performed on a Varian HA-100 nmr spectrometer fitted with a variable temperature probe were determined as a solution in carbon tetrachloride utilizing tetramethylsilane as an internal lock signal. Crystallographic computations were carried out on the IBM 360-75 at the University of Illinois. Computer programs used included NRC-2A (written by F. R. Ahmed), UCLA-LS (written by P. K. Gantzel, R. A. Sparks, and K. N. Trueblood), ALF (Ames Laboratory Fourier Program), and ORTEP (written by C. K. Johnson).

Acknowledgment. We wish to express our thanks to the Petroleum Research Fund, administered by the American Chemical Society, Grant No. 2994-A1 (B. M. T. and P. L. K.), and to the General Medical Sciences Institute of the National Institutes of Health, Grant No. GM12470 (C. A. M. and I. C. P.), for their generous support.

The X-Ray Structures of 7-Aminofurazano[3,4-*d*]pyrimidine and 7-Amino-1,2,5-thiadiazolo[3,4-*d*]pyrimidine

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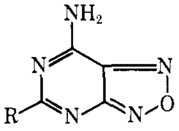
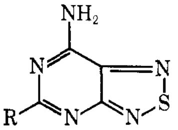
Princeton, New Jersey 08540. *Received January 20, 1971*

Abstract: X-Ray crystallographic analyses of 7-aminofurazano[3,4-*d*]pyrimidine (I, R = H) and 7-amino-1,2,5-thiadiazolo[3,4-*d*]pyrimidine (II, R = H) are reported, and the results correlated with both the chemical and biological activities of these adenine isosters. In particular, the remarkable reactivity of I and its derivatives toward nucleophilic displacement of the 7-amino grouping and toward photoreduction is discussed in the light of the bonding parameters determined by the X-ray analyses.

Continuing investigation of the novel heterocyclic system I (*e.g.*, 7-aminofurazano[3,4-*d*]pyrimidine, R = H) reveals a number of unusual physical and chemical properties of this fused pyrimidine. Like the 7-amino-1,2,5-thiadiazolo[3,4-*d*]pyrimidines (II)[1] and reminiscent of the isoelectronic 4-aminopteridines (III), the 7-aminofurazano[3,4-*d*]pyrimidines (hereafter referred to as 7-aminoFZP) undergo nucleophilic displacement of the 7-amino group. Unlike these related systems, however, the various representatives of I undergo such displacement with *extreme* facility, as illustrated by the following conversion.[2] This same conversion, when carried out on 7-amino-1,2,5-thiadiazolo[3,4-*d*]pyrimidine (II, R = H), requires 4.5 hr at 90°;[1] analogous amino group exchange in the pteridine series is a well-known reaction requiring even more vigorous conditions.[3] Also unexpected is the ready photoaddition of various solvents to the 6,7 bond of I (R = C_6H_5) described in an earlier communication[5] and summarized below. This reaction has no reported analog in systems II, III, or IV.


I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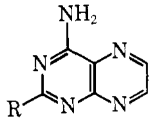
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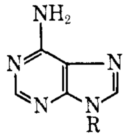
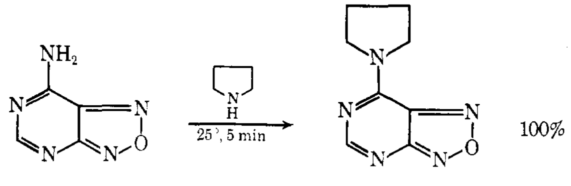
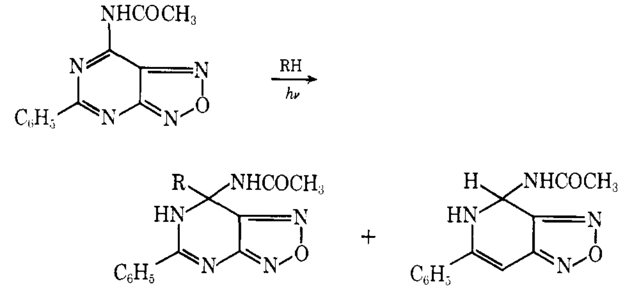

