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Nucleic-Acid Constituents.

VI. The Crystal and Molecular Structure of 3',5'-Di-*O*-acetyluridine at -170°C

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3',5'-Di-*O*-acetyluridine, $\text{C}_{13}\text{H}_{16}\text{O}_8\text{N}_2$, crystallizes with two molecules in a monoclinic unit cell with space group $P2_1$; $a = 10.456$ (3), $b = 8.645$ (3), $c = 8.644$ (3) Å, $\beta = 109.2$ (3) $^{\circ}$ at -170°C . Diffractometer data (Mo $K\alpha$ radiation) were collected at -170°C . The structure was obtained by direct methods and refined by least squares ($R_w = 3.95\%$), taking into account a disorder of the acetyl group bonded to O(3'). The orientation of the nucleobase with respect to the sugar is *anti* ($\chi_{\text{CN}} = 60.4^{\circ}$). The uracil ring is planar within 0.02 Å. Base-base stacking is absent. The ribose ring has a C(2')-*endo* conformation and the orientation of the acetyl group bonded to C(5') is *gauche-gauche* (g^+) with respect to O(1') and C(3').

Introduction

Nucleic-acid constituents are currently investigated in this laboratory by means of NMR studies (part I: Altona, van Boom, de Jager, Koeners & van Binst, 1974; part II: Altona, Koeners, de Jager & van Boom, 1974; part V: Altona, van Boom & Haasnoot, 1976), synthesis (part III: van Boom, Burgers, den Hartog & van der Marel, 1976) and crystal structure determinations (part IV: de Kok, Romers, de Leeuw, Altona & van Boom, 1977). The present paper (part VI) reports the structure determination of 3',5'-di-*O*-acetyluridine (abbreviated DAU). Knowledge of its conformation and geometry is pertinent to the interpretation of physical data on nucleosides and their correlation with nucleic-acid structures. The numbering of atoms is indicated in Fig. 1.

Experimental

DAU was obtained by means of the method of Fromageot, Griffin, Reese & Sulton (1967).

Evaporation at 44°C of a solution of DAU in *n*-butanol resulted after a few days in the appearance of clusters of lath-shaped crystals. The colourless monoclinic crystals are elongated along [010] and cleave easily perpendicular to the needle axis. The lattice

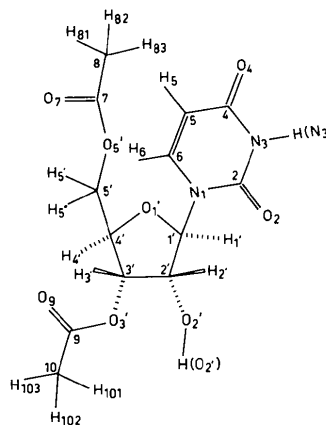


Fig. 1. The numbering of atoms in 3',5'-di-*O*-acetyluridine.

Table 1. *Crystal data of 3',5'-di-O-acetyluridine*

	20°C	-170°C
<i>a</i> (Å)	10.529 (3)	10.456 (5)
<i>b</i> (Å)	8.745 (3)	8.645 (5)
<i>c</i> (Å)	8.703 (3)	8.644 (5)
β (°)	108.45 (2)	109.20 (4)
<i>V</i> (Å ³)	760.2	737.9
<i>d_c</i> (g cm ⁻³)	1.434	1.477
<i>Z</i> = 2, μ (Mo <i>K</i> α) = 1.34 cm ⁻¹		
Space group: <i>P</i> 2 ₁		
Observed reflexions: 1867		
Non-significant reflexions: 12		
Mo <i>K</i> α radiation: λ = 0.71069 Å		
Scanning mode: $\theta/2\theta$		
Scanning range: θ_{\min} = 5°, θ_{\max} = 30°.		

dimensions at 20 and -170°C (Table 1) were determined with a three-circle diffractometer using Cu *K* α radiation (λ = 1.54178 Å). The space group *P*2₁ is deduced from the absence of *Ok0* reflexions for *k* odd and from the chirality of DAU. Assuming two molecules per unit cell, one calculates $d_x^{20} = 1.434$ g cm⁻³, a reasonable value confirmed by the ultimate diffraction analysis.

