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The Crystal and Molecular Structure of Sodium Tetrazolate Monohydrate

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Sodium tetrazolate monohydrate forms orthorhombic crystals in the space group *Pmcm* with unit cell dimensions $a=5\cdot868\pm0\cdot006$, $b=5\cdot624\pm0\cdot005$, $c=6\cdot450\pm0\cdot007$ Å. With two molecules per unit cell, the tetrazolate ion is required to have *mm* symmetry. The distances in the tetrazolate anion are C–N(1) = 1·329, N(1)–N(2) = 1·348 and N(2)–N(2′) = 1·310 Å. The final agreement factor R for the observed reflections was 5·0%.

Introduction

Tetrazole is a non-oxygen-containing weak organic acid with $K_A=1\times10^{-5}$. The acidity is undoubtedly due to reasonance stabilization of the anion, which is isoelectronic with cyclopentadienide. However, ferrocene-type analogs of the tetrazolate anion have not been prepared, although some metal complexes of substituted tetrazoles have been reported by Daugherty & Brubaker (1961) and Brubaker (1960).

The structure determination of sodium tetrazolate monohydrate, $Na^+HCN_4^-.H_2O$, was undertaken to determine precisely the structure of the tetrazolate anion and to assess the contribution of the various resonance forms to the ground state. In addition, the determination of the structure of the tetrazolate anion would provide a basis for the study of some metal–tetrazole complexes.

Experimental

Sodium tetrazolate is a typical salt-like substance, insoluble in most organic solvents. From an aqueous solution, sodium tetrazolate forms poorly developed crystals of the monohydrate. An ill-formed fragment was used to determine approximate cell constants and a tentative orthorhombic space group. A spherical crystal, 0·34 mm in diameter, was ground from a larger fragment with a slightly modified version of the grinder described by Bond (1951). Weissenberg photographs taken with the spherical crystal confirmed the extinction observed on the first crystal namely:

hkl no absences
$0kl$ no absences
$h0l$ absent if $l=2n+1$
$hk0$ no absences.

Thus the possible space groups were *P2cm*, *Pmc*2_1 and *Pmcm*.

The cell constants were determined on the G.E. single-crystal orienter with a narrow beam of Mo $K\alpha$ ($\lambda=0\cdot7107$) radiation. The following values were found:

$$a=5\cdot868\pm0\cdot006,\ b=5\cdot624\pm0\cdot005,\ c=6\cdot450\pm0\cdot007\ \text{Å}\ .$$

The density was determined by flotation in a mixture of carbon tetrachloride and methyl iodide to be 1·74 g.cm^{-3}, corresponding to 2·03 molecules of the monohydrate per unit cell. The density calculated for two molecules per cell was 1·72 g.cm^{-3}.

A total of 758 reflections with $2\theta\le80\cdot0°$ was measured on the G.E. single-crystal orienter, the stationary-crystal stationary-counter technique being used. Molybdenum radiation was used in conjunction with a reverter, a simple type of pulse height analyzer, and zirconium filters to provide approximately monochromatic radiation. A correction for the α_1–α_2 splitting was made by the slow scanning of a number of reflections and by comparing the resulting values with the stationary-crystal values. The background corrections were made by measuring the background count at a number of places in the octant of reciprocal space studied.

The raw intensity data were processed by an IBM 709 to obtain the usual structure amplitudes F_o, using programs written by the author. The intensity distribution of F_o^2 was investigated to determine whether a center of symmetry existed in the crystal. The calculated values are given below together with the theoretical values from Lipson & Cochran (1953) for the two possibilities.

Theory 1	9·5	18·1	25·9	33·0	39·3	45·1	50·3	55·1	59·3
Theory $\bar{1}$	24·8	34·5	41·9	47·4	52·0	56·1	59·7	62·9	65·7
Observed	22·3	34·8	40·7	47·0	51·0	56·3	60·5	63·1	67·0

The most probable space group appeared to be *Pmcm* (D_{2h}^5). Because the atoms will not be in general positions regardless of the space group, these results were used only as a guide in the following analysis.

