JENSEN, B. L., JEWETT-BRONSON, J., HADLEY, S. B. & FRENCH, L. G. (1982). *Synthesis*, **9**, 732–735.
JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
KIPPING, S. F. & HILL, A. (1899). *J. Chem. Soc.* **75**, 144–153.
KRONEBUSCH, P., GLEASON, W. B. & BRITTON, D. (1976). *Cryst. Struct. Commun.* **5**, 17–20; 839–842.
LECTARD, A., PETRISSANS, J. & HAUW, C. (1973). *Cryst. Struct. Commun.* **2**, 1–4.
LICHANOT, A., PETRISSANS, J., HAUW, C. & GAULTIER, J. (1974). *Cryst. Struct. Commun.* **3**, 223–225.
PRAKASH, A. (1967). *Acta Cryst.* **22**, 439–440.
RUTHERFORD, K. & STEVENS, C. L. (1955). *J. Am. Chem. Soc.* **77**, 3278–3280.
SEN, S. N. (1948). *Indian J. Phys.* **22**, 347–348.
SIMON, K. & SASVÁRI, K. (1973). *Cryst. Struct. Commun.* **2**, 481–484.
SMITH, G., KENNARD, C. & WHITNALL, J. (1977). *Cryst. Struct. Commun.* **6**, 131–136.
WILLIAMS, P. P. (1973). *Cryst. Struct. Commun.* **2**, 15–18.
YOON, N. M. & BROWN, H. C. (1968). *J. Am. Chem. Soc.* **90**, 2927–2938.

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cis-Thymidine 3′,5′-Cyclic *N,N*-Dimethylphosphoramidate Acetone Solvate, a Cyclic Nucleotide with an Axial Dimethylamino Substituent on Phosphorus

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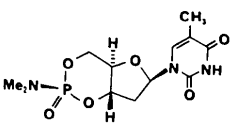
Abstract. $C_{12}H_{18}N_3O_6P.C_3H_6O$, $M_r = 389{\cdot}34$, orthorhombic, $P2_12_12_1$, $a = 12{\cdot}004$ (9), $b = 13{\cdot}702$ (9), $c = 23{\cdot}557$ (7) Å, $V = 3875$ (4) Å^3, $Z = 8$, $D_x = 1{\cdot}33$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, μ(Mo $K\alpha$) = 1·81 cm^{-1}, $F(000) = 1648$, $T = 298$ K, $R = 0{\cdot}091$ for 3306 unique data, 2531 of which were considered observed. There are two independent hydrogen-bonded (base-paired) nucleotide molecules and two acetone molecules in the asymmetric unit. The dioxaphosphorinane ring of each cyclic nucleotide adopts a distorted chair conformation with the pyramidal dimethylamino substituent axial. The pyrimidine ring exists in an *anti* conformation.

Introduction. There is considerable interest in the understanding of the effects of heteroatom substitution on the conformational properties of saturated six-membered rings. We have been concerned with the effects of various substituents on P on the solid-state conformations of 1,3,2-dioxa- (Day, Bentrude, Yee, Setzer, Deiters & Holmes, 1984; Warrent, Caughlan, Hargis, Yee & Bentrude, 1978; Haque, Caughlan, Hargis & Bentrude, 1970) and 1,3,2-oxazaphosphorinanes (Holmes, Day, Setzer, Sopchik & Bentrude, 1984; Bentrude, Day, Holmes, Quin, Setzer, Sopchik & Holmes, 1984; Newton, Pantaleo, Bentrude & Chandrasekaran 1982; Bajwa, Bentrude, Pantaleo, Newton & Hargis, 1979). Recently we have extended our studies to include the conformational analysis of neutral derivatives of nucleoside 3′,5′-cyclic monophosphates using NMR (Nelson, Sopchik & Bentrude, 1983; Sopchik, Bajwa, Nelson & Bentrude, 1981; Sopchik & Bentrude, 1980; Bajwa & Bentrude, 1978, 1980) and X-ray techniques (Newton, Pantaleo, Bajwa & Bentrude, 1977).

