Acta Cryst. (1959). **12**, 59

The Stereochemistry of Deoxyribonucleic Acid: I. Covalent Bond Lengths and Angles

By M. Spencer

Medical Research Council Biophysics Research Unit, King's College, London, England

(*Received* 3 *July* 1958)

Reasons are given for requiring accurate prior knowledge of bond lengths and angles in the components of the deoxyribonucleic acid molecule before a satisfactory molecular model can be built. Probable structures for thymine, cytosine, adenine and guanine are arrived at by an extension of a method used by Pauling & Corey. Their postulate that the bond lengths and angles in a pyrimidine ring may be predicted from a knowledge of the bonds formed outside the ring is shown to be confirmed by recent results. It is shown that each atom in such a ring may be thought of as having a 'ring radius', applying to bonds formed in the ring, which depends on the extra-annular bond formed by the atom. The most likely structure for deoxyribose is also considered. Experimental results for furanose rings are reviewed and it is concluded that there is a definite preference for such rings to pucker in a particular way. It is shown that the observed pucker is that expected on theoretical grounds.

Introduction

The structure of deoxyribonucleic acid (DNA) has in the main been made clear by combining chemical results (Chargaff & Davidson, 1955), X-ray diffraction data, which showed its helical configuration (Wilkins, Stokes & Wilson, 1953; Franklin & Gosling, 1953), and a study of the stereochemistry (Watson & Crick, 1953). The molecular model built by Watson & Crick enabled a detailed comparison to be made of observed X-ray diffraction and that calculated from a model. Present work in this laboratory is directed towards obtaining agreement between observed and calculated diffraction.

Three main types of diffraction pattern have so far been obtained with the sodium and lithium salts of DNA by varying the relative humidity (Langridge *et al.*, 1957; Wilkins, 1957; Marvin *et al.*, 1958). It is possible to bring about reversible changes from one form to another by varying only the relative humidity. Since also one form is found in both the salts referred to, it is concluded that the three forms differ only in the relative orientations of the bonds within the molecules.

In deducing the structure of DNA it is not at present possible to use a method in which the observed diffraction is used to refine an initially rough model of the structure. This is because DNA gives only a 'fibre diagram' in which some spots overlap, and in which large-angle diffraction is very weak. It is therefore impossible to obtain directly the coordinates of atoms in the molecule; one must combine X-ray diffraction analysis with a study of the stereochemistry. The method adopted is to build a molecular model in which certain sub-units are assumed to have structures which are fixed within narrow limits, and to vary the way in which the units are oriented relative to each other. A Fourier transform is calculated from the model and compared with the observed diffraction; discrepancies are then progressively reduced by changing the configuration of the model and studying the way in which the Fourier transform changes. It will be seen that if all bond lengths and angles were assumed to be variable the task of refining the structure would be extremely tedious. It is therefore far more important than it is in a normal crystal-structure determination to have accurate prior knowledge of bond lengths and angles in the sub-units.

It is possible to determine unit-cell dimensions to an accuracy of about 0·1 Å (Langridge *et al.*, 1957). The distances between centres of molecules in a crystallite are therefore known to a similar accuracy. One may use this knowledge to test whether a proposed model leads to reasonable distances between the atoms of adjacent molecules. Since the available information is so limited, this test is an important one in deciding whether a model is likely to be correct. Since the distances between centres of molecules are several times the length of any covalent bond, the error in the length of each bond in a model should be considerably less than 0·1 Å. It is, in practice, desirable for bond lengths to be known to within about 0·02 Å. It is also desirable for bond angles to be known to within about 2°, because a variation in a bond angle at the centre of a model has a large effect on the positions of the outer atoms. It is, however, impossible to predict exact values because some angles will almost certainly be distorted by strains inherent in the structure. It is nevertheless important to know the most likely values so that the energy involved in the distortions may be kept to a minimum. Having built a model with bond lengths and angles at their most likely values, one may be confident that unacceptably short distances between atoms are not due to errors in the assumed structure of the sub-units.

