molecules. Fig. 4 presents a stereodiagram of the packing arrangement of the molecules in the unit cell and Fig. 5 is a simplification of the packing diagram where only the molecular centers are shown. All hexaphenylbenzene molecules in this structure are positioned with their molecular sixfold axes roughly parallel to the a axis. The hexagonal packing near $y = 0$ and $y = 1/2$ corresponds to the packing in the hexaphenylbenzene structure (Bart, 1968). These regions are separated by body-centered packing layers containing anisole molecules in the 'octahedral holes'. Two hexaphenylbenzene molecules from adjacent unit cells along a serve to form the top and bottom of a cavity with the anisole perpendicular to the central C_6 rings, and four other hexaphenylbenzene molecules are the sides of the hole. Thus, the anisole is surrounded by six individual host molecules arranged in a pseudo-octahedron (Fig. 5), unlike the other reported structures for hexa-host compounds. In most of the other known clathrate structures, the solvated molecules are enclosed within a cage formed by just two host molecules. While some of the previous studies have shown some disorder in the solvated molecule, none is observed in the case of hexaphenylbenzene anisole. A refinement of the occupancy of anisole produced a value of 0·992 (6), thus this clathrate is stoichiometric. A search of the distances yielded no intermolecular or intramolecular contacts shorter than the sum of the van der Waals radii for the atoms.

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Structure of 2-Amino-6-chloromethyl-3-cyano-5-ethoxycarbonyl-4-(2-furyl)-4*H*-pyran

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Abstract. Ethyl 6-amino-2-chloromethyl-5-cyano-4-(2-furyl)-4*H*-pyran-3-carboxylate, $C_{14}H_{13}ClN_2O_4$, $M_r = 308·7$, triclinic, $P\bar{1}$, $a = 11·356\ (6)$, $b = 9·066\ (4)$, $c = 8·390\ (3)$ Å, $\alpha = 105·55\ (3)$, $\beta = 104·89\ (4)$, $\gamma = 110·09\ (4)°$, $V = 721·1$ Å^3, $Z = 2$, $D_x = 1·421$, $D_m = 1·42$ Mg m^{-3}. $\lambda(\mathrm{Cu}\ K\alpha) = 1·54178$ Å, $\mu = 1·18$ mm^{-1}, $F(000) = 320$, $T = 293$ K, final $R = 0·056$ for 1631 unique observed reflections. The molecular structure is analyzed in detail and results are compared with those of three analogues reported earlier with variations in ring substitutions, as well as with results of closely related 1,4-dihydropyridines.

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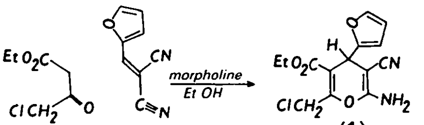
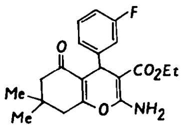
The substituted 4*H*-pyran ring in the title compound assumes a flat-boat conformation. The ethoxycarbonyl and furyl groups are twisted out of the pyran ring plane by 16·2 and 88·5° respectively.

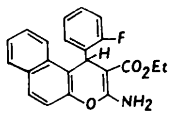
Introduction. The present structure (1) relates to our continuing study on the relationship between ring substitution pattern and the conformation of the 4*H*-pyran ring. It was prepared by a cycloaddition reaction of 2-furylidenepropanedinitrile with ethyl 4-chloro-3-oxobutanoate in the presence of morpholine (Marchalín, Pavlíková & Ilavský, 1989). The structures of (2), (3) and (4) (Sharanina, Nesterov, Klokol, Rodinovskaya, Shklover, Sharanin, Struchkov & Promonenkov, 1986; Klokol, Sharanina, Nesterov, Shklover, Sharanin & Struchkov, 1987; Ukhin, Bessonov, Yanovskii, Timofeeva, Furmanova & Struchkov, 1980), analogues of the present compound, have been reported previously.



