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The Crystal and Molecular Structure of the Polymethine Dye 1,3-Bis(dimethylamino)-trimethinium Perchlorate: a Comparison of Optical and X-ray Crystal Structure Determination

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The crystal and molecular structure of the polymethine dye 1,3-bis(dimethylamino)trimethinium perchlorate has been determined by X-ray diffraction techniques and refined to a residual of 6·9%. The space group is *Cc* and the unit-cell parameters are $a=7{\cdot}86\pm0{\cdot}04$, $b=18{\cdot}93\pm0{\cdot}12$, $c=7{\cdot}70\pm0{\cdot}05$ Å, $\beta=103{\cdot}55\pm0{\cdot}18°$. From the refined coordinates, the transition moments of the two non-parallel molecules in the unit cell were found to have direction cosines of 0·431, 0·879, 0·205 and 0·431, −0·879, 0·205 relative to orthogonal axes parallel to **a***, **b** and **c**. The orientation of the dye molecules in the crystal is compared with predictions made by P. Gramaccioni and W. T. Simpson (unpublished results) on the basis of spectroscopic measurements, and the agreement between the X-ray and the optical studies is found to be excellent.

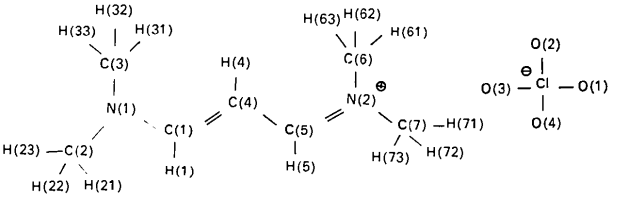
Introduction

The crystals of certain polymethine dyes are of interest because of their most unusual optical properties (Anex & Simpson, 1960; Fanconi, Gerhold & Simpson, 1969). For incident light polarized in one direction and frequency near an intense transition of the isolated molecule, these crystals have reflection properties akin to metals, whereas for light polarized in a different direction the crystals are essentially transparent.

Metallic reflection also occurs from suitable crystal faces of a number of organic molecules with conjugated π-electron systems, but only one, anthracene, has an accurately determined crystal structure (Cruickshank, 1956). Thus, attempts to construct theories describing the spectral characteristics of metal-like reflection have been hampered by a lack of detailed crystal structure determinations, particularly in the case of the polymethinium dyes (Philpott, 1970, 1971). For anthracene the observed metallic reflection is thought to arise from the second singlet transition, whereas in the polymethinium dyes it is the first singlet that is the strong one and which gives a metallic reflection band (Clark & Philpott, 1970; Philpott, 1972). The interpretation of the metallic reflection phenomena is therefore expected to be less complex in the case of the polymethinium dyes.

The purpose of this crystal structure determination of the polymethine dye 1,3-bis(dimethylamino)trimethinium perchlorate (BDTP) was therefore twofold. Firstly to verify the orientation of the molecules in the crystal as determined by Gramaccioni & Simpson (1972) from the reflection spectra of the crystals, and to check the precision of the optical method. Secondly to provide accurate coordinates for further, more detailed, analysis of the optical properties of the polymethine dyes.

The schematic formula of BDTP, with the atom numbering used in this study, is given below.



Experimental

Crystals of BDTP, kindly provided by Drs W. T. Simpson and P. Gramaccioni, were typically well developed monoclinic prisms with the (010) face most prominent. Systematic absences, determined from Weissenberg and Buerger precession photographs, were $h+k=2n+1$ for the hkl reflections; and h odd and l odd for the $h0l$ reflections. The space group could therefore be either $C2/c$ or Cc. From the unit-cell dimensions and density data (Table 1) there were four BDTP molecules per unit cell. If the space group were $C2/c$, the dye molecules and the perchlorate ions would be constrained to lie on twofold axes with the long axes of the polymethinium chains perpendicular to **b**. This would not be consistent with the optical data of Gramaccioni & Simpson (1972) which suggests that there are at least two optically non-equivalent molecules in the unit cell. On the other hand if the space group were Cc there would be one molecule per asymmetric unit, with no restriction on its orientation. The four molecules in the unit cell would be parallel in pairs, consistent with the optical studies.

