picric acid (Herbstein & Kaftory, 1976). (2) 2-Bromo-4,6-dinitrophenol (Neustadt & Cagle, 1975). (3) 2,4-Dinitrophenol (this work). (4) 2,6-Dinitrophenol (Iwasaki, Sato & Aihara, 1976). (5) 2-Nitro-4-chlorophenol (Kawai, Kashino & Haisa, 1976). (6) Salicylic acid (Sundaralingam & Jensen, 1965). (7) *p*-Hydroxybenzaldehyde (Iwasaki, Sato & Aihara, 1973). (8) 3-Hydroxy-4-methoxybenzaldehyde (Iwasaki, 1973). (9) *p*-Hydroxybenzoic acid monohydrate (Fukuyama, Ohkura, Kashino & Haisa, 1973). (10) Piperidinium *p*-hydroxybenzoate (Fukuyama, Kashino & Haisa, 1973). (11) *p*-Chlorophenol, α -form (Perrin & Michel, 1973a). (12) *m*-Nitrophenol (Pandarese, Ungaretti & Coda, 1975). (13) 2,6-Dimethylphenol (Antona, Longchambon, Vandendorre & Becker, 1973). (14) 3,5-Dichlorophenol (Bavoux & Thozet, 1973). (15) 2,5-Dichlorophenol (Bavoux & Perrin, 1973). (16) 2,6-Dichlorophenol (Bavoux & Michel, 1973). (17) *m*-Aminophenol (De Rango, Brunie, Tsoucaris, Declercq & Germain, 1974). (18) *m*-Cresol (Bois, 1973). (19) *o*-Cresol (Bois, 1972). (20) 3,4-Dimethylphenol (Vandendorre, Gillier-Pandraud, Antona & Becker, 1973). (21) *p*-Chlorophenol, β -form (Perrin & Michel, 1973b). (22) *p*-Cresol, metastable form (Perrin & Thozet, 1974). (23) *p*-Cresol (Bois, 1970). (24) 2,5-Dimethylphenol (Neuman & Gillier-Pandraud, 1973). (25) 2,3-Dimethylphenol (Neuman & Gillier-Pandraud, 1973). (26) 2-Methyl-3-bromophenol (Maze-Baudet, 1973). (27) Salicylaldehyde (Bourre-Maladière, 1953). (28) Salicylamide (Sasada, Takano & Kakudo, 1964). The pK_a values for salicylaldehyde (27) and salicylamide (28) were taken from Ågren (1956), and those for the other phenols were estimated from the table of Brown, McDaniel & Häfliger (1955).

In accordance with the structure, the crystals have developed (010) planes.

The sheets are stacked along the *b* axis by weak van der Waals interactions; the shortest contacts are found between the atoms $O(4) \cdots H(4^{IV})$ and $O(5) \cdots H(3^{VII})$. These contacts and $O(4) \cdots C(1^{II})$ may co-operatively inhibit the nitro group at the C(4) atom causing it to undergo torsional librations about the C(4)-N(2) bond.

Molecular structure

Bond lengths and angles are shown in Fig. 3. The least-squares planes and the displacements of the atoms from the planes are listed in Table 2. The benzene ring is planar within 0.004 Å and makes dihedral angles of 2.2 and 4.9° with the nitro groups at the C(2) and C(4) positions, respectively, and 2.8° with the chelate ring.

The *o*-quinonoid nature of the benzene ring is remarkable, as in 2-nitro-4-chlorophenol and 2-bromo-4,6-dinitrophenol (Neustadt & Cagle, 1975). The C-N bond lengths are rather short but agree well with the values C(2)-N(1) 1.457, C(4)-N(2) 1.460 Å calculated from the O-N-O angle by the formula proposed by Kawai, Kashino & Haisa (1976). The C(1)-O(1) length is appreciably shortened as compared with the normal phenolic C-O length 1.368 Å (Brown, 1959) and agrees well with the value expected for a pK_a of 4.0 (Kolesnik, 1974) from the plot of Andersen & Andersen (1975). Fig. 4 shows the phenolic $C(sp^2)$ -O bond lengths of phenols vs the pK_a values based on the complementary data for the Andersen & Andersen plot. Thus the contraction of the phenolic C-O bond is possibly related to high conjugation in *o*-nitrophenols and to the mechanism of their uncoupling action.

