Acta Cryst. (1970). B**26**, 1736

The Crystal Structure of 2-Methylaminobenzothiazole

BY M. FEHLMANN*

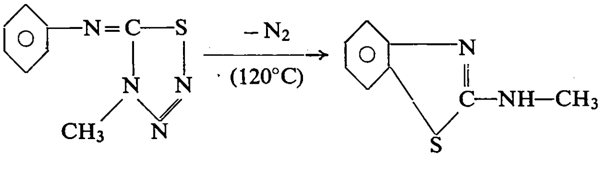
Mineralogisches Institut der Universität Karlsruhe, Germany

(*Received* 23 *July* 1969)

The crystal structure of 2-methylaminobenzothiazole, $C_8H_8N_2S$, has been determined and refined by three-dimensional Fourier and least-squares methods. The crystals are monoclinic, space group $P2_1/c$, with $a=5{\cdot}585$, $b=7{\cdot}073$, $c=20{\cdot}292$ Å, $\beta=93{\cdot}22°$; $Z=4$. The conventional R value on F for 1244 observed reflexions is 0·034. The atoms of the benzene ring are coplanar within experimental errors; the C–C bond lengths, however, vary significantly from 1·372 to 1·391 Å. The other non-hydrogen atoms are out of the benzene-ring plane in the same direction by 0·01 to 0·08 Å. No intermolecular distances shorter than the sums of corresponding van der Waals radii are found. Maximum residual electron density of about 0·20 e.Å^{-3} is found on the S–C bonds.

Introduction

Heating of a solution of 4-methyl-5-phenylimino-1,2,3,4-thiatriazole (I) at 120°C gives the product $C_8H_8N_2S$ (Tauber, 1969). Colourless, prismatic crystals of this compound may be obtained from a saturated solution in toluene. There has been some doubt as to the structure of this product and several models have been proposed. An X-ray diffraction investigation has been undertaken to determine the form, bond lengths and bond angles of this compound; the correct structure established is that shown in (II).



(I) (II)

Experimental

Crystals of the compound were kindly prepared by Dr J. Tauber. A crystal specimen of dimensions 0·03 by 0·06 by 0·06 cm was mounted about the c^* axis. Preliminary examination of precession photographs showed systematic absences for $0k0$ reflexions with k odd and for $h0l$ reflexions with l odd. The density was measured by flotation in a mixture of methanol and carbon tetrachloride. The crystal was then transferred to a Picker four-circle diffractometer. Twelve reflexions were accurately centred and their angle-readings on the four circles formed the basis for a least-squares refinement of cell-parameters and orientation. The results are listed in Table 1.

Table 1. *Crystal data for 2-methylaminobenzothiazole*

($\lambda_{\text{Mo }K\bar{\alpha}}=0{\cdot}71069$ Å)

Monoclinic, space group $P2_1/c$

a	5·585 ± 0·007 Å
b	7·073 ± 0·008
c	20·292 ± 0·022
β	93·22 ± 0·05°
V	800·3 Å^3
Z	4
D_o	1·360 ± 0·010 g.cm^{-3}
D_c	1·363 ± 0·006 g.cm^{-3}

Intensity data with Nb-filtered Mo $K\alpha$ radiation were collected by the θ–2θ scan technique at a scan rate of 1·0° min^{-1}. The scan range was increased towards greater θ values to allow for the $\alpha_1-\alpha_2$ separation. Background measurements of 40 seconds were made at each end of the scan. Up to five copper foils were used as attenuators for strong reflexions. A total of 3655 reflexions with $2\theta \le 50°$ was measured. All intensities were placed on the same scale, then background, Lorentz–polarization (Lp) and absorption corrections were applied. The linear absorption coefficient μ for Mo $K\alpha$ is 3·1 cm^{-1}, the absorption factors (A) range from 0·845 to 0·921. Reflexions with net counts (Q) less than 5% of the total background count (Bg) or less than a specified threshold count were classified as unobserved and their net counts were replaced by the threshold count. Individual standard deviations $\sigma(F_o)$ were assigned to the structure amplitudes:

$$\sigma(F_o)=\tfrac{1}{2}\text{Lp}(a+b^2)^{1/2}(F_o)^{-1}\,,$$

where $a=Q+2\text{Bg}$ accounts for statistical counting errors, and $b=0{\cdot}01\,Q$, allowing for systematic errors, has been determined from the differences among equivalent reflexions. The F_o, $\sigma(F_o)$ and T values ($T=-A^{-1}\text{d}A/\text{d}\mu$, is a parameter in Zachariasen's (1967) structure amplitude formula) were averaged for equivalent reflexions. The number of independent reflexions thus obtained was 1400, of which 156 were classified as unobserved.

---

* Present address: School of Physics, University of Melbourne, Parkville, Victoria 3052, Australia.

Structure determination and refinement

The coordinates of the sulphur atom were found from a three-dimensional Patterson synthesis. Structure amplitudes were calculated for the sulphur atom and a subsequent Fourier synthesis revealed all non-hydrogen atoms. After two more cycles of structure amplitude calculations and Fourier syntheses, least-squares refinement (two cycles with isotropic and two cycles with anisotropic thermal parameters) were carried out. Zachariasen's structure amplitude formula which includes the kinematical approximation F_k as well as an extinction factor E was used for the calculation of structure amplitudes. A least-squares program (Busing, Martin & Levy, 1962*a*) was modified so that structure amplitudes F_z were calculated according to Zachariasen's (1967) general formulae (46*a*) to (46*d*), and the extinction parameter r^* could be varied. The equations used are:

$$F_z = F_k \times E$$

$$E = \left[1 + X\,\frac{2(1+\cos^4 2\theta)}{(1+\cos^2 2\theta)}\right]^{-1/4}$$

$$X = \left|\frac{e^2F_k}{mc^2V}\right|^2 \frac{\lambda^2}{\sin 2\theta}\, r^*T\,,$$

where T is the mean path length defined above, and the other symbols have their usual meaning.

The sites of eight hydrogen atoms were found from a difference synthesis computed at this stage ($R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0{\cdot}07$). Including the eight hydrogen atoms with isotropic thermal parameters ($R_1 = 0{\cdot}055$), three more cycles of least-squares refinement reduced R_1 and R_2 (weighted R value) to 0·035 and 0·032, respectively. A further cycle af least-squares refinement was carried out in which the hydrogen atoms were also assigned variable anisotropic thermal parameters; this reduced the R_1 and R_2 values to 0·034 and 0·031 respectively. The R_1 and R_2 values for all reflexions, including the 156 classified as unobserved, were 0·040 and 0·039.