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Table 1. *Crystallographic data*

Unit-cell dimensions:	$a = 7{\cdot}86 \pm 0{\cdot}04$ Å
	$b = 18{\cdot}93 \pm 0{\cdot}12$
	$c = 7{\cdot}70 \pm 0{\cdot}05$
	$\beta = 103{\cdot}55 \pm 0{\cdot}18°$
	$V_c = 1114$ Å^3
Space group:	Cc
Four molecules per unit cell	
Density (calculated):	1·350 g cm^{-3}
Density (observed):	1·33

The lattice constants were determined by centering 21 reflections and subsequent least-squares refinement.

Three-dimensional diffraction data were first measured by visual estimation of Weissenberg photographs taken with Cu $K\alpha$ radiation. The crystal used was approximately 0·1 mm in each direction. These diffraction data were used for an initial determination of the structure, but, as will be described below, did not lead to a very satisfactory refinement. The diffraction data were therefore remeasured using a card controlled Enraf–Nonius three-circle diffractometer. Filtered Mo $K\alpha$ radiation ($\lambda = 0{\cdot}7107$ Å) was used, and data were recorded to $\sin\theta/\lambda = 0{\cdot}66$, *i.e.* equivalent to the observable limit for Cu $K\alpha$ radiation. The crystal used measured $0{\cdot}20 \times 0{\cdot}25 \times 0{\cdot}62$ mm, no correction being made for absorption. The intensities were measured in the usual way be scanning across each reflection and subtracting the background measured on either side of the peak. A θ–2θ scan was used, the scan width being increased as a function of the Bragg angle to allow for the splitting of the $K\alpha_1$ and $K\alpha_2$ lines. Peak and background counts were accumulated for a total time of about 60 sec each. A reflection was considered to be observed if the peak counts exceeded the appropriately normalized background count by twice the statistical counting error. Using this criterion 1036 reflections out of a possible 1285 with $\sin\theta/\lambda$ less than 0·66 were observable.

Structure determination

During the early stages of the structure determination the optical analysis of the crystals was not complete, and was not used to resolve the $C2/c$, Cc space-group ambiguity mentioned above. Also, since the molecule itself was highly symmetrical, we felt that statistical

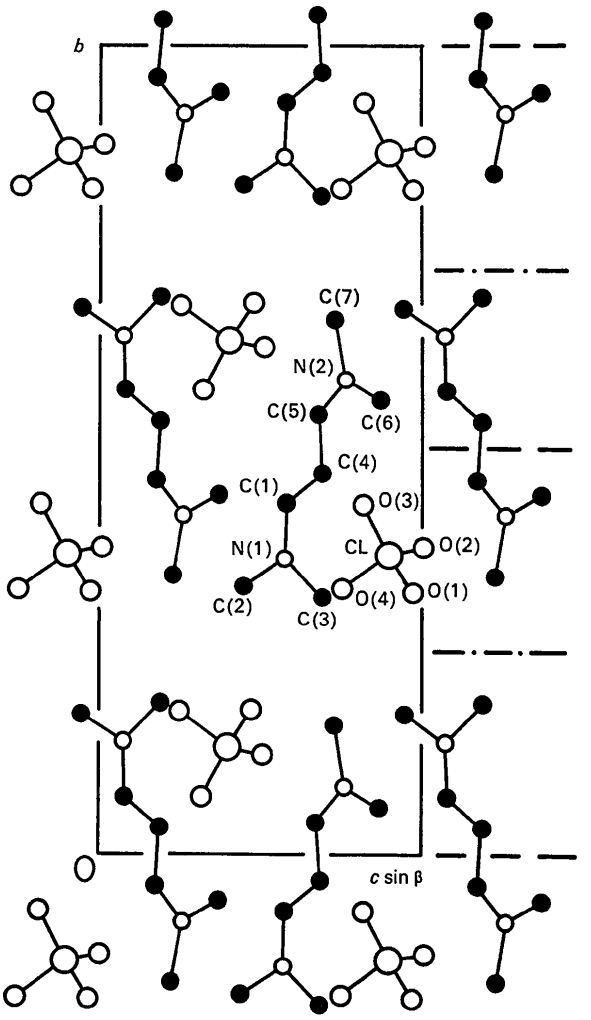

Fig. 1. The molecular packing.

