également expliquer pourquoi l'enthalpie molaire de polymérisation de certains uréthanes est inférieure à la valeur théorique (Eckhardt, Prusik & Chance 1983). A ce sujet, il serait intéressant qu'une étude calorimétrique spécifique soit réalisée pour permettre de déterminer la chaleur molaire de polymérisation du 1*p*CPU.

En conclusion, il existe donc pour le 1*p*CPU plusieurs facteurs défavorables à la polymérisation: la distance d'empilement des chaînes diacétylèniques qui s'accroît au cours de la polymérisation, et l'accroissement des contraintes de van der Waals sur les chaînes latérales *R*. La conjugaison de ces deux facteurs, stérique et énergétique, peut donc ainsi justifier que l'on ne puisse atteindre la polymérisation totale pour le 1*p*CPU forme rouge.

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Structures of the 4-Cyano and 4-Methylamidate Analogs of Tiazofurin

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Abstract

4-Cyanotiazofurin [2-(β-D-ribofuranosyl)thiazole-4-carbonitrile, (1)], $C_9H_{10}N_2O_4S$, $M_r = 242.3$, monoclinic, $P2_1$, $a = 7.329$ (1), $b = 8.295$ (1), $c = 8.697$ (1) Å, $\beta = 90.90$ (1)°, $V = 528.7$ (1) Å^3, $Z = 2$, $D_x = 1.52$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1.54178$ Å, $\mu = 27.2$ cm^{-1}, $F(000) = 252$, $T = 293$ K, $R = 0.0487$ for all 1171 unique reflections. 4-Methylamidatetiazofurin [methyl 2-(β-D-ribofuranosyl)thiazole-4-carboximidate, (2)], $C_{10}H_{14}N_2O_5S$, $M_r = 274.3$, orthorhombic, $P2_12_12_1$, $a = 8.596$ (1), $b = 11.060$ (1), $c = 26.064$ (1) Å, $V = 2478.1$ (2) Å^3, $Z = 8$, $D_x = 1.47$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1.54178$ Å, $\mu = 24.5$ cm^{-1}, $F(000) = 1152$, $T = 293$ K, $R = 0.0374$ for all 2902 unique reflections. Compound (2) crystallizes with two crystallographic unique structures in the asym-

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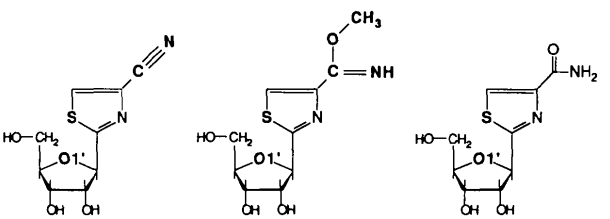
metric unit [(2*a*) and (2*b*)]. All three structures show a close contact between the thiazole sulfur and the pentose oxygen O(1′). S···O(1′) distances are 2.936 (3) Å in (1), 2.773 (2) Å in (2*a*) and 2.878 (2) Å in (2*b*), resulting from *C*-glycosidic torsion angles of 34.5 (4), 15.6 (3) and 27.2 (3)° respectively. This interesting feature is conserved in the crystal structures of other thiazole nucleosides [Burling & Goldstein (1992). *J. Am. Chem. Soc.* **114**, 2313–2320].

Introduction

Examples of nonbonded intermolecular sulfur–nucleophile close contacts are seen in a number of small-molecule crystal structures (Rosenfield, Parthasarathy & Dunitz, 1977). The crystallographic literature also contains numerous examples of compounds that exhibit *intra*molecular nonbonded sulfur–oxygen close contacts. Recent surveys of the Cambridge Structural Database (1991) (Kucsman & Kapovits, 1985; Burling & Goldstein, 1992*b*) have found over 250 structures with intramolecular 1,4 sulfur–oxygen contacts less than the sum of the sulfur and oxygen van der Waals radii (3.30 Å) (Bondi, 1964). In many of the structures displaying S···O close contacts, the S atom is part of a conjugated ring system. For example, close S···O contacts are seen in structures containing thiophene (Ramasubbu & Parthasarathy, 1989), thiazolium (Sax, Pulsinelli & Pletcher, 1974), and thiazole rings (discussion below).