The reflexion intensities were recorded at -170°C on a three-circle diffractometer using graphite-monochromatized Mo *K* α radiation (consult Table 1 for technical details). The reflexions were reduced to structure factors in the usual way. No absorption correction was applied. An overall *B* value of 1.53 Å² was obtained by means of a Wilson plot.

Refinement

With the program *MULTAN*, described by Germain, Main & Woolfson (1971), the solution of the structure was obtained in a routine way. The least-squares refinement was executed by means of a block-diagonal approximation to the matrix of normal equations, taking 9 × 9 blocks (positional and anisotropic thermal parameters) for the heavy atoms and 4 × 4 blocks (positional parameters and isotropic *B* values) for the H atoms. The H atoms were located on difference Fourier maps. The scattering factors of the heavy atoms were taken from *International Tables for X-ray Crystallography* (1962), those of H from Stewart, Davidson & Simpson (1965). The anisotropic temperature factors are defined as $\exp[-2\pi^2 \sum_{ij} a_i^* a_j^* h_i h_j U_{ij}]$, *i, j* = 1, 2, 3, the unweighted and weighted *R* values are $R = \sum |F_o| - |F_c| / \sum |F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}$. The weights *w* are calculated from $1/w = \sigma^2[(\text{counting statistics}) + 0.03F_o^2]$.

With 1867 observed reflexions the refinement rapidly converged to minimum values of *R* = 4.91 and *R_w* = 4.12%. However, the tensor components *U*₂₂ (0.233 Å²) and *U*₂₃ (0.065 Å²) of O atom O(9) were suspiciously high. This effect might indicate disorder. Since O(9) of molecule *x, y, z* is hydrogen-bonded to N(3) of

molecule -1 + *x, y, z* (see *Packing*), disorder in which O(9) and C(10) change their roles seems impossible. The bond distance of the carbonyl group C(9)—O(9) being rather short (1.17 Å) a possible explanation might be a statistical distribution of atoms O(9*A*) and O(9*B*) above and below the plane defined by the acetyl moiety O(8), C(9), O(9) and C(10). The line connecting O(9*A*) and O(9*B*) should be perpendicular to this plane and almost perpendicular to the vector O(9)···N(3). In order to verify this hypothesis two half-atoms O(9*A*) and O(9*B*) (*i.e.* assuming occupation numbers 0.500) were located at positions $x \pm \epsilon_x, y \pm \epsilon_y, z \pm \epsilon_z, x, y, z$ being the position of the original atom O(9). Furthermore, through slack constraints (Waser, 1963) the carbonyl bond distances C(9)—O(9*A*) and C(9)—O(9*B*) were constrained to values deviating only slightly from the 'ideal' value of 1.21 Å.

The refinement converged to substantially lower minimum values of *R* = 4.75 and *R_w* = 3.95%, indicating that the ordered model must be rejected (Hamilton, 1965) on a significance level of 99.9%. The separation O(9*A*)···O(9*B*) amounts to 0.707 Å. Although the *U*₂₂ components (0.080 and 0.110 Å) are still somewhat large, all *U*_{*ij*} components have decreased to physically acceptable values. The positional parameters of the heavy atoms are tabulated in Table 2,* while the

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32497 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Fractional coordinates (× 10⁴) of the heavy atoms*

E.s.d.'s (× 10³, in Å) are given in parentheses. An asterisk indicates occupation numbers equal to $\frac{1}{2}$.