3′,5′-Cyclic nucleotides play an important role in cell metabolism; adenosine 3′,5′-cyclic monophosphate (cAMP) and guanosine 3′,5′-cyclic monophosphate (cGMP) are important bioregulator molecules. There has been growing interest in the synthesis and biological activity of cyclic nucleotides in which the P centers are derivatized as triesters or phosphoramidates (Bajwa & Bentrude, 1978, and references therein). These derivatives may potentially act as cyclic nucleotide mimics, as antagonists of cyclic nucleotide action, or as storage forms of the natural diester nucleotides themselves (Nargeot, Nerbonne, Engels & Lester, 1983, and references therein).

This paper reports the crystal structure of *cis*-thymidine 3′,5′-cyclic *N,N*-dimethylphosphoramidate, (1), a cyclic nucleotide with an axially disposed dimethylamino group on the P atom of the dioxaphosphorinane ring.



(1)

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Experimental. *Preparation of thymidine 3′,5′-cyclic N,N-dimethylphosphoramidate.* Dimethyl chloramine (0·5 mL) (Bock & Kompa, 1966) was added to a cooled (195 K) stirred solution of methyl thymidine 3′,5′-cyclic phosphite (1·0 g, 3·31 mmol) (Bajwa & Bentrude, 1978) in anhydrous dichloromethane (20 mL). The reaction mixture was allowed to warm to room temperature and stirred for 3 h. All volatile materials were removed from the reaction mixture *in vacuo* and the residue chromatographed by MPLC on a 15 × 1000 mm column of silica gel (Merck, 230-400 mesh), eluting with $CHCl_3/CH_3OH$ (97:3), to give 500 mg of pure *trans*-phosphoramidate: ^{31}P NMR ($CDCl_3$) δ 8·63 (Baschang & Kvita, 1973) and 200 mg of pure *cis*-phosphoramidate: ^{31}P NMR ($CDCl_3$) δ 7·22 (Sopchik & Bentrude, 1980). Crystals of the *cis*-phosphoramidate, suitable for X-ray crystallography, were obtained by slow evaporation of a solution of the compound in acetone.

Structure determination. Syntex $P\bar{1}$ diffractometer; cell parameters refined by least-squares method from the setting angles of 15 reflections in the 2θ range 5·7–21·7°; intensities collected with Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71073$ Å), $4{\cdot}0 \le 2\theta \le 50{\cdot}0°$, θ–2θ scan; no absorption or extinction correction; data reduced to F_o^2 and $\sigma(F_o^2)$, data with $I \ge 3\sigma(I)$ considered observed (2531 of 3306 unique data); structure solved (Cyber 172 computer) by *MULTAN*78 (Main, Lessinger, Woolfson, Germain & Declercq, 1978); all but two of the nonhydrogen atoms in the two nucleotides were obtained from the solution with the highest FOM; difference maps revealed the two remaining atoms and the two acetone molecules; structure refined by block-matrix least squares; neutral-atom scattering factors for all species (*International Tables for X-ray Crystallography*, 1974); H atoms added in geometrically ideal positions and not refined, methyl H atoms were assumed to be staggered if the methyl C was bonded to an sp^3-hybridized atom, the H atoms on C(7) were positioned assuming H and C(6) to be *anti*, acetone H atoms were not added; final conventional $R = 0{\cdot}091$, $wR = 0{\cdot}096$, $w = 4F_o^2/[\sigma^2(F_o^2) + (0{\cdot}04F_o^2)^2]$ (Corfield, Doedens & Ibers, 1967); largest peak in final difference map = 0·5 e Å^{-3}. Range of *hkl*: *h* 0–14, *k* 0–16, *l* 0–28. $(\Delta/\sigma)_{max} = 0{\cdot}9$. Three standard reflections (600, 060, 0,0,12) monitored every 97 reflections; no discernible decomposition of the crystal. Major programs used during structure determination were *FORDAP* (Fourier summation program by A. Zalkin) and *NUCLS* [structure factor calculations and least-squares refinement by J. A. Ibers, itself a modification of *ORFLS* (Busing, Martin & Levy, 1962)].

Discussion. The final atomic parameters with their standard deviations are listed in Table 1.* There are two independent hydrogen-bonded (base-paired) nucleotide molecules and two acetone molecules in the asymmetric

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and bond lengths, bond angles, and torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42541 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates and isotropic thermal parameters* (Å^2 × 10^3) *for* (1)

Estimated standard deviations are in parentheses. U_{iso} is given for atoms bearing H, and $U_{eq} = (U_{11} + U_{22} + U_{33})/3$ for atoms not bearing H.