At the conclusion of the refinement a three-dimensional difference map was calculated; a section through the plane of the planar part of the molecule is shown in Fig. 3. The final positional and thermal parameters are listed in Table 2, the calculated and observed structure amplitudes are given in Table 3. The extinction parameter r^* obtained from the least-squares refinement is $0{\cdot}869 \times 10^{-5}$ cm. Atomic scattering amplitudes for neutral atoms of S, N, C and H were taken from *International Tables for X-ray Crystallography* (1962).

Discussion

The geometry of the molecule

A mean plane has been calculated for the carbon atoms of the benzene ring. The results are given in Table 4; they show that the atoms of the benzene ring are coplanar within experimental crrors, whereas the other non-hydrogen atoms are significantly out of the benzene ring plane and all are displaced in the same direction.

The bond distances and angles calculated from the parameters of Table 2 are shown in Fig. 1. The estimated standard deviations are 0·003 Å and 0·2° for non-hydrogen atom bonds and angles, 0·025 Å and 1·5° for bonds and angles involving hydrogen atoms. The six C–C bonds in the benzene ring vary in length from 1·372 to 1·391 Å, thus indicating a significant distortion from a standard benzene ring. The mean value of 1·383 Å for these bond distances is significantly short of the value 1·397 Å expected from electron diffraction (Almenningen, Bastiansen & Fernholt,

Table 2. *The final positional and thermal parameters*

The parameters and standard deviations (in parentheses) of the hydrogen atoms have been multiplied by 10^4; those of the non-hydrogen atoms by 10^5. The expression for the temperature factor is

$$\exp\left[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)\right].$$

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
S	07703 (11)	08333 (09)	13966 (03)	3656 (25)	2116 (16)	223 (02)	−589 (16)	376 (05)	−14 (04)
N(1)	44007 (29)	15885 (25)	06902 (09)	2481 (64)	1813 (44)	263 (06)	−530 (44)	206 (15)	−145 (13)
N(2)	23894 (34)	−11923 (25)	03928 (09)	3801 (79)	1666 (45)	269 (06)	−867 (49)	308 (16)	−129 (14)
C(1)	57847 (44)	45679 (38)	12089 (13)	3406 (92)	2524 (66)	364 (08)	−709 (67)	274 (22)	−304 (20)
C(2)	54417 (46)	59028 (34)	16896 (14)	4090 (107)	2623 (71)	405 (09)	−640 (73)	46 (25)	−371 (22)
C(3)	35879 (45)	57287 (38)	21111 (12)	4242 (106)	2568 (68)	286 (08)	482 (74)	−112 (22)	−298 (19)
C(4)	20495 (43)	42164 (37)	20582 (11)	3990 (97)	2582 (67)	206 (06)	470 (68)	75 (19)	−98 (17)
C(5)	23985 (35)	28838 (30)	15743 (09)	2892 (76)	1899 (52)	177 (06)	170 (54)	48 (16)	−1 (14)
C(6)	42456 (35)	30280 (30)	11457 (10)	2584 (76)	1872 (53)	221 (06)	−104 (54)	28 (17)	−106 (15)
C(7)	27287 (35)	03476 (30)	07667 (10)	2722 (77)	1832 (52)	205 (06)	−136 (54)	98 (17)	3 (15)
C(8)	05667 (52)	−25838 (39)	04963 (14)	5032 (111)	2085 (61)	307 (07)	−1320 (71)	221 (23)	−9 (18)
H(1)	7018 (42)	4664 (38)	0900 (12)	384 (77)	183 (50)	37 (06)	−106 (52)	38 (16)	−45 (15)
H(2)	6442 (43)	7018 (40)	1724 (13)	397 (81)	175 (56)	39 (07)	−110 (55)	16 (19)	−47 (16)
H(3)	3453 (43)	6668 (38)	2453 (12)	345 (79)	270 (51)	29 (06)	46 (52)	5 (17)	−46 (14)
H(4)	0695 (42)	4111 (33)	2378 (12)	354 (77)	208 (49)	19 (05)	20 (53)	11 (14)	−6 (15)
H(5)	3468 (41)	−1403 (34)	0026 (12)	384 (74)	129 (42)	30 (05)	−135 (46)	42 (15)	−22 (12)
H(6)	0514 (45)	−3423 (37)	0160 (12)	601 (90)	194 (49)	33 (06)	−264 (56)	44 (18)	−20 (14)
H(7)	0891 (44)	−3232 (37)	0906 (13)	484 (86)	275 (49)	34 (06)	−224 (54)	22 (18)	20 (14)
H(8)	−0943 (45)	−1890 (38)	0564 (12)	414 (92)	199 (51)	43 (06)	−90 (54)	48 (18)	5 (14)

1958) and neutron diffraction (Bacon, Curry & Wilson, 1964) results. This may be partly due to the omission of libration correction and partly to the neglect of bonding electrons in the atomic scattering amplitudes; it has only recently been appreciated that the use of 'spherical' scattering amplitudes not only affects bond lengths to terminal atoms but also shortens bonds such as carbon–carbon in benzene (*e.g.* O'Connell, Rae & Maslen, 1966). Much the same can be said of the mean value for carbon–hydrogen bond lengths of 0·968 Å.

The C–S distances of 1·739 and 1·763 Å can be considered as pure single bonds (if the shortening of the bonds due to hydridization is taken into account); this can also be said of the C(6)–N(1) distance. The NH–CH_3 distance of 1·440 Å is in accord with similar bonds

Table 3. *Observed and calculated structure amplitudes* (×10).

Asterisks denote reflexions classified as unobserved.