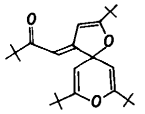
(1)



(2)



(3)



(4)

Table 1. *Final atomic coordinates* (× 10^4) *with e.s.d.'s in parentheses and equivalent isotropic thermal parameters* (Å^2)

$$B_{eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j B_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Cl(1)	1543 (1)	9015 (1)	9115 (1)	5·04
Cl(2)	3889 (1)	9472 (1)	10389 (1)	6·74
O(1)	1950 (1)	5868 (1)	8301 (2)	5·03
O(2)	3893 (1)	4378 (2)	10880 (2)	6·19
O(3)	1563 (1)	5765 (2)	13734 (2)	5·26
O(4)	2735 (1)	8317 (1)	13782 (2)	5·08
N(1)	1138 (2)	3609 (2)	5781 (2)	4·97
N(2)	− 158 (2)	−41 (2)	6913 (2)	9·59
C(2)	1357 (2)	4134 (2)	7515 (2)	3·86
C(3)	1083 (2)	3188 (2)	8495 (2)	3·71
C(4)	1612 (2)	3996 (2)	10523 (2)	3·42
C(5)	1918 (2)	5860 (2)	11125 (2)	3·67
C(6)	2085 (2)	6689 (2)	10036 (2)	4·50
C(7)	411 (2)	1409 (2)	7617 (2)	5·36
C(8)	2840 (2)	3802 (2)	11393 (2)	3·49
C(9)	3187 (2)	3213 (3)	12645 (2)	5·34
C(10)	4540 (2)	3439 (3)	12948 (3)	6·11
C(11)	4919 (2)	4127 (3)	11859 (3)	7·19
C(12)	2047 (2)	6637 (2)	12990 (2)	3·93
C(13)	2451 (3)	8510 (3)	10370 (3)	7·23
C(14)	2867 (2)	9105 (2)	15635 (2)	5·84
C(15)	3610 (3)	10983 (3)	16242 (3)	7·58

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

O(1)—C(2)	1·360 (2)	C(10)—C(11)	1·316 (4)
C(2)—C(3)	1·354 (3)	C(11)—O(2)	1·369 (3)
C(3)—C(4)	1·516 (2)	O(2)—C(8)	1·357 (3)
C(4)—C(5)	1·510 (3)	C(5)—C(12)	1·478 (2)
C(5)—C(6)	1·340 (3)	C(12)—O(3)	1·208 (2)
C(6)—O(1)	1·387 (2)	C(12)—O(4)	1·321 (2)
C(2)—N(1)	1·329 (2)	O(4)—C(14)	1·470 (2)
C(3)—C(7)	1·398 (3)	C(14)—C(15)	1·482 (3)
C(7)—N(2)	1·140 (3)	C(6)—C(13)	1·483 (3)
C(4)—C(8)	1·491 (3)	C(13)—Cl(1)	1·551 (3)
C(8)—C(9)	1·333 (3)	C(13)—Cl(2)	1·558 (3)
C(9)—C(10)	1·423 (4)		

C(6)—O(1)—C(2)	120·4 (2)	C(8)—C(9)—C(10)	107·0 (2)
O(1)—C(2)—C(3)	120·5 (2)	C(9)—C(10)—C(11)	106·7 (2)
C(2)—C(3)—C(4)	121·7 (2)	C(10)—C(11)—O(2)	110·1 (2)
C(3)—C(4)—C(5)	109·7 (1)	C(11)—O(2)—C(8)	106·9 (2)
C(4)—C(5)—C(6)	121·1 (2)	C(4)—C(5)—C(12)	113·8 (2)
C(5)—C(6)—O(1)	121·7 (2)	C(6)—C(5)—C(12)	125·2 (2)
O(1)—C(2)—N(1)	110·7 (2)	C(5)—C(12)—O(3)	121·1 (2)
C(3)—C(2)—N(1)	128·8 (2)	C(5)—C(12)—O(4)	116·1 (2)
C(2)—C(3)—C(7)	118·6 (2)	O(3)—C(12)—O(4)	122·8 (2)
C(4)—C(3)—C(7)	119·4 (2)	C(12)—O(4)—C(14)	116·6 (2)
C(3)—C(7)—N(2)	178·5 (2)	O(4)—C(14)—C(15)	108·1 (2)
C(3)—C(4)—C(8)	112·1 (1)	C(5)—C(6)—C(13)	130·2 (2)
C(5)—C(4)—C(8)	110·4 (1)	O(1)—C(6)—C(13)	108·1 (2)
C(4)—C(8)—C(9)	134·5 (2)	C(6)—C(13)—Cl(1)	120·6 (2)
C(4)—C(8)—O(2)	116·1 (2)	C(6)—C(13)—Cl(2)	112·5 (2)
O(2)—C(8)—C(9)	109·4 (2)		