	First molecule				Second molecule			
	x	*y*	*z*	U_{iso} or U_{eq}	*x*	*y*	*z*	U_{iso} or U_{eq}
P	0·3609 (3)	1·1562 (2)	0·4775 (1)	66 (2)	0·4595 (3)	0·1315 (2)	0·2594 (1)	55 (2)
O(4′)	0·6669 (5)	1·0337 (5)	0·4154 (3)	58 (4)	0·3709 (6)	0·4008 (5)	0·3408 (3)	58 (4)
O(3′)	0·3763 (6)	1·0587 (5)	0·4428 (3)	55 (4)	0·3440 (6)	0·1596 (4)	0·2861 (3)	58 (4)
O(5′)	0·4673 (8)	1·2194 (5)	0·4655 (3)	74 (5)	0·5457 (5)	0·2063 (5)	0·2831 (3)	65 (5)
N′	0·3716 (10)	1·1240 (7)	0·5437 (4)	83 (7)	0·4487 (8)	0·1597 (6)	0·1921 (4)	65 (6)
O′	0·2629 (8)	1·2074 (7)	0·4601 (4)	96 (7)	0·4911 (8)	0·0314 (5)	0·2752 (3)	77 (5)
C(8)	0·4077 (16)	1·1934 (14)	0·5871 (7)	115 (6)	0·5498 (14)	0·1646 (12)	0·1602 (7)	101 (5)
C(9)	0·2941 (14)	1·0470 (12)	0·5636 (7)	97 (5)	0·3589 (14)	0·1163 (13)	0·1611 (7)	107 (5)
C(1′)	0·6292 (8)	0·9499 (6)	0·3860 (4)	44 (2)	0·2576 (8)	0·3835 (8)	0·3569 (5)	53 (3)
C(2′)	0·5079 (7)	0·9336 (7)	0·4053 (4)	44 (2)	0·2203 (9)	0·2934 (8)	0·3242 (5)	56 (3)
C(3′)	0·4878 (7)	1·0198 (6)	0·4436 (4)	40 (2)	0·3238 (8)	0·2646 (7)	0·2909 (4)	50 (3)
C(4′)	0·5653 (8)	1·0918 (7)	0·4223 (4)	48 (2)	0·4144 (8)	0·3063 (7)	0·3251 (4)	48 (3)
C(5′)	0·5787 (10)	1·1785 (9)	0·4631 (6)	74 (4)	0·5190 (10)	0·3078 (8)	0·2947 (5)	63 (3)
N(1)	0·7080 (7)	0·8733 (6)	0·4051 (4)	53 (5)	0·1984 (7)	0·4732 (6)	0·3429 (3)	47 (4)
C(2)	0·7916 (8)	0·8481 (7)	0·3663 (4)	46 (6)	0·1420 (8)	0·5184 (7)	0·3881 (4)	46 (6)
O(2)	0·7972 (6)	0·8796 (5)	0·3186 (3)	67 (5)	0·1358 (7)	0·4883 (5)	0·4347 (3)	64 (5)
N(3)	0·8666 (6)	0·7806 (5)	0·3889 (3)	44 (2)	0·0847 (7)	0·6023 (6)	0·3699 (4)	52 (2)
C(4)	0·8663 (9)	0·7402 (7)	0·4406 (4)	48 (6)	0·0869 (8)	0·6446 (7)	0·3163 (4)	45 (5)
O(4)	0·9416 (6)	0·6812 (5)	0·4541 (3)	60 (4)	0·0312 (7)	0·7201 (5)	0·3084 (3)	71 (5)
C(5)	0·7772 (9)	0·7714 (7)	0·4786 (4)	49 (6)	0·1524 (9)	0·5977 (7)	0·2751 (5)	57 (6)
C(6)	0·7044 (9)	0·8356 (7)	0·4585 (4)	50 (3)	0·2046 (9)	0·5128 (8)	0·2899 (5)	54 (3)
C(7)	0·7719 (12)	0·7308 (10)	0·5370 (6)	79 (4)	0·1642 (9)	0·6409 (8)	0·2164 (5)	63 (3)
O(A)	0·5311 (15)	0·5953 (14)	0·4981 (8)	185 (6)	0·7177 (11)	0·6020 (10)	0·7830 (6)	140 (5)
C(1A)	0·4956 (16)	0·5182 (15)	0·5135 (9)	122 (7)	0·6845 (15)	0·5767 (12)	0·7383 (8)	106 (5)
C(2A)	0·4086 (17)	0·4733 (14)	0·4801 (9)	127 (6)	0·7437 (16)	0·6028 (15)	0·6861 (9)	128 (6)
C(3A)	0·5334 (23)	0·4787 (22)	0·5623 (13)	190 (10)	0·5837 (23)	0·5189 (21)	0·7347 (12)	178 (10)

