Note added in proof: The Technical Editor revealed during a routine check for structure duplication that the crystal structure of TETRA had already been published (Spek, 1972). Our e.s.d.'s for the TETRA structure are, however, about three times smaller than those in the above publication.

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1-(2,3-Dideoxy-erythro- β -D-hexopyranosyl)cytosine: an Example of the Conformational and Stacking Properties of Pyranosyl Pyrimidine Nucleosides. A Crystallographic and Computational Approach*

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Abstract

$C_{10}H_{15}N_3O_4$, $M_r = 241.25$, orthorhombic, $P2_12_12_1$, $a = 7.4013$ (4), $b = 8.7563$ (5), $c = 17.392$ (1) Å, $V = 1127.1$ (1) Å³, $Z = 4$, $D_m = 1.42$, $D_x = 1.422$ Mg m⁻³, Ni-filtered Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å, $\mu =$

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0.895 mm⁻¹, $F(000) = 512$, $T = 293$ K, final $R = 0.044$ for 1024 unique observed [$F \geq 6\sigma(F)$] reflections. The conformational parameters are in accordance with the IUPAC-IUB Joint Commission on Biochemical Nomenclature [Pure Appl. Chem. (1983), **55**, 1273–1280] guidelines. In order to assess the possible use of pyranosyl-modified pyrimidine nucleosides in the design of new synthetic oligonucleotides, the conformational and packing proper-

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heptane/ CCl_4 . Weissenberg photographs showed systematically absent reflections $h00$ with h odd, $0k0$ with k odd and $00l$ with l odd. Hilger & Watts computer-controlled diffractometer, cell constants by least-squares refinement of the θ angles of 30 reflections with $30 \leq 2\theta \leq 50^\circ$, ω scan, $[(\sin\theta)/\lambda]_{\max} = 0.5878 \text{ \AA}^{-1}$, $-8 \leq h \leq 0$, $-10 \leq k \leq 10$, $-20 \leq l \leq 20$. Intensities of four standard reflections (008, 041, 124, 231) monitored every 50 reflections showed no significant decrease in intensity, 4018 reflections measured, 1102 unique reflections of which 1024 were considered observed with $F \geq 6\sigma(F)$. Data reduction with a locally modified version of the REDU4 (Stoe & Co., 1985) program, Lorentz and polarization corrections. No absorption corrections. Scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B) and for H from Stewart, Davidson & Simpson (1965). Anomalous-dispersion corrections were included for all non-H atoms (Ibers & Hamilton, 1964). The structure was solved by MULTAN11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982). Refined on F by full-matrix least squares, first with isotropic temperature factors and finally anisotropically. All H atoms were found in a difference synthesis and they were included in the refinement with a fixed temperature factor B 1.3 times the B_{eq} value of their parent atoms. Final $R = 0.044$, $wR = 0.060$, with $w = 1/[\sigma^2(F_o) + 0.0004F_o^2]$, $S = 0.83$. Largest parameter shift/e.s.d. = 0.05. Minimum and maximum residual electron density -0.24 and $0.15 \text{ e \AA}^{-3}$. The number of reflections per refined parameter $1024/199 = 5.1$. All calculations were performed on a Digital PDP-11/73 microcomputer using SDP (B. A. Frenz & Associates, Inc., 1985) and PARST (Nardelli, 1983).

Discussion

A PLUTO view (Motherwell & Clegg, 1978) of the title compound with the atomic numbering scheme is shown in Fig. 1. The final atomic coordinates and equivalent isotropic thermal parameters are given in

Table 1. Atomic coordinates and equivalent isotropic temperature factors ($\text{\AA}^2 \times 10^4$) for the title compound, with e.s.d.'s in parentheses

$$U_{\text{eq}} = \frac{1}{3} \sum_i U_{ii} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
N1	0.5129 (3)	0.9855 (3)	-0.0399 (1)	393 (4)
C2	0.4900 (4)	0.9302 (3)	0.0346 (1)	392 (7)
O2	0.3340 (3)	0.9197 (3)	0.0617 (1)	527 (5)
N3	0.6362 (3)	0.8908 (3)	0.0762 (1)	432 (5)
C4	0.8003 (4)	0.9097 (3)	0.0473 (2)	412 (7)
N4	0.9411 (3)	0.8744 (3)	0.0926 (1)	515 (7)
C5	0.8282 (4)	0.9646 (4)	-0.0283 (2)	485 (7)
C6	0.6837 (4)	1.0013 (4)	-0.0700 (1)	467 (7)
C1'	0.3574 (4)	1.0220 (3)	-0.0876 (1)	405 (7)
C2'	0.3352 (5)	1.1928 (3)	-0.0987 (2)	511 (8)
C3'	0.1894 (5)	1.2273 (4)	-0.1580 (2)	524 (8)
C4'	0.2191 (4)	1.1364 (3)	-0.2313 (2)	457 (7)
C5'	0.2406 (4)	0.9667 (3)	-0.2109 (1)	396 (7)
O5'	0.3886 (3)	0.9487 (2)	-0.15883 (9)	416 (5)
O44'	0.0676 (3)	1.1606 (3)	-0.2787 (1)	676 (7)
C55'	0.2848 (4)	0.8667 (3)	-0.2796 (2)	471 (8)
O55'	0.2932 (3)	0.7090 (2)	-0.2593 (1)	540 (5)