Experimental. Crystal used 0·4 × 0·2 × 0·15 mm; D_m by flotation in bromoform/cyclohexane; Syntex $P2_1$ diffractometer; accurate unit-cell parameters by least-squares refinement of 15 reflections, $15 < \theta < 45°$; intensity data (h 0–12, $k \pm 9$, $l \pm 8$) by θ–2θ scans, variable rate 4·9 to 29·3° min^{-1} in 2θ, background-to-scan-time ratio = 1·0, scan width 2° plus α_1–α_2 dispersion, Cu $K\alpha$ radiation filtered by graphite monochromator; two standards every 98 reflections: no appreciable changes; 1755 unique reflections, $3 < \theta \leq 55°$, 1631 with $I \geq 2\sigma(I)$ considered observed and included in the refinement; Lp correction but none for absorption or extinction; structure solved by direct methods using *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and refined by block-diagonal least-squares methods, anisotropic thermal parameters for non-H atoms, H atoms appeared on a difference Fourier map but were included in calculated positions, not refined, with common isotropic thermal parameter, $B = 4·0$ Å^2; in final cycle $R = 0·056$, $wR = 0·063$ for observed reflections only, $S = 1·45$, max. shift/e.s.d. = 0·12, function minimized $\sum w(\Delta F)^2$, where $w = 1$ if $|F_o| < 15$ and $w = 15/|F_o|$ if $|F_o| \geq 15$, max. and min. height in final $\Delta\rho$ synthesis 0·21 and $-0·29$ e Å^{-3}; scattering factors for neutral atoms from *International Tables for X-ray Crystallography* (1974); all calculations except *MULTAN* performed with a local version of the *NRC* system (Ahmed, Hall, Pippy & Huber, 1973).

Discussion. Final atomic coordinates of non-H atoms and equivalent isotropic *B*'s for the title compound (1) are listed in Table 1,* bond distances and angles in Table 2. A view of the molecule with atom numbering is shown in Fig. 1. The Cl atom of the chloromethyl group is disordered between two well defined sites [Cl(1) and Cl(2)], the sum of the refined occupancy factors being close to unity (1·02). However, the C(13)—Cl(1) and C(13)—Cl(2) bond lengths are very short (1·55 and 1·56 Å respectively). This might be caused by unresolved disorder of C(13) as indicated by its high thermal motion, which is substantially higher than that of the surrounding atoms.

There is some delocalization involving the donors O(1) and N(1) and the acceptor (cyano group) as reflected in the molecular dimensions. The C(2)—C(3) bond distance of 1·354 (3) Å is slightly but significantly longer than the C=C bond in ethylene [1·336 (2) Å (Bartell, Roth, Hollowell, Kuchitsu & Young, 1965)]. There is a corresponding shortening of the O(1)—C(2) [1·360 (2) Å] and N(1)—C(2) [1·329 (2) Å] bonds relative to the normal C(sp^2)—O (1·403 Å) and C(sp^2)—N (1·426 Å) bonds (Ammon, Mazzocchi, Regan & Colicelli, 1979). On the acceptor side, C(3)—C(7) is 1·398 (3) Å, which is shorter than usually observed in nitriles (Fallon, Fitzmaurice, Jackson & Perlmutter, 1986; Durant, Bufkens, Lefevre, Evrard & Michel, 1985). The remaining distances within the pyran ring correspond approximately to the integer bond orders. Similarly, the bond lengths and angles within the substituent groups are close to those generally expected.

