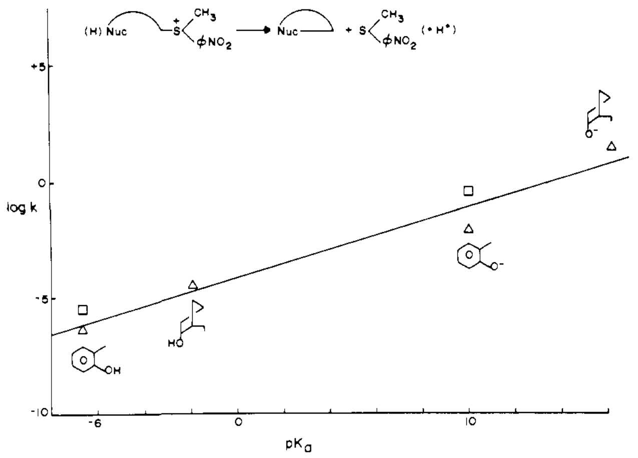
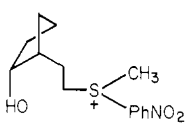
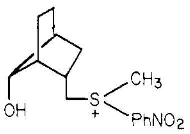


Figure 5. Brønsted plot of log k_{ROH} or log k_{RO^-} vs. pK_a of the conjugate acid. pK_a data: phenol, Arnett, E. M. *Prog. Phys. Org. Chem.* **1963**, *1*, 223; alcohol, Perdoncin, G.; Scorrano, G. *J. Am. Chem. Soc.* **1977**, *99*, 6983; phenoxide, this research; alkoxide, ref 1. In the phenol–phenoxide pairs, the dimethyl system (**3**) is indicated by open squares.

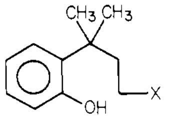
They observed catalysis by borate, but not by acetate, and presented a three-point Brønsted plot (H_2O, borate, OH^-) with β = 0.25. More recently, our studies with the cyclopentanol derivative **18** established general base catalysis by a variety of oxyanion buffers with β = 0.27. Subsequent studies by Irie and Tanida[17] with **19** extended the observations of general base catalysis. An unusual finding in the latter study was the apparent catalysis by general acids (e.g., acetic acid); similar general-acid catalysis has not been observed in our studies of **18**. The present work has extended the observation of general-base catalysis of S_N2 reactions further by demonstrating the susceptibility of phenols such as **1** and **3** to this type of catalysis. Previous studies by Borchardt and Cohen[3] failed to provide evidence for buffer catalysis in cyclization reactions of molecules of type **20**. The main difference between **20** and the phenols (**1** and **3**) studied in the present work is the nature of the leaving group. The leaving groups in **20** are all negatively charged (from a neutral starting material), whereas the leaving group in **1** and **3** is neutral (from a previously charged starting material). Although slightly different reaction conditions prevailed in the studies with **20** (40% dioxane–60% H_2O) vs. the present work (100% H_2O), it is not clear why no general-base catalysis was observed in the reactions of **20**. Additional research will be required to deliniate structural features which lead to general catalysis in S_N2 reactions. As part of this research effort, we have recently completed the synthesis of compounds which are similar to **3** but contain a poorer alkyl thioether leaving group (e.g., 5′-(methylthio)adenosine).



18



19



20

X = $-OSO_2CH_3$, $-OPO(OEt)_2$, $-COOCl_3$

Acknowledgment. This research was supported by a grant from the United States Public Health Service, NIH.

Registry No. 1, 81246-41-5; **2**, 81246-42-6; **3**, 81246-43-7; **4**, 254-04-6; **5**, 40614-27-5; **6**, 1849-36-1; **7**, 81246-44-8; **8**, 81246-45-9; **9**, 1481-92-1; **10**, 81246-46-0; **11**, 10493-37-5; **12**, 81246-47-1; **13**, 81246-48-2; **14**, 40614-20-8; **14** 1-mesylate, 40614-15-1; **14** 1-tosylate, 81255-45-0; **15**, 81246-49-3; **16**, 81246-50-6; **17**, 81246-51-7; 3,4-dihydrocoumarin, 119-84-6.

