

Stereochemistry of Unsaturated Amino Sugars.
IV. The Structure of Peracetylated 2,3-Dideoxy- α -D-erythro-aldopyranose, C₁₆H₂₁NO₉

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Abstract

1,4,6-Tri-*O*-acetyl-2-(*N*-acetylacetamido)-2,3-dideoxy- α -D-erythro-hex-2-enopyranose crystallizes in the space group $P2_12_12_1$ with $a = 9.711$ (5), $b = 23.337$ (26), $c = 8.277$ (6) Å, $Z = 4$. The structure was refined to an R of 0.058. The sugar ring exhibits a half-chair 0H_5 conformation; the substituents are attached to C(1) in quasi-axial, C(4) in quasi-equatorial and C(5) in equatorial positions. Owing to the absence of free hydroxyl groups, O—H...O hydrogen bonds are not possible. In the crystal the molecules are joined by van der Waals interactions only.

Introduction

Increasing interest in the chemistry of carbohydrates is due to the fact that sugars have been established as constituents of numerous natural heteropolymers, even as potential carriers of biological information. Conformational analysis of sugars is of special importance for the understanding of their chemical and biological reactions. Unsaturated sugars are interesting from the theoretical point of view as intermediates in certain processes and also as useful reactive components for many syntheses.

A series of stable peracetylated unsaturated 1,2- and 2,3-amino sugars (Pravdić & Fletcher, 1967; Pravdić, Židovec & Fletcher, 1973; Pravdić, Franjić-Mihalić & Danilov, 1975) and some 2-acetamido unsaturated (2',3'-) nucleosides (with theophylline as a base) (Kojić-Prodić, Danilov & Pravdić, 1976; Pravdić, 1979) were synthesized. X-ray structure determinations of the above series are being carried out to provide information on configuration and conformation (Kojić-Prodić, Rogić & Ružić-Toroš, 1976;

Rogić, Ružić-Toroš, Kojić-Prodić & Pravdić, 1977; Kojić-Prodić & Rogić, 1978; Kojić-Prodić, 1979; Kojić-Prodić, Coffou & Ružić-Toroš, 1979).

The half-chair conformation, as an expected consequence of the presence of the double bond in these ring systems, was found to be predominant. The 0H_5 , 5H_0 (in 2,3-unsaturated derivatives) and 4H_5 (in 1,2-unsaturated derivatives) conformations occurred in regular or distorted shape depending on the spatial relationship of the substituents at C(4) and C(5).

Experimental

The space group was determined as $P2_12_12_1$ from Weissenberg photographs recorded with Cu $K\alpha$ radiation. Table 1 lists the crystallographic and physical data.

The intensities were collected on a Philips PW 1100 computer-controlled diffractometer in the ω -scan mode [scan width = 0.6° (θ), scan speed = 0.02° (θ) s⁻¹] with graphite-monochromated Cu $K\alpha$ radiation. 1351 independent reflexions [$I > 2\sigma(I)$] in the range $3 < \theta <$

Table 1. *Crystallographic and physical data*

Numbers in parentheses here and throughout this paper are the e.s.d.'s in the least significant digit.

1,4,6-Tri-*O*-acetyl-2-(*N*-acetylacetamido)-2,3-dideoxy- α -D-erythro-hex-2-enopyranose, C₁₆H₂₁NO₉

M_r	371.35	Z	4
Space group	$P2_12_12_1$	D_m	1.32 (1) Mg m ⁻³
a	9.711 (5) Å	D_c	1.32
b	23.337 (26)	μ (Cu $K\alpha$)	0.975 mm ⁻¹
c	8.277 (6)	Crystal shape	Prismatic
U	1875.78 Å ³	Crystal size	0.195 × 0.165 × 0.150 mm

70° were used in the calculations. Three standard reflexions were measured every 2 h. The data were corrected for background, Lorentz and polarization effects but not for absorption.