Table 2. *Fractional coordinates* $\times 10^4$

The thermal parameters, $B_{ij} \times 10^4$, are the coefficients in the expression $\exp[-\sum B_{ij}h_ih_j]$.

Here and elsewhere in this paper the estimated standard deviations in the last figure are given in parentheses.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
Cl	0 (0)	−8679 (1)	4000 (0)	186 (2)	40 (1)	232 (2)	−44 (2)	98 (3)	− 9 (2)
O(1)	1442 (13)	−8220 (6)	4710 (14)	322 (17)	82 (4)	510 (26)	−21 (16)	−53 (32)	−130 (14)
O(2)	−1169 (21)	−8777 (7)	5078 (21)	562 (34)	92 (5)	632 (32)	−51 (20)	827 (60)	−59 (20)
O(3)	0510 (17)	−9292 (4)	3189 (17)	576 (30)	54 (3)	571 (27)	−74 (14)	558 (47)	59 (14)
O(4)	−0900 (18)	−8242 (7)	2471 (13)	575 (34)	91 (5)	382 (22)	19 (16)	−118 (43)	135 (22)
N(1)	3228 (7)	−1394 (3)	5697 (7)	192 (8)	33 (1)	229 (9)	19 (5)	65 (14)	4 (5)
N(2)	5931 (8)	0823 (3)	7619 (8)	240 (10)	36 (1)	258 (10)	13 (6)	23 (17)	14 (7)
C(1)	3401 (7)	−0708 (3)	5785 (7)	180 (9)	35 (2)	167 (8)	−12 (5)	34 (13)	2 (7)
C(2)	1757 (9)	−1724 (4)	4472 (10)	218 (12)	42 (2)	292 (14)	−38 (9)	− 3 (20)	−16 (8)
C(3)	4421 (11)	−1866 (4)	6885 (11)	282 (15)	35 (2)	289 (15)	− 8 (8)	66 (24)	− 6 (8)
C(4)	4759 (7)	−0331 (3)	6887 (7)	172 (8)	35 (2)	205 (8)	− 4 (6)	83 (13)	−10 (6)
C(5)	4739 (8)	0388 (3)	6745 (8)	186 (8)	33 (2)	212 (9)	−25 (6)	136 (15)	−17 (6)
C(6)	7543 (10)	0566 (5)	8760 (12)	205 (12)	50 (3)	333 (15)	26 (10)	110 (21)	57 (9)
C(7)	5775 (15)	1577 (4)	7302 (15)	431 (23)	29 (2)	422 (23)	37 (11)	345 (39)	8 (12)

tests for centrosymmetry might not reliably indicate the true space group. Our approach was essentially to attempt a structure determination in both space groups, assuming that in only one case a satisfactory solution would be obtained. This subsequently proved to be the case.

The Patterson function for space groups $C2/c$ and Cc has symmetry $C2/m$ and in this case had its highest non-origin peak at $(\frac{1}{2},0{\cdot}236,\frac{1}{2})$ consistent with a chlorine–chlorine Harker peak. The chlorine coordinates could therefore be tentatively assigned, whether the space group was $C2/c$ or Cc. Also, the Patterson function showed a prominent feature in the $(10\bar{2})$ plane through the origin, which appeared to be the vector image of the planar group of four atoms N(1), C(1), C(2) and C(3) [or the corresponding atoms centered on N(2)]. Assuming, as a first alternative, space group $C2/c$, it was possible to place the polymethinium chain in the cell so that good agreement with the assumed coordinates for N(1), C(1), C(2) and C(3) was obtained, but structure factor calculations using the photographic data led to R values of about 0·57. On the other hand, if space group Cc were assumed, the dye molecule could be placed in many ways consistent with the assumed coordinates for the atoms about N(1), and it was not obvious which of these orientations was to be preferred. We therefore used as a starting model the set of five atoms Cl, N(1), C(1), C(2) and C(3) to calculate structure factors. (If the space group were Cc it was essential to include atoms in addition to chlorine in the phasing, as the chlorine atoms were in a centrosymmetric arrangement.) Two arrangements were possible, depending on the sense chosen for the vector from the chlorine to the light atom motif. Using the photographic data, one choice gave an R value of 0·43, the other 0·36. An F_o synthesis calculated using the latter phases revealed the remainder of the dye moiety. Further F_o syntheses suggested coordinates for three of the four perchlorate oxygen atoms, and resulted in an R value of 0·33, but the coordination of the oxygens was not very satisfactory. We therefore decided to collect more accurate data using the diffractometer, before proceeding with the refinement of the structure. All subsequent discussion will refer to these data.