Determination of the structure

A sharpened three-dimensional Patterson function with the origin peak removed was calculated. The Patterson function contained peaks only in the sections $W=0$, $\frac{1}{4}$ and $\frac{1}{2}$, in agreement with the distribution expected for the space group *Pmcm*. The sodium atom was placed at the origin and the water molecule and the tetrazolate anion were located in the mirror plane at $Z=\frac{1}{4}$. The only ambiguity was with respect to the y parameter of the oxygen atom in the water molecule. In one position the oxygen to ring nitrogen distance would be quite short and appeared to be unreasonable, nevertheless this possibility was not immediately discarded. Two Fourier syntheses were calculated for the two possibilities, using all the observed reflections. The f-curve for the sodium ion given by Tomiie & Stam (1958), the f-curve for nitrogen given by Hoerni & Ibers (1954), and the f-curve for carbon–graphite from McWeeny (1951) were used in the calculation of the structure factors. The respective R values for the two models were 19 and 34%, clearly indicating the correct position for the oxygen atom.

Refinement of the trial structure

A second set of parameters was obtained from the Fourier synthesis and was used as the starting parameters for four cycles of least squares. The full matrix was computed for all positional and thermal parameters and then the symmetry-determined parameters were deleted from the matrix and vector. A total of 7·2 minutes of computing time on an IBM 7090 was required for the four cycles of least squares using the 691 observed reflections.

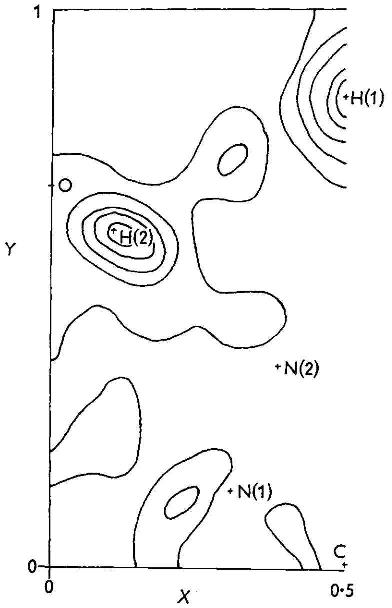

Fig. 1. Section of the difference electron density at $z=\frac{1}{4}$, illustrating the two hydrogen atoms. The contours are drawn at intervals of 0·1 e.Å^{-3} with the lowest contour at 0 e.Å^{-3}. The final least squares positions of the atoms are indicated by crosses.

A difference-Fourier synthesis was calculated and is illustrated in Fig. 1. The two hydrogen atoms were then included in the final least-squares refinement. The heavy atoms were refined anisotropically, while the hydrogens were refined isotropically. After the fourth least-squares cycle, the matrix was inverted and the errors computed from the diagonal elements of the inverse matrix. The final positional and thermal parameters and errors are given in Table 1. The structure factors given in Table 2 were calculated

Table 1. *Final atomic parameters and their probable errors in fractions of the cell edges*

(The temperature factor for each atom is of the form $T_i=\exp-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)$)

Atom	X	Y	Z	B_{11}	B_{22}	B_{33}	B_{12}
Na+	0·00*	0·00*	0·00*	0·0109	0·0180	0·0109	0·00*
σ				0·0002	0·0002	0·0002	
O	0·00*	0·6820	0·25*	0·0130	0·0110	0·0226	0·00*
σ		0·0003		0·0003	0·0003	0·0005	
C	0·50*	0·0069	0·25*	0·0110	0·0120	0·0167	0·00*
σ		0·0004		0·0003	0·0004	0·0004	
N(1)	0·3118	0·1383	0·25*	0·0085	0·0153	0·0160	−0·0019
σ	0·0002	0·0002		0·0002	0·0003	0·0003	0·0003
N(2)	0·3884	0·3643	0·25*	0·0110	0·0131	0·0197	0·0032
σ	0·0002	0·0002		0·0002	0·0003	0·0003	0·0004
H(1)	0·50*	−0·155	0·25*	1·15†			
σ		0·007		0·66			
H(2)	0·109	0·604	0·25*	2·19†			
σ	0·006	0·006		0·62			

* Value determined by the symmetry of the space group.

† Represents the value of the isotropic temperature factor. The values of B_{13} and B_{23} are not given, since they are determined for all the atoms by symmetry to be identically zero.

