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The Crystal and Molecular Structure of 3-Carbethoxy-1,6-dimethyl-4-oxo-6,7,8,9-tetrahydrohomopyrimidazolium Methyl Sulphate, $C_{14}H_{22}O_7N_2S$

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3-Carbethoxy-1,6-dimethyl-4-oxo-6,7,8,9-tetrahydrohomopyrimidazolium methyl sulphate is known as a new analgesic drug (Probon^R). It crystallizes in the monoclinic space group $P2_1/c$ with $a=7{\cdot}645$, $b=16{\cdot}837$, $c=15{\cdot}905$ Å and $\beta=122{\cdot}0°$; $Z=4$. The phase problem was solved by direct methods, and the final atomic parameters were obtained by three-dimensional least-squares refinement; the final conventional $R=0{\cdot}113$ for the observed reflexions. The right-hand ring of the bicyclic part of the molecule with two nitrogen atoms, and the carbethoxy group, with the exception of the methyl carbon atom, are both planar. These two planes are twisted relative to each other at an angle of 16·6°. The left-hand ring occurs in two different conformations. The same is true for the methyl sulphate ion insofar as three atoms, the sulphur, the methyl carbon and one oxygen, are common and the other three oxygen atoms are approximate mirror images reflected through the plane formed by the three common atoms. The two different conformations of the molecule are statistically distributed in the lattice with equal weight.

Introduction

In the course of the preparation of different homopyrimidazole derivatives was sought one which has an analgesic action, is soluble in water and remains stable in aqueous solution. The title compound 3-carbethoxy-1,6-dimethyl-4-oxo-6,7,8,9-tetrahydrohomopyr imidazolium methyl sulphate, Probon^R, Chinoin (Negwer, 1971) has been found to satisfy these requirements.

Experimental

The crystals used for X-ray diffraction were obtained by recrystallization from a solution in isopropyl alcohol. The colourless transparent crystals are very thin plates parallel to (010) and elongated in the direction of the crystallographic c axis.

The cell dimensions were determined from Buerger precession photographs taken about the crystallographic axes with Cu $K\alpha$ radiation.

Crystal data

$a=7{\cdot}645$ (2), $b=16{\cdot}837$ (1), $c=15{\cdot}905$ (4) Å, $\beta=122{\cdot}0$ (1)°; $F(000)=768$; M.W. 362·41; $D_m=1{\cdot}35$, $D_x=1{\cdot}39$ g cm^{-3}; $Z=4$; $\mu(\text{Cu } K\alpha)=15{\cdot}8$ cm^{-1}.

The space group $P2_1/c$ was determined from the systematic absences $h0l$ l odd and $0k0$ k odd. Intensity data were originally recorded on an equi-inclination Weissenberg camera with the multiple-film technique. The intensities were estimated visually with calibrated intensity scales. In total, 2353 reflexions were collected. For reflexions with zero intensity the value $I_0=\frac{1}{4}I_{\min}$ was taken. For the crystal samples used the condition $\mu R\le 0{\cdot}3$ was satisfied and no absorption correction was made. To bring intensities to a common scale, multiple-film and the Lorentz-polarization correction with interlayer scaling were applied. The absolute scale and overall approximate temperature factor $B=2{\cdot}571$ Å^2 were determined by a Wilson plot using all three-dimensional data.

At the refinement stage it was found that some atoms could not be located unambiguously. This was thought to be due to errors in the intensity data. Therefore the data collection was repeated on a Stoe–Güttinger two-circle single-crystal diffractometer. In total, 2849 independent reflexions were collected out of which 1242 were classified as unobserved. The measurement and evaluation of intensities was accomplished in the manner described previously (Sasvári, Simon, Bognár & Makleit, 1974). These new data, brought to absolute scale, proved to be equivalent to those collected by the film method. Thus the difficulty encountered in the first attempt at structure refinement cannot be considered to be due to the intensity data. For the final structure determination the diffractometer data were used.

Determination of the structure

The structure was solved by the symbolic addition method with the program *LSAM* of Main, Woolfson & Germain (1968). For sign determination 488 reflexions with $E \geq 1{\cdot}20$ were used, with the criterion $P_{\min} = 0{\cdot}88$. Four possible sets of sign combinations have been obtained. With that of the highest figure of merit the E map revealed 15 peaks out of the 24 non-hydrogen atoms, resulting in an initial structure-factor agreement of $R = 0{\cdot}45$. With repeated Fourier calculations all missing non-hydrogen atoms could be located.

Refinement of the atomic positional and temperature parameters was carried out with the block-diagonal least-squares method, minimizing the function $\Phi = \sum_{\mathbf{h}} w_{\mathbf{h}}(F_{o\mathbf{h}} - (1/G)|F_{c\mathbf{h}}|)^2$, where G is the scaling factor. The weighting scheme of Cruickshank (1961), $w_{\mathbf{h}} = 1/(a + bF + cF^2)$, was used with $a = 8{\cdot}0$, $b = 1$ and $c = 0{\cdot}02$. After three cycles with isotropic and a further three cycles with anisotropic thermal parameters the structure-factor agreement decreased to $R = 0{\cdot}15$.