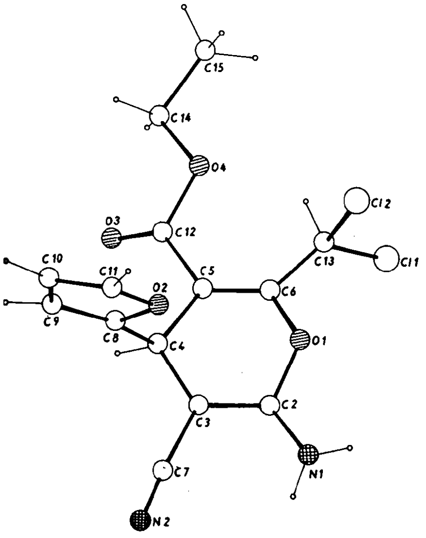


Fig. 1. Perspective view of molecule (1) showing the numbering of the atoms.

The 4*H*-pyran ring has a flat-boat conformation; the flatness of the boat is evident from the small deviations of O(1) [−0·125 (2) Å] and C(4) [−0·265 (2) Å] from the least-squares plane defined by C(2), C(3), C(5) and C(6); all substituents attached to the base of the boat are on the opposite side. Similar observations were noted in the solid-state structures of (2) and (3) (Sharanina, Nesterov, Klokol, Rodinovskaya, Shklover, Sharanin, Struchkov & Promonenkov, 1986; Klokol, Sharanina, Nesterov, Shklover, Sharanin & Struchkov, 1987) while the pyran ring in (4) was found to be essentially planar (Ukhin, Bessonov, Yanovskii, Timofeeva, Furmanova & Struchkov, 1980). Based on these results it appears that the 4*H*-pyran derivatives bear close conformational similarity to substituted 1,4-dihydropyridines for which it has been suggested that C4-unsubstituted (or, by analogy, C4-disubstituted) dihydropyridines are planar, while the C4-monosubstituted ones adopt flat-boat conformations (Fonseca, Martínez-Carrera & García-Blanco, 1986).

The twists about the ethylenic bonds are consistent with the observed bond orders; thus, while the bonds around C(5)—C(6) are nearly coplanar [O(1)—C(6)—C(5)—C(12) 179·8 (2), C(4)—C(5)—C(6)—C(13) −176·7 (2)°], substantial twists about C(2)—C(3) occur [O(1)—C(2)—C(3)—C(7) 176·9 (2), C(4)—C(3)—C(2)—N(1) 169·6 (2)°].

The furan ring is nearly perpendicular to the least-squares plane of the pyran ring [88·5 (3)°]. The C(12), O(3), O(4) moiety of the ethoxycarbonyl group is inclined at an angle of 16·2 (4)° to the pyran ring.

There is one short intermolecular [2·929 (2) Å] distance between the amino N(1) atom and a symmetry-related (x, y, $z-1$) O(3) of the ethoxycarbonyl group, consistent with a hydrogen-bond interaction. The other packing distances are longer than 3·2 Å.

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* Lists of structure factors, anisotropic thermal parameters, H-atom positions, least-squares planes and selected torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52493 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structures of Four Pyrazolo[3,4-*b*]pyridine Nucleosides