L	FO	FC
H=	0, K=	0
4	716	-728
6	57	74
8	72	-63
10	347	-343
12	257	-254
14	274	267
16	22*	-5
18	80	-77
H=	0, K=	1
1	387	355
2	590	-537
3	422	397
4	201	206
5	435	-440
6	589	603
7	220	223
8	95	94
9	305	-307
10	24	-28
11	211	-216
12	157	156
13	189	188
14	12*	-5
15	136	139
16	154	-155
17	102	-101
18	52	-50
19	155	-159
H=	0, K=	2
0	227	227
1	328	-325
2	289	-286
3	158	-153
4	136	-135
5	257	265
6	14	16
7	21	25
8	104	110
9	10	-16
10	117	114
11	279	273
12	64	-68
13	148	152
14	156	159
15	160	-160
16	13*	3
17	158	-164
18	134	-138
H=	0, K=	3
1	69	-67
2	311	-311
3	181	-176
4	97	-95
5	33	-36
6	239	233
7	138	130
8	11	-5
9	26	20
10	116	-113
11	70	70
12	214	217
13	49	53
14	122	129
15	37	-43
16	202	-206
17	13	-17
H=	0, K=	4
0	185	-185
1	258	-256
2	27	26
3	104	-98
4	13*	-11
5	321	317
6	100	-102
7	21	24
8	21	-21
9	155	-155
10	66	65
11	69	72
12	60	62
13	56	57
14	61	-64
15	91	-95
16	15	14
17	17	-12
18	70	74
19	36	37
20	12*	-11
21	24	21
H=	0, K=	5
1	180	-181
2	134	-134
3	99	100
4	57	55
5	131	132
6	153	149
7	257	-255
8	67	-70
9	12*	0
10	79	-79
11	156	158
12	24	25
13	13	13
14	13	6
15	12*	4
16	70	-68
17	27	27
18	17	14
19	22	21
H=	0, K=	6
0	209	-202
1	50	49
2	99	101
3	12*	9
4	79	77
5	147	-148
6	149	-149
7	61	-64
8	60	-61
9	22	22
10	84	87
11	12*	13
12	100	100
13	14*	14
14	71	-71
15	13	-11
16	22	27
H=	0, K=	7
1	44	43
2	72	-67
3	16*	13
4	104	-103
5	49	46
6	62	-62
7	106	-104
8	16*	6
9	17	-15
10	36	37
11	37	37
12	27	-24
13	27	-25
H=	0, K=	8
0	58	-55
1	23	21
2	59	55
3	13*	-8
4	64	63
5	78	-76
6	17	-16
7	13*	-7
H=	1, K=	0
0	139	-124
2	794	-765
4	11*	-11
6	70	-68
8	100	97
10	381	-384
12	67	64
14	168	163
16	184	-172
18	58	-56
20	89	88
22	121	129
-2	895	900
-4	90	80
-6	589	583
-8	286	278
-10	249	-250
-12	367	-360
-14	138	137
-16	103	105
-18	293	-286
-20	103	90
-22	132	127
-24	78	-69
H=	1, K=	1
0	291	-273
1	295	289
2	340	330
3	1272	-1180
4	966	931
5	51	-51
6	25	32
7	406	407
8	161	-163
9	97	-96
10	16	-15
11	46	-44
12	48	-47
13	12*	-16
14	176	-174
15	50	56
16	91	-92
17	121	-124
18	44	45
19	12*	-3
20	50	54
21	112	115
22	32	35
23	13*	3
-1	427	415
-2	147	146
-3	14*	-16
-4	215	-214
-5	114	-116
-6	300	-295
-7	450	448
-8	100	102
-9	270	269
-10	105	106
-11	397	-398
-12	172	-167
-13	36	-37
-14	50	-50
-15	88	86
-16	130	130
-17	30	31
-18	40	-39
-19	73	-75
-20	78	-81
-21	21	-26
-22	59	57
-23	60	60
H=	1, K=	2
0	9*	-4
1	23	-33
2	56	-55
3	95	-95
4	140	-142
5	592	598
6	96	-99
7	196	194
8	274	287
9	365	-370
10	57	-53
11	65	-64
12	28	33
13	11*	-6
14	94	95
15	124	-127
16	104	-106
17	47	-50
18	60	-62
19	128	131
20	46	49
21	15	15
22	16	23
-1	50	53
-2	82	-80
-3	346	348
-4	208	-211
-5	163	-168
-6	184	182
-7	247	-244
-8	15	25
-9	313	314
-10	28	-23
-11	124	125
-12	51	-53
-13	254	-257
-14	72	76
-15	121	-125
-16	157	161
-17	83	86
-18	69	-72
-19	16	-15
-20	44	-49
-21	58	-63
-22	13*	-11
-23	73	72
H=	1, K=	3
0	27	-35
1	10	5
2	335	-340
3	14	-20
4	272	268
5	109	106
6	90	87
7	10*	2
8	141	-138
9	30	-27
10	99	-99
11	40	38
12	116	121
13	12*	13
14	51	-51
15	13	14
16	109	-114
17	12*	-4
18	108	111
19	25	-28
20	30	33
21	16	-23
22	49	-49
-1	224	214
-2	497	490
-3	163	161
-4	77	-75
-5	152	-153
-6	30	-37
-7	221	-207
-8	177	179
-9	72	-70
-10	128	130
-11	51	-54
-12	170	-173
-13	79	77
-14	198	-208
-15	70	75
-16	35	36
-17	27	26
-18	38	41
-19	12*	7
-20	62	-64
-21	12*	5
-22	13*	-1
H=	1, K=	4
0	11*	-6
1	199	-198
2	119	112
3	29	27
4	150	146
5	234	235
6	17	15
7	87	-89
8	145	-149
9	167	-166
10	81	83
11	153	154
12	74	77
13	49	45
14	80	-83
15	77	-75
16	11*	5
17	63	-63
18	17	20
19	57	54
20	19	-22
-1	82	-74
-2	38	35
-3	348	345
-4	101	103
-5	15	-16
-6	120	-119
-7	185	-184
-8	226	-224
-9	151	152
-10	105	-110
-11	35	-32
-12	46	47
-13	204	-215
-14	12*	19
-15	31	32
-16	13	-17
-17	127	133
-18	79	85
-19	38	-40
-20	32	36
-21	28	-34
H=	1, K=	5
0	108	-107
1	40	-39
2	91	-90
3	221	223
4	90	85
5	125	-124
6	27	-30
7	64	-56
8	21	22
9	247	251
10	61	63
11	52	53
12	36	36
13	62	-65
14	43	-43
15	67	-67
16	48	-47
17	27	25
18	33	36
-1	169	-172
-2	68	66
-3	21	17
-4	26	-18
-5	82	80
-6	56	-58
-7	152	-154
-8	12*	11
-9	80	-79
-10	25	26
-11	139	145
-12	72	-72
-13	70	-75
-14	16	-12
-15	60	-66
-16	85	86
-17	82	91
-18	58	56
-19	60	64
H=	1, K=	6
0	179	-179
1	110	-109
2	13	5
3	135	-136
4	36	36
5	41	37
6	29	25
7	91	94
8	23	-21
9	15	-9
10	152	151
11	13*	14
12	25	25
13	15	13
14	87	-85
15	14	18
16	22	17
-1	28	-31
-2	123	-120
-3	12*	-8
-4	179	178
-5	12*	-2
-6	11*	7
-7	24	26
-8	78	-78
-9	20	20
-10	35	32
-11	53	59
-12	84	84
-13	13	11
-14	51	-52
-15	29	-34
-16	68	-73
H=	1, K=	7
0	52	-50
1	116	-114
2	35	35
3	98	91
4	44	-40
5	17	-18
6	42	-39
7	85	-82
8	53	51
9	35	32
10	24	24
11	31	32
12	22	-23
-1	59	-59
-2	156	-156
-3	83	80
-4	12*	5
-5	92	89
-6	110	104
-7	19	-18
-8	48	47
-9	44	-42
-10	13	-9
-11	63	61
-12	15*	16
-13	18	-20
H=	1, K=	8
0	18	16
1	13*	2
2	41	39
3	52	50
4	21	-22
5	15*	-11
6	48	-47
-1	62	-59
-2	15*	-13
-3	52	-52
-4	56	53
-5	24	25
-6	13*	5
H=	2, K=	0
0	149	157
2	285	-290