Table 1.* Bond lengths, bond angles and selected torsion angles are given in Table 2. Table 3 summarizes all the intermolecular hydrogen bonds. All bond lengths and bond angles are within the normal range (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987). The orientation of the χ torsion angle ($\text{O5}'\text{—C1}'\text{—N1—C2}$) along the *N*-glycosidic bond is in the *anti* range [$229.4 (2)^\circ$]. The chair puckering for the sequence $\text{C1}'\text{—C2}'\text{—C3}'\text{—C4}'\text{—C5}'\text{—O5}'$ can be described using the method of Cremer & Pople (1975) with phase angles $\varphi_2 = 84 (2)$ and $\theta_2 = 174.3 (2)^\circ$ and a total puckering amplitude $Q = 0.569 (2) \text{ \AA}$.

The crystal packing is determined partly by hydrogen bonds (Table 3) and partly by base-stacking forces between bases related to each other by the 2_1 axis along b [d_{mean} between the planes = $3.1 (1) \text{ \AA}$, dihedral angle = $4.6 (1)^\circ$]. A PLUTO plot (Motherwell & Clegg, 1978) of the crystal packing is shown in Fig. 2.

Conformational analysis

Experimental

The compound names and the abbreviations used throughout this paper are listed in Table 4. Although they are not pyranosyl nucleosides in the chemical sense, the crystal structures of 1-[(2*R*,6*R*)-6-hydroxy-methyl-1,4-dioxan-2-yl]uracil and its 5-bromouracil analog were also subjected to investigation since the overall conformations of the molecules strongly

* Lists of structure factors, anisotropic thermal parameters, bond lengths and angles involving H atoms, least-squares planes and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54567 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: GE0271]

Fig. 1. A PLUTO plot (Motherwell & Clegg, 1978) of the title compound with atomic numbering scheme.

Table 4. List of the compounds in this study, with average bond-length e.s.d.'s, base types and abbreviations used

Code	Chemical name	Mean σ (Å)	Base*
α-Enantiomers			
GSII118	1-(2,3-Dideoxy-erythro- α -D-hexopyranosyl)-thymine ^b	0.003	T
NORDA	1-(2-Deoxy- α -D-ribo-hexopyranosyl)uracil ^c	0.005	U
LKI59A	1-(2-Deoxy-2-fluoro- α -D-arabinopyranosyl)-5-iodouracil ^f	0.006	U
β-Enantiomers			
LKI60	1-(2-Deoxy-erythro- β -D-pentopyranosyl)-5-iodouracil ^a	0.005	U
GSII115	1-(2,3-Dideoxy-erythro- β -D-hexopyranosyl)-thymine ^b	0.004	T
NORDB	1-(2-Deoxy- β -D-ribo-hexopyranosyl)uracil ^c	0.005	U
LKII5	1-(2-Deoxy-2-fluoro- β -D-arabinopyranosyl)-thymine ^d	0.002	T
LKI70	1-(2-Deoxy-2-fluoro- β -D-arabinopyranosyl)-5-ethyluracil ^f	0.005	U
AVII52	1-[(2R,6R)-Hydroxymethyl-1,4-dioxan-2-yl]uracil ^g	0.003	U
AVII56	5-Bromo-1-[(2R,6R)-6-Hydroxymethyl-1,4-dioxan-2-yl]uracil ^g	0.01	U
GS121	1-(2,3-Dideoxy-erythro- β -D-hexopyranosyl)-cytosine ^e	0.003	C
C-SUBST†	4-Amino-1-[4-amino-2-oxo-1(2H)-pyrimidinyl]-1,4-dideoxy- β -D-glucopyranuronic acid ^h	0.006	C

References: (a) De Winter *et al.* (1991a). (b) De Winter *et al.* (1991b). (c) Nord *et al.* (1987). (d) De Winter *et al.* (1991c). (e) De Winter *et al.* (1991d). (f) De Winter *et al.* (1991e). (g) This paper. (h) Swaminathan *et al.* (1980).