It is unfortunate that the structures of most of the components of DNA are not known as accurately as desired. One must therefore deduce the most probable structures from data on related substances. It is the purpose of this paper to arrive at likely values for covalent bond lengths and angles in all the sub-units of the DNA molecule. The lengths of the hydrogen bonds which are believed to be an important feature of the structure of DNA cannot be accurately predicted, and it is likely that they may be anywhere within certain limits. The effect of this uncertainty on the range of molecular models that can be built will be considered in a later paper. The components to be considered here are the pyrimidines thymine and cytosine, the purines adenine and guanine, the phosphate group and the deoxyribose ring.

Pyrimidines

Available data

Structure determinations for cytidine (Furberg, 1950) and for deoxythymidine (Huber, 1957) have been made, but in neither case is the maximum error in bond length less than 0·1 Å. It seems best to rely on more accurate data for related compounds. The method of deducing probable structures will be an extension of that used by Pauling & Corey (1956). From a study of certain pyrimidine structures they concluded that one could predict the bond lengths and angles in a pyrimidine ring from a knowledge of the attachments to the ring. In view of the fact that more structure determinations for heterocyclic compounds have been made since the publication of their paper, it has been felt worth while to review again the available data with a view to drawing more detailed conclusions than was possible at that time. The structure determinations to be referred to are listed below. The standard deviation in bond length is given after each reference. (ii), (iv), (v) and (vii) were the results of three-dimensional refinements.

(i) 2-amino-4, 6-dichloropyrimidine (Clews & Cochran, 1948) (0·04 Å max.).
(ii) 4-amino-2, 6-dichloropyrimidine (Clews & Cochran, 1949) (0·02 Å).
(iii) 5-bromo-4, 6-diaminopyrimidine (Clews & Cochran, 1949) (0·04 Å).
(iv) Uracil (Parry, 1954) (0·014 Å).
(v) 6-amido-3-pyridazone (Cucka & Small, 1954) (0·014 Å).
(vi) 4,5-diamino-2-chloropyrimidine (White & Clews, 1956) (0·03–0·04 Å).
(vii) Pyrazine (Wheatley, 1957) (0·003 Å).

Not all these compounds are pyrimidines, but they all contain a single ring in which there are four carbon and two nitrogen atoms. The justification for this grouping will be discussed later. Bond lengths and angles in the rings of all the compounds listed are classified in Table 1 according to the extra-annular attachments of the ring atoms. The following notation has been used: C(*D*) = carbon atom forming a bond outside the ring which has a large amount of double-bond character, C(*S*) = carbon atom forming a mainly single bond outside the ring, N(*S*) = nitrogen atom forming a single bond outside the ring, N(*Z*) = nitrogen atom forming no bond outside the ring. All values have been checked from atomic coordinates, and the re-calculated values given where they differ appreciably from published ones. Averages have been calculated without weighting in favour of the more accurate determinations, because this would bias the

Table 1. *Ring bond lengths and angles in pyrimidines and related compounds, checked from atomic coordinates*

For notation see text

Bond type	Experiment	Bond lengths (Å)	Average (Å)
C(*S*)–N(*Z*)	(i)	1·32*, 1·34*, 1·28*, 1·30	$1·32_5$
	(ii)†	1·314, 1·304, 1·331, 1·324*	
	(iii)	1·34*, 1·33, 1·36, 1·36	
	(v)†	1·32	
	(vi)	1·30, 1·32, 1·36, 1·31	
	(vii)†	1·334 (average of 4)	
C(*S*)–N(*S*)	(iv)	1·341	
C(*D*)–N(*S*)	(iv)	1·374, 1·384, 1·344	$1·37_1$
	(v)	1·38	
C(*S*)–C(*S*)	(i)	1·40*, 1·40*	$1·38_4$
	(ii)†	1·411*, 1·347	
	(iii)	1·37, 1·36	
	(iv)†	1·408	
	(v)†	1·40, 1·34	
	(vi)	1·36, 1·44	
	(vii)†	1·378 (average of 2)	
C(*D*)–C(*S*)	(iv)†	1·411	$1·42_6$
	(v)†	1·44	
N(*S*)–N(*Z*)	(v)†	1·35*	