	<i>x</i>	<i>y</i>	<i>z</i>
N(1)	10226 (2)	2662 (2)	5292 (2)
N(3)	12346 (2)	2643 (3)	4977 (2)
C(2)	10999 (2)	3008 (3)	4303 (2)
C(4)	13010 (3)	2051 (3)	6520 (3)
C(5)	12122 (3)	1694 (3)	7457 (3)
C(6)	10806 (2)	2018 (3)	6825 (2)
C(1')	8789 (2)	3031 (3)	4695 (2)
C(2')	7845 (2)	1665 (3)	4620 (2)
C(3')	6576 (2)	2529 (3)	4618 (2)
C(4')	7144 (2)	3849 (3)	5818 (3)
C(5')	7203 (2)	3583 (3)	7568 (3)
C(7)	8198 (3)	1797 (3)	9725 (3)
C(8)	9260 (3)	598 (4)	10335 (3)
C(9)	4723 (2)	3297 (3)	2240 (3)
C(10)	4417 (3)	3974 (4)	564 (3)
O(2)	10537 (2)	3584 (2)	2957 (2)
O(4)	14238 (2)	1838 (2)	6969 (2)
O(1')	8503 (2)	4129 (2)	5769 (2)
O(2')	7699 (2)	671 (2)	3292 (2)
O(3')	6054 (2)	3169 (2)	2978 (2)
O(5')	8124 (2)	2316 (2)	8218 (2)
O(7)	7477 (2)	2311 (2)	10441 (2)
O(9 <i>A</i>)*	3920	2536	2689
O(9 <i>B</i>)*	3943	3293	3005

Table 3. Fractional coordinates ($\times 10^3$) and isotropic B values ($\times 10$ in \AA^2) of the hydrogen atoms

E.s.d.'s ($\times 10^2$ in \AA for coordinates and $\times 10$ in \AA^2 for B values) are given in parentheses.

	x	y	z	B
H(N3)	1279 (3)	283 (3)	438 (3)	18 (6)
H(5)	1246 (3)	122 (3)	842 (3)	25 (7)
H(6)	1019 (2)	180 (3)	734 (2)	4 (5)
H(1')	869 (2)	344 (3)	365 (2)	1 (5)
H(2')	820 (2)	106 (3)	564 (3)	15 (6)
H(3')	589 (2)	194 (2)	484 (2)	0 (5)
H(4')	660 (2)	481 (3)	547 (3)	9 (6)
H(5')	756 (2)	448 (3)	822 (2)	7 (5)
H(5'')	640 (3)	333 (3)	763 (3)	24 (6)
H(O2')	753 (2)	125 (3)	247 (3)	15 (6)
H(101)	489 (3)	352 (3)	-4 (3)	18 (6)
H(102)	348 (3)	400 (3)	5 (3)	20 (7)
H(103)	470 (3)	511 (4)	71 (3)	44 (9)
H(81)	929 (3)	0 (4)	951 (4)	51 (10)
H(82)	1015 (4)	91 (4)	1061 (3)	53 (10)
H(83)	921 (3)	5 (3)	1131 (3)	17 (6)

coordinates and isotropic B values of the H atoms are listed in Table 3.

Discussion of the structure

The mean positional estimated standard deviations (e.s.d.'s) are 0.0019, 0.0022, 0.0028 and 0.031 \AA for O, N, C and H atoms respectively. Taking into account a 40% underestimation due to the block-diagonal refinement we arrive at e.s.d.'s of 0.0056, 0.0050 and 0.0048 \AA for C-C, C-N and C-O bonds and at e.s.d.'s of 0.04 \AA for bonds involving H atoms. For valency and torsion angles the e.s.d.'s are about 0.3 and 0.4 $^\circ$. Interatomic bond lengths and valency angles may be found in Fig. 2(a) and (b). Torsion angles defin-

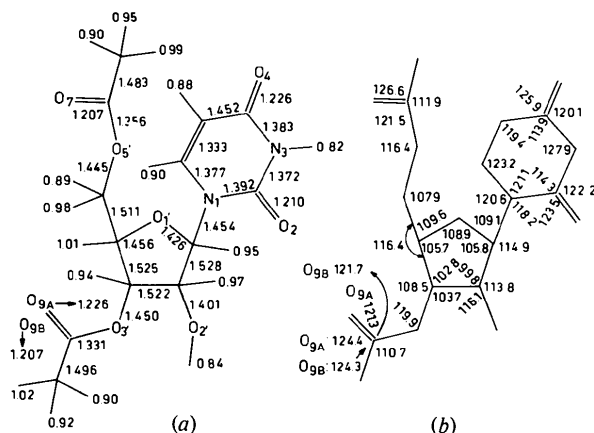


Fig. 2. (a) Bond lengths in \AA units and (b) bond angles in degrees. Estimated standard deviations are approximately 0.005 \AA and 0.3 $^\circ$, respectively, for bonds not involving hydrogen atoms.