Structure determination and refinement

An overall temperature factor ($B = 2.88 \text{ \AA}^2$) and a scale factor were determined (Wilson, 1942) and used to compute normalized structure amplitudes by the routine *NORMAL* included in *MULTAN 77*. The structure was solved with *MULTAN 77* (Main, Lessinger, Woolfson, Germain & Declercq, 1977). The solution was based on 250 reflexions with $|E| > 1.29$. The E map corresponding to the solution with the best figure of merit (ABS FOM = 1.395, PSI ZERO = 42.6, RESID = 37.06) revealed the positions of all the non-hydrogen atoms. Refinement was by full-matrix least squares minimizing $\sum w||F_o| - |F_c||^2$. The weighting scheme of type 3 from the XRAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) was used. The weights were assigned as: $w = w_1 w_2$, where $w_1 = 1$ for $|F_o| \leq 30$ and $w_1 = 30/|F_o|$ for $|F_o| > 30$; $w_2 = 1$ for $\sin \theta \geq 0.4$ and $w_2 = (\sin \theta)/0.4$ for $\sin \theta < 0.4$. Anisotropic refinement and a subsequent difference synthesis were performed to locate the H atoms; those bonded to C(10) did not appear clearly in a difference map and therefore were not determined. A scale factor, heavy-atom coordinates and anisotropic

Table 2. Final atomic coordinates for non-hydrogen atoms ($\times 10^4$)

	x	y	z
O(0)	8588 (4)	1203 (2)	4836 (5)
O(1)	6828 (5)	637 (2)	3716 (6)
O(2)	6418 (7)	309 (3)	6241 (8)
O(3)	3543 (5)	1454 (3)	1312 (7)
O(4)	5631 (5)	2312 (2)	4763 (7)
O(5)	10065 (4)	1498 (2)	904 (5)
O(6)	10717 (6)	2400 (2)	393 (7)
O(7)	11214 (4)	640 (2)	5144 (6)
O(8)	13426 (6)	877 (3)	5231 (10)
C(1)	7197 (6)	1196 (3)	4339 (8)
C(2)	6944 (6)	1595 (3)	2947 (8)
C(3)	7935 (6)	1820 (3)	2090 (8)
C(4)	9414 (6)	1678 (3)	2416 (7)
C(5)	9552 (6)	1156 (3)	3525 (8)
C(6)	10981 (7)	1162 (3)	4223 (8)
C(7)	6430 (7)	230 (3)	4815 (12)
C(8)	6028 (9)	-294 (3)	3948 (13)
C(9)	4794 (7)	1427 (3)	1401 (9)
C(10)	5627 (8)	1083 (4)	206 (11)
C(11)	4920 (7)	2136 (3)	3687 (11)
C(12)	3530 (7)	2373 (3)	3308 (12)
C(13)	10695 (7)	1905 (3)	4 (8)
C(14)	11301 (9)	1653 (3)	-1457 (8)
C(15)	12531 (7)	556 (3)	5590 (9)
C(16)	12692 (10)	20 (5)	6550 (13)
N	5500 (5)	1716 (2)	2638 (6)

Table 3. Positional parameters ($\times 10^3$) for the hydrogen atoms

	x	y	z
H(1)	646	130	552
H(3)	783	214	140
H(4)	992	207	312
H(5)	950	78	288
H(6,1)	1167	129	320
H(6,2)	1104	154	500
H(8,1)	563	-57	500
H(8,2)	542	-43	320
H(8,3)	675	-50	372
H(12,1)	354	271	400
H(12,2)	292	214	360
H(12,3)	354	250	200
H(14,1)	1187	126	-140
H(14,2)	1167	186	-240
H(14,3)	1104	146	-220
H(16,1)	1208	-7	720
H(16,2)	1290	-28	560
H(16,3)	1360	7	688

thermal parameters (235 variables in all) were refined. The H atoms were included in structure factor calculations only. For H atoms the isotropic thermal parameters are those of the bonded atoms. The final $R = 0.058$ and $R_w = 0.056$.

Scattering factors given by Cromer & Mann (1968) and (for H) by Stewart, Davidson & Simpson (1965) were used.

The calculations were carried out on a Univac 1110 computer at the University Computing Centre in Zagreb with the XRAY system (Stewart *et al.*, 1972).

Heavy-atom coordinates are listed in Table 2, H atom coordinates in Table 3.*

Description and discussion of the structure

The structural formula with the atom numbering and interatomic distances are given in Fig. 1. Bond angles are listed in Table 4. The molecular packing is illustrated in Fig. 2. The conformation of the pyranose ring is shown in Fig. 3 and Table 5. In the preparation of the title substance, a D compound was used as the starting material, *i.e.* *N*-acetyl-D-mannosamine (Pravdić & Fletcher, 1967; Pravdić, Židovec, Franjić & Fletcher, 1973). There is no reason to expect conversion from the D to L enantiomer. During the structure determination the D enantiomer was chosen, and the configuration and conformation were defined in accordance with its torsion angles (Table 6).