IV





R = CH_2OH, $CH(CH_3)OH$, $C(CH_3)_2OH$, $CH_2C(CH_3)_2$, $CHOCH_2CH_2OCH_2$

That the uv spectra of the thiadiazolopyrimidines II resemble closely those of the corresponding pteridines III has been demonstrated by Shealy, Clayton, and Montgomery[6] who inferred from this similarity a matching resemblance in π-electronic structure between systems II and III. The uv spectra of the furazanopyrimidines I are characterized by three absorptions of nearly equal intensity (log ε = 3–4) occurring in the regions 210–240, 250–290, and 330–380 nm, fitting remarkably well the pattern described by Shealy and coworkers[6] for II and III. This similarity suggests that the isoelec-

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[1] Y. F. Shealy and C. A. O'Dell, *J. Org. Chem.*, **29**, 2135 (1964).

[2] E. C. Taylor, Y. Maki, and B. E. Evans, unpublished results.

[3] Representative conditions cited in ref 4 are 180° in EtOH for 18–20 hr.

[4] R. C. Elderfield and A. C. Mehta, *Heterocycl. Compounds*, **9**, 64 (1967).

[5] E. C. Taylor, Y. Maki, and B. E. Evans, *J. Amer. Chem. Soc.*, **91**, 5181 (1969).

[6] Y. F. Shealy, J. D. Clayton, and J. A. Montgomery, *J. Org. Chem.*, **27**, 2154 (1962).

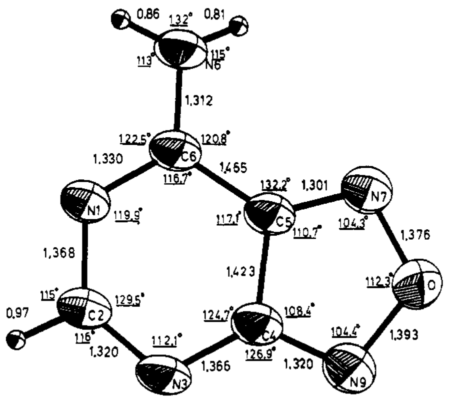


Figure 1. I (R = H) showing intramolecular bonding parameters corrected for thermal motion. Thermal ellipses are drawn at the 50% probability level for nonhydrogen atoms in this and all subsequent illustrations.

tronic relationship between systems II and III extends to I as well.

Likewise, the morphological kinship of these systems to one another, as well as to the purines (*i.e.*, adenine IV, R = H), has been substantiated by the demonstrated activity of all these compounds as substrates for, or inhibitors of, adenosine deaminases. Such activity is thought to be dependent on structural and electronic similarity of the potential substrate–inhibitor to the natural substrate, adenosine IV (R = β-D-ribofuranosyl).[7,8]

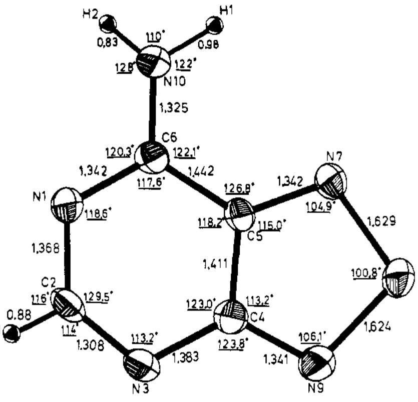
Why, then, do derivatives of I undergo anomalously facile displacement of the 7-amino group by nucleophiles, and photochemical addition of alcohols and dioxane to the 6,7-(*amidine*) bond (a reaction without precedent)? In an attempt to find an answer to these questions, we have undertaken X-ray crystallographic analyses of both 7-aminoFZP (I, R = H) and its thio analog (II, R = H). The results of these analyses are presented in the following paragraphs and their significance is discussed.