Fig. 3. An ORTEP projection of 3',5'-di-O-acetyluridine based upon the ordered model.

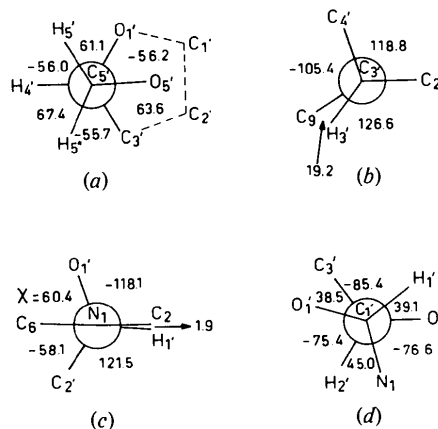


Fig. 4. Newman projections along (a) C(5')-C(4'), (b) C(3')-O(3'), (c) N(1)-C(1') and (d) C(1')-C(2').

ing the conformation of the sugar ring and backbone are listed in Table 4. The overall shape of the molecule is depicted in an ORTEP projection (Fig. 3). Finally a number of important Newman projections are given in Fig. 4.

The resulting pattern of bond lengths and valency angles does not occasion special remarks. A comparison of the uracil ring with corresponding uracil and thymine moieties occurring in known structures indicates no significant deviations. The corresponding entities of uracil in DAU and the 'averaged structure' obtained from literature data (see Table 5) display mean deviations of 0.005 \AA for bond lengths and 0.4 $^\circ$ for bond angles. Nor does the nucleobase exhibit a substantial deviation from planarity: the largest distance from the least-squares plane is 0.020 \AA for C(4). On the other hand the 'outer' atoms O(4) and C(1') are significantly displaced at -0.042 and -0.054 \AA from the least-squares plane. Moreover, nearly all observed deviations from planarity (Table 6) show the same trend in DAU, 2',3'-O-methoxymethylneuridine (MMU) and in 3',5'-di-O-acetyl-2'-deoxy-2'-fluorouridine (DAF, see literature in Table 5).

In agreement with 22 earlier observations [see de Kok *et al.* (1977) and papers quoted by Sundaralingam (1973)] the observed difference [$\delta = 0.028 \text{ \AA}$, $\sigma(\delta) = 0.0065 \text{ \AA}$] between the lengths of bonds C(4')-O(1') and C(1')-O(1') in the ribose ring is highly significant and can be attributed to the anomeric effect occurring in sugars and halogeno-substituted dioxane compounds (Lemieux, 1964; Romers, Altona, Buys & Havinga, 1969; Zefirov & Shekhtman, 1971; Jeffrey, Pople & Radom, 1972).

Inspection of the endocyclic torsion angles (Table 4) indicates that the sugar ring has an *S*-type conformation with a phase angle of pseudorotation $P = 165.3^\circ$ (Altona & Sundaralingam, 1972) and with C(2') *endo* with respect to the C(5') side chain. The calculated maximum puckering angle ϕ_{\max} (41.2°) is slightly larger than the average (38.2°) obtained from 36 independent observations on *S*-type ribosides tabulated by Altona & Sundaralingam (1972). The glycosidic torsion angle $\chi_{\text{CN}} = 60.4^\circ$ (see Fig. 4c) indicates the usual *anti* connexion between the sugar and the base. Its value lies in

the normal range for *S*-type ribonucleosides ($38\text{--}73^\circ$, observed by Altona & Sundaralingam). The orientation of O(5') (Fig. 4a) is *gauche-gauche* (g^+) with respect to C(3') and O(1').