Table 2. *Observed and calculated structure factors*

The three columns in each group contain the values, reading from left to right, of h, $10F_o$, and $10F_c$. The values of k and l are given at the beginning of each column. A negative sign on F_o means a 'less than'.

	0, 0	
1	43	-60
2	233	259
3	307	371
4	112	118
5	87	91
6	119	122
7	53	55
8	47	45
9	8	5
10	61	62
	1, 0	
0	192	228
1	72	86
2	86	87
3	86	89
4	178	175
5	46	-47
6	107	107
7	30	29
8	5	-3
9	27	25
10	20	20
	2, 0	
0	110	108
1	49	47
2	143	155
3	10	8
4	97	102
5	23	25
6	48	49
7	5	5
8	31	30
9	2	2
10	11	10
	3, 0	
0	236	251
1	118	117
2	276	295
3	83	84
4	85	87
5	148	149
6	41	40
7	11	11
8	91	90
9	9	-9
10	22	21
	4, 0	
0	58	-48
1	141	144
2	140	143
3	45	-47
4	122	123
5	22	21
6	41	38
7	-1	1
8	35	34
9	14	13
	5, 0	
0	63	65
1	7	-6
2	71	70
3	8	-4
4	22	22
5	22	26
6	7	6
7	-1	-6
8	28	28
9	12	-14
	6, 0	
0	120	126
1	24	25
2	68	65
3	61	61
4	51	48
5	19	19
6	47	45
7	15	14
8	23	23
	7, 0	
0	43	44
1	28	27
2	15	16
3	22	20
4	59	59
5	35	-35
6	47	45
7	14	14
	8, 0	
0	51	54
1	34	-36
2	5	4
3	13	13
4	5	-7
5	3	-5
6	7	7
	9, 0	
0	25	24
1	11	11
2	24	24
3	8	8
4	21	22
	10, 0	
0	-1	-0
1	13	13
2	20	21
	1, 1	
0	192	-207
1	267	296
2	173	160
3	74	-63
4	110	107
5	35	39
6	15	13
7	10	11
8	20	21
9	19	20
10	16	-16
	2, 1	
0	100	-85
1	153	-135
2	61	48
3	91	-87
4	104	-110
5	87	87
6	72	-76
7	35	-35
8	42	43
9	39	-38
10	8	-9
	3, 1	
0	155	-149
1	67	56
2	12	1
3	76	-69
4	15	18
5	12	-7
6	11	-12
7	8	-7
8	2	-0
9	3	4
10	16	-17
	4, 1	
0	45	48
1	70	64
2	16	22
3	60	50
4	47	42
5	-1	3
6	28	26
7	26	26
8	6	-5
9	16	16
	5, 1	
0	79	79
1	73	-73
2	54	-50
3	54	51
4	53	-52
5	9	-9
6	4	-4
7	-1	0
8	12	-13
9	11	-11
	6, 1	
0	25	-25
1	9	7
2	55	-49
3	5	4
4	13	13
5	55	-54
6	17	17
7	4	6
8	33	-34
	7, 1	
0	32	32
1	14	14
2	14	14
3	30	30
4	3	3
5	21	20
6	5	6
7	12	12
	8, 1	
0	9	-8
1	4	-4
2	2	2
3	3	-4
4	19	-18
5	19	18
6	13	-12
	9, 1	
0	48	-48
1	15	14
2	4	-4
3	26	-27
4	2	4
	0, 2	
0	384	-445
1	303	344
2	81	85
3	73	-58
4	95	92
5	71	68
6	17	-4
7	26	24
8	12	10
9	32	31
10	30	-31
	1, 2	
0	145	141
1	233	229
2	197	203
3	159	156
4	27	35
5	178	181
6	6	4
7	45	45
8	53	53
9	11	11
10	7	6
	2, 2	
0	180	190
1	212	224
2	113	114
3	193	196
4	74	74
5	100	102
6	45	45
7	58	60
8	17	17
9	29	30
10	13	12
	3, 2	
0	14	17
1	115	118
2	59	-50
3	98	97
4	58	58
5	30	-29
6	40	40
7	46	45
8	42	-43
9	38	37
10	-1	0
	4, 2	
0	201	206
1	37	38
2	25	21
3	167	168
4	10	-7
5	61	60
6	23	25
7	44	43
8	-1	0
9	12	11
	5, 2	
0	54	58
1	118	118
2	39	40
3	97	93
4	53	53
5	36	35
6	38	39
7	39	39
8	-1	-0
9	31	32
	6, 2	
0	34	-35
1	54	52
2	12	10
3	8	5
4	6	7
5	25	24
6	8	-9
7	12	11
8	-1	-2
	7, 2	
0	8	8
1	22	23
2	30	29
3	21	21
4	18	-20
5	61	61
6	18	-19
7	5	4
	8, 2	
0	17	-19
1	62	62
2	23	24
3	13	12
4	28	28
5	23	24
6	8	7
	9, 2	
0	2	-3