---

(17) Irie, T.; Tanida, H. *J. Org. Chem.* **1979**, *44*, 325-330.

(18) Bell, R. P. "The Proton in Chemistry", 2nd ed.; Cornell University Press: Ithaca, N.Y., 1973; Chapter 10.

Molecular Structures of Nucleosides and Nucleotides. 2. Orthogonal Coordinates for Standard Nucleic Acid Base Residues

Robin Taylor* and Olga Kennard*[1]

Contribution from the Crystallographic Data Centre, University Chemical Laboratory, Cambridge CB2 1EW, England. *Received July 27, 1981*

Abstract: A least-squares minimization procedure was used to derive orthogonal coordinates for "standard" nucleic acid base residues. The dimensions of the standard residues are as close as possible to the average dimensions observed in crystal structures, subject to the necessity for ring closure. The residues were assumed to be precisely planar, and an examination of 67 nucleoside and nucleotide crystal structures suggests that this assumption is justified.

The use of "standard" nucleic acid base residues has many applications in model-building calculations and in the determination, refinement, and interpretation of nucleoside and nucleotide crystal structures.[2] In the present context, a standard residue is defined as one whose molecular dimensions are as close as possible to the average dimensions observed in crystal structures, subject to the necessity for ring closure. The standard residues in current use are generally derived from mean bond lengths and valence angles reported by Voet and Rich in 1970.[3] The large number of structure determinations that have appeared in the literature since then has prompted a recent redetermination of these values,[4] using 90 crystal structures[5] retrieved from the

---

(1) External Staff, Medical Research Council.

(2) Arnott, S.; Hukins, D. W. L. *J. Mol. Biol.* **1973**, *81*, 93-105.

(3) Voet, D.; Rich, A. *Prog. Nucleic Acid Res. Mol. Biol.* **1970**, *10*, 183-265.

(4) Taylor, R.; Kennard, O. *J. Mol. Struct.* **1982**, *78*, 1-28.

(5) A complete bibliography of these structures is given in ref 4.

0002-7863/82/1504-3209$01.25/0

Table I. Orthogonal Coordinates for Standard Nucleic Acid Base Residues (in Angstroms)

	neutral		protonated			neutral		protonated	
	x	*y*	*x*	*y*		*x*	*y*	*x*	*y*
	Cytosine					Uracil			
N1	0.0000	0.0000	0.0000	0.0000	N1	0.0000	0.0000		
C2	0.0000	1.3990	0.0000	1.3809	C2	0.0000	1.3791		
N3	1.1871	2.0550	1.2581	1.9646	N3	1.2462	1.9560		
C4	2.3303	1.3673	2.4287	1.2882	C4	2.4662	1.3042		
C5	2.3500	-0.0585	2.3668	-0.1236	C5	2.3823	-0.1333		
C6	1.1739	-0.6943	1.1614	-0.7115	C6	1.1787	-0.7172		
O2	-1.0799	2.0023	-1.0098	2.0494	O2	-1.0194	2.0456		
N4	3.4753	2.0576	3.5603	1.9542	O4	3.5058	1.9558		
	Adenine					Guanine			
N1	-2.3548	1.2363	-2.3151	1.1999	N1	-2.3158	1.1867	-2.3171	1.1980
C2	-2.1991	-0.0930	-2.1996	-0.1571	C2	-2.2136	-0.1842	-2.2130	-0.1689
N3	-1.0733	-0.8054	-1.0758	-0.8223	N3	-1.0615	-0.8426	-1.0562	-0.8228
C4	0.0000	0.0000	0.0000	0.0000	C4	0.0000	0.0000	0.0000	0.0000
C5	0.0000	1.3817	0.0000	1.3853	C5	0.0000	1.3772	0.0000	1.3721
C6	-1.2563	2.0196	-1.2441	2.0381	C6	-1.2362	2.0659	-1.2278	2.0873
N7	1.2954	1.8718	1.2865	1.8793	N7	1.2986	1.8698	1.3213	1.7829
C8	2.0408	0.7921	2.0435	0.8027	C8	2.0457	0.8010	2.0877	0.6984
N9	1.3246	-0.3724	1.3156	-0.3672	N9	1.3265	-0.3697	1.3124	-0.3934
N6	-1.4074	3.3480	-1.4243	3.3477	N2	-3.3684	-0.8660	-3.3726	-0.8464
					O6	-1.4337	3.2891	-1.4142	3.2980