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34896 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

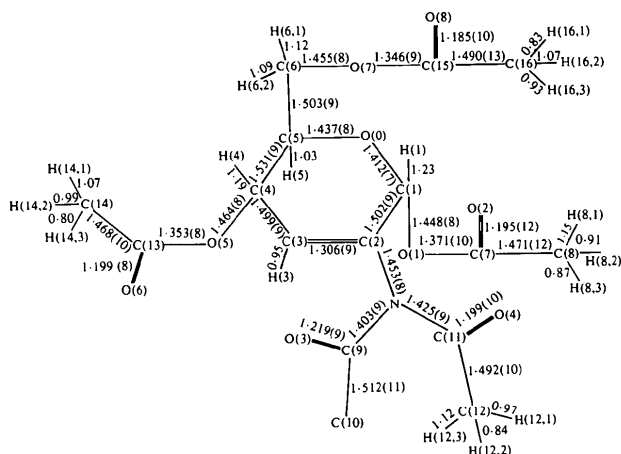
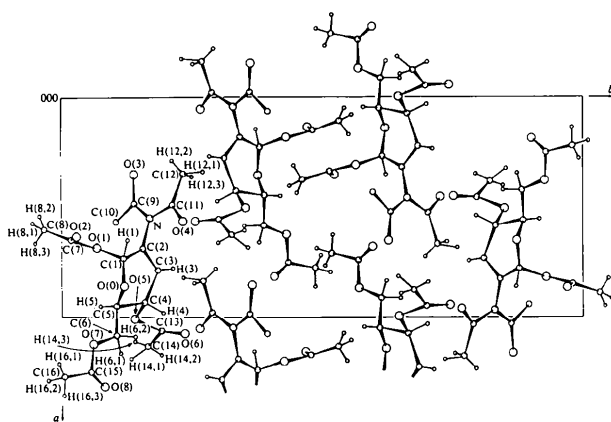
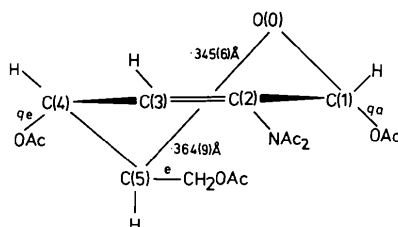


Fig. 1. The structural formula and intramolecular distances (Å).


 Fig. 2. A view of the crystal structure along *c*.

 Fig. 3. Schematic drawing of 0H_5 half-chair conformation illustrating the displacement of O(0) (above) and C(5) (below) the plane defined by C(1), C(2), C(3) and C(4), and orientation of substituents.

The sugar ring in the crystal structure of the α -D-erythro compound exhibits a rather symmetrical half-chair 0H_5 conformation with O(0) displaced by 0.345 and C(5) by -0.364 Å (Fig. 3 and Table 5). The acetoxy groups are attached to C(1) in quasi-axial, C(4) in quasi-equatorial and C(5) in equatorial positions (Fig. 3) (Stoddart, 1971). The conformation found is in agreement with the 1H NMR spectral data

 Table 4. Bond angles ($^\circ$)