At this stage most of the bond lengths and angles were in satisfactory agreement with the corresponding values in other homopyrimidazole derivatives, but some in the left-hand ring involving C(6), C(7), C(8), the methyl carbon atom C(16) and O(21), O(22), O(23) and C(24) of the methyl sulphate group were unexpectedly different. Therefore these atoms were temporarily deleted from the refinement. Without them and with anisotropic thermal parameters $R = 0{\cdot}341$ for the observed reflexions.

The three-dimensional difference function now showed definitely that near each of the probable positions of C(7) and C(16) were two prominent peaks. Both pairs of peaks could be regarded as equally reliable. It was concluded that C(7) and C(16) must appear in the crystal lattice at two different positions, resulting in two different conformations of the molecule with a statistical distribution.

With the double positions of C(7) and C(16) the bond lengths associated with these atoms still remained unreliable. Although the electron density peaks of the neighbouring C(6) and C(8) atoms were not doubled but only somewhat elongated, it seemed reasonable to assign also two atomic positions in the electron density peaks to C(6) and C(8). This gave more reliable bond lengths.

The latter four carbon atoms with the assigned double positions and with a weight of 0·5 for each position reduced R to 0·310.

With all the previously located atoms in a new difference function we could locate unambiguously only three atoms of the methyl sulphate group, namely S(19), O(20) and C(24), by their sharp and strong electron density peaks. There were, however, six weaker, diffuse electron density peaks for the remaining three oxygen atoms of the sulphate group. Assuming also in this case that the three oxygen atoms

Table 1. *The final fractional coordinates* ($\times 10^4$) *and anisotropic thermal parameters* ($\times 10^4$) *for the non-hydrogen atoms*

The estimated standard deviations are in parentheses. Primed serial numbers refer to atoms of conformation *B* of the molecule. The b_{ij} are defined by: $T = \exp\left[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)\right.$.

	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
N(1)	−283 (7)	2485 (3)	−2102 (4)	152 (8)	22 (2)	44 (3)	−1 (7)	81 (7)	2 (4)
C(2)	−1681 (10)	1905 (5)	−2570 (5)	199 (11)	33 (3)	48 (3)	−2 (10)	119 (8)	3 (5)
C(3)	−1113 (10)	1140 (5)	−2539 (5)	225 (13)	35 (3)	61 (4)	−35 (11)	129 (10)	−12 (6)
C(4)	1041 (12)	924 (5)	−1961 (7)	322 (17)	27 (3)	107 (5)	11 (12)	205 (13)	−9 (7)
N(5)	2413 (8)	1596 (4)	−1506 (4)	181 (10)	35 (3)	67 (3)	39 (9)	120 (8)	7 (5)
C(6)	4639 (22)	1361 (11)	−1071 (11)	186 (28)	55 (7)	52 (8)	49 (24)	81 (22)	−17 (13)
C(6′)	4731 (20)	1372 (10)	−769 (12)	134 (26)	44 (6)	81 (9)	29 (21)	102 (22)	−17 (12)
C(7)	5808 (19)	2081 (13)	−1084 (12)	119 (22)	66 (10)	64 (9)	12 (26)	74 (20)	9 (16)
C(7′)	5813 (22)	2061 (15)	4 (12)	197 (26)	99 (13)	65 (9)	−17 (32)	122 (21)	7 (18)
C(8)	5468 (24)	2708 (11)	−595 (15)	245 (34)	41 (7)	101 (14)	−86 (26)	76 (34)	26 (16)
C(8′)	5510 (23)	2890 (12)	−523 (14)	169 (31)	54 (8)	85 (12)	16 (27)	67 (30)	−10 (17)
C(9)	3212 (11)	3012 (5)	−1124 (6)	191 (14)	41 (3)	69 (5)	−31 (12)	89 (12)	7 (7)
C(10)	1759 (9)	2328 (5)	−1576 (5)	153 (10)	36 (3)	40 (3)	−7 (10)	74 (8)	2 (5)
C(11)	−2664 (13)	515 (6)	−3122 (7)	323 (19)	38 (3)	111 (6)	−82 (14)	187 (15)	−51 (7)
O(12)	−2325 (13)	−81 (5)	−3341 (7)	484 (23)	50 (3)	180 (6)	−30 (15)	203 (18)	−92 (7)
O(13)	−4500 (10)	770 (5)	−3416 (7)	317 (15)	73 (3)	248 (7)	−160 (12)	280 (16)	−159 (8)
C(14)	−6408 (22)	265 (10)	−4184 (11)	536 (38)	95 (8)	149 (10)	−164 (28)	215 (28)	−9 (15)
C(15)	−7015 (26)	−70 (13)	−3681 (10)	1166 (48)	151 (11)	165 (9)	−428 (35)	602 (26)	−59 (16)
C(16)	5355 (27)	1066 (13)	−4 (12)	394 (42)	76 (10)	59 (9)	202 (32)	149 (30)	76 (15)
C(16′)	5601 (31)	1260 (20)	−1417 (14)	430 (44)	136 (19)	95 (11)	95 (48)	268 (29)	−39 (23)
O(17)	1777 (10)	266 (4)	−1813 (6)	345 (15)	31 (2)	183 (6)	46 (10)	221 (14)	−7 (7)
C(18)	−1052 (11)	3300 (5)	−2173 (6)	214 (15)	28 (3)	81 (5)	50 (11)	81 (13)	−1 (6)
S(19)	1833 (3)	2295 (2)	961 (2)	176 (3)	73 (1)	61 (1)	−65 (4)	116 (2)	−25 (2)
O(20)	4017 (9)	2293 (6)	1534 (6)	180 (12)	126 (5)	160 (6)	−110 (15)	152 (12)	−96 (10)
O(21)	925 (20)	2295 (8)	−40 (8)	526 (33)	56 (6)	60 (6)	−24 (25)	225 (20)	8 (10)
O(21′)	753 (18)	2293 (10)	1426 (8)	418 (25)	106 (8)	63 (6)	57 (26)	253 (16)	−8 (11)
O(22)	1041 (20)	2927 (11)	1382 (10)	354 (26)	99 (10)	125 (8)	42 (28)	262 (20)	−19 (15)
O(22′)	909 (25)	2855 (11)	98 (10)	648 (45)	91 (8)	98 (8)	89 (34)	289 (26)	82 (13)
O(23)	1044 (21)	1529 (12)	1258 (9)	442 (31)	131 (11)	62 (7)	−163 (30)	175 (20)	36 (13)
O(23′)	1142 (22)	1502 (12)	273 (11)	367 (33)	147 (10)	151 (10)	−193 (32)	268 (26)	−200 (15)
C(24)	1792 (30)	759 (11)	943 (13)	970 (73)	62 (8)	200 (13)	−19 (42)	375 (46)	11 (18)