* U for uracil, T for thymine and C for cytosine.

† With two molecules in the asymmetric unit, C-SUBST1 and C-SUBST2.

ring fragment from the pyranosyl nucleoside structures. Following this procedure each pyranose ring was initially fitted with *BMFIT* (Nyburg, 1974; the fitting involved all six ring atoms) to a reference ring (*in casu* the LKII5 fragment) and subsequently to the weighted average of these fitted rings. This second fitting was then iterated until no change in the geometry of the averaged fragment was observed; the average r.m.s. deviation converged to less than 0.03 (2) Å.

Theoretical calculations were performed with the molecular-mechanics programs *ALCHEMYII* (Tripos Associates, 1989) and *CHEMMOD* (U-Microcomputers Ltd., 1989) and with the semi-empirical quantum-chemical program *AM1* (Dewar, Zoebisch, Healy & Stewart, 1985), which is part of the *MOPAC* package (Stewart, 1989). *ALCHEMYII* was run on an IBM AT compatible, *CHEMMOD* on its dedicated U-MAN 1000 system and *MOPAC* was implemented on the IBM 3090 of the Leuven Universitair Rekencentrum. The energy of each conformation was fully optimized until (1) the energy difference between successive iterations dropped below 0.01 kcal mol⁻¹ (1 kcal mol⁻¹ = 4.184 kJ mol⁻¹) (*ALCHEMY*), (2) the r.m.s. value of the function gradient was <0.01 kcal mol⁻¹ Å⁻¹ (*CHEMMOD*) or (3) the difference in heat of formation between consecutive iterations was <0.3 kcal mol⁻¹ (*AM1*).

Discussion

The pyrimidine base. For a description of the pyrimidine-base geometry, the reader is referred to the paper of Taylor & Kennard (1982), where an accurate depiction of the base geometry of furanosyl nucleosides is given. Since for the pyranosyl bases under study the weighted means of the bond lengths and angles do not differ by more than 2 σ from their comparable furanosyl-base values, it is obvious that the bases are conformationally identical and that the sugar ring type (furanosyl- or pyranosyl-like) has little or no influence on the base geometry. Only for the cytosine pyranosyls (GS121 and C-SUBST), some mean values such as the N1—C2 bond length and the C1'—N1—C2 and C1'—N1—C6 bond angles deviate by more than 5 σ from their reference furanosyl values. This, however, has little physical significance since these parameters have been calculated from only three observations, two of which (C-SUBST1 and 2) have e.s.d.'s twice as large as the third (GS121). Consequently, the contribution of the former observations to the weighted mean is relatively small and the mean is biased in favor of only one observation, GS121.

The pyranosyl sugar ring. The conformation of the six-membered pyranosyl ring is different for α - and β -nucleosides. In the former a 4C_1 conformation is adopted while for the latter the conformation is 4C_1 so that the base moiety is always oriented equatorially. In a study of the pyranosyl-ring geometry, it is important that both anomers are distinguished and treated separately or converted to the correct anomeric form. In order to increase the data set the latter solution was chosen and three additional β -anomers were generated by simple inversion of the α -anomers; in total 11 β -nucleosides were investigated [obviously, 1-[(2R,6R)-6-hydroxymethyl-1,4-dioxan-2-yl]uracil and its 5-bromo analog were excluded from the calculations]. In order to reveal some common properties or to identify outliers in the data set, the iterative fitting procedure as described by Sheldrick & Akrigg (1980) was used to calculate an averaged pyranosyl rigid-body fragment. Bond lengths, bond angles and torsion angles for this ring are tabulated in Table 2. From the small average r.m.s. deviation of only 0.03 (2) Å and from the observation that all deviations fall within 1 σ from the mean (minimum and maximum of 0.01 and 0.05 Å for LKI60 and GSII118 respectively), it is clear that the 11 rings are all conformationally very similar; the reason for this lies most probably in the rigidity of the pyranose ring. Results from research done by Sheldrick & Akrigg (1980) and Jeffrey (1990) point in the same direction. The Cremer & Pople (1975) puckering parameters for the sequence C1'—C2'—C3'—C4'—C5'—O5' of the ' β -fragment'

(semi-empirical quantum chemical). The molecular-mechanics calculations were performed on the uncharged model. Fig. 5(a) summarizes the results of these calculations and the experimental conformations are represented by arrows. From this figure it can be seen that the experimental conformations fall within the preferred conformation range as predicted from *AM1*. The semi-empirical quantum-chemical results thus agree much better than the molecular-mechanics calculations, which predict two energy minima at $\chi = 50$ and 220 – 230° , respectively. Therefore, the idea was raised that, aside from steric interactions, electrostatic forces could play a determining role in the orientation of the base moiety relative to the sugar ring. In this context, a *CHEMMOD* molecular-mechanics recalculation, but this time with net atomic charges from *AM1*, was performed (Fig. 5b). Since the net charges on O2 and O5' are highly dependent upon the conformation (Fig. 6), the charges assigned to the model are from