Cambridge Crystallographic Database.[6] The new mean values agree quite well with those reported by Voet and Rich, but there are occasional discrepancies of up to 0.02–0.03 Å for bond lengths and 1–3° for valence angles. These discrepancies are statistically significant when compared with the standard errors of the means, which average about 0.004 Å for bond lengths and 0.2° for valence angles.[4] We have therefore used the redetermined average dimensions to calculate orthogonal coordinates for standard nucleic acid base residues. The results are reported herein.

Methods and Results

The coordinates for each residue (protonated and neutral cytosine, adenine, and guanine residues, and the neutral uracil residue; Figure 1) were calculated by minimization of the expression

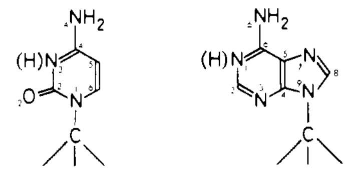
$$\sum_i (l_i - \bar{l}_i)^2/\sigma_i^2 + \sum_j (\theta_j - \bar{\theta}_j)^2/\sigma_j^2$$

$\sum_i$ and $\sum_j$ represent summations over all the bond lengths and valence angles, respectively. l_i is the value of the ith bond length, and $\bar{l}_i$ and σ_i are, respectively, the mean and standard deviation of the bond length in the crystal structures. Similarly, θ_j is the value of the jth valence angle, and $\bar{\theta}_j$ and σ_j are its mean and standard deviation in the crystal structures. The residues were assumed to be precisely planar.

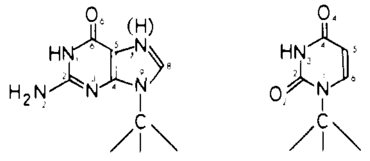
The coordinates are listed in Table I.[7] The dimensions of the standard residues are summarized in Table II, together with the mean dimensions observed in the crystal structures.[4] The maximum discrepancy for bond lengths, $|l_i - \bar{l}_i|_{\max}$, is 0.001 Å, while the corresponding figure for valence angles is 0.1°. These discrepancies are within the uncertainties of the observed average dimensions.

Base Planarity

The similarity between the dimensions of the standard residues and the average dimensions observed in the crystal structures suggests that the assumption of exact base planarity is justified. However, at the request of one of the referees we examined the validity of this assumption in detail. From the original sample of 90 crystal structures, we selected 67 that crystallize in Sohncke groups[8] and in which the chirality of the nucleoside or nucleotide molecule can be inferred from the known configuration of the sugar residue. Calculations of the furanose residue torsion angles revealed that in five cases[9] the configuration at the C4′ atom was that of an L sugar, although the authors had named the sugar as D.[15] We therefore reversed the signs of all the torsion angles in these molecules. We then computed the means and standard errors



Cytosine. Adenine.



Guanine. Uracil.

Figure 1. Atom labeling scheme for nucleic acid base residues.