Pyranose ring	C(6)—O(7)—acetyl group		
C(5)—O(0)—C(1)	113.7 (5)	O(7)—C(6)—H(6,1)	122
O(0)—C(1)—C(2)	111.9 (5)	O(7)—C(6)—H(6,2)	111
O(0)—C(1)—O(1)	110.5 (5)	H(6,1)—C(6)—H(6,2)	101
O(0)—C(1)—H(1)	109	C(6)—O(7)—C(15)	114.4 (5)
O(1)—C(1)—C(2)	104.2 (5)	O(7)—C(15)—O(8)	122.4 (7)
O(1)—C(1)—H(1)	108	O(7)—C(15)—C(16)	111.6 (7)
C(2)—C(1)—H(1)	113	O(8)—C(15)—C(16)	126.0 (8)
C(1)—C(2)—C(3)	123.1 (6)		
C(1)—C(2)—N	114.4 (5)	O(1)—acetyl group	
C(3)—C(2)—N	122.5 (6)	C(1)—O(1)—C(7)	117.2 (6)
C(2)—C(3)—C(4)	121.3 (6)	O(1)—C(7)—O(2)	123.5 (7)
C(2)—C(3)—H(3)	124	O(1)—C(7)—C(8)	109.1 (8)
C(4)—C(3)—H(3)	113	O(2)—C(7)—C(8)	127.4 (8)
C(3)—C(4)—C(5)	111.6 (5)	O(5)—acetyl group	
C(3)—C(4)—O(5)	108.9 (5)	C(4)—O(5)—C(13)	117.7 (5)
C(3)—C(4)—H(4)	108	O(5)—C(13)—O(6)	122.4 (6)
C(5)—C(4)—O(5)	104.3 (5)	O(5)—C(13)—C(14)	110.7 (6)
C(5)—C(4)—H(4)	106	O(6)—C(13)—C(14)	126.9 (7)
O(5)—C(4)—H(4)	117		
O(0)—C(5)—C(4)	109.6 (5)	N-acetyl groups	
O(0)—C(5)—C(6)	108.1 (5)	C(2)—N—C(9)	120.5 (5)
O(0)—C(5)—H(5)	115	C(2)—N—C(11)	114.1 (5)
C(4)—C(5)—C(6)	107.7 (5)	C(9)—N—C(11)	125.4 (5)
C(4)—C(5)—H(5)	111	O(3)—C(9)—C(10)	121.3 (7)
C(6)—C(5)—H(5)	105	O(3)—C(9)—N	120.6 (7)
C(6)—O(7)—acetyl group		C(10)—C(9)—N	118.1 (6)
C(5)—C(6)—O(7)	109.7 (5)	O(4)—C(11)—C(12)	123.4 (7)
C(5)—C(6)—H(6,1)	105	O(4)—C(11)—N	117.4 (6)
C(5)—C(6)—H(6,2)	106	C(12)—C(11)—N	119.0 (7)

Table 5. Displacements from the least-squares plane (Å)

Atoms included in the calculation of the plane are denoted by an asterisk.

C(1)*	0.004 (9)	C(4)*	-0.004 (9)
C(2)*	-0.008 (9)	O(0)	0.345 (6)
C(3)*	0.008 (9)	C(5)	-0.364 (9)

($J_{3,4}$ and $J_{4,5}$ coupling constants of 2.0 and 8.5 Hz) (Pravdić, Židovec & Fletcher, 1973).

A half-chair conformation is found to be predominant; for 2,3-unsaturated α -D-aldopyranoses the 0H_5 conformation can be expected. It is found in, for example, 1,4,6-tri-*O*-acetyl-2-(*N*-acetylacetamido)-2,3-dideoxy- α -D-*threo*-hex-2-enopyranose (Kojić-Prodić, Rogić & Ružić-Toroš, 1976) and in a nucleoside with an analogous sugar moiety, 7-(methyl 2-acetamido-6-*O*-acetyl-2,3,4-trideoxy- α -D-*threo*-hex-2-enopyranosid-4-yl)theophylline (Kojić-Prodić, 1979).

The puckering of the sugar ring required by the 0H_5 conformation can be described by the values of the C(2)—C(3)—C(4)—C(5) (13.6°) and C(3)—C(4)—C(5)—O(0) (-44.2°) torsion angles (Table 6); these values are similar to the 7.1 and -40.5° in the α -D-*threo* isomer of the title compound (Kojić-Prodić,

Table 6. *Torsion angles* ($^{\circ}$)