O(21), O(22) and O(23) are doubly positioned, two conformations could be assigned to the methyl sulphate group, in which S(19), O(20) and C(24) are common.

With the two conformations for the methyl sulphate group, and with a weighting factor of 0·5 for the doubly positioned atoms, R decreased to 0·244. Three cycles of least-squares refinement with isotropic thermal parameters for the doubly positioned atoms and three cycles with anisotropic thermal parameters for all atoms resulted in $R=0·131$.

From the difference function no hydrogen positions could be determined. Therefore all the hydrogen atoms but those of the methyl groups were geometrically generated and were given the isotropic temperature factors of their corresponding carbon atoms.

Taking into account the generated hydrogen atoms and deleting two reflexions (020 and $\bar{1}14$) affected by extinction two further cycles of anisotropic least-squares refinement of non-hydrogen atoms resulted in final R values of 0·113 and 0·170 for observed and for all the reflexions, respectively. With the doubly positioned atoms the refinement was convergent and no trend towards superimposition of the two conformations was observed. This seems to be a satisfactory sign that the molecule adopts two different conformations in a statistical distribution, although this is an unexpected phenomenon. The final atomic parameters are given in Tables 1 and 2. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962).*

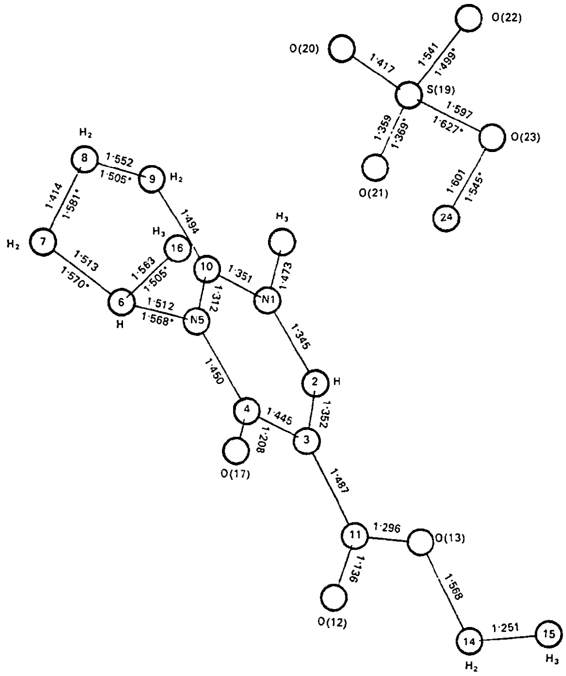

Fig. 1. The atomic numbering and identification of the atoms of the two conformations of the molecule (A and B), with bond lengths. The bond lengths for conformation B are indicated by asterisks.