The thiazole nucleoside tiazofurin (3) is an antitumor drug whose crystal structure exhibits an interesting sulfur–furanose-oxygen close contact. The S···O(1′) distance in tiazofurin is 2.958 (1) Å (Goldstein, Takusagawa, Berman, Srivastava & Robins, 1983). This is considerably less than the sum of the sulfur and oxygen van der Waals radii (Bondi, 1964). Similar close sulfur–oxygen contacts are seen in the crystal structures of six ribose-modified thiazole nucleosides (Goldstein *et al.*, 1983; Goldstein, Mao & Marquez, 1988; Burling, Gabrielsen & Goldstein, 1991). Analogous sulfur–oxygen close contacts are also seen in two related thiazole amino- and thiazole thionucleoside structures (Sanghvi *et al.*, 1988). The observation of this feature in a number of compounds, each in different packing environments, indicates that the S···O(1′) close contact is due to an intramolecular interaction and not to external crystal packing forces. Computational studies (Burling & Goldstein, 1992*a*) were performed on several thiazole nucleoside model fragments. These studies suggest that the S atom is positively charged due to donation of electron density to the π system of the thiazole ring. An attractive electrostatic interaction results between the positively charged sulfur and the nucleophilic O(1′). This interaction is in part responsible for the observed close contacts. These computations also indicate that a 1–4 S···O(1′) interaction would constrain rotation of the thiazole ring about the *C*-glycosidic bond. Such a conformational restriction would have important consequences with regard to the antitumor activity of tiazofurin (Goldstein, Bell & Marquez, 1990). In this study we examine the structures of two base-substituted tiazofurin analogs: 4-cyanotiazofurin (1) and 4-methylamidatetiazofurin (2). Close sulfur–oxygen contacts are seen in the crystal structures of these compounds as well. The observation of S···O(1′) close contacts in (1) and (2), together with those seen in the ribose-modified thiazole nucleosides, suggests that this conformational feature results from structural properties shared by all of the thiazole nucleosides studied to date. These common structural elements include a thiazole heterocycle linked by a *C*-glycosidic bond to a furan moiety.



(1) (2) (3)

Experimental

The synthesis of (1) and (2) will be described elsewhere (Gabrielsen *et al.*, 1992). Compound (1) was crystallized by slow evaporation at 277 K from isopropanol. Compound (2) was crystallized from ethyl acetate by slow evaporation at 277 K. Both crystals were colorless. Data collection and refinement variables are given in Table 1.

Data were collected at room temperature for both structures. A half sphere of data was collected for (1), a quarter sphere was collected for (2) and equivalent reflections averaged for both data sets. The data were corrected for Lorentz and polarization factors. Corrections were applied for variation in beam intensity *via* a polynomial fit to three standards. Data were corrected for anisotropy of absorption using the semi-empirical ψ-scan technique (North, Phillips & Mathews, 1968). Both structures were solved using standard Patterson and Fourier methods. All hydrogen positions were determined from difference Fourier maps computed from low-angle data ($\sin\theta/\lambda < 0.4$ Å^{-1}). Refinement of (1) employed full-matrix least-squares techniques. Refinement of (2) employed block-diagonal least squares with each of the two independent molecules

Table 1. *Data collection and refinement for* (1) *and* (2)

	(1)	(2*a*), (2*b*)
Crystal size (mm)	0.13 × 0.45 × 0.47	0.17 × 0.30 × 0.35
Diffractometer	CAD-4	CAD-4
Scan type	ω–2θ	ω–2θ
Scan width in ω (°)	0.90 + 0.14tanθ	0.75 + 0.14tanθ
Lattice parameter refinement	25 reflections (19.2 < θ < 30.9°)	25 reflections (23.0 < θ < 31.8°)
Transmission factor (on *I*)	0.981–1.000	0.744–1.000
Net variation in standards (%)	−1.1	−1.4
Data collection		
θ range (°)	1.5 < θ < 78.0	1.5 < θ < 78.0
hkl range	0→9, −10→10, −9→10	−10→7, 0→13, 0→32
Total reflections	2350 [2328 > 3σ(*I*)]	5568 [5120 > 3σ(*I*)]
Unique reflections	1171	2902
R_{merge}	0.033	0.032
R (all data)	0.0487	0.0374
wR (all data)	0.0560	0.0480
No. of variables	185	438
S	1.1397	0.983
$(\Delta/\sigma)_{max}$	0.02	0.30
$(\Delta\rho)_{max}$ (e Å^{-3})	0.51	0.43
Extinction parameter *G* (× 10^{-4})	17 (2)	1.2 (4)

in a single block. In both structures anisotropic refinement of all non-H atoms and isotropic refinement of all hydrogens minimized the function $\sum w(\Delta F)^2$. Weights were $w = 1/\sigma'^2$ with $\sigma' = \sigma\{0.5(A_1|F_o| + A_2) + 0.5[B_1(\sin\theta/\lambda) + B_2]\}$. Values of σ were acquired from counting statistics. Values of A and B were obtained from least-squares minimization of the function $|\Delta F|^2 - \sigma'^2$ in 20 separate segments in $|F_o|$ and $(\sin\theta)/\lambda$ for each data set. Final refinements utilized all data and included a type I isotropic extinction correction (Coppens & Hamilton, 1970). Atomic scattering factors and f' and f'' for S atoms were from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 99–102, 149–150). All programs were from the *DNA* system (Takusagawa, 1981).