4	136	-139
6	247	252
8	120	-122
10	209	-210
12	59	53
14	50	41
16	67	63
18	42	40
20	72	68
22	22	16
-2	386	382
-4	598	-607
-6	265	-259
-8	606	597
-10	56	55
-12	214	-208
-14	11*	-2
-16	254	255
-18	72	-64
-20	162	-150
-22	125	117
H=	2, K=	1
0	25	27
1	206	-204
2	185	183
3	148	-151
4	189	-185
5	239	242
6	65	-55
7	91	89
8	81	-74
9	139	-132
10	111	-108
11	124	-125
12	41	41
13	162	161
14	30	-17
15	38	36
16	12*	10
17	82	-81
18	14	19
19	84	83
20	17	17
21	51	47
22	16	-21
-1	11*	3
-2	303	305
-3	273	-277
-4	208	206
-5	147	-149
-6	260	-266
-7	53	57
-8	201	-197
-9	303	303
-10	171	167
-11	93	-102
-12	36	40
-13	77	-74
-14	210	-210
-15	241	239
-16	80	77
-17	53	-46
-18	155	150
-19	95	-93
-20	94	-91
-21	29	25
-22	46	-48
-23	71	68
H=	2, K=	2
0	91	-87
1	372	-374
2	439	-425
3	12*	7
4	115	-114
5	166	168
6	461	471
7	517	-524
8	101	108
9	80	-81
10	177	-177
11	139	138
12	45	46
13	55	56
14	41	39
15	49	-50
16	61	-57
17	14	8
18	30	-31
19	79	80
20	30	32
21	54	-54
-1	204	207
-2	67	69
-3	326	323
-4	194	-205
-5	63	51
-6	20	10
-7	139	-139
-8	231	234
-9	187	188
-10	10*	10
-11	41	41
-12	13*	6
-13	151	-151
-14	62	-62
-15	40	39
-16	16	16
-17	50	46
-18	24	23
-19	30	-31
-20	12*	-8
-21	105	-105
-22	43	39
H=	2, K=	3
0	395	-395
1	62	-63
2	54	-58
3	75	73
4	99	98
5	10*	3
6	15	22
7	45	-48
8	339	-339
9	82	85
10	66	-66
11	46	48
12	283	283
13	68	-73
14	93	-95
15	90	-91
16	33	-31
17	12*	3
18	79	78
19	22	25
20	15	17
-1	86	-84
-2	279	279
-3	71	66
-4	282	274
-5	194	190
-6	134	-138
-7	153	151
-8	64	66
-9	47	49
-10	217	219
-11	135	-135
-12	62	63
-13	162	-163
-14	194	-195
-15	12*	-13
-16	11*	-2
-17	12	7
-18	31	35
-19	23	21
-20	113	-118
-21	27	30
H=	2, K=	4
0	57	-59
1	79	-72
2	124	124
3	107	109
4	81	78
5	145	143
6	106	-108
7	135	-138
8	25	27
9	56	58
10	78	78
11	43	-46
12	141	-141
13	68	-68
14	84	-85
15	14	-14
16	33	30
17	21	20
18	30	28
19	76	74
-1	48	46
-2	43	43
-3	12	20
-4	245	241
-5	73	-74
-6	54	51
-7	162	-167
-8	75	-74
-9	217	214
-10	23	-21
-11	169	171
-12	85	-89
-13	164	-163
-14	141	-141
-15	77	-81
-16	49	-55
-17	63	68
-18	48	49
-19	12*	11
-20	59	60
H=	2, K=	5
0	138	-139
1	50	55
2	121	120
3	129	134
4	194	193
5	51	54
6	121	119
7	18	20
8	67	-64
9	41	-40
10	70	-70
11	11*	-8
12	29	25
13	59	-60
14	69	-66
15	39	-41
16	13	-2
17	43	42
-1	97	-96
-2	37	-32
-3	12*	5
-4	12*	-11
-5	129	126
-6	146	-149
-7	49	-53
-8	56	-58
-9	187	-191
-10	105	108
-11	85	85
-12	64	64
-13	88	93
-14	81	-81
-15	146	-152
-16	13*	4
-17	18	-21
-18	35	39
H=	2, K=	6
0	52	-46
1	24	24
2	157	160
3	89	87
4	73	73
5	62	64
6	106	-104
7	28	-23
8	40	38
9	18	15
10	90	85
11	15	19
12	63	-64
13	12*	2
14	35	-32
-1	54	-54
-2	153	-150
-3	99	-101
-4	58	58
-5	44	-48
-6	13	9
-7	16	13
-8	123	-127
-9	12*	4
-10	47	48
-11	13*	-13
-12	91	94
-13	38	43
-14	12*	6
-15	13*	13
H=	2, K=	7
0	32	34
1	29	27
2	15*	10
3	84	81
4	20	-20
5	62	-63
6	12	-11
7	69	-64
8	14*	22
9	43	44
10	13*	10
-1	86	-85
-2	32	-29
-3	12*	2
-4	42	-44
-5	25	21
-6	13	6
-7	12*	-13
-8	14	-20
-9	38	-34
-10	13*	-8
-11	52	49
H=	2, K=	8
0	14*	-10
1	109	103
-1	13*	-5
-2	31	-31
H=	3, K=	0
0	18	-11
2	119	-118
4	9	-10
6	127	127
8	53	45
10	121	-123
12	91	85
14	132	126
16	62	-61
18	43	-46
20	33	29
-2	163	165
-4	94	86
-6	285	-280
-8	63	74
-10	141	137
-12	221	-221
-14	72	-80
-16	156	153
-18	20	19
-20	94	-89
-22	134	122
H=	3, K=	1
0	177	-173
1	199	-200
2	31	-34
3	120	-119
4	141	144
5	317	311
6	116	118
7	65	62
8	128	-122
9	162	-160
10	30	34
11	58	59
12	38	39
13	102	100
14	24	-24
15	20	-23
16	42	-42
17	52	-45
18	13	9
19	16	16
20	52	48
-1	266	276
-2	142	-132
-3	21	-13
-4	124	123
-5	397	-398
-6	53	-59
-7	10*	0
-8	45	-42
-9	182	183
-10	74	72
-11	22	-20
-12	76	81
-13	166	-166
-14	14	-11
-15	96	90
-16	58	-57
-17	99	97
-18	80	78
-19	71	-67
-20	13*	-8
-21	13*	-2
H=	3, K=	2
0	13	4
1	345	-345
2	63	60
3	171	169
4	178	176
5	11*	-11
6	47	46
7	67	-61
8	124	-128
9	48	50
10	23	-16
11	103	101
12	95	96
13	28	26
14	27	-25
15	118	-115
16	58	-54
17	75	76
18	50	51
19	38	33
20	15	13
-1	205	-205
-2	85	-81
-3	65	66
-4	244	-248
-5	13*	13
-6	160	-162
-7	117	-118
-8	169	174
-9	87	87
-10	66	65
-11	344	347
-12	71	-76
-13	106	-102
-14	112	109
-15	119	-111
-16	71	75
-17	126	125
-18	65	-66
-19	13	5
-20	88	-83
-21	73	-73
H=	3, K=	3
0	220	-222
1	16	16
2	85	-84
3	37	40
4	59	57
5	11*	-3
6	107	-108
7	20	-16
8	144	-145
9	85	-88
10	240	246
11	107	-112
12	12*	4
13	12*	0
14	49	-53
15	101	98
16	70	71
17	33	35
18	16	17
19	13*	-7
-1	18	20
-2	28	30
-3	32	37
-4	208	208
-5	53	-57
-6	250	-255
-7	96	-97
-8	44	44
-9	66	69
-10	267	267
-11	205	203
-12	12*	9
-13	11	10
-14	69	-69
-15	87	-85
-16	12*	3
-17	39	-34
-18	114	112
-19	39	-37
-20	85	-85
H=	3, K=	4
0	47	46
1	91	-94
2	135	134
3	151	150
4	15	-14
5	24	-25
6	142	-143
7	150	-151
8	94	-93
9	115	-112
10	41	-37
11	85	79
12	33	-37
13	121	123
14	17	20
15	83	-79
16	61	62
17	20	21
-1	12*	-3
-2	68	-65
-3	161	168
-4	83	87
-5	108	110
-6	93	94
-7	176	-177
-8	53	-56
-9	192	-191
-10	18	19
-11	187	185
-12	102	99
-13	20	12
-14	28	-30