unit. An *ORTEP* perspective view (Johnson, 1965) of the hydrogen-bonded pair is shown in Fig. 1. The numbering scheme, including average bond lengths and selected bond angles, is given in Fig. 2.

The two independent nucleotide molecules are hydrogen bonded to each other by way of mutual N(3)—H(3)···O(4) hydrogen bonds (Fig. 1). The N(3)···O(4) intermolecular distances are 2·86 (1) and 2·84 (1) Å. The acetone molecules both appear to have attractive dipole–dipole interactions with nucleotide 4-carbonyl groups: in the first molecule, the C(4) of the carbonyl group is 3·33 (2) Å from an acetone O whereas, in the second molecule, the nucleotide carbonyl oxygen, O(4), is 3·51 (2) Å from the C of the other acetone.

The conformation adopted by the thymine base in compound (1) is *anti*. The glycosyl torsion angles, χ[O(4′)—C(1′)—N(1)—C(2)], for the two independent molecules are 252·8 and 233·1°.* The *anti* conformation is found in crystalline thymidine (Young, Tollin & Wilson, 1969), thymidylyl thymidylate (Camerman, Fawcett & Camerman, 1976), and 6-azathymidine (Banerjee & Saenger, 1978). Uridine 3′,5′-cyclic monophosphate (Coulter, 1969) and *trans*-5-isopropyl-2′-deoxyuridine 3′,5′-cyclic *N*-benzylphosphoramidate (Béres, Bentrude, Párkányi, Kálmán & Sopchik, 1985) also crystallize with *anti* orientations of the base. The *anti* orientation has been calculated to be about 13 kJ mol^{-1} more stable than the *syn* alternative for pyrimidine cyclic nucleotides (Yathindra & Sundaralingam, 1974). Interestingly, however, the benzyl triester of 2′-acetyluridine 3′,5′-cyclic monophosphate (Depmeier, Engels & Klaska, 1977), *trans*-thymidine 3′,5′-cyclic *N,N*-dimethylphosphoramidate (Newton, Pantaleo, Bajwa & Bentrude, 1977) and 5-iodouridine 3′,5′-cyclic monophosphate (Béres, Bentrude, Kálmán, Párkányi, Balzarini & De Clercq, 1985) have *syn* conformations about the glycosidic bond.

The geometrical parameters (bond lengths and bond angles) in the ribose ring and the base are comparable to those found in thymidine itself (Young, Tollin & Wilson, 1969) with the exception of the C(3′)—C(4′) bond length. In thymidine this bond length is 1·53 Å, whereas in (1) it is 1·45 (1) and 1·47 (1) Å. The 1,3,2-dioxaphosphorinane ring in (1) shows bond lengths and bond angles similar to those of other neutral cyclic nucleotide derivatives (Béres, Sándor, Kálmán, Koritsánszky & Ötvös, 1984; Cotton, Gillen, Gohil, Hazen, Kirchner, Nagyvary, Rouse, Stanislowski, Stevens & Tucker, 1975).

The ribose rings of (1) adopt severely twisted $_4T^3$, C(4′)-*exo*/C(3′)-*endo*, conformations (Sundaralingam & Abola, 1972) as evidenced by the relatively small O(4′)—C(1′)—C(2′)—C(3′) torsion angles, ν_1, of 1·0 and 2·1°, and the large C(4′)—O(4′)—C(1′)—C(2′) torsion angles, ν_0, of −27·2 and −29·3°. The 1,3,2-dioxaphosphorinane ring of (1) is in a distorted chair conformation, although in solution the twist conformation is populated to the extent of 64–75%. The P end of the six-membered ring is flattened as is generally observed in 1,3,2-dioxaphosphorinanes (Warrent, Caughlan, Hargis, Yee & Bentrude, 1978). The P—O(3′)—C(3′) angles are 114·5 (6) and 114·7 (6)° while the P—O(5′)—C(5′) angles are opened to 123·0 (7) and 123·4 (7)°. These bond angles are similar to those found in other cyclic nucleotides (Newton, Pantaleo, Bajwa & Bentrude, 1977, and references therein).