Table 2. *Generated fractional coordinates and isotropic thermal parameters* (Å^2) *of the hydrogen atoms not belonging to the methyl groups*

The temperature parameters are those of the corresponding carbon atoms to which the hydrogen atoms are bonded and were obtained in the last isotropic least-squares refinement. Primed serial numbers refer to conformation B.

	x	y	z	B
H(2)	−0·319	0·205	−0·296	3·8
H(6)	0·479	0·092	−0·145	4·1
H(6′)	0·478	0·087	−0·044	4·1
H(71)	0·730	0·197	−0·074	4·1
H(72)	0·525	0·225	−0·179	4·1
H(71′)	0·528	0·211	0·045	4·3
H(72′)	0·737	0·197	0·044	4·3
H(81)	0·591	0·254	0·010	5·1
H(82)	0·641	0·317	−0·049	5·1
H(81′)	0·619	0·332	−0·002	4·8
H(82′)	0·606	0·285	−0·097	4·8
H(91)	0·296	0·329	−0·064	3·7
H(92)	0·296	0·340	−0·166	3·7
H(91′)	0·279	0·335	−0·074	3·7
H(92′)	0·287	0·343	−0·165	3·7
H(141)	−0·600	−0·014	−0·452	8·2
H(142)	−0·755	0·063	−0·471	8·2

The geometry of the molecule

A schematic view of the molecule with the atomic numbering and bond lengths is given in Fig. 1. In the molecule two atomic groups can be regarded as coplanar. The atoms of the right-hand ring of the bicyclic part of the molecule, containing two nitrogen atoms, together with O(17) and C(18) are in one plane, $P1$. The second plane $P2$ is formed by the atoms of the carbethoxy group if C(15) in this group is neglected. The plane constants of the least-squares planes referred to crystal axes along with the deviations of the atoms from the planes are given in Table 3. The maximum deviations from planes $P1$ and $P2$ are 0·05 and 0·07 Å, respectively.

The left-hand ring of the bicyclic part of the molecule is distorted but along the structure the distortions occur in two different ways with a distribution of equal weights, resulting in two different conformations (A and B) of the molecule. The two conformations differ in the positions of C(6), C(7), C(8) and C(16). The least-squares planes of the atoms forming the two conformations of the left-hand ring have been calculated ($P3$ and $P4$ in Table 3), for on the basis of the deviations of atoms from these planes one can obtain some information on the distortion of the ring in question. It is found that in the two different conformations the relative positions of the atoms with respect to their

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30908 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

least-squares planes are almost identical (Table 3), with the difference that the corresponding atoms of the two conformations are on opposite sides of the planes (Fig. 2). The planes *P*3 and *P*4 are twisted relative to *P*1 in opposite directions with angles of 14·0 and 12·5°, respectively, resulting in an inclination angle of 26·3° for *P*3 and *P*4. Consequently *P*1 seems to be a mirror plane for the two conformations. This can be understood in the sense that the mirror image is always on a succeeding equivalent molecule in the lattice with the above-mentioned statistical distribution. That the two conformations of the left-hand ring are mirror images relative to *P*1 can be seen from Table 3, by comparing the normal distances of the double positions from *P*1. An exception is found for C(8), which shows rather small deviations for its two C(8) and C(8′) representations. The inclination angles of the different least-squares planes are given in Table 3.

To a rough approximation the distorted ring may be considered to be in a boat conformation in which C(7) and C(10) are the upper atoms. The dihedral angles, *i.e.* the inclination angles of the plane N(5)C(6)C(8)C(9) with the planes C(6)C(7)C(8) and N(5)C(9)C(10) are 53·2 and 3·1° in conformation *A*, and 53·5 and 7·3° in conformation *B*, respectively.

Similarly the methyl sulphate ion occurs in two different conformations, where the doubly positioned atoms O(21), O(22) and O(23) are approximate mirror images of each other through the plane *P*5, formed by the three atoms S(19), O(20) and C(24), common to both conformations. This can be seen in Fig. 3. Comparison of the interatomic distances of the same oxygen atoms of the two conformations of the methyl sulphate group with the sum of their normal distances to the mirror plane (*P*5 in Table 3), shown in Table 4, indicates an accurate mirror symmetry, the mirror images having the same sense as those described for the homopyrimidazole rings. Both conformations of the sulphate tetrahedron are rather distorted and are in relative positions to the main molecule as can be seen in Fig. 4. The bond lengths and bond angles of the molecule can be seen in Tables 5 and 6.

Table 3. *Least-squares planes of the molecule with atomic deviations from the planes*

The plane constants ($Ax+By+Cz=D$) are referred to crystal axes and coordinates in Å.