The angle C(5)-C(4)-C(3) is close to, and the angles C(1)-C(2)-C(3) and C(6)-C(1)-C(2) are smaller than the values predicted from the electronegativity of the substituents (Domenicano, Mazzeo & Vaciago, 1975).

On the geometry of intramolecular hydrogen bonding in *o*-nitrophenols, it may generally be said from Table 3 that the $O(1) \cdots O(2)$ contact remains short, the torsion angles about the $O(1)-C(1)$, $C(1)-C(2)$ and $C(2)-N(1)$ bonds are relatively small, and the widening of the bond angles C(2)-C(1)-O(1) and N(1)-C(2)-C(1) is significant. The H(1) atom in the present compound twists appreciably against the C(2) atom about the C(1)-O(1) bond.

References

- ÅGREN, A. (1956). *Svensk Kem. Tidskr.* **68**, 189-199.
 ANDERSEN, E. K. & ANDERSEN, I. G. K. (1975). *Acta Cryst.* **B31**, 387-390.
 ANTONA, D., LONGCHAMBON, F., VANDENBORRE, M. T. & BECKER, P. (1973). *Acta Cryst.* **B29**, 1372-1376.
 ASHIDA, T. (1973). *The Universal Crystallographic Computing System - Osaka*. The Computation Center, Osaka Univ.
 BAVOUX, C. & MICHEL, P. (1973). *Acta Cryst.* **B30**, 2043-2045.
 BAVOUX, C. & PERRIN, M. (1973). *Acta Cryst.* **B29**, 666-668.
 BAVOUX, C. & THOZET, A. (1973). *Acta Cryst.* **B29**, 2603-2605.
 BOIS, C. (1970). *Acta Cryst.* **B26**, 2086-2092.
 BOIS, C. (1972). *Acta Cryst.* **B28**, 25-31.
 BOIS, C. (1973). *Acta Cryst.* **B29**, 1011-1017.
 BOURRE-MALADIÈRE, P. (1953). *C. R. Acad. Sci. Paris*, **237**, 825-827.
 BROWN, H. C., MCDANIEL, D. H. & HÄFLIGER, O. (1955). *Determination of Organic Structures by Physical Methods*, edited by E. A. BRAUDE & F. C. NACHOD, pp. 567-662. New York: Academic Press.

- BROWN, M. G. (1959). *Trans. Faraday Soc.* **55**, 694–701.
- DE RANGO, C., BRUNIE, S., TSOUCARIS, G., DECLERCQ, J. P. & GERMAIN, G. (1974). *Cryst. Struct. Commun.* **3**, 485–487.
- DOMENICANO, A., MAZZEO, P. & VACIAGO, A. (1975). *Acta Cryst.* **A31**, S117.
- FUKUYAMA, K., KASHINO, S. & HAISA, M. (1973). *Acta Cryst.* **B29**, 2713–2717.
- FUKUYAMA, K., OHKURA, K., KASHINO, S. & HAISA, M. (1973). *Bull. Chem. Soc. Japan*, **46**, 804–808.
- HERBSTEIN, F. H. & KAFTORY, M. (1976). *Acta Cryst.* **B32**, 387–396.
- International Tables for X-ray Crystallography* (1962). Vol. III, pp. 202–203. Birmingham: Kynoch Press.
- IWASAKI, F. (1973). *Chem. Lett.* pp. 227–228.
- IWASAKI, F., SATO, M. & AIHARA, A. (1973). *Chem. Lett.* pp. 249–250.
- IWASAKI, F., SATO, M. & AIHARA, A. (1976). *Acta Cryst.* **B32**, 102–106.
- JÖNSSON, P.-G. & KVICK, Å. (1972). *Acta Cryst.* **B28**, 1827–1833.
- KAWAI, R., KASHINO, S. & HAISA, M. (1976). *Acta Cryst.* **B32**, 1972–1975.
- KOLESNIK, M. I. (1974). *Zh. Fiz. Khim.* **48**, 1114–1118.
- MAZE-BAUDET, M. (1973). *Acta Cryst.* **B29**, 602–614.
- NEUMAN, A. & GILLIER-PANDRAUD, H. (1973). *Acta Cryst.* **B29**, 1017–1023.
- NEUSTADT, R. J. & CAGLE, F. W. JR (1975). *Acta Cryst.* **B31**, 2727–2729.
- PANDARESE, F., UNGARETTI, L. & CODA, A. (1975). *Acta Cryst.* **B31**, 2671–2675.
- PERRIN, M. & MICHEL, P. (1973a). *Acta Cryst.* **B29**, 253–258.
- PERRIN, M. & MICHEL, P. (1973b). *Acta Cryst.* **B29**, 258–263.
- PERRIN, M. & THOZET, A. (1974). *Cryst. Struct. Commun.* **3**, 661–664.
- SASADA, Y., TAKANO, T. & KAKUDO, M. (1964). *Bull. Chem. Soc. Japan*, **37**, 940–946.
- SUNDARALINGAM, M. & JENSEN, L. H. (1965). *Acta Cryst.* **18**, 1053–1058.
- VANDENBORRE, M. T., GILLIER-PANDRAUD, H., ANTONA, D. & BECKER, P. (1973). *Acta Cryst.* **B29**, 2488–2492.
- WHITE, A., HANDLER, P. & SMITH, E. L. (1973). *Principles of Biochemistry*, 5th ed., p. 367. New York: McGraw-Hill.