The dimethylamino substituent on P adopts an axial orientation and is pyramidal rather than planar with a relatively long P—N bond. These effects have been previously observed. Dialkylamino substituents on P are planar if the group is equatorial but pyramidal when the group is axial in phosphorinanes (Newton, Pantaleo, Bentrude & Chandrasekaran, 1982, and references therein; Holmes, Day, Setzer, Sopchik & Bentrude, 1984).

The uncommonly high *R* factor in this structure may be due in part to the observed large degree of thermal motion, or possibly disorder, present in the acetone solvent molecules and in the dimethylamino substituent on P. Because of the relatively small number of observed data per number of variables, non-hydrogen atoms bearing H were refined isotropically in order to keep the ratio of the number of data per number of variables approximately eight. It may be that much of the thermal motion is anisotropic and is not well accommodated by isotropic refinement, also accounting for the high *R*.

* The atom labeling and definitions of χ, ν_0 and ν_1 are according to *Eur. J. Biochem.* (1983), **131**, 9–15.

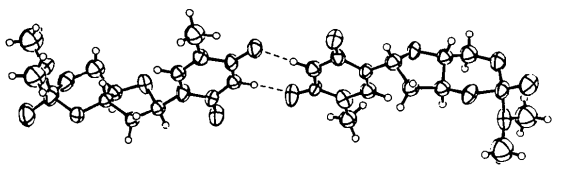

Fig. 1. *ORTEP* perspective view of the hydrogen-bonded pair of (1).

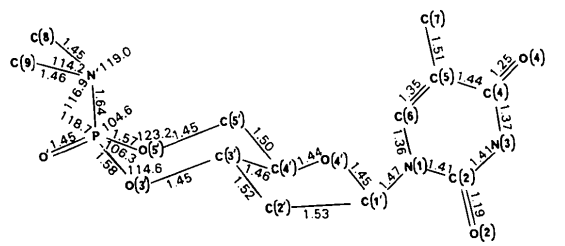

Fig. 2. Labeling scheme with average bond lengths (Å) and selected bond angles (°) for (1).

References

BAJWA, G. S. & BENTRUDE, W. G. (1978). *Tetrahedron Lett.* pp. 421–424.

BAJWA, G. S. & BENTRUDE, W. G. (1980). *Tetrahedron Lett.* pp. 4683–4686.

BAJWA, G. S., BENTRUDE, W. G., PANTALEO, N. W., NEWTON, M. G. & HARGIS, J. H. (1979). *J. Am. Chem. Soc.* **101**, 1602–1604.

BANERJEE, A. & SAENGER, W. (1978). *Acta Cryst.* B**34**, 1294–1298.

BASCHANG, G. & KVITA, V. (1973). *Angew. Chem. Int. Ed. Engl.* **12**, 71–72.

BENTRUDE, W. G., DAY, R. O., HOLMES, J. M., QUIN, G. S., SETZER, W. N., SOPCHIK, A. E. & HOLMES, R. R. (1984). *J. Am. Chem. Soc.* **106**, 106–111.

BÉRES, J., BENTRUDE, W. G., KÁLMÁN, A., PÁRKÁNYI, L., BALZARINI, J. & DE CLERCQ, E. (1985). *J. Med. Chem.* Submitted.

BÉRES, J., BENTRUDE, W. G., PÁRKÁNYI, L., KÁLMÁN, A. & SOPCHIK, A. E. (1985). *J. Org. Chem.* **50**, 1271.

BÉRES, J., SÁNDOR, P., KÁLMÁN, A., KORITSÁNSZKY, T. & ÖTVÖS, L. (1984). *Tetrahedron*, **40**, 2405–2414.

BOCK, H. & KOMPA, K. (1966). *Chem. Ber.* **99**, 1347–1356.

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS.* Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.

CAMERMAN, N., FAWCETT, J. K. & CAMERMAN, A. (1976). *J. Mol. Biol.* **107**, 601–621.

CORFIELD, P. W. R., DOEDENS, R. J. & IBERS, J. A. (1967). *Inorg. Chem.* **6**, 197–204.