Discussion

Crystal structures of compounds (1) and (2) are shown in Fig. 1. Compound (2) crystallized with two unique molecules per asymmetric unit [*cf.* structures (2*a*) and (2*b*) in Fig. 1] Atomic coordinates of these structures are given in Table 2. Bond lengths are listed in Table 3. Bond angles and selected torsion angles are given in Table 4.

Close S···O(1′) *contacts*

All three structures show close S···O(1′) contacts. In these, as in the earlier thiazole nucleoside structures, the thiazole S and ribose O(1′) are *cis* to one another. The S···O(1′) distances seen previously range from 2.826 (3) to 3.158 (4) Å. In (1) the sulfur–oxygen distance is 2.936 (3) Å. Structure (2*a*) exhibits the smallest S···O(1′) distance [2.773 (2) Å] seen in any thiazole nucleoside to date. In structure (2*b*) this distance is 2.878 (2) Å. These S···O(1′) close contacts are related to the glycosidic torsion angle χ [O(1′)—C(1′)—C(2)—S]. In previous thiazole nucleoside structures absolute values of χ ranged from 5.2 (3) to 55.2 (5)°. Structure (2*a*) exhibits a relatively small value of the glycosidic torsion angle [χ = 15.6 (3)°]. The corresponding torsion angles in (1) and (2*b*) are somewhat larger, χ = 34.5 (4) and 27.2 (3)° respectively. Close S···O(1′) contacts have now been observed in nine thiazole nucleoside compounds. Seven of these were from compounds with a carboxamide group at the thiazole C(4) (Goldstein *et al.*, 1983; Goldstein *et al.*, 1988; Burling *et al.*, 1991), while the two presented here contain different substituents at C(4). The thiazole nucleosides studied to date have all crystallized in different packing environments. In spite of this, S···O(1′) close contacts are seen in all of these structures. This indicates that the S···O(1′) close contact is due to an intramolecular

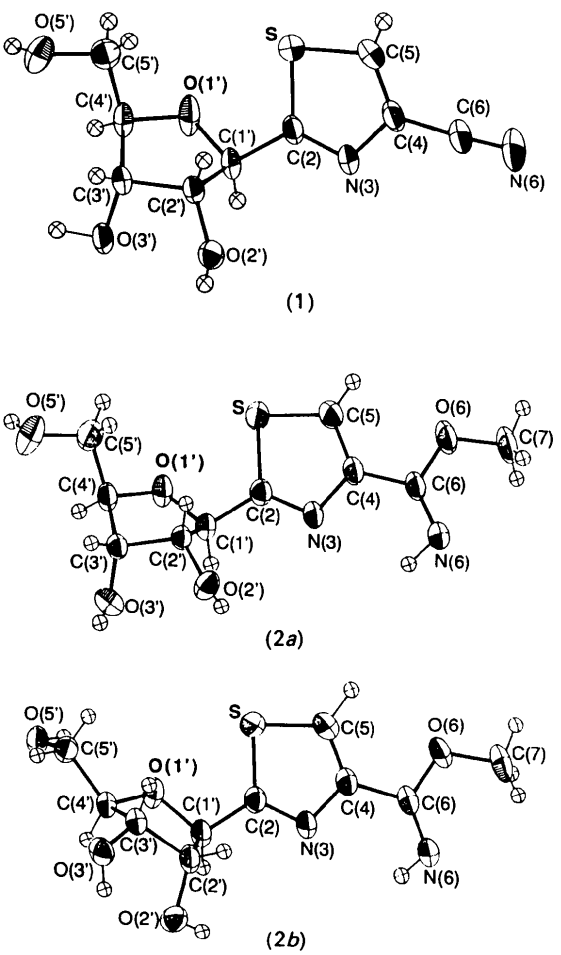


Fig. 1. Molecular structures of 4-cyanotiazofurin (1) and 4-methylamidatetiazofurin [(2*a*) and (2*b*)]. Thermal ellipsoids of non-H atoms are drawn at the 50% probability level.