Experimental Section

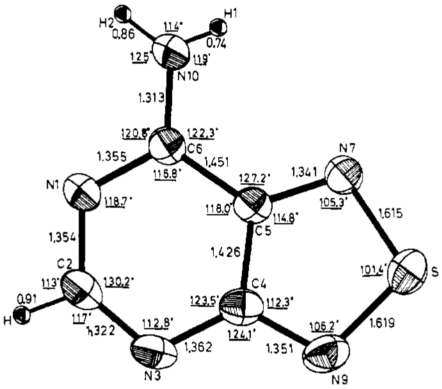
Colorless prisms of I (R = H)[9] were obtained by crystallization from acetic acid, while II (R = H)[11] crystallized from pyridine as yellow monoclinic prisms. Crystallographic data measured at room temperature for these two compounds are summarized in Table I.

Table I

	I (R = H)	II (R = H)
a, Å	3.703 (1)	10.998 (1)
b, A	12.463 (2)	7.104 (1)
c, A	11.989 (3)	15.950 (2)
β, deg	101.92 (3)	101.58 (1)
Density (measd), g/cm^3	1.690	1.668
Density (calcd), g/cm^3	1.681	1.666
Z (no. of molecules in unit cell)	4	8
Space group	$P2_1/c$	$P2_1/c$



MOLECULE A



MOLECULE B

Figure 2. Thermally corrected bond lengths and angles for the two unique molecules (A and B) of II (R = H).

The intensity data were collected by the stationary counter–stationary crystal technique[12] on a General Electric XRD-6 diffractometer equipped with a single-crystal orientor. Balanced filters for Cu Kα radiation were utilized for the measurement of peak intensities and backgrounds; Ni against Co. The range of measurement in both cases was from 0 to 140° in 2θ, which encompasses 1080 and 2319 independent reflections for I (R = H) and II (R = H), respectively. Only about 10% of the reflections had intensities which were not significantly greater than their background counts; these were given zero weight throughout the computations. In both cases, the intensities were corrected for absorption by applying a factor to correct for the anisotropy of transmission of the X-ray beam about the ϕ axis of each crystal as measured at $\chi = 90°$. The other factors applied to convert the data to structure factor amplitudes, $|F|$'s, were Lorentz polarization and α_1–α_2 splitting corrections.

Direct methods were employed to obtain the phases of a number of reflections for both I (R = H) and II (R = H) so that the structures could be solved. A program written by R. Long[13] which makes use of the Sayre relationships,[14] which in turn are similar to the Σ_2 equations of Hauptman and Karle,[15] was used. The phases of 301 reflections for II (R = H) having $|E|$ values of 1.50 or greater and 120 reflections for I (R = H) with $|E|$ values greater than 1.60 were determined. The *E* maps calculated for these compounds enabled the nonhydrogen atoms to be located. After initial refinement of the atomic positions for the two compounds [I (R = H) has one molecule in the asymmetric unit cell while II (R = H) has two independent molecular species in the asymmetric unit], the hydrogen atoms of the respective molecules were located in difference electron density maps. The final cycles of least-squares refinement were then carried out using a weighting scheme designed

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[7] B. Evans and R. Wolfenden, *J. Amer. Chem. Soc.*, **92**, 4751 (1970), and references contained therein.

[8] R. Wolfenden, J. Kaufman, and J. B. Macon, *Biochemistry*, **8**, 2412 (1969).

[9] This compound was prepared by lead tetraacetate oxidation of 4,6-diamino-5-nitrosopyrimidine in glacial acetic acid.[10]

[10] (a) Ben E. Evans, Ph.D. Thesis, Princeton University, Princeton, N. J., 1970; (b) E. C. Taylor, G. P. Beardsley, and Y. Maki, *J. Org. Chem.*, **36**, 3211 (1971).

[11] This compound was prepared by the procedure of Shealy, Clayton, and Montgomery.[6]

[12] T. C. Furnas and D. Harker, *Rev. Sci. Instrum.*, **26**, 449 (1955).