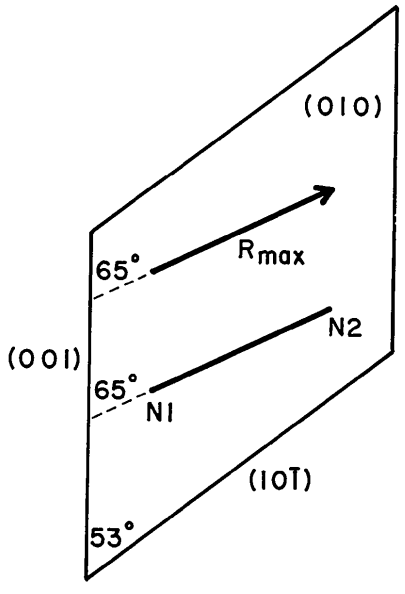

Fig. 2. Schematic diagram comparing the optical and X-ray results. The parallelogram illustrates the morphology of a typical crystal viewed parallel to **b**. The polarization direction for maximum reflectivity is shown by R_{max}, and the molecular orientation is illustrated by the line N1, N2, drawn parallel to the projection of the vector joining the nitrogen atoms N(1) and N(2).

A difference map using the remeasured data, and subtracting out the contribution of the chlorine atom plus the polymethine chain, clearly showed the positions of the four perchlorate oxygens. Also several cycles of block-diagonal least-squares refinement using isotropic temperature factors led to $R=0{\cdot}15$, also indicating the overall correctness of the structure determination in space group Cc, and the improved quality of the diffractometer data. Use of anisotropic temperature factors reduced R to 0·114. At this stage it appeared that eight of the intense low-angle reflections were affected by extinction. Omitting these, R dropped to 0·076. A difference map, also omitting these reflections, showed all the expected hydrogen atoms. At a late stage in the structure analysis, a careful check of the data processing revealed typographical errors which had caused incorrect attenuation factors to be applied to the eight intense reflections mentioned above. On correction, the agreement between F_o and F_c improved dramatically, suggesting that none of the reflections in the data set were seriously affected by extinction. Final block-diagonal least-squares refinement, in which the hydrogen atoms were refined with isotropic thermal parameters and other atoms anisotropically, led to a residual $R=0{\cdot}069$ for the 1036 observable intensities. The weighting scheme used for the least-squares refinement was similar to that described by Stout & Jensen (1968) for diffractometer data.

The atomic coordinates with their standard devia-

Table 3. *Fractional hydrogen coordinates* ($\times 10^3$) *and thermal parameters* (Å^2)

	x	y	z	B
H(21)	127 (9)	−142 (3)	392 (9)	1·5 (10)
H(22)	205 (18)	−202 (6)	363 (16)	2·8 (22)
H(23)	080 (12)	−198 (5)	505 (11)	5·5 (16)
H(1)	242 (24)	−045 (9)	439 (21)	4·2 (37)
H(33)	409 (29)	−238 (11)	636 (27)	11·8 (52)
H(32)	552 (40)	−207 (16)	674 (34)	9·1 (84)
H(31)	421 (20)	−157 (9)	832 (20)	8·7 (30)
H(4)	580 (15)	−051 (6)	752 (15)	3·9 (22)
H(5)	411 (12)	058 (5)	616 (12)	4·5 (14)
H(72)	455 (30)	180 (11)	653 (29)	4·3 (50)
H(71)	693 (21)	160 (9)	692 (20)	5·2 (34)
H(73)	493 (37)	185 (13)	836 (37)	27·3 (70)
H(63)	842 (22)	028 (9)	825 (22)	8·6 (37)
H(61)	770 (26)	018 (9)	935 (22)	9·1 (41)
H(62)	784 (14)	090 (6)	966 (13)	6·2 (21)

Table 4. *Observed and calculated structure factors*

Units are in electrons multiplied by 10. Reflections considered as unobserved (see text) are indicated with an asterisk.