Table 2. *Fractional coordinates and equivalent isotropic thermal parameters for non-*H *atoms*

$B_{eq} = (4/3)\sum_i\sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B_{eq}
4-Cyanotiazofurin				
S	0.4011 (1)	0.25	1.0118 (1)	4.18 (2)
C(2)	0.2881 (4)	0.1204 (4)	0.8888 (3)	2.4 (1)
N(3)	0.1268 (3)	0.0781 (4)	0.9313 (3)	2.81 (9)
C(4)	0.0887 (4)	0.1530 (5)	1.0687 (3)	2.8 (1)
C(5)	0.2174 (5)	0.2512 (6)	1.1282 (4)	3.7 (1)
C(6)	−0.0818 (5)	0.1242 (6)	1.1425 (4)	3.9 (1)
N(6)	−0.2137 (5)	0.1036 (8)	1.2056 (5)	5.7 (2)
C(1′)	0.3693 (4)	0.0761 (4)	0.7378 (3)	2.42 (9)
C(2′)	0.3342 (4)	0.2039 (4)	0.6130 (3)	2.23 (9)
C(3′)	0.5078 (4)	0.1974 (4)	0.5169 (3)	2.21 (9)
C(4′)	0.6546 (4)	0.1493 (4)	0.6334 (3)	2.6 (1)
C(5′)	0.7646 (4)	0.2882 (5)	0.7007 (4)	3.2 (1)
O(1′)	0.5631 (3)	0.0693 (4)	0.7577 (3)	3.53 (8)
O(2′)	0.1703 (3)	0.1812 (3)	0.5288 (3)	2.82 (8)
O(3′)	0.4803 (3)	0.0793 (3)	0.4013 (3)	2.91 (8)
O(5′)	0.8647 (3)	0.3676 (4)	0.5844 (3)	3.65 (9)
4-Methylamidatetiazofurin (Mol. *a*)				
S	0.7806 (1)	0.66741 (7)	0.46466 (3)	4.23 (5)
C(2)	0.8526 (3)	0.8064 (2)	0.44556 (9)	2.7 (2)
N(3)	0.8906 (3)	0.8782 (2)	0.48299 (7)	2.9 (1)
C(4)	0.8639 (4)	0.8223 (3)	0.52960 (9)	3.0 (2)
C(5)	0.8052 (5)	0.7095 (3)	0.5271 (1)	3.9 (2)
C(6)	0.8954 (4)	0.8878 (3)	0.57769 (9)	3.0 (2)
N(6)	0.9525 (4)	0.9919 (2)	0.58256 (8)	3.7 (1)
O(6)	0.8517 (4)	0.8212 (3)	0.61800 (7)	4.8 (1)
C(7)	0.8716 (7)	0.8737 (5)	0.6677 (1)	5.4 (2)
C(1′)	0.8549 (3)	0.8368 (2)	0.38962 (8)	2.5 (1)
C(2′)	1.0103 (3)	0.8222 (2)	0.36128 (9)	2.4 (1)
C(3′)	0.9506 (3)	0.8051 (2)	0.30607 (9)	2.6 (2)
C(4′)	0.8155 (3)	0.7199 (3)	0.31507 (9)	2.8 (2)
C(5′)	0.8576 (4)	0.5864 (3)	0.3153 (1)	3.7 (2)
O(1′)	0.7544 (2)	0.7517 (2)	0.36485 (6)	3.1 (1)
O(2′)	1.1182 (3)	0.9174 (2)	0.36718 (8)	3.1 (1)
O(3′)	0.8883 (3)	0.9148 (2)	0.28665 (8)	3.5 (1)
O(5′)	0.8821 (3)	0.5448 (3)	0.2645 (1)	4.7 (2)
4-Methylamidatetiazofurin (Mol. *b*)				
S	1.0639 (2)	1.46107 (7)	0.53561 (3)	5.1 (1)
C(2)	1.0001 (3)	1.3190 (2)	0.55139 (9)	2.8 (2)
N(3)	0.9921 (3)	1.2435 (2)	0.51342 (7)	2.9 (1)
C(4)	1.0365 (3)	1.2996 (2)	0.46877 (9)	2.9 (2)
C(5)	1.0799 (6)	1.4157 (3)	0.4732 (1)	4.6 (2)
C(6)	1.0338 (3)	1.2293 (3)	0.42035 (9)	2.9 (2)
N(6)	0.9994 (4)	1.1197 (3)	0.41578 (9)	4.2 (2)
O(6)	1.0776 (3)	1.2988 (2)	0.38084 (7)	3.7 (1)
C(7)	1.0845 (5)	1.2418 (4)	0.3311 (1)	4.1 (2)
C(1′)	0.9666 (3)	1.2876 (3)	0.60616 (9)	2.8 (2)
C(2′)	1.1051 (4)	1.2325 (3)	0.63557 (9)	2.9 (2)
C(3′)	1.1486 (3)	1.3313 (3)	0.67413 (9)	2.6 (2)
C(4′)	0.9928 (3)	1.3949 (2)	0.68221 (8)	2.5 (1)
C(5′)	1.0001 (4)	1.5238 (3)	0.7011 (1)	2.9 (2)
O(1′)	0.9244 (2)	1.3972 (2)	0.63227 (7)	3.1 (1)
O(2′)	1.0588 (4)	1.1304 (2)	0.66403 (8)	4.1 (1)
O(3′)	1.2163 (3)	1.2869 (2)	0.71946 (7)	3.1 (1)
O(5′)	0.8485 (3)	1.5716 (2)	0.71082 (7)	3.0 (1)