Plane	*A*	*B*	*C*	*D*
*P*1	−0·56405	−0·13609	0·99033	−3·73523
*P*2	−0·44855	−0·39526	0·91751	−4·02611
*P*3	−0·34963	−0·18308	0·96455	−3·48877
*P*4	−0·71377	−0·02008	0·97200	−3·62068
*P*5	−0·54572	−0·00445	0·99979	0·74620

Plane		Distances to plane (Å)			
*P*1	N(1), C(2), C(3), C(4)	−0·0004	−0·0071	−0·0349	−0·0058
	N(5), C(10), O(17), C(18)	−0·0286	−0·0179	0·0547	0·0400
–	C(6), C(7), C(8), C(9)	−0·2516	−0·9346	−0·1558	−0·0831
	C(6′), C(7′), C(8′), C(11)	0·1820	0·7813	−0·1005	−0·1468
	O(12), O(13), C(14), C(15)	−0·5068	0·1257	−0·1501	0·9777
	C(16), C(16′)	1·1852	−1·1892		
*P*2	C(3), C(11), O(12), O(13)	−0·0561	0·0410	0·0018	0·0718
	C(14)	−0·0585			
–	C(2), C(4), C(18), O(17)	−0·4156	0·1925	−0·9803	0·5940
	C(15)	1·1066			
*P*3	N(5), C(6), C(7), C(8)	0·0415	0·1863	−0·3681	0·2797
	C(9), C(10)	−0·0226	−0·1168		
–	C(4), C(6′), C(7′), C(8′)	−0·0827	0·6216	1·3059	0·3228
	N(1), C(18), C(16), C(16′)	−0·4263	−0·5809	1·7227	−0·5706
*P*4	N(5), C(6′), C(7′), C(8′)	−0·0775	−0·1947	0·3870	−0·2905
	C(9), C(10)	0·0295	0·1462		
	C(4), C(6), C(7), C(8)	−0·0099	−0·6110	−1·2930	−0·3728
	N(1), C(18), C(16), C(16′)	0·4414	0·7235	0·6580	−1·6672
*P*5	S(19), O(20), C(24)	0·0	0·0	0·0	
–	O(21), O(22), O(23)	−1·2129	0·9952	0·8072	
	O(21′), O(22′), O(23′)	1·1900	−0·9910	−0·7998	

Inclination angles of least-squares planes of the molecule

*P*1,*P*2	16·6°	*P*1,*P*3	14·0°
*P*3,*P*4	26·3	*P*1,*P*4	12·5

Table 4. *Interatomic distances and sums of normal distances to the mirror plane (P5 in Table 3) of the two positions of the same atoms in the two conformations of the methyl sulphate group*

Two positions of the same atom	Interatomic distance	Sum of normal distances to mirror plane
O(21)-O(21′)	2·404 Å	2·403 Å
O(22)-O(22′)	1·994	1·986
O(23)-O(23′)	1·608	1·607

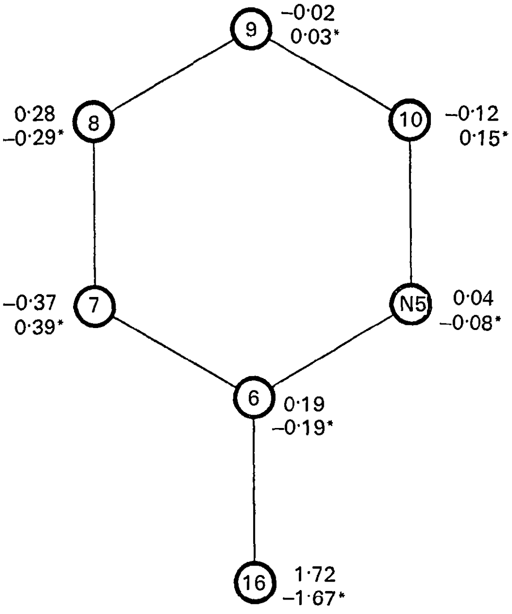

Fig. 2. A schematic view of the two conformations of the left-hand ring of the bicyclic part of the molecule showing the deviations (Å) of the atoms from their least-squares planes. Deviations referring to conformation *B* are marked with asterisks.

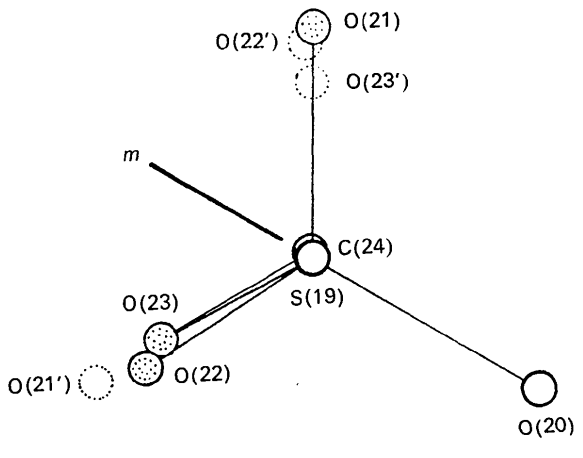

Fig. 3. The orthogonal projections of the two conformations of the methyl sulphate group onto the plane (010). The atoms of conformation *B* are represented by dotted spheres. The thick line *m* represents the intersection of the mirror plane, formed by S(19), O(20) and C(24), with (010).