1	7	8
2	3	-4
3	8	8
4	4	-6
	10, 2	
0	12	12
	1, 3	
0	121	117
1	175	-172
2	108	-100
3	53	45
4	80	-76
5	28	-30
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7	7	-8
8	18	-18
9	15	-16
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1	91	82
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3	64	62
4	80	81
5	70	-70
6	59	62
7	29	29
8	37	-36
9	32	32
10	6	8
	3, 3	
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1	44	-39
2	7	-1
3	55	51
4	11	-14
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6	9	10
7	8	6
8	-1	-0
9	1	-3
	4, 3	
0	33	-34
1	50	-46
2	12	-14
3	42	-38
4	34	-32
5	-1	-2
6	20	-21
7	21	-22
8	4	5
9	13	-13
	5, 3	
0	63	-63
1	57	57
2	43	40
3	43	-43
4	42	42
5	8	8
6	-1	2
7	-1	-1
8	11	11
	6, 3	
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1	6	-6
2	43	41
3	4	-4
4	10	-11
5	45	45
6	15	-15
7	3	-5
8	27	29
	7, 3	
0	24	-26
1	10	-11
2	11	-11
3	22	-25
4	-1	-2
5	16	-16
6	4	-5
7	10	-10
	8, 3	
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1	4	3
2	-1	-2
3	-1	3
4	16	15
5	16	-15
6	13	10
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1	12	-12
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3	22	23
4	3	-3
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0	388	408
1	24	29
2	140	134
3	186	193
4	73	73
5	52	52
6	84	82
7	37	37
8	31	30
9	4	4
	1, 4	
0	123	127
1	66	74
2	68	66
3	61	62
4	113	108
5	28	-27
6	75	74
7	21	20
8	-1	-1
9	20	19
	2, 4	
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1	48	50
2	97	96
3	9	15
4	69	68
5	18	18
6	36	36
7	5	4
8	24	23
9	3	2
	3, 4	
0	135	136
1	69	70
2	167	166
3	47	47
4	57	55
5	97	97
6	27	27
7	7	6
8	65	65
9	<	-6
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2	94	92
3	28	-29
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5	16	15
6	29	27
7	-1	0
8	27	26
9	10	9
	5, 4	
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5	18	18
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	6, 4	
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	9, 4	
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2	17	17
3	5	5
	1, 5	
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1	84	80
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3	31	-28
4	44	44
5	19	19
6	3	4
7	2	4
8	11	13
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1	41	-38
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3	36	-36
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5	51	49
6	41	-42
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9	21	-22
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1	26	23
2	5	2
3	34	-31
4	9	9
5	2	-2
6	5	-7
7	3	-4
8	-1	0
9	-1	2
	4, 5	
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1	28	26
2	6	6
3	26	24
4	22	20
5	-1	0
6	13	13
7	14	15
8	3	-4