-15	57	-63
-16	118	-117
-17	65	68
-18	18	-18
H=	3, K=	5
0	101	102
1	92	98
2	86	88
3	103	100
4	12*	-15
5	117	-119
6	77	-79
7	90	-88
8	75	-76
9	54	49
10	43	47
11	12*	9
12	15*	-15
13	61	-59
14	14*	-9
15	13*	-1
-1	91	-84
-2	66	68
-3	27	-23
-4	81	86
-5	107	110
-6	114	-114
-7	41	40
-8	110	-115
-9	65	-68
-10	24	-29
-11	15*	4
-12	12*	5
-13	67	67
-14	12*	-3
-15	41	-43
-16	13*	9
H=	3, K=	6
0	16	-12
1	24	18
2	42	40
3	45	45
4	12*	-13
5	40	-38
6	39	-38
7	43	-39
8	34	38
9	32	35
10	62	56
11	30	24
12	29	-30
-1	41	46
-2	77	-71
-3	52	54
-4	41	45
-5	14	-12
-6	96	99
-7	56	-56
-8	71	-72
-9	26	-27
-10	51	-55
-11	14*	3
-12	91	90
-13	13*	-8
H=	3, K=	7
0	51	47
1	55	50
2	20	17
3	13*	11
4	52	-45
5	77	-72
6	13*	3
7	35	34
-1	69	-71
-2	20	-20
-3	12*	-6
-4	24	-20
-5	94	94
-6	56	53
-7	19	-20
-8	13*	7
H=	4, K=	0
0	54	52
2	64	-62
4	109	115
6	125	122
8	224	-224
10	96	-94
12	152	147
14	12*	-21
16	65	-67
18	13*	1
-2	242	244
-4	39	-39
-6	184	-182
-8	27	21
-10	76	68
-12	72	-65
-14	77	-78
-16	50	46
-18	23	22
-20	140	-129
H=	4, K=	1
0	102	100
1	20	-17
2	47	46
3	56	53
4	89	90
5	78	77
6	81	-78
7	73	-72
8	66	-62
9	39	-35
10	71	74
11	11*	5
12	25	22
13	48	44
14	60	-59
15	48	-46
16	15	-11
17	34	-30
18	69	66
-1	127	129
-2	43	41
-3	124	125
-4	24	-21
-5	150	-155
-6	76	-75
-7	166	-168
-8	158	-157
-9	109	113
-10	13*	-10
-11	13	13
-12	11*	8
-13	151	-154
-14	12*	-7
-15	67	66
-16	32	34
-17	103	100
-18	91	86
-19	106	-100
H=	4, K=	2
0	43	-46
1	34	-33
2	115	-119
3	160	158
4	55	53
5	14	-15
6	52	45
7	48	-45
8	40	-39
9	23	24
10	31	31
11	87	83
12	43	42
13	27	-31
14	17	-15
15	13*	7
16	13*	12
17	19	18
-1	171	-172
-2	227	232
-3	194	195
-4	24	27
-5	26	-27
-6	243	-243
-7	226	-227
-8	53	-51
-9	95	-100
-10	103	107
-11	109	105
-12	30	-29
-13	57	52
-14	36	-40
-15	79	-78
-16	80	80
-17	121	117
-18	43	45
-19	75	78
H=	4, K=	3
0	166	-167
1	14	7
2	12*	-2
3	49	-56
4	119	120
5	90	-91
6	83	-85
7	50	-50
8	12*	12
9	32	32
10	118	113
11	100	102
12	41	29
13	64	63
14	12*	-6
15	35	-33
16	42	-40
-1	29	-29
-2	127	-128
-3	12*	4
-4	200	204
-5	92	95
-6	48	46
-7	43	46
-8	285	-287
-9	74	-70
-10	116	115
-11	49	-45
-12	129	129
-13	48	48
-14	83	-86
-15	32	33
-16	26	-26
-17	39	36
-18	98	98
H=	4, K=	4
0	14*	-1
1	51	-53
2	11*	-10
3	31	28
4	107	-111
5	49	-51
6	95	-90
7	15	-7
8	46	51
9	68	70
10	40	39
11	83	85
12	13*	11
13	80	-85
14	35	37
-1	95	-103
-2	48	-47
-3	103	106
-4	73	72
-5	13*	2
-6	106	109
-7	12	8
-8	73	-67
-9	23	25
-10	36	-34
-11	12*	12
-12	67	65
-13	21	-23
-14	32	29
-15	109	-107
-16	32	-35
H=	4, K=	5
0	55	-61
1	37	33
2	24	-31
3	12	1
4	50	51
5	61	-61
6	32	-28
7	12*	-3
8	14*	-5
9	50	47
10	38	35
11	13*	-1
12	15*	-15
-1	48	-47
-2	34	-36
-3	31	-30
-4	90	92
-5	19	21
-6	89	93
-7	12*	14
-8	72	-68
-9	50	-48
-10	12*	1
-11	19	21
-12	13*	9
-13	105	100
H=	4, K=	6
0	24	21
1	12*	5
2	78	79
3	24	-22
4	24	-17
5	37	-35
6	38	-37
7	40	40
-1	43	-48
-2	113	-113
-3	22	21
-4	26	-27
-5	64	64
-6	62	65
-7	22	24
-8	34	-30
-9	22	-16
H=	5, K=	0
0	12*	-5
2	173	-169
4	56	-52
6	12*	3
8	73	-71
10	62	69
12	33	26
14	25	-31
-2	169	170
-4	163	167
-6	70	-68
-8	44	48
-10	108	110
-12	152	-152
-14	122	-118
-16	66	68
H=	5, K=	1
0	121	-122
1	190	-190
2	20	22
3	25	25
4	87	84
5	41	38
6	27	-23
7	39	-41
8	12*	7
9	44	-38
10	13	16
11	51	50
12	42	-42
13	30	26
14	32	-29
-1	35	31
-2	64	60
-3	214	215
-4	126	124
-5	19	24
-6	13	-4
-7	55	-56
-8	73	-70
-9	12*	9
-10	12*	8
-11	39	43
-12	12*	-1
-13	104	-104
-14	88	-88
-15	46	-51
-16	53	-51
H=	5, K=	2
0	61	-65
1	59	62
2	39	38
3	60	59
4	52	51
5	12	11
6	13	9
7	23	-20
8	12*	-4
9	48	47
10	34	35
11	36	29
12	16	-15
13	64	-62
-1	131	-131
-2	61	-60
-3	34	-37
-4	78	80
-5	162	163
-6	18	-21
-7	25	-22
-8	38	-39
-9	76	-77
-10	46	47
-11	29	27
-12	39	-35
-13	13*	-2
-14	46	-47
-15	138	-133
H=	5, K=	3
0	89	-85
1	50	-47
2	93	99
3	13	-1
4	39	37
5	47	50
6	46	-45
7	48	49
8	57	57
9	21	23
10	31	23
11	15	-13
12	27	-31
-1	16	-17
-2	58	-61
-3	12*	-11
-4	36	31
-5	32	-34
-6	47	49
-7	22	-20
-8	72	-71
-9	19	21
-10	13*	7
-11	33	34
-12	88	88
-13	13*	10
-14	92	-85
H=	5, K=	4
0	12*	7
1	19	22
2	12*	11
3	78	76
4	15	-10
5	29	29
6	12*	10
7	61	-59
8	33	34
9	17	8
-1	97	-97
-2	42	-44
-3	16	13
-4	56	-60
-5	99	97
-6	61	55
-7	87	-86
-8	21	18
-9	61	-59
-10	68	-65
-11	50	57
-12	25	25
H=	5, K=	5
0	15	-13
1	78	78
2	54	57
3	13*	2
4	13*	8
5	45	-44
-1	65	-60
-2	13	-11
-3	58	-61
-4	14	-15
-5	84	76
-6	13*	-5
-7	13*	-5
H=	6, K=	0
0	186	-186
2	62	-53
4	179	178
6	26	-24
8	66	-59
-2	13*	-9
-4	62	62
-6	12*	-10
-8	13*	-14
-10	149	148
H=	6, K=	1
0	29	29
1	13	-8
2	110	109
3	20	23
4	13	-10
5	24	20
6	79	-77
7	15	9
8	19	-15
-1	85	-90
-2	58	-59
-3	27	24
-4	30	30
-5	15	-15
-6	40	40
-7	28	-29
-8	44	-47
-9	95	90
-10	13*	-12
-11	78	80
H=	6, K=	2
0	13*	-9
1	26	33
2	13*	-3
3	56	52
4	43	39
5	19	-24
6	13*	-6
7	40	-39
-1	17	-9
-2	14	6
-3	18	14
-4	14	9
-5	34	32
-6	13*	-8
-7	54	-48
-8	49	-47
-9	40	-42
H=	6, K=	3
0	13*	11
1	13*	9
2	46	48
3	26	28
4	13*	-7
-1	13*	-13
-2	53	-50
-3	15*	16
-4	17	21
-5	22	24
-6	56	55
-7	13*	-2