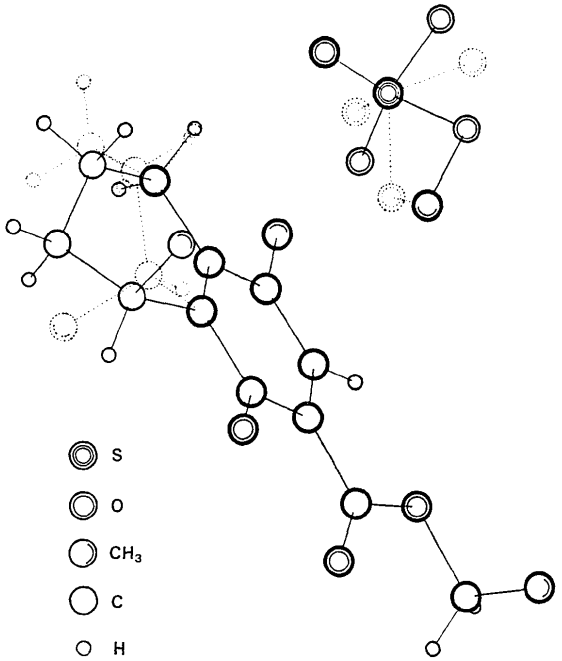

Fig. 4. Stereoscopic projection of the two conformations of the whole molecule and the methyl sulphate group in their relative positions. The atoms of conformation *B* are represented by dotted spheres.

Table 5. *Bond lengths* (Å) *with their estimated standard deviations in parentheses*

Primed numbers refer to atoms of conformation *B* of the molecule.

N(1)–C(2)	1·345 (9)	C(8)—C(9)	1·552 (22)
N(1)–C(10)	1·351 (9)	C(8′)–C(9)	1·505 (22)
N(1)–C(18)	1·473 (10)	C(9)—C(10)	1·494 (12)
C(2)–C(3)	1·352 (11)	C(11)–O(12)	1·136 (14)
C(3)–C(4)	1·445 (12)	C(11)–O(13)	1·296 (14)
C(3)–C(11)	1·487 (13)	O(13)–C(14)	1·568 (19)
C(4)–N(5)	1·450 (12)	C(14)–C(15)	1·251 (26)
C(4)–O(17)	1·208 (12)	S(19)–O(20)	1·417 (9)
N(5)–C(6)	1·512 (19)	S(19)–O(21)	1·359 (14)
N(5)–C(6′)	1·568 (18)	S(19)–O(21′)	1·369 (15)
N(5)–C(10)	1·312 (10)	S(19)–O(22)	1·541 (17)
C(6)–C(7)	1·513 (25)	S(19)–O(22′)	1·499 (18)
C(6′)–C(7′)	1·570 (27)	S(19)–O(23)	1·597 (17)
C(6)–C(16)	1·563 (27)	S(19)–O(23′)	1·627 (18)
C(6′)–C(16′)	1·505 (32)	C(24)–O(23)	1·601 (26)
C(7)–C(8)	1·414 (27)	C(24)–O(23′)	1·545 (27)
C(7′)–C(8′)	1·581 (29)		

Discussion of the structure

In several homopyrimidazole derivatives, *e.g.* $C_{12}H_{12}N_2O_3$ (Sasvári, Csonka Horvai & Simon, 1972), $C_{12}H_{16}N_2O_3$ (Sasvári & Simon, 1973) and $C_{13}H_{20}N_2O_3$ (Simon & Sasvári, 1972) the left-hand rings with one nitrogen atom show marked differences in their conformations. This is especially striking in the title molecule in which two different conformations occur within the symmetry-related positions with an equal distribution, as described above.

In the title molecule, as in the above-mentioned homopyrimidazole derivatives, N(5) is coplanar with its immediate three neighbouring carbon atoms, in spite of the change in conformation and individual bond distances from one derivative to the other. In the cases of $C_{13}H_{20}N_2O_3$ and the title molecule, however, where a methyl group is linked to N(1), the deviation from the plane of the three neighbouring carbon atoms is slightly greater than in the other two cases, as can be seen in Table 7. In the latter two cases also N(1) is coplanar with its three neighbouring carbon atoms.

In the title molecule the three individual N(5)–C bond lengths, in both conformations, deviate from the corresponding ones in the above three derivatives but their average for the two conformations, 1·434 Å, compares with the averages of the three derivatives (1·428, 1·426 and 1·438 Å) within 1σ.