Table 3. *Bond distances* (Å)

	(1)	(2*a*)	(2*b*)
C(2)—N(3)	1.292 (4)	1.300 (3)	1.297 (3)
N(3)—C(4)	1.380 (4)	1.382 (3)	1.373 (3)
C(4)—C(5)	1.343 (5)	1.348 (4)	1.342 (4)
C(5)—S	1.696 (3)	1.706 (3)	1.707 (3)
S—C(2)	1.719 (3)	1.730 (3)	1.715 (3)
C(2)—C(1′)	1.496 (4)	1.496 (3)	1.497 (3)
C(4)—C(6)	1.432 (5)	1.473 (4)	1.482 (3)
C(6)—N(6)	1.131 (5)	1.259 (4)	1.254 (4)
C(6)—O(6)	–	1.337 (3)	1.339 (3)
O(6)—C(7)	–	1.430 (4)	1.443 (4)
C(1′)—C(2′)	1.536 (4)	1.535 (4)	1.542 (4)
C(2′)—C(3′)	1.533 (4)	1.539 (3)	1.532 (4)
C(3′)—C(4′)	1.519 (4)	1.514 (4)	1.528 (4)
C(4′)—O(1′)	1.442 (4)	1.443 (4)	1.428 (3)
C(4′)—C(5′)	1.517 (5)	1.520 (4)	1.510 (4)
O(1′)—C(1′)	1.428 (3)	1.431 (3)	1.437 (3)
C(2′)—O(2′)	1.409 (3)	1.412 (3)	1.408 (3)
C(3′)—O(3′)	1.416 (4)	1.420 (3)	1.406 (3)
C(5′)—O(5′)	1.421 (4)	1.418 (4)	1.429 (4)

interaction common to all of the thiazole nucleosides and is not a result of packing interactions. Results from quantum chemical calculations (Burling & Goldstein, 1992*a*) suggest that the thiazole S and the ribose O(1′) carry partial positive and negative charges respectively. These calculations show that an attractive electrostatic interaction exists between the oppositely charged S and O(1′). This attractive interaction along with a repulsive electrostatic interaction between the ribose O(1′) and the negatively charged thiazole nitrogen, produces the S···O(1′) *cis* conformation seen in the thiazole nucleoside crystal structures.

Thiazole rings

In all three structures, the thiazole rings are planar (see supplementary material).* With one exception, all bond lengths and bond angles in the three thiazole rings are within three standard deviations of those seen in the eight previously determined thiazole nucleoside structures. The N(3)—C(4)—C(5) bond angle [117.2 (3)°] in (1) is marginally larger than the average seen in the other thiazole nucleosides [116.0 (3)°]. Computational studies show that the thiazole sulfur participates in π bonding with the flanking carbon atoms (Burling & Goldstein, 1992*a*). This is consistent with the finding that the thiazole S—C(2) and S—C(5) bond lengths in all three structures are shorter than single S—C(sp^2) bond lengths seen in thiazolidine and thiazolidinone ring structures, which show little resonance character (Espenbetov, Yanovskii, Struchkov, Tsoi & Cholpankulova, 1981; Adman, Jensen & Warrener, 1975). In all thiazole nucleoside structures observed to date, the S—C(5) bond length is shorter than the S—C(2) distance. This suggests greater contribution from the C(5)=S^+—C(2) resonance form. The S—C(5) bond length [1.696 (3) Å] in (1) is marginally shorter than the average S—C(5) bond length [1.706 (5) Å] obtained from the other thiazole nucleosides. In addition, the C(4)—C(6) bond length

* Lists of structure factors, anisotropic thermal parameters, variables used in the weighting scheme, deviations from least-squares planes and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54929 (30 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. *Bond angles* (°) *and selected torsion angles* (°)