Ring atom	Experiment	Angles in ring (°)	Average (°)
C(*S*)	(i)	105*, 129*, 127*, 132*	122
	(ii)†	132·3, 120·0*, 126·2*, 116·0*	
	(iii)	122·5, 129·5, 122, 119·5	
	(iv)†	116·4, 121·5	
	(v)†	122, 119, 120	
	(vi)	130, 119·5, 124, 116	
	(vii)†	122·4 (average of 4)	
C(*D*)	(iv)†	118·1, 115·6	116
	(v)†	114	
N(*Z*)	(i)	113*, 114*	114
	(ii)†	115·0, 110·2	
	(iii)	114, 113*	
	(v)†	118	
	(vi)	112·5, 118	
	(vii)†	115·1 (average of 2)	
N(*S*)	(iv)†	124·7, 123·6	125
	(v)†	126	

* Differs from published value.
† Three-dimensional refinement.

results in favour of particular compounds. It cannot be anticipated that bonds of a given type will be identical in all compounds, because of the effects of strains in the structures; we wish to know whether the averages for different bond types involving the same ring atoms differ significantly from each other.

The most striking feature of the results is the dependence of ring angle on extra-annular attachment. Pauling & Corey (1956) showed that the differences between average values could be qualitatively explained in terms of bond orbitals, and the arguments will not be repeated here. The additional results quoted add further support to their arguments. From the results for bond lengths it will be seen that, as Pauling & Corey (1956) observed, there is a difference between the average lengths of C(*S*)–N(*Z*) and C(*D*)–N(*S*) which is probably significant. This difference can also be explained in terms of bond orbitals; the ring bonds formed by both atoms in the former case have, on average, more double-bond character than in the latter case, and one would therefore expect C(*S*)–N(*Z*) to be the shorter bond. Pauling & Corey (1956) did not distinguish between C(*D*)–C(*S*) and C(*S*)–C(*S*), though by the same arguments one would expect the latter bond to be the shorter. The results in Table 1 show that, though there are only two values for C(*D*)–C(*S*), they are both significantly larger than the average for C(*S*)–C(*S*). The significance of the departures of individual values from the averages cannot be assessed until more accurate results are available. It is, however, interesting to note that all bond lengths and angles from experiment (vii), which is the most accurate of all, agree closely with the average values from all experiments.

One may explain all the average bond lengths in Table 1 by postulating that each atom has a 'ring radius', applying only to ring bond lengths, which depends on the type of bond formed by the atom outside the ring. The length of a ring bond may then be predicted by adding the radii of the two atoms concerned in the same way as is done for single and double bonds. The idea of a ring radius in a resonating system is not strictly justified on theoretical grounds, but for rings of a given composition it is reasonable as a first approximation (Coulson (1958), private communication). Although the bond formed by a ring atom outside the ring will have some effect on all ring bonds it will mainly affect those adjacent to the atom. If resonance is present it will tend to affect these two bonds equally. One would not expect the same radii to apply exactly in rings of different compositions.

From the average value of C(*S*)–C(*S*) one obtains a ring radius of $0{\cdot}69_2$ Å for C(*S*). From the average for C(*S*)–N(*Z*) one then obtains a ring radius of $0{\cdot}63_3$ for N(*Z*). There are too few values for other bond types to deduce from them reliable radii for C(*D*) and N(*S*), but one would expect these to be greater than for C(*S*) and N(*Z*) respectively by approximately equal amounts, because of the increased bond formation outside the ring. If the ring radii for C(*D*) and N(*S*) are taken as 0·72 and 0·66 Å respectively, the expected lengths for all the bonds considered are as in Table 2.

Table 2. *Bond lengths in pyrimidine rings*

Bond type	Predicted length (Å)	Observed length (Å)
C(*S*)–N(*Z*)	1·33	1·33 (average of 27)
C(*D*)–N(*Z*)	1·35	No data
C(*S*)–N(*S*)	1·35	1·34
C(*D*)–N(*S*)	1·38	1·37 (average of 4)
C(*S*)–C(*S*)	1·38	1·38 (average of 13)
C(*D*)–C(*S*)	1·41	1·41, 1·44
N(*S*)–N(*Z*)	1·29	1·35

It will be seen that the predicted values agree quite well with the observed values, with the exception of the single value for N(*S*)–N(*Z*). It may be noted here that, in constructing probable structures for thymine and cytosine, Pauling & Corey (1956) took C(*D*)–N(*Z*) and C(*S*)–N(*S*) bonds to be of length 1·34–1·36 Å. They gave no details of how these values were arrived at.