The most critical bond length of the homopyrimidazole derivatives is C(4)–N(5) in the right-hand ring. This bond is very long (1·472 Å) in $C_{12}H_{12}N_2O_3$ and causes an opening of the ring in aqueous solution (Sasvári, Csonka Horvai & Simon, 1972). In $C_{12}H_{16}N_2O_3$ with the left-hand ring saturated, however, this bond is shortened to 1·411 Å so that in aqueous solution no ring opening occurs (Sasvári & Simon, 1973). Saturation and methylation causes this bond to become still shorter 1·372 Å, in $C_{13}H_{20}N_2O_3$ (Simon & Sasvári, 1972). In the present derivative this bond is again increased to 1·450 Å and is only 0·022 Å shorter than in $C_{12}H_{12}N_2O_3$ but is apparently strong enough to keep the ring stable in aqueous solution. It may be, however, that it is not only this bond length which is responsible for the stability of the ring. C(10)–N(1) and C(10)–N(5) with length of 1·351 and 1·312 Å are, in reverse sequence, almost the same as those in $C_{12}H_{16}N_2O_3$ (1·322 and 1·359 Å). Although the double bond is assumed to be between C(10) and N(1), because of similar short bond lengths, the possibility cannot be excluded that the double bond also belongs to the atom pairs C(10) and N(5).

All the atoms of the right-hand ring of the title molecule similar to $C_{12}H_{16}N_2O_3$ are in one plane with deviations less than 0·02 Å, while in $C_{12}H_{12}N_2O_3$ the C(4) and in $C_{13}H_{20}N_2O_3$ the C(10) atoms are out of the least-squares plane of the ring.

Considering saturation conditions the atomic bond lengths involved in the common part of the two conformations compare with those of the other homopyrimidazole derivatives. Significant differences were found only at the end of the ethoxy group with bond lengths of 1·568 and 1·251 Å for C(13)–C(14) and C(14)–C(15) respectively, in comparison with 1·450–1·489 and 1·414–1·489 Å in the other derivatives, respectively. These deviations cannot be explained but may have the same origin as that which resulted in the two conformations of the molecule.

Table 6. *Bond angles* (°) *with their estimated standard deviations in parentheses*

Primed numbers as in Table 5.

C(2)—N(1)–C(10)	121·4 (6)	C(7′)—C(8′)—C(9)	104·6 (14)
C(2)—N(1)–C(18)	117·8 (6)	C(8)—C(9)—C(10)	109·7 (10)
C(10)–N(1)–C(18)	120·9 (6)	C(8′)—C(9)—C(10)	121·4 (10)
N(1)—C(2)–C(3)	121·7 (7)	C(9)—C(10) –N(1)	118·0(7)
C(2)—C(3)–C(4)	119·9 (8)	C(9)—C(10) –N(5)	122·0 (7)
C(2)—C(3)–C(11)	121·1 (8)	N(1)—C(10) –N(5)	120·0 (7)
C(4)—C(3)–C(11)	118·9 (8)	C(3)—C(11) –O(12)	125·5 (10)
C(3)—C(4)–N(5)	113·7 (8)	C(3)—C(11) –O(13)	110·2 (9)
C(3)—C(4)–O(17)	127·7 (9)	O(12)–C(11) –O(13)	124·1 (11)
N(5)—C(4)–O(17)	118·6 (8)	C(11) –O(13)–C(14)	119·0 (10)
C(4)—N(5)–C(6)	111·5 (9)	O(13)–C(14) –C(15)	104·7 (14)
C(4)—N(5)–C(6′)	114·8 (8)	O(20)–S(19)—O(21)	116·8 (7)
C(4)—N(5)–C(10)	123·2 (7)	O(20)–S(19)—O(21′)	119·6 (7)
C(10)–N(5)–C(6)	124·8 (9)	O(20)–S(19)—O(22)	108·8 (7)
C(10)–N(5)–C(6′)	121·2 (8)	O(20)–S(19)—O(22′)	114·5 (8)
N(5)—C(6)–C(7)	108·3 (13)	O(20)–S(19)—O(23)	108·0 (7)
N(5)—C(6′)–C(7′)	109·1 (13)	O(20)–S(19)—O(23′)	106·5 (8)
N(5)—C(6)–C(16)	104·1 (13)	O(21)–S(19)—O(22)	115·7 (9)
N(5)—C(6′)–C(16′)	104·6 (14)	O(21′)-S(19)—O(22′)	111·7 (9)
C(7)—C(6)–C(16)	113·5 (15)	O(21)–S(19)—O(23)	107·9 (9)
C(7′)–C(6′)–C(16′)	112·8 (16)	O(21′)-S(19)—O(23′)	106·7 (9)
C(6)—C(7)–C(8)	108·0 (16)	O(22)–S(19)—O(23)	97·6 (9)
C(6′)–C(7)′–C(8′)	111·6 (16)	O(22′)-S(19)—O(23′)	94·1 (10)
C(7)—C(8)–C(9)	115·0 (16)	S(19)—O(23)–C(24)	108·0 (12)
		S(19)—O(23′)–C(24)	109·2 (13)

Table 7. *Deviations* (Å) *of the nitrogen atoms* [N(5) *and* N(1)] *from the planes of their three neighbouring carbon atoms in different homopyrimidazole derivatives*