In the pyranose ring		On the pyranose ring		Acetyl groups	
O(0)—C(1)—C(2)—C(3)	13.9 (9)	H(1)—C(1)—C(2)—C(3)	137	C(4)—O(5)—C(13)—C(14)	167.4 (9)
C(1)—C(2)—C(3)—C(4)	2 (1)	N—C(2)—C(3)—H(3)	16	H(5)—C(5)—C(6)—O(7)	-55
C(2)—C(3)—C(4)—C(5)	13.6 (9)	H(3)—C(3)—C(4)—H(4)	64	C(5)—C(6)—O(7)—C(15)	169.3 (6)
C(3)—C(4)—C(5)—O(0)	-44.2 (7)	H(3)—C(3)—C(4)—O(5)	-65	C(6)—O(7)—C(15)—O(8)	-1 (1)
C(4)—C(5)—O(0)—C(1)	63.6 (7)	H(4)—C(4)—C(5)—H(5)	-158	C(6)—O(7)—C(15)—C(16)	179.1 (6)
C(5)—O(0)—C(1)—C(2)	-47.4 (7)	H(4)—C(4)—C(5)—C(6)	-44	H(6,1)—C(6)—O(7)—C(15)	46
On the pyranose ring		O(5)—C(4)—C(5)—H(5)	-33	H(6,2)—C(6)—O(7)—C(15)	94
O(0)—C(1)—C(2)—N	-165.5 (5)	O(5)—C(4)—C(5)—C(6)	81.1 (6)	Others	
C(1)—C(2)—C(3)—H(3)	-163	Acetyl groups		O(0)—C(1)—O(1)—C(7)	84.7 (6)
C(2)—C(3)—C(4)—H(4)	-103	H(1)—C(1)—O(1)—C(7)	-34	C(2)—C(1)—O(1)—C(7)	-154.9 (5)
C(2)—C(3)—C(4)—O(5)	128.1 (7)	C(1)—O(1)—C(7)—O(2)	-2.5 (9)	C(1)—C(2)—N—C(9)	-99.7 (7)
C(3)—C(4)—C(5)—H(5)	84	C(1)—O(1)—C(7)—C(8)	177.0 (6)	C(1)—C(2)—N—C(11)	80.0 (7)
C(3)—C(4)—C(5)—C(6)	-161.5 (6)	C(2)—N—C(9)—C(10)	-12.0 (9)	C(3)—C(2)—N—C(9)	80.9 (9)
C(5)—O(0)—C(1)—H(1)	-173	C(2)—N—C(9)—O(3)	167.6 (7)	C(3)—C(2)—N—C(11)	-99.5 (8)
C(5)—O(0)—C(1)—O(1)	68.3 (7)	C(2)—N—C(11)—O(4)	-5.2 (9)	C(3)—C(4)—O(5)—C(13)	-174.7 (9)
H(5)—C(5)—O(0)—C(1)	-63	C(2)—N—C(11)—C(12)	169.1 (6)	C(5)—C(4)—O(5)—C(13)	-55.5 (5)
C(6)—C(5)—O(0)—C(1)	-179.3 (5)	C(10)—C(9)—N—C(11)	168.4 (7)	C(4)—C(5)—C(6)—O(7)	-173.7 (5)
H(4)—C(4)—C(5)—O(0)	74	O(3)—C(9)—N—C(11)	-12 (1)	O(0)—C(5)—C(6)—O(7)	68.0 (7)
O(5)—C(4)—C(5)—O(0)	-161.5 (4)	C(12)—C(11)—N—C(9)	-11 (1)	C(4)—C(5)—C(6)—H(6,1)	-41
H(1)—C(1)—C(2)—N	-42	O(4)—C(11)—N—C(9)	174.5 (6)	C(4)—C(5)—C(6)—H(6,2)	-57
O(1)—C(1)—C(2)—N	75.1 (6)	H(4)—C(4)—O(5)—C(13)	62	O(0)—C(5)—C(6)—H(6,1)	-159
O(1)—C(1)—C(2)—C(3)	-105.5 (7)	C(4)—O(5)—C(13)—O(6)	-87.2 (6)	O(0)—C(5)—C(6)—H(6,2)	-175

Rogić & Ružić-Toroš, 1976) as well as 11.4 and -47.0° in the theophylline nucleoside with an analogous sugar moiety (Kojić-Prodić, 1979) appearing in the 0H_5 conformation.

Sundaralingam (1968) has defined the conformation about C(5)—C(6) in pyranosides by the angle $\varphi_{OO} = O(5)—C(5)—C(6)—O(6)$. In the present structure this angle is described by the sequence O(0)—C(5)—C(6)—O(7) and its value of $68.0(7)^{\circ}$ is in the range $\pm 60 \pm 30^{\circ}$ common for pyranoside derivatives.