[13] R. Long, *Dissertation Abstr.*, **26**, 3651 (1966).

[14] D. Sayre, *Acta Crystallogr.*, **5**, 60 (1952).

[15] H. Hauptman and J. Karle, "Solution of the Phase Problem I. The Centrosymmetric Crystal," American Crystallographic Association Monograph, No. 3, Polycrystal Book Service, Pittsburgh, Pa., 1953.

Table II. Positional and Thermal Parameters with Their Respective Estimated Standard Deviations (in Parentheses) Obtained from Least-Squares Refinement[a]

Atom	x	y	z	b_{11}/B_{iso}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
I (R = H)									
N(1)	3592 (9)	1035 (2)	3877 (2)	991 (30)	57 (2)	35 (2)	−25 (13)	37 (13)	−1 (3)
C(2)	1895 (12)	3534 (3)	7858 (3)	983 (37)	68 (3)	35 (2)	−18 (16)	19 (15)	11 (4)
N(3)	1911 (10)	2461 (3)	2495 (2)	1064 (31)	68 (2)	33 (2)	23 (14)	−3 (12)	8 (3)
C(4)	3995 (11)	3116 (3)	3283 (3)	948 (36)	59 (2)	36 (2)	23 (16)	54 (14)	4 (4)
C(5)	5933 (11)	2220 (3)	9372 (3)	888 (33)	59 (2)	34 (2)	7 (15)	65 (14)	3 (4)
C(6)	5592 (11)	3347 (3)	9668 (3)	875 (33)	61 (2)	32 (2)	3 (15)	66 (14)	7 (4)
N(7)	7683 (11)	3579 (3)	4930 (3)	1214 (37)	61 (2)	45 (2)	−51 (15)	70 (15)	1 (4)
O(8)	6920 (9)	4430 (2)	4194 (2)	1426 (33)	57 (2)	57 (2)	−88 (13)	59 (13)	10 (3)
N(9)	4617 (11)	854 (3)	8171 (3)	1260 (37)	63 (2)	49 (2)	8 (15)	54 (15)	−12 (4)
N(6)	7254 (10)	3716 (3)	663 (2)	1235 (36)	56 (2)	33 (2)	77 (14)	−17 (14)	0 (3)
H(C2)	533 (112)	4045 (33)	7321 (35)	4.4 (0.9) Å^2					
H(N6)1	6886 (113)	4392 (34)	10744 (34)	4.4 (0.9) Å^2					
H(N6)2	8284 (106)	3267 (32)	11097 (32)	3.8 (0.8) Å^2					
II (R = H) Molecule A									
N(1)	4014 (3)	2051 (4)	40 (2)	54 (2)	114 (5)	16 (1)	31 (6)	0 (2)	−18 (4)
C(2)	3027 (3)	3233 (5)	−191 (2)	36 (2)	154 (7)	17 (1)	25 (7)	−11 (3)	−13 (5)
N(3)	2819 (2)	4868 (4)	124 (2)	42 (2)	141 (6)	21 (1)	42 (6)	−6 (3)	−14 (4)
C(4)	3760 (3)	5443 (5)	781 (2)	43 (2)	117 (6)	14 (1)	25 (6)	12 (3)	−7 (4)
C(5)	4829 (3)	4360 (4)	1079 (2)	43 (2)	103 (6)	9 (1)	17 (6)	3 (2)	−2 (4)
C(6)	4931 (3)	2561 (4)	686 (2)	48 (3)	97 (6)	12 (1)	26 (6)	8 (3)	11 (4)
N(7)	5662 (3)	5155 (4)	1707 (2)	55 (2)	107 (5)	14 (1)	16 (6)	0 (2)	−3 (4)
S(8)	5063 (1)	7175 (1)	1877 (1)	69 (1)	124 (2)	17 (0.3)	34 (2)	5 (1)	−29 (1)
N(9)	3767 (3)	7094 (4)	1185 (2)	56 (2)	126 (6)	22 (1)	48 (6)	9 (3)	−17 (4)
N(10)	5888 (3)	1431 (4)	942 (2)	57 (2)	113 (5)	22 (1)	53 (6)	−13 (3)	−16 (4)
H(C2)	2479 (39)	2903 (58)	−644 (26)	3.3 (0.8) Å^2					
H(N10)1	6553 (53)	1739 (80)	1428 (35)	5.9 (1.3) Å^2					
H(N10)2	6041 (35)	424 (57)	728 (24)	2.8 (0.8) Å^2					
II (R = H) Molecule B									
N(1)	1063 (3)	1077 (4)	907 (2)	52 (2)	133 (6)	28 (1)	40 (6)	1 (3)	−1 (4)
C(2)	2117 (3)	1280 (6)	1500 (3)	53 (3)	152 (8)	39 (2)	46 (8)	−2 (4)	8 (6)
N(3)	2494 (3)	2680 (5)	2030 (2)	51 (3)	178 (7)	34 (1)	18 (7)	−19 (3)	6 (5)
C(4)	1667 (3)	4117 (5)	1947 (2)	50 (3)	159 (7)	19 (1)	−8 (7)	12 (3)	8 (5)
C(5)	521 (3)	4110 (5)	1351 (2)	50 (3)	133 (6)	13 (1)	17 (7)	14 (3)	6 (4)
C(6)	217 (3)	2474 (5)	810 (2)	53 (3)	127 (6)	17 (1)	24 (7)	14 (3)	5 (4)
N(7)	−168 (3)	5655 (5)	1361 (2)	68 (3)	167 (7)	21 (1)	56 (7)	0 (3)	−31 (4)
S(8)	621 (1)	6977 (2)	2095 (1)	89 (1)	192 (2)	29 (0.4)	45 (2)	9 (1)	−57 (1)
N(9)	1829 (3)	5693 (5)	2426 (2)	67 (3)	199 (7)	21 (1)	−15 (7)	3 (3)	−26 (5)
N(10)	−840 (3)	2305 (5)	267 (2)	58 (3)	159 (7)	29 (1)	62 (7)	−14 (3)	−28 (5)
H(C2)	2625 (39)	266 (64)	1534 (27)	3.8 (1.0) Å^2					
H(N10)1	−1276 (42)	3108 (68)	200 (28)	4.1 (1.1) Å^2					
H(N10)2	−1018 (54)	1424 (90)	−106 (37)	6.8 (1.4) Å^2					