---

(6) Allen, F. H.; Bellard, S.; Brice, M. D.; Cartwright, B. A.; Doubleday, A.; Higgs, H.; Hummelink, T.; Hummelink-Peters, B. G.; Kennard, O.; Motherwell, W. D. S.; Rodgers, J. R.; Watson, D. G. *Acta Crystallogr., Sect. B* **1979**, *B35*, 2331–2339.

(7) Coordinates for the C1′ atom of the furanose ring were not derived. We intend to examine the geometry of the glycosidic linkage in a subsequent study.

(8) Space groups in which homochiral molecules can crystallize.

(9) Arabinofuranosyladenine hydrochloride,[10] sodium deoxyadenosine 5′-phosphate hexahydrate,[11] deoxyadenosine monohydrate,[12] 5-hydroxymethyl-2′-deoxyuridine,[13] and the 1:1 salicylic acid–cytidine complex.[14]

(10) Hata, T.; Sato, S.; Kaneko, M.; Shimizu, B.; Tamura, C. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 2758–2763.

(11) Reddy, B. S.; Viswamitra, M. A. *Acta Crystallogr., Sect. B.* **1975**, *B31*, 19–26.

(12) Watson, D. G.; Sutor, D. J.; Tollin, P. *Acta Crystallogr.* **1965**, *19*, 111–124.

(13) Birnbaum, G. I.; Deslauriers, R.; Lin, T.-S.; Shiau, G. T.; Prusoff, W. H. *J. Am. Chem. Soc.* **1980**, *102*, 4236–4241.

(14) Tamura, C.; Yoshikawa, M.; Sato, S.; Hata, T. *Chem. Lett.* **1973**, 1221–1224.

(15) The procedure used to infer the configuration of the sugar residue was that of Murray-Rust, P.; Motherwell, S. *Acta Crystallogr., Sect. B* **1978**, *B34*, 2534–2546.

Table II. Dimensions of Standard Nucleic Acid Base Residues (Distances in Angstroms, Angles in Degrees)