Fig. 5. Variation of the steric energy (*CHEMMOD* or *ALCHEMY*) or heat of formation (*AM1*) as a function of χ for (a) the uncharged model and (b) the model with *AM1* net charges assigned.

the conformation with $\chi = 240^\circ$. It is noteworthy that mainly the charges on O2 and O5' fluctuate with χ , while the charge shifts on the other base or sugar atoms are less pronounced (results not shown). From Fig. 5(b) it is clear that the introduction of net atomic charges leads to a considerable improvement of the molecular-mechanics results: only one energy minimum is predicted at $\chi = 210^\circ$. Compared with *AM1* the energy minimum is much deeper and narrower, but that is most probably the consequence of the invariability of the assigned charges. Indeed, as Fig. 6 suggests, the closer O2 and O5' come, the more modest the charges on these atoms, which counterbalances for the larger electrostatic repulsion at smaller distances. If, however, the charges are left invariable (as is the case in the molecular-mechanics approach) and thus unable to compensate for the larger electrostatic repulsion at small distances, the repulsion will be overestimated in most of the conformations, and so will be the total energy.

The N1—C1' bond length varies from 1.450 (2) to 1.479 (5) Å with a weighted mean value of 1.459 (2) Å, significantly shorter than the average 1.49 Å for furanosyl pyrimidine nucleosides (Lin, Sundaralingam & Arora, 1971). Unlike the furanosyl pyrimidine nucleosides (Lo, Shefter & Cochran, 1975) no dependency of the glycosyl N1—C1' bond length on χ has been observed.

Construction of the 'standard' model. As already stated above, the scope of this conformational analysis was to elucidate a standard rigid model for a pyranosyl pyrimidine nucleoside which could be used in subsequent molecular-modeling studies of modified oligonucleotides. The fragment does consist of a base moiety linked onto the pyranosyl sugar part by the *N*-glycosidic bond. Averaged geometries for the nucleoside bases can be found in the excellent book by Saenger (1984). For the pyranosyl sugar ring, the geometry of the averaged pyranosyl rigid-body fragment was used and linked onto the base

Fig. 6. Variation of the *AM1* net atomic charges (on O2 and O5') as a function of χ .

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Crystallography of the Even *n*-Alkanes: Structure of C₂₀H₄₂

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Abstract

n-Eicosane, $M_r = 282.55$, triclinic, $P\bar{1}$, $a = 4.293$ (5), $b = 4.84$ (1), $c = 27.35$ (9) Å, $\alpha = 85.3$ (3), $\beta = 68.2$ (1), $\gamma = 72.6$ (1)°, $V = 503.2$ Å³, $Z = 1$, $D_x = 0.932$ Mg m⁻³, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu = 0.34$ mm⁻¹, $F(000) = 162$, $T = 300$ K, $wR = 0.074$, $R = 0.090$ for 649 significant reflections out of a total of 1251 [$I > 2.5\sigma(I)$]. The triclinic even *n*-alkanes up to $n = 22$ form an isostructural series.

Introduction

It is a matter of some difficulty to obtain accurate X-ray crystal structure analyses of long-chain *n*-alkanes. By virtually whatever method they are crystallized, they invariably adopt a thin platy habit, a consequence of their underlying layer structure. Such thin plates are often slightly warped and this prevents their precise alignment on a diffractometer. The best orientation matrix obtainable usually yields

cell parameters with errors substantially larger than those normally acceptable. Nevertheless, accepting these limitations, it is possible to obtain X-ray structure analyses which, although not of the highest accuracy, can yield useful structural information. We report the X-ray crystal structure analysis of *n*-eicosane, C₂₀H₄₂. Its relation to the crystal structures of other even *n*-alkanes is given in the *Discussion*.

Experimental

A large crystalline agglomeration (25 × 10 × 4 mm) of *n*-C₂₀H₄₂ (Aldrich Chemical Company Ltd) was grown from *n*-dodecane, C₁₂H₂₆, by slow cooling (< 0.01 K per day) over a period of two weeks. From this, a flat plate was cut (dimensions 1.5 × 0.5 × 0.1 mm) and mounted on a Picker four-circle diffractometer. Using Ni-filtered Cu $K\alpha$ radiation, unit-cell dimensions were derived from 26 reflections, $34.0 < 2\theta < 80.0^\circ$. Data were collected in the range $3.0 < 2\theta$

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