Table 4. *Least-squares plane*

The equation of the plane through the carbon atoms of the benzene ring is $-0{\cdot}5654x+0{\cdot}5169y-0{\cdot}6428z+1{\cdot}6523=0$. The coefficients are the direction cosines relative to *a*, *b* and *c**. Asterisks denote atoms defining the plane.

Atom	Distance from plane
S	−0·0150 Å
N(1)	−0·0110
N(2)	−0·0243
C(1)*	−0·0009
C(2)*	0·0004
C(3)*	0·0005
C(4)*	−0·0010
C(5)*	0·0005
C(6)*	0·0004
C(7)	−0·0313
C(8)	−0·0855
H(1)	0·0270
H(2)	0·0501
H(3)	−0·0364
H(4)	−0·0078
H(5)	0·0115
H(6)	0·0403
H(7)	−0·9327
H(8)	0·5607

between trigonally hybridized nitrogen and tetrahedral carbon, *e.g.* Goldstein & Trueblood (1967). The C(7)–N(1) bond length of 1·297 Å indicates a rather large double bond character, whereas the C(7)–N(2) distance of 1·335 Å is closer to an aromatic C–N bond (as *e.g.* in pyridine) than to a single bond.

No intermolecular distances are less than the sums of the corresponding atomic van der Waals radii. The shortest distances are: S–N, 3·80; S–C, 3·77; N–N, 3·47; N–C, 3·57; N–H, 3·00; C–C, 3·45; C–H, 2·98; H–H, 2·38 Å; the S–H distance of 2·93 Å occurs between H(4) in the basic molecule and S in the molecule transformed to the symmetry position $1-x,\frac{1}{2}+y,\frac{1}{2}-z$.