	neutral		protonated			neutral		protonated	
	calcd[a]	obsd	calcd	obsd		calcd	obsd	calcd	obsd
	Cytosine					Uracil			
N1-C2	1.399	1.399 (4)	1.381	1.381 (2)	N1-C2	1.379	1.379 (2)		
C2-N3	1.356	1.356 (3)	1.387	1.387 (2)	C2-N3	1.373	1.373 (2)		
N3-C4	1.334	1.334 (2)	1.352	1.352 (2)	N3-C4	1.383	1.383 (2)		
C4-C5	1.426	1.426 (4)	1.413	1.413 (3)	C4-C5	1.440	1.440 (2)		
C5-C6	1.337	1.337 (2)	1.341	1.341 (2)	C5-C6	1.338	1.338 (2)		
C6-N1	1.364	1.364 (2)	1.362	1.362 (3)	C6-N1	1.380	1.380 (2)		
C2-O2	1.237	1.237 (2)	1.211	1.211 (2)	C2-O2	1.218	1.218 (2)		
C4-N4	1.337	1.337 (4)	1.313	1.313 (3)	C4-O4	1.227	1.227 (2)		
C6-N1-C2	120.6	120.6 (1)	121.5	121.5 (1)	C6-N1-C2	121.3	121.3 (1)		
N1-C2-N3	118.9	118.9 (2)	114.9	114.9 (2)	N1-C2-N3	114.8	114.8 (1)		
C2-N3-C4	120.0	120.0 (2)	125.1	125.1 (2)	C2-N3-C4	127.0	127.0 (1)		
N3-C4-C5	121.8	121.8 (2)	117.5	117.5 (2)	N3-C4-C5	114.8	114.7 (2)		
C4-C5-C6	117.6	117.6 (2)	118.5	118.5 (1)	C4-C5-C6	119.2	119.2 (2)		
C5-C6-N1	121.0	121.0 (2)	122.5	122.5 (1)	C5-C6-N1	122.8	122.8 (2)		
N1-C2-O2	119.2	119.2 (2)	123.5	123.5 (2)	N1-C2-O2	123.2	123.2 (2)		
N3-C2-O2	121.9	121.9 (2)	121.6	121.6 (1)	N3-C2-O2	122.0	122.0 (1)		
N3-C4-N4	117.9	117.9 (3)	119.5	119.5 (2)	N3-C4-O4	119.8	119.8 (1)		
C5-C4-N4	120.3	120.3 (2)	123.0	123.0 (3)	C5-C4-O4	125.4	125.4 (2)		
	Adenine					Guanine			
N1-C2	1.338	1.338 (3)	1.362	1.362 (4)	N1-C2	1.375	1.375 (3)	1.371	1.371 (4)
C2-N3	1.332	1.332 (3)	1.306	1.306 (2)	C2-N3	1.327	1.327 (2)	1.329	1.329 (5)
N3-C4	1.342	1.342 (2)	1.354	1.354 (3)	N3-C4	1.355	1.355 (2)	1.339	1.339 (7)
C4-C5	1.382	1.382 (2)	1.385	1.385 (6)	C4-C5	1.377	1.377 (2)	1.372	1.372 (4)
C5-C6	1.409	1.409 (1)	1.405	1.405 (4)	C5-C6	1.415	1.415 (5)	1.421	1.420 (11)
C6-N1	1.349	1.349 (2)	1.360	1.360 (2)	C6-N1	1.392	1.393 (2)	1.406	1.406 (12)
C5-N7	1.385	1.385 (2)	1.378	1.378 (2)	C5-N7	1.389	1.389 (3)	1.384	1.384 (20)
N7-C8	1.312	1.312 (2)	1.316	1.316 (2)	N7-C8	1.304	1.304 (3)	1.328	1.328 (14)
C8-N9	1.367	1.367 (4)	1.378	1.378 (4)	C8-N9	1.374	1.374 (4)	1.339	1.339 (7)
N9-C4	1.376	1.376 (2)	1.366	1.366 (3)	N9-C4	1.377	1.377 (2)	1.370	1.370 (10)
C6-N6	1.337	1.337 (3)	1.322	1.322 (3)	C2-N2	1.341	1.341 (3)	1.343	1.343 (8)
					C6-O6	1.239	1.239 (5)	1.225	1.225 (3)
C6-N1-C2	118.8	118.8 (2)	123.2	123.2 (2)	C6-N1-C2	124.9	124.9 (2)	124.9	124.8 (6)
N1-C2-N3	129.0	129.0 (1)	125.5	125.5 (2)	N1-C2-N3	124.0	124.0 (2)	123.8	123.8 (2)
C2-N3-C4	110.8	110.8 (1)	112.0	112.0 (2)	C2-N3-C4	111.8	111.8 (1)	112.6	112.6 (2)
N3-C4-C5	126.9	126.9 (2)	127.4	127.4 (2)	N3-C4-C5	128.4	128.4 (2)	127.9	127.9 (1)
C4-C5-C6	116.9	116.9 (1)	117.7	117.7 (2)	C4-C5-C6	119.1	119.1 (1)	120.2	120.2 (3)
C5-C6-N1	117.6	117.6 (1)	114.3	114.3 (3)	C5-C6-N1	111.7	111.7 (2)	110.6	110.5 (1)
C4-C5-N7	110.7	110.7 (1)	111.0	111.0 (2)	C4-C5-N7	110.8	110.8 (2)	107.3	107.3 (9)
C5-N7-C8	103.9	103.9 (2)	104.1	104.1 (2)	C5-N7-C8	104.2	104.2 (3)	108.0	108.0 (2)
N7-C8-N9	113.8	113.8 (2)	113.0	113.0 (2)	N7-C8-N9	113.5	113.5 (4)	109.4	109.4 (2)
C8-N9-C4	105.9	105.9 (1)	106.3	106.3 (2)	C8-N9-C4	106.0	106.0 (2)	108.7	108.7 (4)
N9-C4-C5	105.7	105.7 (1)	105.6	105.6 (2)	N9-C4-C5	105.6	105.6 (1)	106.7	106.7 (7)
N3-C4-N9	127.4	127.4 (1)	127.0	127.0 (4)	N3-C4-N9	126.0	126.0 (2)	125.4	125.4 (7)
C6-C5-N7	132.4	132.3 (2)	131.3	131.3 (2)	C6-C5-N7	130.1	130.1 (2)	132.5	132.5 (6)
N1-C6-N6	119.0	119.0 (2)	120.2	120.2 (2)	N1-C2-N2	116.3	116.3 (2)	115.9	115.9 (4)
C5-C6-N6	123.4	123.4 (2)	125.5	125.5 (3)	N3-C2-N2	119.7	119.7 (2)	120.2	120.2 (1)
					N1-C6-O6	120.0	120.0 (2)	120.5	120.5 (13)
					C5-C6-O6	128.3	128.3 (2)	129.0	129.0 (12)