[a] All ×10^4 except B_{iso}. The anisotropic temperature factor is of the form: temp = exp $-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)$.

such that $\langle w\Delta^2 \rangle$ is constant over the whole range of $|F_o|$ values. These are: for I (R = H), $w^{-1} = [(|F_o| - 4)/10]^2 + 1$; for II (R = H), $w^{-1} = [(|F_o| - 8)/13]^2 + 1$. A modified version of the Trueblood, Sparks, and Gantzel block diagonal least squares[16] was used for these computations. The final R values (usual reliability index) for the two structures are 0.067 for the 2144 observed data of II (R = H) and 0.076 for the 863 observed reflections of I (R = H).

The positional and thermal parameters obtained for the two structures are listed in Table II.[17]

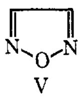
Analysis of the thermal motion of the molecules was accomplished by the Schomaker and Trueblood method.[18] The root-mean-square discrepancy between the observed U_{ij}'s and those calculated for the individual molecular species, assuming rigid body motion, showed that 7-aminoFZP and species A and B (see below) of the thiadiazolopyrimidine II (R = H) behave as rigid bodies. The values of the rms differences in the U_{ij}'s for I (R = H) and molecules A and B of II (R = H) are 0.0023, 0.0013, and 0.0011 Å, respectively. The intramolecular bond distances and angles in the two compounds, shown in Figures 1 and 2, respectively, were corrected for thermal motion; corrections were never greater than two times the esd's of the respective atoms.