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Abstract. 4-Methoxy-1-(2-deoxy-β-D-*erythro*-pentofuranosyl)-1*H*-pyrazolo[3,4-*b*]pyridine (1), $C_{12}H_{15}N_3O_4$, $M_r = 265\cdot27$, orthorhombic, $P2_12_12_1$, $a = 6\cdot9930\,(10)$, $b = 9\cdot231\,(2)$, $c = 19\cdot119\,(4)$ Å, $V = 1234\cdot2\,(4)$ Å^3, $Z = 4$, $D_x = 1\cdot428$ g cm^{-3}, Cu $K\alpha$ ($\lambda = 1\cdot54178$ Å), $\mu = 8\cdot718$ cm^{-1}, $F(000) = 560$, $T = 295$ K, $R = 0\cdot0361$ for 2330 reflections ($F \geq 4\sigma_F$); 1-(2-deoxy-β-D-*erythro*-pentofuranosyl)-1*H*-pyrazolo[3,4-*b*]pyridin-4(7*H*)-one (2), $C_{11}H_{13}N_3O_4$, $M_r = 251\cdot24$, monoclinic, $C2$, $a = 17\cdot506\,(3)$, $b = 8\cdot512\,(2)$, $c = 7\cdot941\,(3)$ Å, $\beta = 110\cdot59\,(3)$°, $V = 1107\cdot7\,(6)$ Å^3, $Z = 4$, $D_x = 1\cdot506$ g cm^{-3}, Cu $K\alpha$ ($\lambda = 1\cdot54178$ Å), $\mu = 9\cdot406$ cm^{-1}, $F(000) = 528$, $T = 295$ K, $R = 0\cdot0369$ for 1874 reflections ($F \geq 4\sigma_F$); 1-β-D-arabinofuranosyl-1*H*-pyrazolo[3,4-*b*]pyridin-4(7*H*)-one (3) dihydrate, $C_{11}H_{13}N_3O_5.2H_2O$, $M_r = 303\cdot27$, monoclinic, $P2_1$, $a = 4\cdot8604\,(3)$, $b = 12\cdot6573\,(15)$, $c = 10\cdot9802\,(17)$ Å, $\beta = 91\cdot17\,(6)$°, $V = 675\cdot36\,(13)$ Å^3, $Z = 2$, $D_x = 1\cdot491$ g cm^{-3}, Cu $K\alpha$ ($\lambda = 1\cdot54178$ Å), $\mu = 10\cdot325$ cm^{-1}, $F(000) = 320$, $T = 295$ K, $R = 0\cdot0291$ for 2692 reflections ($F \geq 4\sigma_F$); 1-β-D-ribofuranosyl-1*H*-pyrazolo[3,4-*b*]pyridine (4), $C_{11}H_{13}N_3O_4$, $M_r = 251\cdot24$, orthorhombic, $P2_12_12_1$, $a = 6\cdot9252\,(6)$, $b = 8\cdot288\,(6)$, $c = 19\cdot431\,(3)$ Å, $V = 1115\cdot2\,(8)$ Å^3, $Z = 4$, $D_x = 1\cdot496$ g cm^{-3}, Cu $K\alpha$ ($\lambda = 1\cdot54178$ Å), $\mu = 9\cdot342$ cm^{-1}, $F(000) = 528$, $T = 295$ K, $R = 0\cdot0298$ for 2045 reflections ($F \geq 4\sigma_F$). The 4-hydroxy compounds (2) and (3) exist as the oxo tautomers with N7 protonated. The pyrazole–pyridine dihedral angles are 0·44 (7), 1·00 (13), 0·47 (7) and 0·95 (6)° for (1)–(4), respectively. Compounds (1) and (3) are in the *syn* conformation with stabilizing intramolecular O5′···N7 hydrogen bonds; (2) and (4) are in the *anti* conformation. The sugar moieties have conformations of ^2E (C2′-*endo*), $_4T^3$ (C4′-*exo*), $^3T_4$ (C3′-*endo*) and $_3T^2$ (C3′-*exo*) for (1)-(4), respectively. Compound (4) has nearly complete, antiparallel base stacking.

Introduction. For two decades the search for beneficial drugs has included the synthesis and biological evaluation of nucleosides containing modified purine rings (Revankar, Gupta, Adams, Dalley, McKernan, Cook, Canonico & Robins, 1984; Meyer, Revankar, Cook, Ehler, Schweizer & Robins, 1980; Cline, Panzica & Townsend, 1978). The pyrazolo[3,4-*b*]pyridine nucleosides presented in this study [(1)–(4)] were synthesized (Sanghvi, Larson, Willis, Robins & Revankar, 1989) as examples of nitrogen modification in the purine ring system. These compounds possess the 1-deaza feature of 1-deazaadenosine [(5)] and the pyrazole ring in place of the imidazole ring as found in 1-β-D-ribofuranosylpyrazolo[3,4-*d*]pyrimidin-4(5*H*)-one [(6), allopurinol ribonucleoside]. Allopurinol ribonucleoside (Lichtenthaler & Cuny, 1981; Cottam, Petrie, McKernan, Goebel, Dalley, Davidson, Robins & Revankar, 1984) and 1-deazaadenosine (Itoh, Kitano & Mizuno, 1972; Cristalli, Franchetti, Grifantini, Vittori, Bordoni & Geroni, 1987) possess significant chemotherapeutic proper-

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