[a] Calcd = value of dimension in standard residue; obsd = mean value of dimension in crystal structures[4] (number in parentheses is standard error of mean, in the units of the least significant digit of the preceding number).

of torsion angles involving the base residue atoms. The results are given in Table III. Of the 86 mean torsion angles calculated, all but 5 are within 2σ of the values expected for precisely planar base residues, and all but 1 are within 3σ. This evidence therefore indicates that the mean geometry of each of the base residues is exactly, or almost exactly planar. In order to confirm this, we conducted Hotelling T^2 significance tests[16] on four of the residues (protonated and neutral cytosine, neutral adenine, and neutral uracil; insufficient data were available for T^2 tests on the other three residues). In this procedure, the null hypothesis

$$H_0:\ \bar{\tau} = \mu_0$$

was tested against the alternative hypothesis

$$H_1:\ \bar{\tau} \neq \mu_0$$

where $\bar{\tau}$ is the vector of observed mean torsion angles and μ_0 is the vector of expected mean torsion angles assuming that the average geometry of the residue is precisely planar. The T^2 values obtained, together with their associated F statistics (degrees of freedom in parentheses), are as follows: protonated cytosine $T^2 = 98.2$, $F(10,1) = 0.982$; neutral cytosine $T^2 = 113.7$, $F(10,2) = 2.068$; neutral adenine $T^2 = 192.9$, $F(13,1) = 1.141$; neutral uracil $T^2 = 9.1$, $F(10,16) = 0.579$. Since the F values are not statistically significant at, or above the 90% level, we accept the null hypothesis and conclude that the average geometry of each of the residues is precisely planar.[17]

Also given in Table III are the means and standard errors of the absolute values of the torsion angles (i.e., of $|\tau|$ rather than

---

(16) Morrison, D. F. "Multivariate Statistical Methods", 2nd ed.; McGraw-Hill Kogakusha: Tokyo, 1976; p 128.

(17) This result is consistent with either of the following hypotheses: (a) the equilibrium geometry of the isolated base residue is precisely planar; (b) the equilibrium geometry of the isolated base residue is not precisely planar, but deviations from planarity occur with equal facility on either side of the base mean plane. We await the publication of additional structural data before attempting to decide between these two alternatives, but note that in either case the optimum geometry of the standard base residue will be planar.