The esd's for the intramolecular bond lengths and angles in the two structures are 0.006 Å and 0.4° on the average (these values include an additional uncertainty for the thermal motion corrections estimated to be approximately 0.001 Å and 0.1°). The bonds involving the hydrogen atoms have errors approximately eight times as great.

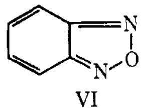
The intermolecular hydrogen bonding found for I (R = H) and II (R = H) is illustrated in Figures 3 and 4, respectively.

Discussion

Bond Lengths. The N–O linkages in I (R = H) (see Figure 1) are quite similar to those reported[19] for furazan (V) itself. The corresponding bonds in benzofurazan (VI) are substantially shorter,[20] most likely reflecting inaccuracy in its structure determination.



V



VI

The 1.384 ± 0.008-Å N–O bond length (average value) in I (R = H) agrees quite well with that found in

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(16) K. N. Trueblood, R. A. Sparks, and P. K. Gantzel, unpublished.

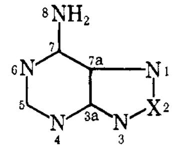
(17) A list of the observed and calculated structure factors is available (ref 10a).

(18) V. Schomaker and K. N. Trueblood, *Acta Crystallogr., Sect. B*, 24, 63 (1968).

(19) A. P. Cox and E. Saegebarth, *U. S. Govt. Res. Develop. Rep.*, 40, 35 (1965); *Chem. Abstr.*, 63, 9253c (1965).

(20) V. Luzzati, *Acta Crystallogr.*, 4, 193 (1951).

Table III. Reported Values for Selected Bond Lengths (in Ångströms) (Listed According to Numbering Scheme in VII below)



VII

Bond	I (R = H)	II (R = H), A	II (R = H), B	IV (R = CH$_3$)	IV (R = H·HCl)	V	VI	Benzo[*c*]-1,2,5-thiadiazole
5-Ring				*a* (*b*)	*c*	*d*	*e*	*e*
CN								
1–7a	1.301	1.342	1.341	1.38 (1.38)	1.37	1.300	1.35	1.34
3–3a	1.320	1.341	1.351	1.36 (1.39)	1.36	1.300	1.35	1.34
NX								
1–2	1.376	1.629	1.615	1.31 (1.32)	1.35	1.380	1.20	1.60
2–3	1.393	1.624	1.619	1.35 (1.36)	1.33	1.380	1.20	1.60
CC								
3a–7a	1.423	1.411	1.426	1.37 (1.37)	1.37	1.421	1.43	1.41
6-Ring								
3a–4	1.366	1.383	1.362	1.34 (1.35)	1.36		1.43[f]	1.46
4–5	1.320	1.308	1.322	1.32 (1.30)	1.30		1.43	1.39[g]
5–6	1.368	1.368	1.354	1.35 (1.36)	1.37		1.43	1.46
6–7	1.330	1.342	1.355	1.35 (1.36)	1.38		1.43	1.39[g]
7–7a	1.465	1.442	1.451	1.40 (1.41)	1.40		1.43	1.46
7a–3a	1.423	1.411	1.426	1.37 (1.37)	1.37		1.43	1.41
Exocyclic CN								
7–8	1.312	1.325	1.313	1.35 (1.34)	1.30			

[a] Reference 31. [b] Reference 32. [c] Reference 33. [d] Reference 19. [e] Reference 20. [f] All carbon–carbon bonds. [g] Value calculated by Ray and Narasimhan (N. K. Ray and P. T. Narasimhan, *Theoret. Chim. Acta*, **5**, 401 (1966)) who question value (1.29 Å) reported in ref 20.

various *N*-oxide structures,[21] but is appreciably shorter than the N–OH bond (1.43 Å).