	(1)	(2*a*)	(2*b*)
C(2)—S—C(5)	89.8 (2)	89.3 (1)	89.1 (1)
S—C(5)—C(4)	109.0 (3)	110.2 (2)	110.0 (2)
C(5)—C(4)—N(3)	117.2 (3)	115.7 (2)	115.9 (2)
C(4)—N(3)—C(2)	108.9 (3)	110.2 (2)	109.9 (2)
N(3)—C(2)—S	115.2 (2)	114.6 (2)	115.1 (2)
C(1′)—C(2)—S	120.4 (2)	119.0 (2)	120.2 (2)
C(1′)—C(2)—N(3)	124.2 (3)	126.2 (2)	124.6 (2)
C(6)—C(4)—C(5)	122.7 (3)	124.4 (2)	125.4 (2)
C(6)—C(4)—N(3)	120.2 (3)	119.8 (2)	118.7 (2)
N(6)—C(6)—C(4)	177.5 (4)	127.4 (2)	126.3 (2)
O(6)—C(6)—C(4)	-	110.3 (2)	110.5 (2)
O(6)—C(6)—N(6)	-	122.3 (2)	123.2 (2)
C(6)—O(6)—C(7)	-	117.0 (3)	116.8 (3)
C(1′)—C(2′)—C(3′)	103.3 (2)	99.9 (2)	103.4 (2)
C(2′)—C(3′)—C(4′)	103.2 (2)	100.8 (2)	101.8 (2)
C(3′)—C(4′)—C(5′)	115.1 (3)	115.0 (2)	116.3 (2)
C(3′)—C(4′)—O(1′)	106.8 (2)	105.5 (2)	104.1 (2)
O(1′)—C(4′)—C(5′)	108.1 (3)	108.6 (2)	107.3 (2)
C(4′)—O(1′)—C(1′)	111.3 (2)	110.2 (2)	108.2 (2)
O(1′)—C(1′)—C(2′)	105.6 (2)	103.8 (2)	107.0 (2)
O(1′)—C(1′)—C(2)	108.1 (2)	106.5 (2)	107.7 (2)
C(2′)—C(1′)—C(2)	112.7 (3)	117.2 (2)	114.6 (2)
C(1′)—C(2′)—O(2′)	114.0 (2)	116.2 (2)	111.1 (2)
C(3′)—C(2′)—O(2′)	114.7 (2)	114.4 (2)	107.2 (2)
C(2′)—C(3′)—O(3′)	107.6 (2)	110.7 (2)	113.7 (2)
C(4′)—C(3′)—O(3′)	112.6 (2)	107.4 (2)	114.1 (2)
C(4′)—C(5′)—O(5′)	110.7 (3)	110.2 (2)	111.6 (2)
χ [O(1′)—C(1′)—C(2)—S]	34.5 (4)	15.6 (3)	27.2 (3)
φ [O(5′)—C(5′)—C(4′)—C(3′)]	296.6 (3)	283.8 (3)	184.2 (2)
κ [N(6)—C(6)—C(4)—N(3)]	*	−3.3 (5)	−2.7 (5)
θ [C(7)—O(6)—C(6)—C(4)]	-	181.4 (3)	178.4 (3)

* This torsion angle is poorly defined due to the fact that the cyano group is nearly linear in (1).

[1.432 (5) Å] is significantly shorter in (1) than in the carboxamide-substituted thiazole nucleosides [average value 1.487 (7) Å] or in the two 4-methylamidate structures [1.473 (4) and 1.482 (3) Å for conformers (2*a*) and (2*b*) respectively]. This suggests that there is conjugation between the triple bond of the cyano group and the thiazole ring of (1).

Cyano group

In (1), the cyano group is bent slightly and is nearly coplanar with the thiazole ring. The C(4)—C(6)—N(6) bond angle is 177.5 (4)°. C(6) and N(6) deviate only 0.036 (4) and 0.074 (5) Å respectively from the calculated least-squares plane of the thiazole ring.

Methylamidate groups

In both (2*a*) and (2*b*), the methylamidate groups are planar. In both structures the C(4) substituent is also nearly coplanar with the thiazole ring (see supplementary material).* With one exception, methylamidate bond distances and angles in (2*a*) and (2*b*) are within two standard deviations of the average values seen in three other compounds containing methylamidate groups (Kolakowski, 1974; Marzilli, Summers, Ramsden, Bresciani-Pahor & Randaccio, 1984; Roesky, Hofmann, Keller, Pinkert, Jones & Sheldrick, 1984). In structures (2*a*) and (2*b*) the C(6)—O(6)—C(7) bond angle is roughly 1.5 (3)° greater than the average value [115.6 (2) Å] of this bond angle seen in the other three methylamidate containing compounds. The N(6) hydrogen H[N(6)] is *cis* to the thiazole nitrogen in both structures, thus