Acta Cryst. (1976). **B32**, 3175

Structure Cristalline de l'Orthotrithioarsénite Trisodique, Na_3AsS_3

PAR MARCEL PALAZZI

Laboratoire de Chimie Minérale Structurale LA 200 (Laboratoire de Physique), Faculté des Sciences Pharmaceutiques et Biologiques de Paris Luxembourg, 4 avenue de l'Observatoire, 75270 Paris Cédex 06, France

(Reçu le 12 mai 1976, accepté le 31 mai 1976)

Na_3AsS_3 crystallizes in the cubic system with $a = 8.566 \text{ \AA}$, space group $P2_13$. The structure was solved and refined to a final R value of 0.032 for 320 independent single-crystal reflexions. The coordination number of Na is six. The position of the unbound electron pair of As^{III} is found at about 1.25 \AA from the As atom.

Introduction

Après l'étude des thioarséniates (As^{V}): anhydre (Palazzi, Jaulmes & Laruelle, 1974) et hydratés (Palazzi, 1976; Jaulmes & Palazzi, 1976), nous avons entrepris celle des thioarsénites (As^{III}).

En étudiant les structures de Na_3AsS_3 et NaAsS_2 nous cherchons, d'une part, à connaître les modes d'enchaînements des atomes d'arsenic (linéaire, ramifié ou cyclique), et d'autre part, à déterminer le rôle stéréochimique éventuel du doublet solitaire de As^{III} .

Préparation

L'orthotrithioarsénite trisodique, Na_3AsS_3 , a été préparé, pour la première fois, par réaction dans l'état solide entre As_2S_3 et Na_2S dans la proportion de 1 mol pour 3 (Palazzi, 1972). Le mélange homogène des deux sulfures est comprimé en pastilles et chauffé sous atmosphère d'azote à 220°C . Les monocristaux utilisés

pour la détermination de la structure ont été obtenus après fusion et recristallisation du produit en poudre par la méthode de Bridgman.

Na_3AsS_3 est très sensible à l'action de l'eau. De couleur marron clair lorsqu'il est maintenu dans une atmosphère sèche il devient marron foncé et se décompose au contact de l'eau.

Afin d'éviter que le monocristal ne se décompose durant les mesures, en présence d'air humide, il est isolé dans un capillaire en pyrex, à parois très minces, scellé aux extrémités.

Données cristallographiques

La mesure du paramètre et la détermination du groupe spatial ont été effectuées à partir des diagrammes d'oscillation, de Weissenberg et de précession avec la radiation $\text{Mo K}\alpha$. Na_3AsS_3 cristallise dans le système cubique.

Les réflexions observées sur les différents clichés de