The acetyl group O(5')-C(7)-O(7)-C(8) is planar within 0.007 \AA . The torsion angle C(5')-O(5')-C(7)-C(8) amounts to -174.8° . We refrain from passing verdict on the shape of the second acetyl group O(3')-C(9)-O(9)-C(10). If we suppose C(9) to be disordered as well $\sim 0.1 \text{ \AA}$ above and below the average acetyl plane - then the two resulting acetyl groups *A* and *B* might be planar. Unfortunately, the separation of atoms C(9A) and C(9B) (about 0.2 \AA) would be too small to verify this hypothesis with a least-squares procedure.

It is interesting to note that the closely related nucleoside DAF studied by Suck, Saenger, Main, Germain & Declercq (1974) displays a totally different conformation. The 2'-deoxy-2'-fluoro ribose ring of DAF is characterized by the C(3')-*endo*-C(4')-*exo* conformation ($P = 38.2^\circ$). The orientation of O(5') is *trans-gauche* (t^-) with respect to O(1') and C(3'), whereas

Table 4. Selected torsion angles ($^\circ$)

Notation	Designation	Angle	Conformation
τ_0	C(4') O(1') C(1')-C(2')	-22.9	<i>S</i> type C(2')- <i>endo</i>
τ_1	O(1')-C(1')-C(2')-C(3')	38.5	$P = 165.3^\circ$
τ_2	C(1')-C(2')-C(3')-C(4')	-38.9	$\phi_{\max} = 41.2^\circ$
τ_3	C(2')-C(3')-C(4')-O(1')	26.9	
τ_4	C(3')-C(4')-O(1')-C(1')	-2.6	
ψ'	O(3')-C(3')-C(4')-C(5')	155.6	
ψ	C(3')-C(4')-C(5')-O(5')	63.6	g^- (<i>gauche-gauche</i>)
ϕ	C(4') C(5')-O(5') C(7)	173.1	<i>t</i>
ω	C(5')-O(5')-C(7)-C(8)	-174.8	<i>t</i>
ϕ'	C(4') C(3')-O(3') C(9)	-105.4	<i>g</i>
ω'	C(3')-O(3')-C(9)-C(10)	-179.6	<i>t</i>
χ	C(6) N(1)-C(1') O(1')	60.4	<i>anti</i>

Table 6. Deviations (\AA) from least-squares planes through the uracil rings of DAU, 2',3'-*O*-methoxymethylneuridine (MMU) and 3',5'-di-*O*-acetyl-2'-deoxy-2'-fluorouridine (DAF)

The plane-defining atoms are marked with an asterisk.

	DAU	MMU	ADF		DAU	MMU	ADF
N(1)*	0.007	0.017	0.016	C(6)*	0.004	0.018	0.004
C(2)*	0.005	0.005	0.010	O(2)	-0.024	0.037	-0.018
N(3)*	0.019	0.026	0.007	O(4)	-0.042	-0.079	-0.068
C(4)*	0.020	0.023	0.018	C(1')	-0.054	0.000	0.007
C(5)*	0.009	0.002	0.013				

Table 5. The geometry of the uracil moiety

Angles α are in degrees, distances l in \AA units. σ - estimated standard deviation; S = estimator = $[(n-1)^{-1} \sum_i (q_i - q_{\text{av}})^2]^{1/2}$. S and σ are given in numbers of the last digit and within parentheses. The average values are computed from thymidine (Hunt & Sabramanian, 1969), 6-methyluridine (two independent molecules; Suck & Saenger, 1972), 1- β -D-arabinofuranosylthymidine (two determinations; Tollin, Wilson & Young, 1973; Sherfinski & Marsh, 1974), uridine-3',5' cyclomonophosphate (Coulter, 1969), 3',5' di-*O*-acetyl-2'-deoxy-2'-fluorouridine (Suck, Saenger, Main, Germain & Declercq, 1974), 2',3'-*O*-methoxymethylneuridine (de Kok, Romers, de Leeuw, Altona & van Boom, 1977) and this work.