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3	30	31
4	26	-28
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3	16	17
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	8, 5	
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3	61	59
4	13	14
5	82	81
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8	28	28
9	7	7
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1	81	78
2	43	41
3	80	75
4	30	29
5	24	45
6	22	20
7	30	30
8	9	8
	3, 6	
0	17	19
1	54	52
2	14	-12
3	50	48
4	28	27
5	9	-10
6	22	21
7	26	25
8	19	-21
	4, 6	
0	79	81
1	20	19
2	9	7
3	77	77
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6	13	13
7	25	23
8	-1	-0
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1	53	52
2	15	15
3	46	44
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7	20	21
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2	6	6
3	4	4
4	2	4
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1	17	16
2	14	-14
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4	26	26
5	29	-30
6	23	25
7	11	12
8	16	-17
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1	12	-13
2	1	-2
3	19	17
4	3	-5
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6	-1	4
7	-1	2
	4, 7	
0	10	-9
1	11	-17
2	-1	-1
3	12	-13
4	10	-10
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7	7	-8
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2	16	16
3	17	-19
4	14	16
5	3	4
6	-1	-0
	6, 7	
0	4	5
1	-1	-2
2	16	17
3	-1	-4
4	3	-4
5	19	19
	7, 7	
0	9	-9
1	-1	-3
2	2	-3
3	8	-10
4	-1	-0
	8, 7	
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1	-1	0
	0, 8	
0	96	96
1	8	7
2	36	34
3	54	52
4	25	23
5	13	12
6	31	30
7	14	13
	1, 8	
0	39	40
1	21	20
2	23	22
3	22	20
4	37	36
5	6	-9
6	28	28
7	9	9
	2, 8	
0	27	26
1	16	16
2	33	32
3	6	6
4	25	24
5	7	7
6	15	15
7	-1	2
	3, 8	
0	36	36
1	19	18
2	52	50
3	12	10
4	19	18
5	32	33
6	10	9
7	-1	2
	4, 8	
0	-1	-4
1	27	27
2	34	33
3	8	-11
4	30	29
5	8	8
6	11	10
	5, 8	
0	17	17
1	-1	1
2	21	20
3	-1	-0
4	8	9
5	9	8
	6, 8	
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1	4	4
2	15	15
3	15	14
4	14	13
	7, 8	
0	15	14
1	6	6
2	5	4
	1, 9	
0	15	-16
1	16	16
2	10	11
3	8	-10
4	9	10
5	4	6
6	-1	-0
	2, 9	
0	7	-8
1	5	-6
2	7	8
3	8	-10
4	11	-12
5	15	16
6	10	-13
	3, 9	
0	14	-14
1	5	6
2	-1	1
3	7	-9
4	-1	2
5	-1	0
6	-1	-2
	4, 9	
0	4	4
1	4	5
2	-1	-0
3	5	6
4	5	4
5	-1	-1
	5, 9	
0	13	13
1	9	-10
2	7	-8
3	9	10
4	6	-7
	6, 9	
0	2	-1
1	-1	1
2	7	-8
	0, 10	
0	10	-13
1	27	27
2	13	13
3	-1	1
4	11	10
5	13	14
	1, 10	
0	9	9
1	19	20
2	17	16
3	13	14
4	4	4
5	22	22
	2, 10	
0	15	14
1	18	18
2	9	9
3	20	19
4	8	7
5	12	12
	3, 10	
0	7	7
1	14	14
2	-1	-2
3	15	16
4	8	8
	4, 10	
0	21	21
1	7	6
2	-1	1
3	21	22
	5, 10	
0	8	6
1	14	14
	1, 11	
0	5	7
1	5	-6
2	3	-5
3	3	5
	2, 11	
0	-1	4
1	-1	2
2	-1	-4
	3, 11	
0	4	6
1	-1	-3