COTTON, F. A., GILLEN, R. G., GOHIL, R. N., HAZEN, E. E. JR, KIRCHNER, C. R., NAGYVARY, J., ROUSE, J. P., STANISLOWSKI, A. G., STEVENS, J. D. & TUCKER, P. W. (1975). *Proc. Natl Acad. Sci. USA*, **72**, 1335–1339.

COULTER, C. L. (1969). *Acta Cryst.* B**25**, 2055–2065.

DAY, R. O., BENTRUDE, W. G., YEE, K. C., SETZER, W. N., DEITERS, J. A. & HOLMES, R. R. (1984). *J. Am. Chem. Soc.* **106**, 103–106.

DEPMEIER, W., ENGELS, J. & KLASKA, K.-H. (1977). *Acta Cryst.* B**33**, 2436–2440.

HAQUE, M., CAUGHLAN, C. N., HARGIS, J. H. & BENTRUDE, W. G. (1970). *J. Chem. Soc. A*, pp. 1786–1791.

HOLMES, R. R., DAY, R. O., SETZER, W. N., SOPCHIK, A. E. & BENTRUDE, W. G. (1984). *J. Am. Chem. Soc.* **106**, 2353–2358.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 71–98. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

JOHNSON, C. K. (1965). *ORTEP.* Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

MAIN, P., LESSINGER, L., WOOLFSON, M. M., GERMAIN, G. & DECLERCQ, J.-P. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain-la-Neuve, Belgium.

NARGEOT, J., NERBONNE, J. M., ENGELS, J. & LESTER, H. A. (1983). *Proc. Natl Acad. Sci. USA*, **80**, 2395–2399.

NELSON, K. A., SOPCHIK, A. E. & BENTRUDE, W. G. (1983). *J. Am. Chem. Soc.* **105**, 7752–7754.

NEWTON, M. G., PANTALEO, N. S., BAJWA, G. S. & BENTRUDE, W. G. (1977). *Tetrahedron Lett.* pp. 4457–4460.

NEWTON, M. G., PANTALEO, N. S., BENTRUDE, W. G. & CHANDRASEKARAN, S. (1982). *Tetrahedron Lett.* pp. 1527–1530.

SOPCHIK, A. E., BAJWA, G. S., NELSON, K. A. & BENTRUDE, W. G. (1981). *Phosphorus Chemistry.* ACS Symp. Ser. No. 171, edited by L. D. QUIN & J. VERKADE, pp. 217–220. Washington: American Chemical Society.

SOPCHIK, A. E. & BENTRUDE, W. G. (1980). *Tetrahedron Lett.* pp. 4679–4682.

SUNDARALINGAM, M. & ABOLA, J. (1972). *J. Am. Chem. Soc.* **94**, 5070–5076.

WARRENT, R. W., CAUGHLAN, C. N., HARGIS, J. H., YEE, K. C. & BENTRUDE, W. G. (1978). *J. Org. Chem.* **43**, 4266–4270.

YATHINDRA, N. & SUNDARALINGAM, M. (1974). *Biochem. Biophys. Res. Commun.* **56**, 119–126.

YOUNG, D. W., TOLLIN, P. & WILSON, H. R. (1969). *Acta Cryst.* B**25**, 1423–1432.

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Structure of Benzamidine Hydrochloride Monohydrate

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Abstract. $C_7H_9N_2^+.Cl^-.H_2O$, $M_r = 174{\cdot}5$, orthorhombic, $P2_12_12_1$, $a = 7{\cdot}328\,(2)$, $b = 8{\cdot}500\,(2)$, $c = 14{\cdot}573\,(3)$ Å, $V = 907{\cdot}7\,(4)$ Å^3, $Z = 4$, D_m(flotation) $= 1{\cdot}279$, $D_x = 1{\cdot}277$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å, $\mu = 3{\cdot}78$ cm^{-1}, $F(000) = 368$, $T = 293$ K, final $R = 0{\cdot}051$ for 707 observed reflections with $I > 2\sigma(I)$. The imine group is protonated. Chlorine is involved in five hydrogen bonds, three of N—H···Cl and two of O(W)—H···Cl type. The terminal C—C$\begin{smallmatrix}\diagup\mathrm{N}\\ \diagdown\mathrm{N}\end{smallmatrix}$ plane makes an angle of 36·6 (8)° with the benzene-ring plane, which prevents conjugation between the two unsaturated systems.

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