Angle	α	σ	α	S	Bond	l	σ	l	S
C(1')-N(1) C(2)	118.2	(3)	118.1	(2)	C(1')-N(1)	1.454	(5 ^a)	1.464	(3 ^b)
C(1')-N(1) C(6)	120.6	(3)	120.7	(1 ^b)	N(1)-C(2)	1.392	(5 ^a)	1.384	(3 ^b)
C(2)-N(1) C(6)	121.1	(3)	121.1	(1 ^b)	C(2)-O(2)	1.210	(4 ^a)	1.208	(3 ^b)
N(1) C(2) O(2)	123.5	(3)	123.3	(2)	C(2)-N(3)	1.372	(5 ^a)	1.373	(1 ^b)
N(1) C(2) N(3)	114.3	(3)	115.0	(1 ^b)	N(3)-C(4)	1.383	(5 ^a)	1.385	(3 ^b)
O(2)-C(2) N(3)	122.2	(3)	121.8	(2 ^b)	C(4)-O(4)	1.226	(4 ^a)	1.223	(3 ^b)
C(2) N(3)-C(4)	127.9	(3)	127.1	(1 ^a)	C(4)-C(5)	1.452	(5 ^a)	1.438	(3 ^b)
N(3) C(4)-O(4)	120.1	(3)	119.7	(2 ^b)	C(5)-C(6)	1.333	(5 ^a)	1.337	(3)
N(3)-C(4) C(5)	113.9	(3)	114.4	(2 ^b)	N(1)-C(6)	1.377	(5 ^a)	1.380	(3 ^b)
O(4) C(4)-C(5)	125.9	(3)	126.0	(1 ^b)					
C(4) C(5) C(6)	119.4	(4)	120.0	(3 ^b)					
C(5)-C(6) N(1)	123.2	(3)	122.4	(3 ^b)					

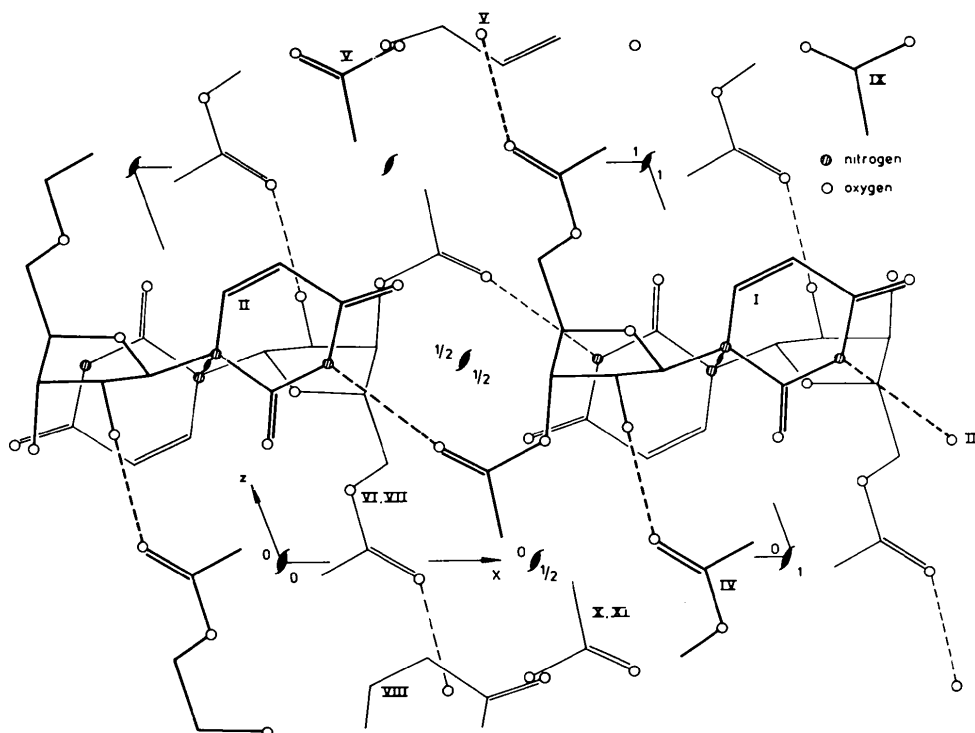


Fig. 5. Projection of the packing along [010].

the uracil base exhibits a *syn* orientation with respect to the ribose ring ($\chi_{\text{CN}} = -108.3^\circ$).