Bond lengths and angles (Fig. 1 and Table 4) are comparable to the values in peracetylated 2,3-dideoxyaldopyranoses (Kojić-Prodić, Rogić & Ružić-Toroš, 1976) or in theophylline nucleosides with analogous sugar moieties (Kojić-Prodić, 1979; Kojić-Prodić, Coffou & Ružić-Toroš, 1979). The asymmetry of the endocyclic C(1)—O(0) [$1.412(7)$ Å] and C(5)—O(0) [$1.437(8)$ Å] bonds is pronounced. The exocyclic anomeric C(1)—O(1), $1.448(8)$ Å, is longer than the normal C—O single bond of 1.428 Å (Sundaralingam, 1968). The exocyclic O(0)—C(1)—O(1) angle is $110.5(5)$ and the endocyclic C(5)—O(0)—C(1) $113.7(5)^{\circ}$.

The shortening of C(1)—C(2) [$1.502(9)$ Å] and C(3)—C(4) [$1.499(9)$ Å] is due to the presence of the C(2)=C(3) [$1.306(9)$ Å] in the ring. In the acetyl groups the mean C—C length of $1.492(11)$ Å is reasonable for a single bond next to a C=O bond. There are two categories of C to O bonds: the C—O bonds range from $1.448(8)$ to $1.464(8)$ Å and the O—C=O bonds from $1.346(9)$ to $1.371(10)$ Å. The carbonyl bonds are in the range $1.185(10)$ to $1.219(9)$ Å.

The mean value of the endocyclic valence angle of a C atom in sp^3 hybridization is $110.8(5)^{\circ}$. The C(sp^3) valence angles exterior to the pyranose ring are in a wider range [$104.2(5)$ to $110.5(5)^{\circ}$] than the interior angles.

All hydroxyl groups are acetylated and O—H...O hydrogen bonds are not possible. The intermolecular distances do not give any evidence of C—H...O contacts. In the crystal structure, molecules are connected by van der Waals forces only.

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The Monoclinic Structure of a Fluorescent Probe: Ammonium 1-Anilino-8-naphthalenesulfonate (ANS) Monohydrate

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Abstract

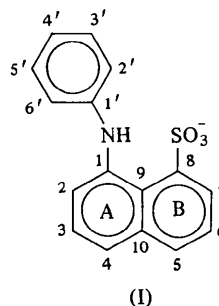
$\text{NH}_4^+ \cdot \text{C}_{16}\text{H}_{12}\text{NO}_3\text{S}^- \cdot \text{H}_2\text{O}$ is monoclinic, $P2_1/c$, with $a = 6.150$ (2), $b = 9.544$ (2), $c = 26.77$ (7) Å, $\beta = 90.35$ (2)°, $Z = 4$, $D_c = 1.413$ Mg m⁻³, $\mu(\text{Mo } K\alpha) = 0.1818$ mm⁻¹. The structure was solved by use of the program *MULTAN* and refined by full-matrix least squares to an R value of 3.5% for 2077 reflections for which $|F| > 3\sigma(|F|)$. The C–N bonds are significantly shorter than the expected single-bonded values. Comparison of independent crystal structures of triclinic ANS and Mg ANS with the present determination revealed that such shortening exists independent of anilino geometry or conformation. The comparison also revealed that ANS probably does not assume a planar conformation, thought possible from its fluorescence properties.

Introduction

N-Arylamino-naphthalenesulfonates have received much attention because of the highly sensitive response of their fluorescence properties to local conditions of chemical environment (Greene, 1975; Kosower, Dodiuk, Tanizawa, Ottolenghi & Orbach, 1975). These compounds have been used as reporter molecules when bound to proteins and other biomacromolecular structures, and they are generally referred to as fluorescent probes (Edelman & McClure, 1968; Brand & Gohlke,

1972). Even though their use has achieved notable popularity, the specific mechanism of their response to environment and their general applicability is still under investigation (De Toma, Easter & Brand, 1976; Dodiuk, Kanety & Kosower, 1979; Johnson, El-Bayoumi, Weber & Tulinsky, 1979; Weber, Tulinsky, Johnson & El-Bayoumi, 1979).

Cody & Hazel (1977*a,b*) have determined the structures of the ammonium and magnesium salts of 1-anilino-8-naphthalenesulfonate (ANS) (I).



Although both salts crystallized in the triclinic system, the former was unusual in that there were two molecules per asymmetric unit. In addition to its fluorescence properties, ANS is also a member of a class of *peri*-substituted naphthalenes which are known to exhibit a distorted naphthyl ring geometry arising from intramolecular steric effects (Balasubramanian, 1966; Robert, Sherfinski, Marsh & Roberts, 1974). Since we were carrying out crystallographic studies of the structure of the ANS- α -chymotrypsin complex

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