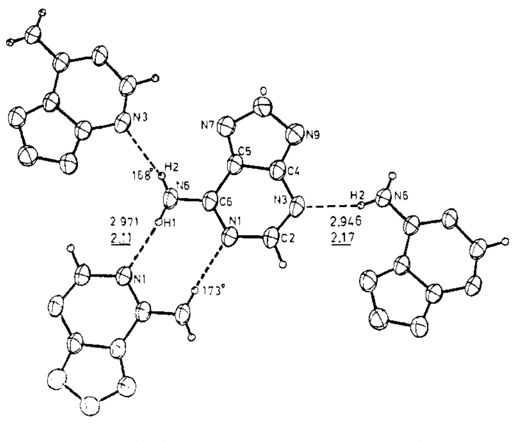


Figure 3. A general view of the hydrogen bonding occurring in the crystals of I (R = H).

In the thio analog II (R = H), the N–S bonds (average length 1.622 ± 0.007 Å) are substantially shorter than the N–S single bond (1.735 Å), falling quite close to the values observed in various sulfonamides.[22–24]

The CN bonds in the furazan ring of I (R = H) (*i.e.*, C_5–N_7 and C_4–N_9 in Figure 1) are significantly shorter than the corresponding bonds in the thio analog II (R = H) (see Figure 2). The latter, in turn, are shorter than the analogous bonds in 9-methyladenine (IV, R = CH$_3$) (see Table III for complete listing of all bond lengths discussed in this section).

The length of a pure CN double bond has been estimated[25] to be 1.265 Å, and the corresponding single bond (sp^2 carbon–sp^2 nitrogen), 1.470 Å.[26] To a first approximation, then, the bond lengths cited in the preceding paragraph would indicate the double bond character of these bonds decreases from 75 to 60 to 50% in going from 7-amino FZP (I, R = H) to thio analog II (R = H) to the carbon analog, 9-methyladenine (IV, R = CH$_3$).

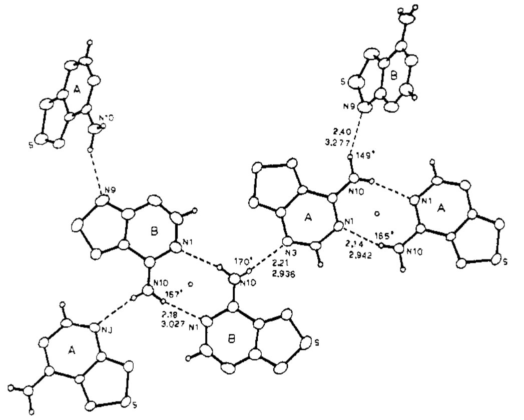


Figure 4. The hydrogen bonding scheme in the crystals of II (R = H). The two unique molecules are so marked.

Differences between the bonding parameters of the two unique molecules of II (R = H) (*i.e.*, molecules

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Table IV. Least-Squares Planes[a] and Displacements Therefrom