Probable structures for thymine and cytosine

Using the average ring angles and the ring radii deduced above, the form of the rings of thymine and cytosine may be predicted. The predicted structures

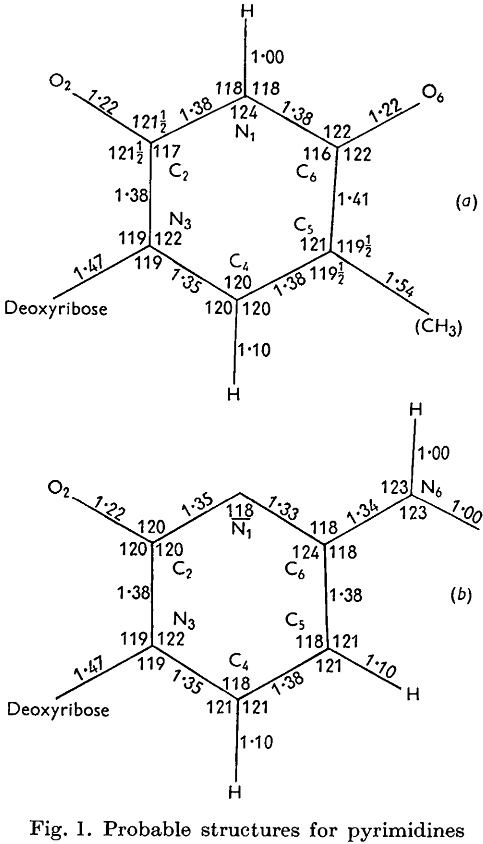

Fig. 1. Probable structures for pyrimidines
(*a*) thymine; (*b*) cytosine.

are shown in Fig. 1. The rings have been assumed to be planar, since there is general agreement that this is so in related compounds. It has been necessary to distort some ring angles by up to 4° in order to make the rings join up, but bond lengths have been assumed fixed. The lengths of $C=O$ and $C{-}NH_2$ bonds formed outside the rings have been put equal to the averages of values found in both purines and pyrimidines (see next section). Extra-annular C–C, C–H and N–H bonds have been given normally accepted lengths. All extra-annular bonds have been assumed to make equal angles with their adjacent ring bonds. The deviations from symmetry observed in crystal structures might be due to the interactions of molecules with each other, and it would be unsafe to draw conclusions from the data on this point. The glycosidic link to N_3 has in both cases been given the normally accepted single-bond length of 1·47 Å. In the structures given by Pauling & Corey (1956) these bonds were of length 1·53 Å, but they gave no reasons for choosing this value.

Purines

Available data

No structure determinations of the required accuracy have been made in the case of adenine or of guanine. An accurate structure is available for a derivative of adenine (see below), but there is deduced to be a hydrogen atom attached to one ring which is absent in the free purine. It is therefore of interest to determine whether the structure of a purine may be predicted in the same way as that of a pyrimidine. Results are available for five compounds which have a pyrimidine ring sharing one ring bond with a five-membered ring; the experiments are listed below with the standard deviation in bond length after each reference.

(viii) Adenine hydrochloride (Cochran, 1951) (0·01 Å).
(ix) Guanine hydrochloride (Broomhead, 1951) (0·04 Å).
(x) Xanthazol (Nowacki & Bürki, 1955) (0·01 Å).
(xi) Theophylline (Sutor, 1958*a*) (0·01 Å).
(xii) Caffeine (Sutor, 1958*b*) (0·01–0·02 Å).

(x) was the result of three-dimensional refinement. All the compounds are purines except xanthazol, which has three nitrogen atoms in its five-membered ring.