Table III. Mean Torsion Angles of Nucleic Acid Base Residues (in Degrees)

	neutral			protonated		
	$\bar{\tau}$(exp)[a]	$\bar{\tau}$(obsd)	$\lvert\bar{\tau}\rvert$(obsd)	$\bar{\tau}$(exp)	$\bar{\tau}$(obsd)	$\lvert\bar{\tau}\rvert$(obsd)
Cytosine						
N1-C2-N3-C4	0	1.4 (0.8)	2.3 (0.4)	0	−0.6 (1.1)	2.1 (0.5)
C2-N3-C4-C5	0	−1.8 (0.7)	2.5 (0.3)	0	−0.7 (0.9)	1.8 (0.4)
N3-C4-C5-C6	0	1.3 (0.8)	2.2 (0.5)	0	1.1 (0.9)	2.2 (0.3)
C4-C5-C6-N1	0	−0.5 (0.5)	1.5 (0.3)	0	−0.2 (0.4)	1.0 (0.2)
C5-C6-N1-C2	0	0.1 (1.0)	2.4 (0.6)	0	−1.1 (0.8)	1.8 (0.4)
C6-N1-C2-N3	0	−0.6 (1.2)	3.1 (0.6)	0	1.4 (1.3)	2.5 (0.6)
C6-N1-C2-O2	180	−179.8 (1.1)	177.4 (0.6)	180	−178.9 (1.0)	178.0 (0.5)
C4-N3-C2-O2	180	−179.4 (0.7)	178.0 (0.3)	180	179.8 (0.9)	178.2 (0.4)
C2-N3-C4-N4	180	178.5 (0.8)	177.5 (0.3)	180	179.4 (0.9)	178.0 (0.4)
C6-C5-C4-N4	180	−179.0 (0.8)	177.8 (0.5)	180	−179.0 (1.1)	177.7 (0.4)
Uracil						
N1-C2-N3-C4	0	0.2 (0.6)	2.3 (0.3)			
C2-N3-C4-C5	0	−0.8 (0.7)	3.1 (0.3)			
N3-C4-C5-C6	0	0.7 (0.7)	2.8 (0.4)			
C4-C5-C6-N1	0	−0.1 (0.4)	1.4 (0.2)			
C5-C6-N1-C2	0	−0.5 (0.5)	2.3 (0.3)			
C6-N1-C2-N3	0	0.4 (0.7)	2.8 (0.4)			
C6-N1-C2-O2	180	−179.8 (0.7)	177.5 (0.4)			
C4-N3-C2-O2	180	−179.6 (0.6)	177.7 (0.3)			
C2-N3-C4-O4	180	179.2 (0.6)	177.2 (0.3)			
C6-C5-C4-O4	180	−179.3 (0.7)	177.4 (0.4)			
Adenine						
N1-C2-N3-C4	0	−0.6 (0.4)	1.1 (0.2)	0	−0.2 (0.3)	0.6 (0.1)
C2-N3-C4-C5	0	0.1 (0.4)	1.0 (0.2)	0	1.4 (0.5)	1.9 (0.3)
N3-C4-C5-C6	0	0.3 (0.4)	1.1 (0.2)	0	−1.4 (0.7)	2.2 (0.4)
C4-C5-C6-N1	0	−0.2 (0.5)	1.3 (0.2)	0	0.0 (0.7)	1.6 (0.4)
C5-C6-N1-C2	0	−0.3 (0.5)	1.3 (0.3)	0	1.1 (0.8)	2.2 (0.4)
C6-N1-C2-N3	0	0.8 (0.5)	0.9 (0.3)	0	−1.1 (0.7)	2.0 (0.4)
N9-C4-C5-N7	0	0.2 (0.3)	0.8 (0.1)	0	0.0 (0.3)	0.6 (0.2)
C4-C5-N7-C8	0	−0.2 (0.2)	0.5 (0.1)	0	0.0 (0.3)	0.6 (0.2)
C5-N7-C8-N9	0	0.2 (0.3)	0.8 (0.1)	0	0.0 (0.4)	0.9 (0.2)
N7-C8-N9-C4	0	−0.1 (0.4)	1.0 (0.2)	0	0.0 (0.3)	0.8 (0.2)
C8-N9-C4-C5	0	−0.1 (0.4)	0.9 (0.2)	0	0.0 (0.3)	0.6 (0.2)
C2-N1-C6-N6	180	180.0 (0.5)	178.5 (0.2)	180	−179.2 (0.6)	178.2 (0.3)
N7-C5-C6-N6	0	−0.5 (0.5)	1.6 (0.2)	0	−0.2 (0.5)	1.1 (0.3)
Guanine						
N1-C2-N3-C4	0	−0.2 (0.8)	1.7 (0.4)	0	−0.4 (1.7)	2.0 (1.0)
C2-N3-C4-C5	0	−1.2 (1.0)	1.6 (0.5)	0	0.9 (2.1)	2.6 (1.2)
N3-C4-C5-C6	0	1.8 (1.0)	1.9 (0.6)	0	−0.7 (0.3)	0.7 (0.3)
C4-C5-C6-N1	0	−0.8 (0.5)	1.3 (0.5)	0	0.0 (2.4)	3.1 (1.1)
C5-C6-N1-C2	0	−0.5 (0.7)	1.3 (0.1)	0	0.4 (2.8)	3.3 (1.6)
C6-N1-C2-N3	0	1.1 (1.0)	1.8 (0.3)	0	−0.2 (0.8)	1.1 (0.3)
N9-C4-C5-N7	0	0.1 (0.4)	0.7 (0.1)	0	0.0 (0.9)	1.1 (0.5)
C4-C5-N7-C8	0	0.3 (0.3)	0.6 (0.2)	0	−0.4 (0.9)	1.0 (0.6)
C5-N7-C8-N9	0	−0.6 (0.3)	0.6 (0.2)	0	0.6 (0.6)	0.6 (0.6)
N7-C8-N9-C4	0	0.6 (0.2)	0.6 (0.1)	0	−0.6 (0.3)	0.6 (0.3)
C8-N9-C4-C5	0	−0.4 (0.3)	0.7 (0.1)	0	0.4 (0.6)	0.7 (0.5)
C6-N1-C2-N2	180	−178.9 (1.2)	178.2 (0.3)	180	178.6 (1.0)	178.6 (1.0)
C4-N3-C2-N2	180	179.7 (0.9)	178.3 (0.4)	180	−179.2 (1.5)	178.1 (0.8)
C2-N1-C6-O6	180	180.0 (0.8)	178.8 (0.2)	180	179.9 (2.4)	177.0 (1.0)
N7-C5-C6-O6	0	−0.1 (0.8)	0.7 (0.3)	0	1.0 (0.9)	1.4 (0.5)