I (R = H)				II (R = H)					
Atoms comprising 1s plane	Displacements, Å	Other atoms	Displacements, Å	Atoms comprising 1s plane	Displacements, Å		Other atoms	Displacements, Å	
					Mol A	Mol B		Mol A	Mol B
N(1)	−0.005	N(7)	−0.018	N(1)	−0.006	−0.002	N(7)	−0.046	0.025
C(2)	−0.004	O(8)	−0.033	C(2)	−0.002	0.000	S(8)	−0.076	0.006
N(3)	0.006	N(9)	−0.016	N(3)	0.006	0.001	N(9)	−0.031	−0.009
C(4)	0.001	N(6)	0.022	C(4)	0.000	0.001	N(10)	0.042	0.058
C(5)	−0.009	H(C2)	−0.04	C(5)	−0.007	−0.003	H(C2)	−0.09	0.02
C(6)	0.011	H(N6)1	0.03	C(6)	0.011	0.004	H(N10)1	0.10	0.01
		H(N6)2	0.08				H(N10)2	−0.01	−0.03
Equation:	$-0.9032x + 0.2067y + 0.3762z - 1.6482\ \text{Å} = 0$				Equations:	$-0.6071x - 0.4442y + 0.6589z + 3.2720\ \text{Å} = 0\ (A)$ $-0.5911x - 0.4240y - 0.6862z - 0.1310\ \text{Å} = 0\ (B)$			
C(4)	0.002	N(1)	−0.032	C(4)	−0.002	−0.007	N(1)	−0.073	0.013
C(5)	−0.004	C(2)	−0.033	C(5)	0.000	0.004	C(2)	−0.074	−0.001
N(7)	0.005	N(3)	−0.010	N(7)	0.002	0.007	N(3)	−0.036	−0.011
O(8)	−0.003	C(6)	0.001	S(8)	−0.003	−0.002	C(6)	−0.017	0.024
N(9)	0.001	N(6)	0.014	N(9)	0.003	−0.002	N(10)	0.019	0.093
Equation:	$-0.8983x + 0.2183y + 0.3813z - 1.7154\ \text{Å} = 0$				Equations:	$-0.5955x - 0.4253y + 0.6815z + 3.1249\ \text{Å} = 0\ (A)$ $-0.5986x - 0.4273y + 0.6776z - 0.0943\ \text{Å} = 0\ (B)$			

[a] Calculated by the method of Schomaker, *et al.* (see ref 35).

A and B in Figures 2a and 2b, respectively) are not *highly* significant.[27] The largest discrepancy, that between the C_4–N_3 bonds, is only significant at the $p = 0.01$ level. The distinctive environment about each of these two molecules (see Figure 4) is probably responsible for these bond-length (and, hence, bond-order) variations.

Ring Planarity. An examination of the least-squares planes calculated through the two fused ring systems I (R = H) and II (R = H) reveals that, in each case, the five- and six-membered rings are tilted from coplanarity about their common bond (see Table IV). This distortion from overall planarity in these heterocyclic systems can be simply described in terms of the dihedral angle between the five- and six-membered rings. These angles are 0.8, 1.8, and 0.7° for I (R = H), II (R = H), molecule A, and II (R = H), molecule B, respectively. Many purine analogs show similar displacements,[28,29] and in all probability such distortions result from the packing forces operating on the molecule in the crystal. To what extent these distortions occur in solution does not appear to be known.

Crystal Hydrogen Bonding. The general features of the hydrogen bonding scheme in the crystals of I (R = H) and II (R = H) are quite similar (see Figures 3 and 4). The amino group in each case donates one proton to N_1 and another to either N_3 or N_9. The lengths of these hydrogen bonds are typical of such interactions.[30–34]

Summary

According to bonding parameters determined by the X-ray analysis, then, 7-amino-1,2,5-thiadiazolo[3,4-*d*]pyrimidine (II) is extensively delocalized throughout, while its oxygen analog I is appreciably delocalized only in the pyrimidine ring. The furazan ring in I may thus be thought of as constituting a pair of strongly electronegative substituents (oximes) on a monocyclic pyrimidine. The remarkable susceptibility of I and its derivatives to nucleophilic attack at C-7 is attributable to this high level of electron deficiency. Similarly, the ease of photoreduction of I and its derivatives might be tentatively ascribed to its high formal oxidation state.

The adenine-like behavior of I (R = H) toward the adenosine deaminases is likewise accounted for by the X-ray results which show vividly the close morphological relationship between I (R = H) and the adenines listed in Table III; the reactivity of II (R = H) toward adenosine deaminases[9] is likewise explicable in terms of the X-ray results.

In conclusion, much of the curious chemistry of system I is gratifyingly explained by the X-ray analysis. A detailed correlation of the chemical reactivity of I with MO calculations (based on the above bonding parameters) will be published independently.

Acknowledgments. The authors are appreciative of the support given to this project by the National Cancer Institute (CA-10104) and the National Science Foundation (predoctoral fellowship to B. E. E.), the technical assistance of Mrs. Phyllis Sackman, and the facilities of the Computing Center of SUNY/B.

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