with the final set of parameters. The usual residual R was 5·0% for only the observed reflections.

The weighting scheme used in the least squares refinement was

$$\text{if } F_o \le F_{\min},\ \sqrt{w} = 1{\cdot}0$$
$$\text{if } F_o > F_{\min},\ \sqrt{w} = F_{\min}/F_o$$

where $F_{\min}$ was taken to be 4·5 (45 on the scale used in Table 2). The unobserved reflections were not included in the refinement. A survey reveals that about half of the unobserved reflections calculate higher than the minimum observable value, the 750 reflection being the worst. The majority of the unobserved reflections represent very low levels of F(observed), 0·1 to 0·2 of an electron, and errors in the model are important at this low level. The approximation of the thermal motion by an ellipsoid in the case of the ring atoms and errors in the scattering curves for the various atoms are possible sources of error in the case of the low level observed structure amplitudes.

Discussion

The tetrazolate ion

The distances and angles in the tetrazolate ion are given in Table 3 and Fig. 2. The ion has *mm* symmetry as required by the space group. This symmetry represents the maximum symmetry possible for the tetrazolate anion.

The six resonance forms which could be expected to contribute significantly to the ground state of the

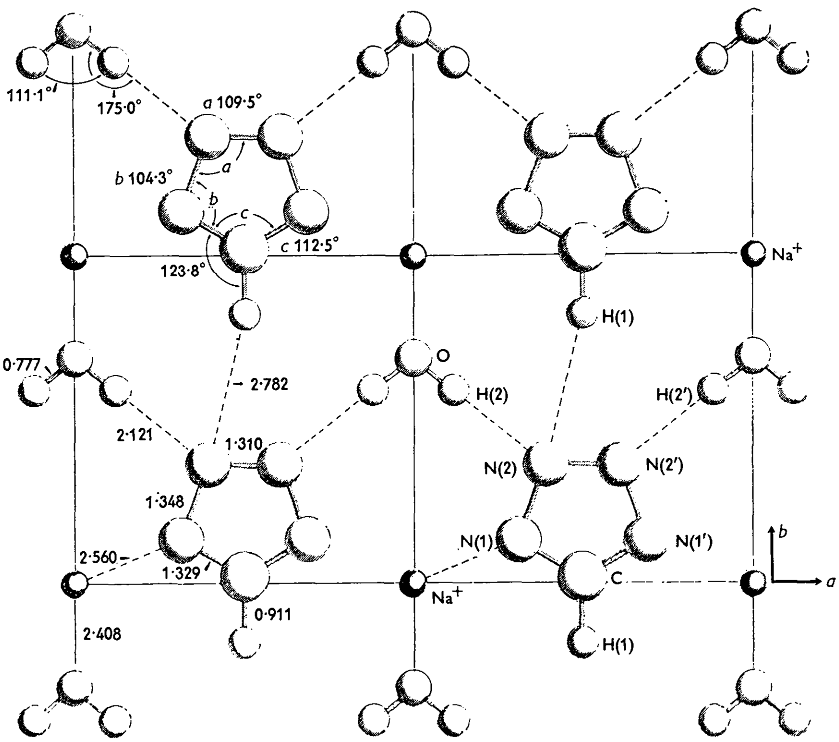

Fig. 2. View down the *c* axis giving the various intra- and intermolecular distances and angles. The tetrazolate ion and the water molecule are in the plane $z=\frac{1}{4}$ and the sodium ions are at $z=0$.

Table 3. *Intra- and intermolecular distance and angles*

Atoms	Distance	Atoms	Angle
C–N(1)	1·329 ± 0·003 Å	C–N(1)–N(2)	104·3 ± 0·2°
N(1)–N(2)	1·348 ± 0·002	N(1)–N(2)–N(2′)	109·5 ± 0·2
N(2)–N(2′)	1·310 ± 0·002	N(1)–C–N(1′)	112·5 ± 0·2
C–H(1)	0·911 ± 0·040	O–H(2)–N(2)	175·0 ± 2·2
Na^+–O	2·408 ± 0·002	N(1)–C–H(1)	123·8 ± 0·4
Na^+–N(1)	2·560 ± 0·002		
O–H(2)	0·777 ± 0·033		
O–N(2)	2·898 ± 0·003		

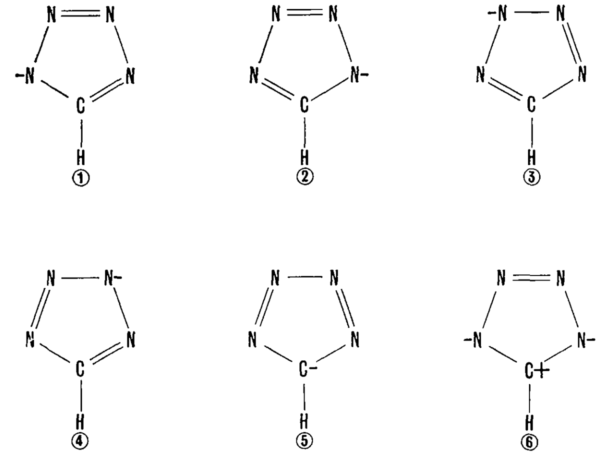

Fig. 3. Six resonance forms of the tetrazolate ion which contribute to the ground state.