[a] $\bar{\tau}$(exp) = expected mean value of torsion angle, assuming average geometry of residue is planar; $\bar{\tau}$(obsd) = observed mean value of torsion angle (number in parentheses is standard error of mean); $\lvert\bar{\tau}\rvert$(obsd) = observed mean of absolute value of torsion angle (number in parentheses is standard error of mean).

τ). These figures are based on all 90 of the crystal structures used in the original survey.[4] The results show that, in any given crystal structure, the torsion angles of a pyrimidine ring are typically within 1–3° of the values expected for a precisely planar residue. The corresponding range for the torsion angles of the imidazole ring in a purine residue is about 0.5–1.0°. These figures, together with those in Table II, indicate that the geometry of any given nucleic acid base residue is likely to be very similar to that of the corresponding standard residue reported in this paper.

Acknowledgment. Financial support was provided by the Medical Research Council. Calculations were performed on the Cambridge University IBM 370/165 computer, with programs written by R.T. and members of the Cambridge Crystallographic Data Centre. We thank one of the referees for constructive comments.

Registry No. Cytosine, 71-30-7; cytosine, protonated, 20791-98-4; adenine, 73-24-5; adenine, protonated, 18444-01-4; guanine, 73-40-5; guanine, protonated, 51460-61-8; uracil, 66-22-8.

Supplementary Material Available: Table IV, listing references for the 67 crystal structures used in the examination of base planarity (5 pages). Ordering information is given on any current masthead page.