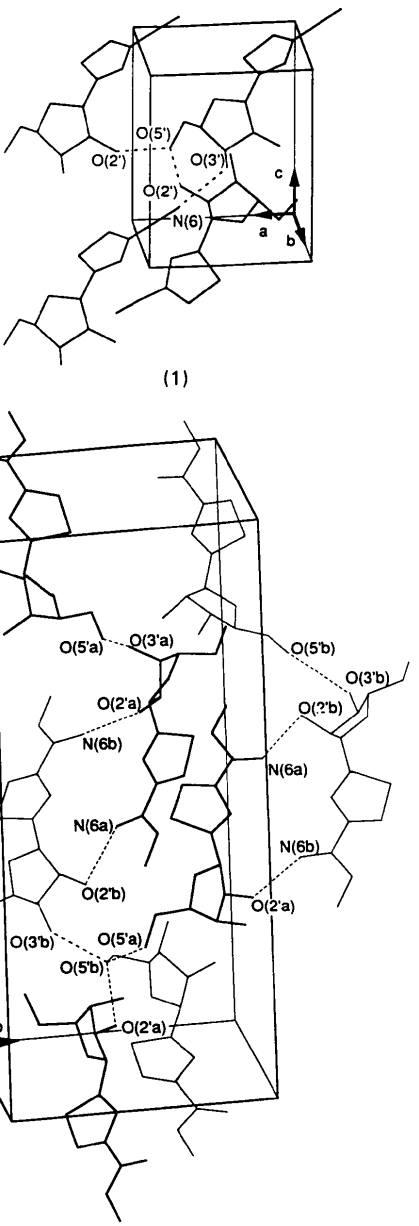


Fig. 2. Crystal packing of 4-cyanotiazofurin (1) and 4-methylamidatetiazofurin (2). Dashed lines represent hydrogen bonds. In (2) the two crystallographically unique conformations (2*a*) and (2*b*) are drawn with heavy and thin lines respectively. Both packing diagrams are drawn to the same scale.

* See deposition footnote.

Table 5. *Hydrogen-bond distances* (Å) *and angles* (°)

D—H···*A*	*D*···*A*	H···*A*	*D*—H···*A*	Symmetry of acceptor *A*
(1) 4-Cyanotiazofurin				
O(2′)—H(O2′)···O(5′)	2.792 (4)	1.92 (6)	169 (5)	$1-x, -\frac{1}{2}+y, 1-z$
O(3′)—H(O3′)···N(6)	2.842 (5)	1.91 (7)	169 (8)	$1+x, y, -1+z$
O(5′)—H(O5′)···O(2′)	2.768 (3)	1.95 (6)	172 (6)	$1+x, y, z$
(2*a*) and (2*b*) 4-Methylamidatetiazofurin				
O(2′*a*)—H(O2′*a*)···N(6*b*)*	2.767 (4)	2.06 (4)	165 (4)	x, y, z
O(3′*a*)—H(O3′*a*)···O(5′*a*)	2.782 (4)	2.05 (5)	169 (5)	$2-x, \frac{1}{2}+y, \frac{1}{2}-z$
O(5′*a*)—H(O5′*a*)···O(5′*b*)	2.747 (4)	2.04 (6)	166 (7)	$\frac{3}{2}-x, 2-y, -\frac{1}{2}+z$
O(2′*b*)—H(O2′*b*)···N(6*a*)	2.773 (3)	2.12 (8)	152 (8)	x, y, z
O(3′*b*)—H(O3′*b*)···O(5′*b*)	3.047 (3)	2.31 (6)	141 (5)	$2-x, -\frac{1}{2}+y, \frac{3}{2}-z$
O(5′*b*)—H(O5′*b*)···O(2′*a*)	2.840 (3)	1.99 (4)	161 (3)	$-\frac{1}{2}+x, \frac{3}{2}-y, 1-z$

* *a* and *b* refer to molecules (2*a*) and (2*b*) respectively.

optimizing any attractive interaction between H(N6) and the lone-pair electron on N(3). The terminal methyl groups are located *cis* across the C(6)—O(6) bond to N(6). In this conformation steric interactions between the C(7) hydrogens and H(C5) are avoided while possible attractive interactions between H(C5) and the O(6) lone pair are maximized.

Furanose rings

Bond lengths and angles in the furanose rings are similar to those seen in 346 ribofuranosidic nucleosides found in a search of the Cambridge Structural Database (1991). In (1) the amplitude and phase angles of pseudorotation (Altona & Sundaralingam, 1972) are $\tau_m = 31.58°$ and $P = 172.02°$ respectively. Compound (1) thus exhibits a C2′-*endo* C3′-*exo* sugar pucker ($^2T_3$). Structures (2*a*) and (2*b*) each display different sugar puckering. In (2*a*) the pseudorotation angles are $\tau_m = 44.11°$ and $P = 172.39°$, while in (2*b*) these angles are $\tau_m = 37.22°$ and $P = 43.45°$. Structure (2*a*) thus assumes a C2′-*endo* C3′-*exo* ($^2T_3$) sugar pucker while (2*b*) exhibits a C3′-*endo* C4′-*exo* ($_4T^3$) conformation. In (1) the conformation around the C(4′)—C(5′) bond is *gauche*, *trans*. In both (2*a*) and (2*b*) the conformation about this bond is *trans*, *gauche*.