Atoms forming the plane	$C_{12}H_{12}N_2O_3$	$C_{12}H_{16}N_2O_3$	$C_{13}H_{20}N_2O_3$	$C_{14}H_{22}O_7N_2S$	
				A	*B*
C(4), C(6), C(10)	−0·023	0·002	−0·150	0·057	−0·074
C(2), C(10), C(18)	—	—	−0·043	—0·004	

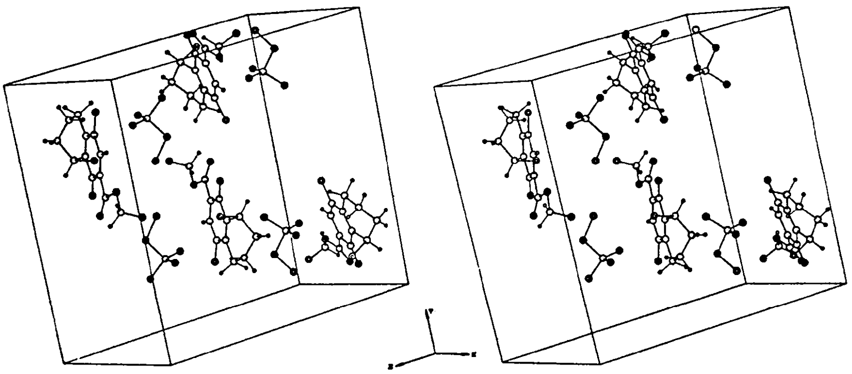

Fig. 5. Stereoscopic projection of the unit-cell contents down a direction deviating from the *c* axis by a rotation of the crystal about *x* and *y* by 20 and −35°, respectively. For simplicity only the *A* conformation is given in the projection. The methyl carbon atoms are represented by double circles and the oxygens by filled circles.

The nearest intermolecular neighbours of the two nitrogen atoms, at distances less than 3·50 Å, are O(21) and O(22) of both conformations of the sulphate group. These N–O distances are given in Table 8. The lengths of N(1)–O(21) and N(1)–O(21′) (2·917 and 2·865 Å) are, within experimental error, equal to the sum of the van der Waals radii (2·90 Å) but N(1)–O(22) and N(1)–O(22′) (3·147 and 3·176 Å) are slightly longer. The lengths of the oxygen contacts to N(5) are greater still.

Table 8. *Nearest intermolecular atomic neighbours to nitrogen atoms with interatomic distances*

From atom in *x,y,z*	To atom	In position	Distance (Å)
N(1)	O(21)	$x, \quad y, \quad z$	2·917
	O(22)	$x, \frac{1}{2}-y, -\frac{1}{2}+z$	3·147
	O(21′)	$x, \frac{1}{2}-y, -\frac{1}{2}+z$	2·865
	O(22′)	$x, \quad y, \quad z$	3·176
N(5)	O(21)	$x, \quad y, \quad z$	3·305
	O(22)	$x, \frac{1}{2}-y, -\frac{1}{2}+z$	3·050
	O(21′)	$x, \frac{1}{2}-y, -\frac{1}{2}+z$	3·393
	O(22′)	$x, \quad y, \quad z$	3·447

N(1) and N(5) of the same molecule are linked to O(21) as well as to O(22) in such a way that the oxygen atoms belong to different symmetry-related positions. This is true for the same distances involving both conformations of the sulphate group, except that in these two cases the corresponding oxygen atoms belong to opposite symmetry-related positions, as is evident from Table 8. It follows that the homopyrimidazole molecules are linked to the sulphate groups in the form N(1)–O(21)–O(22)–N(5)^3, where O(21) and O(22) belong to the same sulphate group and N(5)^3 means the third symmetry-related position relative to that of N(1). This is true for both conformations, as can be seen in Table 8.

Van der Waals and still shorter C–O intermolecular distances exist for the two conformations of the sulphate group. These contacts are given in Table 9.

Table 9. *Shortest intermolecular* O–C *contacts*

From atom in *x,y,z*	To atom	In position	Distance (Å)
O(20)	C(2)	$1+x, \frac{1}{2}-y, \frac{1}{2}+z$	3·117
O(21)	C(10)	$x, \quad y, \quad z$	2·833
O(22)	C(10)	$x, \frac{1}{2}-y, \frac{1}{2}+z$	3·025
O(21′)	C(10)	$x, \frac{1}{2}-y, \frac{1}{2}+z$	2·918
O(22′)	C(10)	$x, \quad y, \quad z$	3·183

It can thus be concluded that the positions of the two conformations of the methyl sulphate group relative to the homopyrimidazole molecule are indistinguishable insofar as the lengths of the corresponding intermolecular N–O and C–O contacts are concerned. This also verifies the reality of the two conformations of the molecule within the symmetry-related positions.

The packing is shown in a stereoscopic projection in Fig. 5, where for simplicity, the molecules are represented by only one of the two conformations (*A*). As the methyl hydrogen atoms could not be located, their carbon atoms are specially marked in the projection.

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