Table 3. *Bond lengths and angles in six-membered rings of purines and related compounds, checked from atomic coordinates*

For notation see,text

Bond type	Experiment	Bond lengths (Å)	Average (Å)	Value used to predict pyrimidine rings (Å)
C(*S*)–N(*Z*)	(viii)	1·30, 1·36	1·34	1·33
	(ix)	1·33, 1·35		
C(*S*)–N(*S*)	(viii)	1·38, 1·37		
	(ix)	1·32		
	(x)†	1·34	1·37	1·35
	(xi)	1·37		
	(xii)	1·42		
C(*D*)–N(*S*)	(ix)	1·41		
	(x)†	1·39, 1·36, 1·35		
	(xi)	1·38, 1·40, 1·35	1·38	1·38
	(xii)	1·36, 1·42, 1·35		
C(*S*)–C(*S*)	(viii)	1·40, 1·37		
	(ix)	1·34		
	(x)†	1·39	1·37	1·38
	(xi)	1·37		
	(xii)	1·32		
C(*D*)–C(*S*)	(ix)	1·40		
	(x)†	1·44		
	(xi)	1·41	1·42	1·41
	(xii)	1·44		

Ring atom	Experiment	Angles in ring (°)	Average (°)	Value used to predict pyrimidine rings (°)
C(*S*)	(viii)	118, 114, 125, 128		
	(ix)	124, 124, 124		
	(x)†	121, 123	122	122
	(xi)	122·6, 121·8		
	(xii)	119·9, 121·4		
C(*D*)	(ix)	108		
	(x)†	112, 119		
	(xi)	112·5, 117·8	114	116
	(xii)	115·8, 112·9		
N(*Z*)	(viii)	112		
	(ix)	113	113	114
N(*S*)	(viii)	123		
	(ix)	126		
	(x)†	127, 119	124	125
	(xi)	126·0, 119·4		
	(xii)	127·6, 122·8		

† Three-dimensional refinement.

Although the results are less numerous than for pyrimidines and related compounds, one may use them to test whether the 'ring radii' and ring bond angles used in predicting pyrimidine structures are applicable to the six-membered rings of purines. One might expect the ring radii for a pyrimidine ring to apply only approximately when it shares a bond with a second ring. Bond lengths and angles in the six-membered rings of the compounds listed above are collected in Table 3. It will be seen that the average values agree to 0·02 Å and 2° with those used in predicting pyrimidine structures. It therefore seems that, until more information on purines is available, it is reasonable to predict the form of the six-membered ring of a purine from the results applicable to pyrimidines. In view of this fact it also seems reasonable to assume that extra-annular bonds of a given type formed by both purines and pyrimidines will have the same length. Lengths of extra-annular $C=O$ and

Table 4. *Lengths of extra-annular bonds in pyrimidines, purines and related compounds, checked from atomic coordinates*

For notation see text

Bond type	Experiment	Bond lengths (Å)	Average (Å)
C=O	(iv)	1·230, 1·241	
	(v)	1·24	
	(ix)	1·20	1·22
	(x)	1·21, 1·24	
	(xi)	1·22, 1·19	
	(xii)	1·26, 1·19	
C–NH_2	(i)	1·27	
	(ii)	1·339	
	(iii)	1·32, 1·39*	
	(vi)	1·34, 1·42	1·34
	(viii)	1·30	
	(ix)	1·32	

* Differs from published value.

C–NH_2 bonds from all the experiments quoted so far are collected in Table 4. It will be seen that there is no obvious difference between values for pyrimidines and those for purines. One may therefore use the average values in predicting structures for both.

Probable structures for adenine and guanine

Probable structures are shown in Fig. 2. Ring radii and ring angles used for pyrimidines have been used to build up the six-membered rings. The form of the five-membered ring has in both cases been taken from the results for adenine hydrochloride obtained by Cochran (1951), as there is not enough information available to draw general conclusions about such rings. Extra-annular C=O and C–NH_2 bonds have been given the average values from Table 4. Other bonds have been given normally accepted lengths.