Thermal motion of the atoms

50% probability ellipsoids to illustrate the thermal motion of the atoms are shown in Fig. 2.

Variable anisotropic thermal parameters for the hydrogen atoms were introduced for the last cycle of least-squares refinement. There seems to be a tendency among crystallographers to add more and more parameters to their structural models solely in order to obtain better agreement between observed and calculated structure amplitudes. In the present investigation, however, the introduction of anisotropic thermal parameters for the hydrogen seems to be justified. First, errors due to extinction (which seriously affect positional and thermal parameters mainly of hydrogen atoms) have been eliminated by using a corrected formula for the structure amplitude calculation; secondly, Hamilton's (1965) significance test on the R_2-value ratio (1·04) indicates that we can reject the hypothesis that the hydrogen atoms vibrate isotropically at the 0·005 level ($R_{40,1073,0\cdot005}=1\cdot031$); and thirdly, the resulting thermal motions of the hydrogen atoms seem to be quite realistic.

An interesting feature of these results is that the thermal motions for the hydrogen atoms H(1) to H(5) are almost the same (in direction and magnitude) as the thermal motions of the atoms to which they are

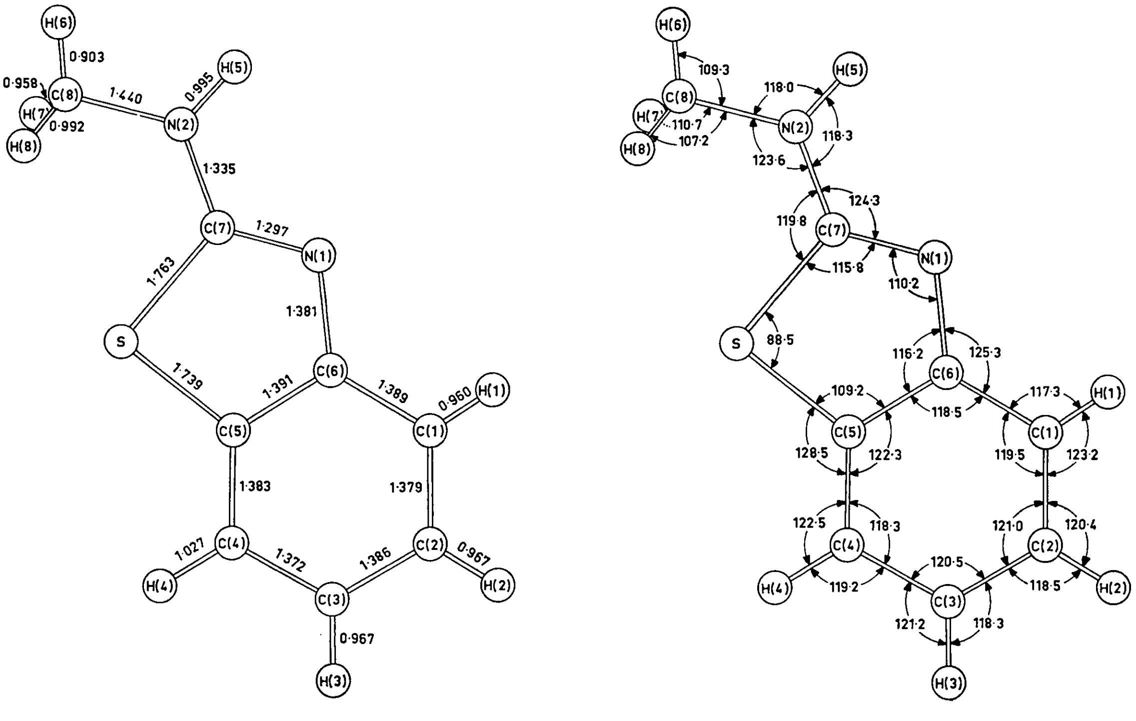


Fig. 1. Bond lengths (Å) and bond angles (°).

bonded. For the methyl hydrogen atoms the maximum 'thermal' motions are approximately perpendicular to the N(2)–C(8) bond direction, thus indicating a possible oscillation about this direction.

Residual electron density

A section of the final difference synthesis through the almost planar part of the molecule is shown in Fig. 3. The largest residual peaks of about 0·20 e.Å^{-3} occur on the S–C bonds, and two peaks of about 0·16 e.Å^{-3} occur on the N(1)–C bonds. These peaks seem to be due to the bonding electrons. A discussion of the distribution of bonded electron density is given by O'Connell, Rae & Maslen (1966). These authors also show that the electron density in bonds between hydrogen-substituted carbon atoms is lower than in bonds between carbon-, nitrogen- or sulphur-substituted carbon atoms, which is in accord with the findings in the present investigation.

In addition to the programs mentioned in the text, the following programs were used: *ORFFE* (Busing, Martin & Levy, 1962*b*) and some of the NCR-Crystallographic programs (Ahmed, Hall, Pippy & Huber, 1966).

I would like to extend my thanks to Professor A. Niggli of the University of Zürich, in whose department the intensity measurements were performed, and to Dr J. Tauber for useful discussion.

References

Ahmed, F. R., Hall, S. R., Pippy, M. E. & Huber, C. P. (1966). *World List of Crystallographic Programs*. Second Edition, Appendix p. 52.

Almenningen, A., Bastiansen, O. & Fernholt, L. (1958). *Kgl. Norske Vid. Selsk. Skr.* No. 3.

Bacon, G. E., Curry, N. A. & Wilson, S. A. (1964). *Proc. Roy. Soc.* A **279**, 98.

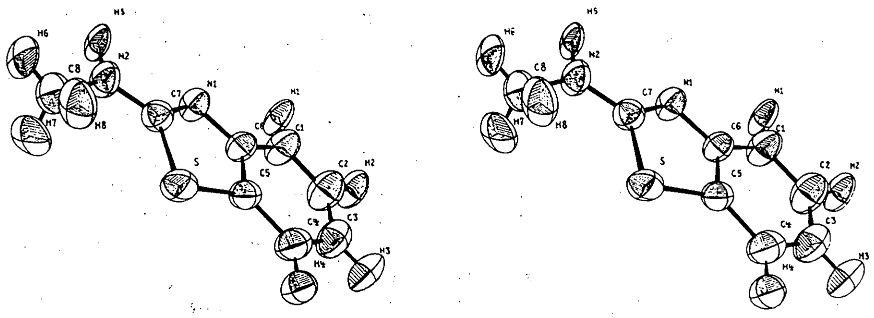


Fig. 2. Stereoscopic (Johnson, 1965) illustration of 2-methylaminobenzothiazole showing the ellipsoids of thermal motion.