tetrazolate ion are illustrated in Fig. 3. Forms 1–4 are expected to make the major contribution to the ground state of the ion because of the higher electronegativity of nitrogen as compared with carbon. The observed distances were used to calculate the bond orders of the three independent bonds in the ion. The resonance forms were then weighted and a set of calculated bond orders and distances were computed. If the first four resonance forms are weighted equally at 22·5%, the fifth at 7·0% and the sixth at 3·0%, the following distances and bond orders were obtained:

	Observed		Calculated	
	Distance	Bond order	Distance	Bond order
C–N(1)	1·329	0·43	1·326	0·45
N(1)–N(2)	1·348	0·27	1·342	0·295
N(2)–N(2′)	1·310	0·43	1·301	0·48

The two sets of distances and bond orders are in fair agreement. The above assumptions regarding the resonance forms lead to a slight excess of negative charge on N(1) compared with N(2). The fact that N(1) and not N(2) is in close proximity to the positively charged sodium atom is consistent with a slight excess of negative charge on N(1).

Although the structures of several substituted tetrazoles have been reported, the tetrazolate ion can only be compared with the 5-aminotetrazole ion reported by Bryden (1958). These are the only two cases where there are no substituents on the ring nitrogens. The average C–N(1) of 1·310, N(1)–N(2) of 1·351 and N(2)–N(3) of 1·295 were found in the 5-aminotetrazolate ion. The present results are in fair agreement with the above distances, considering the fact that the amino group appears to perturb the ring resonance forms. In addition the 5-aminotetrazolate ion was refined by generalized projections and least squares using only the *hk*0 and *hk*1 data, and the results are probably less accurate than the values quoted in the present study.

Intermolecular packing

The structure of sodium tetrazolate monohydrate consists essentially of layers of water molecules hydrogen-bonded to tetrazolate ions separated by the positive sodium ion. The water molecule forms hydrogen bonds to two tetrazolate ions in the same layer. The result is an infinite chain of water molecules and tetrazolate ions. The only contact between chains is the van der Waals contact of the hydrogen on the carbon of one ring with the two N(2) atoms of another tetrazolate ion. Fig. 4 illustrates the packing of the water molecules and tetrazolate ions of one layer. For drawing this figure the van der Waals radii given by Pauling (1960) were used.

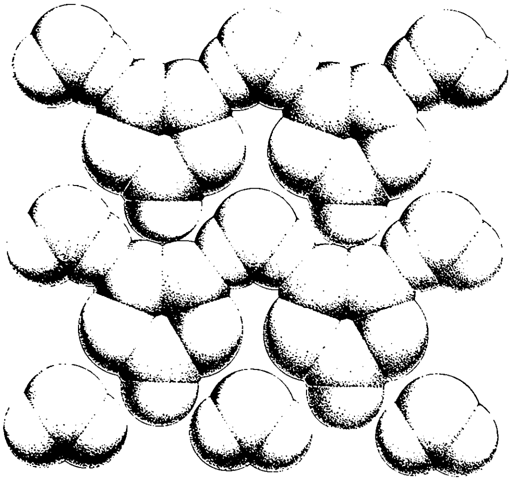

Fig. 4. Packing drawing through the water molecule and tetrazolate ion at $z=\frac{1}{4}$, illustrating the van der Waals contacts between molecules.

The hydrogen bond from the water molecule to N(2) is asymmetric with an overall length of 2·898 Å. This distance is about average for O–H ··· N hydrogen bonds. The O–H distance of 0·777 Å is much shorter than would be expected from the sum of the covalent radii. The shortening of A–H bonds determined by X-ray diffraction is fairly well known. The short C–H distance 0·91 reported by Marsh (1958) is in agreement with our value for the C–H bond. The N–H bond distance reported by Marsh (1958), when corrected for the change in radius of O and N, is in fair agreement with our O–H distance. The shortening of A–H bonds has been discussed in more detail by Tomiie (1958) and Ibers (1961).

The sodium cation is situated between the layers of water molecules and tetrazolate ions. The coordination around the sodium is a distorted octahedron composed of four nitrogens and two oxygens. The distances Na^+ to O or N are slightly longer than the distances predicted from the ionic radius of Na^+ and the van der Waals radii for O or N.

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