Packing

An illustration of the packing is given in a projection along [010] (Fig. 5). It is seen that the reference molecule I at x, y, z has close contacts ($<3.50 \text{ \AA}$) with ten neighbouring molecules. We also note that parallel base-base stacking is absent. The molecules are stacked in layers parallel to (010) and in these layers each molecule is hydrogen-bonded to four neighbours. Disregarding the hydrogen bonds there is only one short interaction (at 3.228 \AA) between O(7) of the reference molecule and O(3') of molecule IV at $x, y, 1 + z$. The hydrogen bridges (see Fig. 5) occur (i) between N(3)-H and O(9A) (2.962 \AA) and O(9B) (2.807 \AA) and (ii) between O(2')-H and O(7) (2.787 \AA), the former translating the molecule in the direction [100], the latter in the direction [001]. Only weak interactions involving the two acetyl groups are observed between succeeding layers. This explains why (010) is a perfect plane of cleavage.

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Structures of Nitrogen-Containing Aromatic Compounds. IV. 1,4,5,8-Pyridazino[1,2-*a*]pyridazinetetrone

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$C_8N_2O_4H_4$ (DIAZAN) is monoclinic, $P2_1/c$, $a = 13.805$ (10), $b = 8.360$ (5), $c = 21.500$ (15) Å, $\beta = 107.3$ (1)°, $V = 2369$ Å³, $D_m = 1.58$ (1) g cm⁻³, $Z = 12$, $R = 0.054$ for 3104 observed data (diffractometer, monochromated Mo $K\alpha$), all C, N and O atoms anisotropic, all H's included. Mean bond lengths (not corrected for thermal motion, ranges in parentheses): N–N 1.428 (5), N–C 1.418 (20), C–C 1.461 (15), C=C 1.317 (20), C=O 1.209 (10) Å. Although each N atom is trigonal sp^2 -hybridized, the molecule is far from planar. The bond lengths show that DIAZAN is not aromatic although there is some electron delocalization in the O=C–N–C=O system. The structure is layered with the molecules lying in sheets at approximately $z = \frac{1}{12}$, $\frac{1}{4}$ and $\frac{5}{12}$. There are two types of short intermolecular C...O separations of 2.95 to 3.15 Å: (a) the O atom of a carbonyl group of a molecule in one layer is close to the C atom of a carbonyl group of a molecule in the adjacent layer; (b) the O atom of a carbonyl group of a molecule is in close contact with one H atom of another molecule within the same layer. A detailed description is given of the solution of the structure by direct methods.

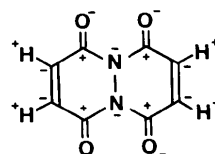
Introduction

The preparation and properties of 1,4,5,8-pyridazino[1,2-*a*]pyridazinetetrone were described by Kealy (1962). The analogous 1,4-dione was reported by Sasaki, Kanematsu & Ochiai (1972), and the crystal structure of the related compound 8b,8c-diazacyclo-pent[*fg*]acenaphthylene was reported by Atwood, Hrnčir, Wong & Paudler (1974).

DIAZAN is readily formed by thermal decomposition of 3,6-pyridazinedione, and its reported melting point (247°C) suggests not only stability of the molecule but unusually large intermolecular attractions in the solid. However, DIAZAN is rapidly hydrolysed in boiling water and Kealy (1962) concluded that it had 'a strained ring system', inferred from the position of the carbonyl stretching frequency in the infrared

spectrum. Its UV–visible absorption spectrum is remarkably similar to that of 1,4-naphthaquinone (Sasaki *et al.*, 1972), suggesting aromatic character.

Consideration of electronegativities (Pauling, 1960) gives the charge distribution shown in (I), and a π -electron count suggests that the compound could be 'antiaromatic' (Lewis & Peters, 1975). Therefore, the crystal structure of DIAZAN has been determined to obtain accurate C–C, C–N and N–N bond lengths and thus an estimate of their bond orders and the degree of aromaticity of the compound.



(I)

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