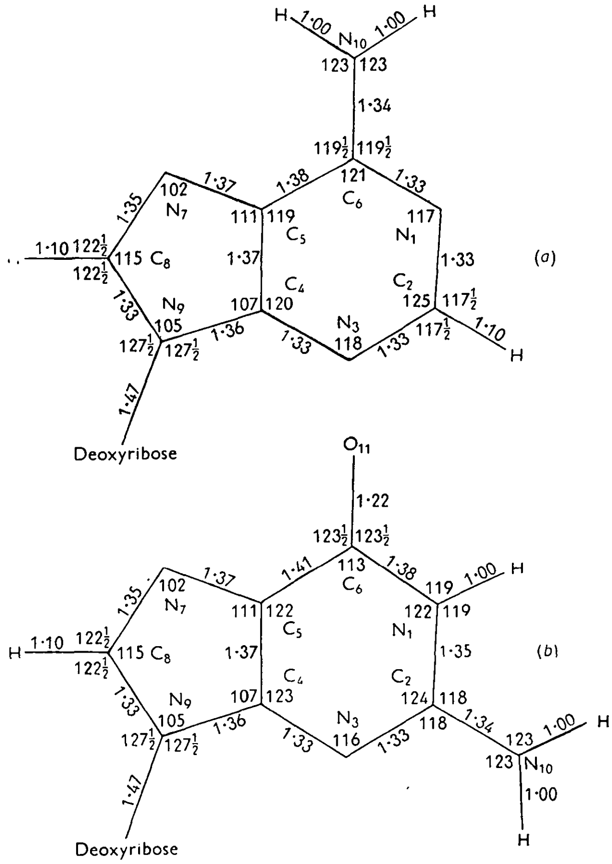

Fig. 2. Probable structures for purines (*a*) adenine; (*b*) guanine.

The phosphate group

The structure of dibenzyl phosphoric acid has been determined with a standard deviation in bond length of less than 0·01 Å (Dunitz & Rollett, 1956). The phosphate group in DNA probably differs from the one in this substance only in that the P–O bonds formed by the non-esterified oxygen atoms are of equal length, due to a sharing of the charge carried by the group.

The deoxyribose ring

Available data

The structure of a compound containing 2-deoxyribose has been determined (iii, below) but the maximum error in bond length was 0·2 Å. No other results are yet available for deoxyribose, but the structures of a few compounds containing other furanose rings have been determined. Substances for which results are available are listed below. The standard deviations in bond length were in all cases 0·04 Å or greater.

(i) Sucrose sodium bromide dihydrate (Beevers & Cochran, 1947).
(ii) Cytidine (Furberg, 1950).
(iii) 5′-bromo-5′-deoxythymidine (Huber, 1957).
(iv) Muscarine iodide (Jellinek, 1957).

A study of the results shows that, in all cases except (i), the bond lengths in the ring were not found to be significantly different from normal single-bond values. All the results indicate that furanose rings are not planar. The reasons for this will be discussed later. The consequences are that the average ring angle is less than 108°, and the angles between extra-annular and ring bonds are greater than the expected tetrahedral value. Bond angles observed in the compounds listed above are collected in Table 5.

Ring pucker

The structures referred to above all indicate that, in a furanose ring, there is a tendency for one ring atom to be displaced from a plane containing the other four. It is of interest to investigate whether there is a preference for the displacement of particular atoms, as the pucker of the ring in DNA is found to have a profound effect on the range of models that can be built. It is first worth discussing the probable reason for the pucker. A pucker is observed in the five-

Table 5. *Bond angles in furanose rings, checked from atomic coordinates*

Angle	Experiment	Values (°)	Average (°)
Ring C	(i)	104, 100, 102, 107	105
	(ii)	112*, 100*, 104*, 102*	
	(iii)	113*, 100*, 102*, 105	
	(iv)	106, 104, 106, 107*	
Ring O	(i)	113	108
	(ii)	106	
	(iii)	103	
	(iv)	109	
Between extra-annular and ring bonds	(i)	115, 110, 112, 117, 114, 122, 109, 118, 114, 104	112
	(ii)	110*, 115, 112*, 110*, 116*, 109*, 120*, 107*	
	(iii)	108, 108*, 102, 109*, 110, 105	
	(iv)	110, 113*, 109, 110, 114, 116	

* Differs from published value.