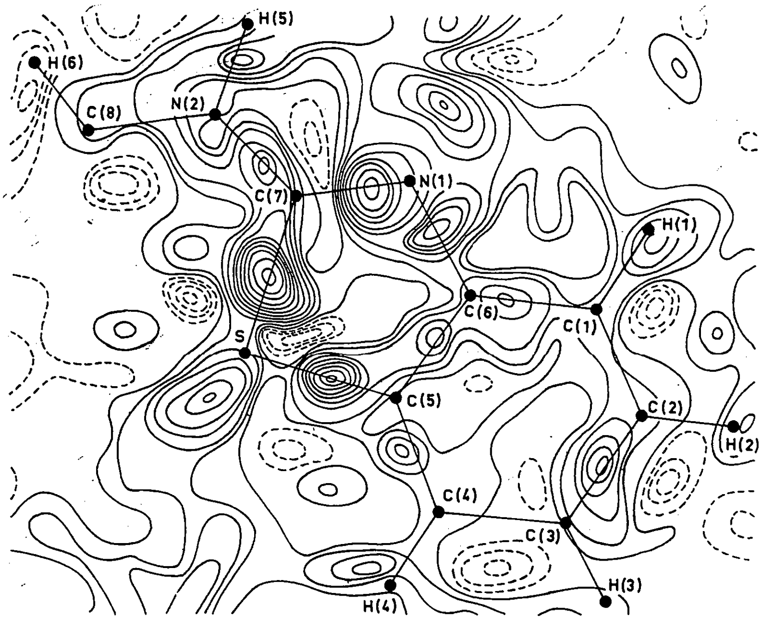


Fig. 3. Section of final difference synthesis through the mean plane of the molecule. Contours are at intervals of 0·02 e.Å^{-3}; negative contours are shown as broken lines.

Busing, W. R., Martin, K. O. & Levy, H. A. (1962*a*). Report ORNL-TM-305. Oak Ridge National Laboratory.
Busing, W. R., Martin, K. O. & Levy, H. A. (1962*b*). Report ORNL-TM-306. Oak Ridge National Laboratory.
Goldstein, P. & Trueblood, K. N. (1967). *Acta Cryst.* **23**, 148.
Hamilton, W. C. (1965). *Acta Cryst.* **18**, 502.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
Johnson, C. K. (1965). Report ORNL-TM-3794. Oak Ridge National Laboratory.
O'Connell, A. M., Rae, A. I. M. & Maslen, E. N. (1966). *Acta Cryst.* **21**, 208.
Tauber, J. (1969). Doctoral Thesis, Univ. of Marburg, Germany.
Zachariasen, W. H. (1967). *Acta Cryst.* **23**, 558.

Acta Cryst. (1970). B**26**, 1741

The Crystal Structure of 4,6-Dideoxy-4-(*N*,*N*-dimethylamino)-α-D-talopyranoside Methiodide

By Richard E. Cook and Milton D. Glick

Department of Chemistry, Wayne State University, Detroit, Michigan 48202, *U.S.A.*

(*Received* 8 *August* 1969)

The crystal structure of 4,6-dideoxy-4-(*N*,*N*-dimethylamino)-α-D-talopyranoside methiodide has been determined by X-ray diffraction. The crystals belong to the orthorhombic space group $P2_12_12_1$ with unit-cell dimensions $a = 13{\cdot}179$ (9), $b = 10{\cdot}604$ (8) and $c = 9{\cdot}770$ (7) Å. The structure was solved by Patterson–Fourier techniques; least-squares refinement yielded a final discrepancy index of $R = 0{\cdot}031$. The structure was found to occur in the 1*C* *trans* chair conformation owing to the presence of a trimethylammonium group in the 4 position.

Introduction

A series of antibiotics, isolated between 1953 and 1958, (Flynn, Hinman, Carol & Woolf, 1953; Haskell, Ryder, Frohardt, Fusari, Jakubawski & Bartz, 1958) has been shown to contain a new class of carbohydrates, the 4-amino-4,6-dideoxyaldohexoses. The antibiotics, amicetin (Stevens, Blumbergs & Daniher, 1963) and bamicetin (Haskell, 1958; Stevens, Blumbergs, Daniher, Otterbach & Taylor, 1966) contained respectively the *N*,*N*-dimethyl and *N*-monomethyl sugar derivative in the D-gluco configuration. The isolation of the parent 4,6-dideoxy-4-amino-D-glucose from the cell wall of the bacteria *Chromobacterium violaceum* (Stevens, Blumbergs, Daniher, Wheat, Kiyomoto & Rollins, 1963) and from *E. coli* strain B (Stevens, Blumbergs, Daniher, Strominger, Matsuhashi, Dietzer, Suzuki, Okazaki, Sugimoto & Okazaki, 1964) increased the biological interest in these compounds. Further, the isolation of the D-galacto derivative from the cell wall of *E. coli* strain Y10 (Stevens, Blumbergs, Otterbach, Strominger, Matsuhashi & Dietzler, 1964) and the D-manno derivative from an antifungal antibiotic (Lee & Schaffner, 1966; Stevens, Gupta, Glinski, Taylor, Blumbergs, Schaffner & Lee, 1968) indicated the wide occurrence of these sugars.

Chemical synthesis of all eight possible configurations has been accomplished by Stevens and co-workers. The relationship of basicity to configuration and conformation is under investigation because of the possible importance in biological activity. The most interesting case to date involves the isolation of the crystalline α and β forms of the 4,6-dideoxy-4-dimethylaminotalose (Stevens, Glinski & Taylor, 1968). It was found that on initial dissolution of these sugars, which mutarotate in aqueous solution, the β-form (*pKa* 8·22) is four times more basic than the α-form (7·60).

The three-dimensional X-ray analysis of 4,6-dideoxy-4 (*N*,*N*-dimethylamino)-α-D-talopyranoside methiodide, reported herein, confirms the general formulation of this class of sugars and suggests a possible explanation for the difference in basicity mentioned previously. In the crystalline state we find this salt exists in the 1*C* geometry; if the α-form of the 4,6-dideoxy-4-dimethylamino talose retains this geometry and the β-form exists in the more usual *C*1 geometry, the difference in basicity may be a result of the different environment (*i.e.* equatorial *vs.* axial) of the dimethyamino group.

Experimental

Transparent, colorless, needle-shaped crystals of 4,6-dideoxy-4-(*N*,*N*-dimethylamino)-D-talopyranoside methiodide were crystallized from a methanol–ethyl ether mixture. Lattice parameters were obtained with *M*o *K*α radiation on a previously aligned Picker four-circle automatic X-ray diffractometer. Fifteen reflections