Packing interactions

Hydrogen-bond distances and angles are listed in Table 5 and illustrated in Fig. 2. The only close intermolecular contacts are those resulting from hydrogen bonding. No intramolecular hydrogen bonding was observed. In (1) the cyano N(6) atom acts as an acceptor for one hydrogen bond. Compound (2) crystallized with two molecules per asymmetric unit. The packing arrangement for this molecule shows that the methylamidate N(6) from one conformer acts as an acceptor for the O(2′) H from the other. In (2), the O(5′*b*) atom acts as a donor for one hydrogen bond and as an acceptor for both HO(5′*a*) and HO(3′*b*).

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Structures of Three Diaryl-Substituted Triphenylphosphazines

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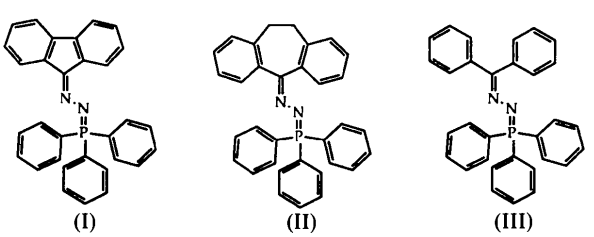
Abstract

9-Fluorenone triphenylphosphazine (I), $C_{31}H_{23}N_2P$, $M_r = 454.51$, orthorhombic, *Pbca*, $a = 22.312$ (11), $b = 11.510$ (10), $c = 18.744$ (9) Å, $V = 4813$ (5) Å^3, $Z = 8$, $D_x = 1.25$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 1.31$ cm^{-1}, $F(000) = 1904$, $T = 294$ K, $R = 0.047$ for 2531 observed reflections. 10,11-Dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5-one triphenylphosphazine (II), $C_{23}H_{27}N_2P$, $M_r = 482.57$, orthorhombic, $P2_12_12_1$, $a = 22.645$ (5), $b = 9.190$ (10), $c = 12.568$ (2) Å, $V = 2615$ (3) Å^3, $Z = 4$, $D_x = 1.23$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 1.24$ cm^{-1}, $F(000) = 1016$, $T = 294$ K, $R = 0.054$ for 2710 observed reflections. Benzophenone triphenylphosphazine (III), $C_{31}H_{25}N_2P$, $M_r = 456.53$, monoclinic, $P2_1/c$, $a = 13.730$ (5), $b = 17.205$ (10), $c = 10.914$ (4) Å, $\beta = 109.36$ (1)°, $V = 2432$ (1) Å^3, $Z = 4$, $D_x = 1.25$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 1.30$ cm^{-1}, $F(000) = 960$, $T = 294$ K, $R = 0.058$ for 2541 observed reflections. The results confirm that the C—N—N—P phosphazine link is planar, implying strong conjugation, and that in (III) one of the C-phenyl substituents lies in a plane orthogonal to the C—N—N—P plane; both these findings accord with predictions made on the basis of kinetic studies of phosphazine formation.

Introduction

Phosphazines are prepared by the reaction of equimolar amounts of aliphatic diazo compounds with phosphines in what is generally regarded as a biphilic reaction, *i.e.* both reagents acting simultaneously as nucleophile and electrophile (Kirby & Warren, 1967). The reaction has attracted interest as a means of characterizing labile diazo compounds (Huisgen, 1955), and its biphilic nature has been explored by examining structural effects on the kinetics of reaction of diazoalkanes with triphenylphosphine and some substituted analogues (Goetz & Juds, 1964). Most recently frontier molecular orbital (FMO) theory has been used to interpret the reactivity of a group of α,α-diaryl-substituted diazoalkanes with triphenylphosphine (Bethell, Dunn, Khodaei & Newall, 1989), but this required assumptions to be made about the trajectory of approach of the reactants in order to select the interacting frontier orbitals. The trajectory, it was felt, should be reflected in the molecular structure of the product, but it was found that little was known about the structure of phosphazines, in particular about the extent of conjugation between the diazo-C and P atoms. A crystallographic investigation of compounds (I), (II) and (III) was therefore undertaken to answer this question. Information was also sought on the conformational situation of C-aryl groups in triphenylphosphazines. The rate of formation of (III) was found to be an order of magnitude faster than predicted by FMO theory and showed unexpected increases when substituents both with electron-donating and electron-withdrawing character were introduced into the diaryldiazoalkane precursor; this was thought to be the result of conformational changes in passing from the reactant to the transition state which would again be evident in the structure of (III).



(I) (II) (III)

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