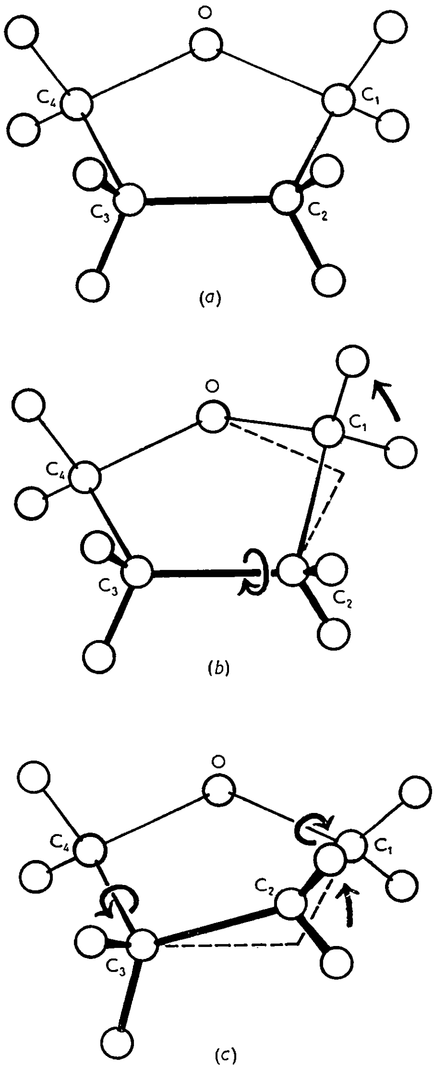

Fig. 3. Configurations of a furanose ring (*a*) unpuckered; (*b*) C_1 displaced from plane; (*c*) C_2 displaced from plane.

membered ring compound cyclopentane (see, for example, Dauben & Pitzer, 1956) and it is thought to be due to unacceptably short distances between the hydrogen atoms attached to adjacent ring atoms. Puckering the ring relieves these 'short contacts', though it distorts the ring angles from their expected tetrahedral values. Similar short contacts will occur in a planar furanose ring (Fig. 3(*a*)). If the atom C_1 is displaced from the plane (Fig. 3(*b*)) C_2 also rotates about the bond C_2C_3, thus relieving short contacts between hydrogen atoms attached to C_1, C_2 and C_3. Atoms attached to C_3 and C_4 do not, however, change their relative orientations and short contacts between them are not relieved. They could be relieved by sideways displacement of the atoms attached to C_4, but this would involve energy additional to that required to distort the ring bond angles. Displacement of atoms C_4 or O also leaves two ring atoms unaffected. Displacement of C_2, however, relieves all short contacts (Fig. 3(*c*)), and displacement of C_3 has a similar effect. One would therefore expect to observe a preference for displacement of one of these two atoms.

A study of published data shows that in experiments (i), (ii) and (iv) above the out-of-plane atom is C_2 or C_3. Published coordinates for air-dried vitamin B_{12} (Hodgkin *et al.*, 1957) indicate clearly that in the ribose ring of this substance the out-of-plane atom is C_2. In (iii) it is stated by Hubert to be C_3, but from his coordinates it appears to be C_4; however, the plane containing the other atoms is not very clearly defined. In no case is it found to be C_1 or O. There therefore seems firm ground for preferring displacement of C_2 or C_3 in building a model of DNA. The amount of displacement observed is generally about 0·5 Å.

Probable structure of deoxyribose

A fixed structure cannot be predicted as in the case of pyrimidines and purines, because of the possibility of rotation about single bonds, but certain likely features of the structure may be noted. It seems best to assume normal single-bond lengths for all bonds, and to assume that bond angles do not depart greatly from the average values given in Table 5. It also seems preferable that there should be a pucker in that C_2 or C_3 lies out of a plane containing the other ring atoms by about 0·5 Å. The direction of the displacement probably depends only on the requirements of the whole structure which contains the ring. It may be noted that displacement of one carbon atom introduces an asymmetry into the ring, so that it is impossible for all carbon ring angles to have the same value. The departures from the average are, however, no more than a few degrees.

Conclusions

Evidence has been collected which supports the assumption of Pauling & Corey (1956) that the structure of a pyrimidine ring, and that of the six-membered ring of a purine, may be fairly well predicted from a knowledge of the extra-annular bonds formed by ring atoms. The values of bond lengths and angles arrived at have been similar to, but not identical with, those used by Pauling & Corey (1956) in predicting likely structures. It is believed that they are accurate to 0·02 Å in bond length and about 4° in bond angle. The exact accuracy cannot be estimated until more accurate structure determinations have been made. It has been noted, however, that the bond lengths and angles found in the most accurate of the experiments quoted agree very closely with the average values from all results. It is thus possible that, in the case of pyrimidines, all the observed deviations from average values are due mainly to experimental errors.

Probable structures for the purines and pyrimidines found in DNA have been described. The phosphate group has not been considered at length as only one accurate structure determination has been reported. The structure of deoxyribose is less certain. Its bonds are probably all of normal single-bond length; it has been shown that the ring is very likely to be puckered, one carbon atom lying out of a plane containing the other ring atoms. The out-of-plane atom is likely to be C_2 or C_3; this is expected because more short contacts are relieved by displacement of one of these atoms than in the case of any other.

A final conclusion may be drawn that it is possible to construct a model of DNA in which errors in the positions of its outer atoms, due to inaccuracy in assumed covalent bond lengths and angles, are no greater than the probable errors in the observed distances between molecules.

I am indebted to Dr D. June Sutor for access to results prior to publication; to Prof. C. A. Coulson, F. R. S., Mrs D. C. Hodgkin, F. R. S. and Mr W. Cochran for helpful discussions, and to Dr M. H. F. Wilkins for constant advice and encouragement.

References

Beevers, C. A. & Cochran, W. (1947). *Proc. Roy. Soc.* A, **190**, 257.

Broomhead, J. M. (1951). *Acta Cryst.* **4**, 92.

Chargaff, E. & Davidson, J. N. (1955). *The Nucleic Acids*. New York: Academic Press.

Clews, C. J. B. & Cochran, W. (1948). *Acta Cryst.* **1**, 4.

Clews, C. J. B. & Cochran, W. (1949). *Acta Cryst.* **2**, 46.

Cochran, W. (1951). *Acta Cryst.* **4**, 81.

Cucka, P. & Small, R. W. H. (1954). *Acta Cryst.* **7**, 199.

Dauben, W. G. & Pitzer, K. S. (1956). *Steric Effects in Organic Chemistry*, p. 35 (ed. Newman). New York: Wiley.

Dunitz, J. D. & Rollett, J. S. (1956). *Acta Cryst.* **9**, 327.

Franklin, R. E. & Gosling, R. G. (1953). *Nature, Lond.* **171**, 740.

Furberg, S. (1950). *Acta Cryst.* **3**, 325.

Hodgkin, D. C., Kamper, J., Lindsey, J., Mackay, M., Pickworth, J., Robertson, J. H., Shoemaker, C. B., White, J. G., Prosen, R. J. & Trueblood, K. N. (1957). *Proc. Roy. Soc.* A, **242**, 228.

Huber, M. (1957). *Acta Cryst.* **10**, 129.

Jellinek, F. (1957). *Acta Cryst.* **10**, 277.

Langridge, R., Seeds, W. E., Wilson, H. R., Hooper, C. W., Wilkins, M. H. F. & Hamilton, L. D. (1957). *J. Biophys. Biochem. Cytol.* **3**, 767.

Marvin, D. A., Spencer, M., Wilkins, M. H. F. & Hamilton, L. D. (1958). *Nature, Lond.* **182**, 387.

Nowacki, W. & Burki, H. (1955). *Z. Kristallogr.* **106**, 339.

Parry, G. S. (1954). *Acta Cryst.* **7**, 313.

Pauling, L. & Corey, R. B. (1956). *Arch. Biochem. Biophys.* **65**, 164.

Sutor, D. J. (1958*a*). *Acta Cryst.* **11**, 83.

Sutor, D. J. (1958*b*). *Acta Cryst.* **11**, 453.

Watson, J. D. & Crick, F. H. C. (1953). *Nature, Lond.* **171**, 737.

Wheatley, P. J. (1957). *Acta Cryst.* **10**, 182.

White, N. E. & Clews, C. J. B. (1956). *Acta Cryst.* **9**, 586.

Wilkins, M. H. F. (1957). (Special publications.) *N.Y. Acad. Sci.* **5**, 180.

Wilkins, M. H. F., Stokes, A. R. & Wilson, H. R. (1953). *Nature, Lond.* **171**, 737.