L	FO	FC
H= 1, K= 0		
0	213	239
1	168	146
2	170	172
3	82	76
4	111	110
5	52	57
6	113	117
7	57	56
8	176	29
9	78	4
H= 2, K= 0		
0	160	156
1	144	138
2	195	173
3	144	139
4	53	49
5	49	44
6	31	35
7	259	33
H= 3, K= 0		
0	159	159
1	188	173
2	101	112
3	150	148
4	49	46
5	72	67
6	25	23
7	48	44
8	27	25
H= 4, K= 0		
0	277	256
1	104	103
2	40	31
3	56	42
4	87	78
5	79	8
6	72	79
8	31	27
H= 5, K= 0		
0	311	359
1	251	238
2	198	183
3	211	187
4	62	55
5	106	111
6	176	167
7	40	41
H= 6, K= 0		
0	127	155
1	87	92
2	102	109
3	225	216
4	70	57
5	157	155
6	46	60
7	51	51
8	31	30
9	139	23
H= 7, K= 0		
0	271	272
1	117	175
2	40	46
3	353	365
4	249	28
5	35	36
6	46	60
7	31	42
8	57	52
9	29	29
H= 8, K= 0		
0	179	6
1	159	184
2	188	210
3	39	34
4	179	155
5	200	16
H= 9, K= 0		
0	62	64
1	76	17
2	44	61
3	70	47
4	53	59
5	49	80
6	28	28
7	139	23
H= 10, K= 0		
0	239	239
1	146	146
2	172	172
3	82	76
4	110	110
5	57	57
6	113	117
7	56	56
8	29	5
9	4	4
H= 11, K= 0		
0	146	156
1	173	173
2	173	167
3	144	139
4	49	49
5	44	44
6	41	35
7	25	33
H= 12, K= 0		
0	159	159
1	173	173
2	148	148
3	41	35
4	206	217
5	137	144
6	124	114
7	64	42
H= 13, K= 0		
0	159	159
1	139	1
2	40	37
3	150	148
4	49	46
5	214	235
6	159	31
7	41	81
8	179	3
9	40	44
H= 14, K= 0		
0	310	310
1	119	117
2	44	44
3	35	37
4	138	110
5	25	25
6	21	14
7	15	12
H= 15, K= 0		
0	98	111
1	74	81
2	179	16
3	47	34
4	79	24
H= 16, K= 0		
0	100	97
1	85	95
2	96	107
3	82	87
4	67	60
5	77	75
6	68	67
7	40	30
H= 17, K= 0		
0	97	48
1	61	56
2	112	112
3	41	35
4	54	62
5	0*	8
6	0*	13
7	2*	15
H= 18, K= 0		
0	37	48
1	96	91
2	22*	17
3	36	35
4	51	52
5	26*	30
6	40	48
H= 19, K= 0		
0	0*	12
1	96	91
2	40	44
3	10*	23
4	51	52
5	26*	30
6	40	48
H= 20, K= 0		
0	43	61
1	71	70
2	64	63
3	49	43
4	78	74
5	18*	24
6	31	34
7	21*	26
H= 21, K= 0		
0	30	42
1	49	49
2	47	54
3	18*	24
4	0*	10
5	23*	24
6	44	45
7	0*	21
H= 22, K= 0		
0	47	30
1	47	47
2	37	31
3	25*	24
4	0*	10
5	44	44
6	31	34
7	0*	21
H= 23, K= 0		
0	0*	12
1	0*	21
2	47	45
3	57	62
4	21*	24
5	19*	24
6	31	34
7	40	38
H= 24, K= 0		
0	37	48
1	61	56
2	112	112
3	41	35
4	54	62
5	0*	8
6	0*	13
7	2*	15
H= 25, K= 0		
0	63	61
1	71	70
2	64	63
3	49	43
4	78	74
5	18*	24
6	31	34
7	21*	26
H= 26, K= 0		
0	30	42
1	49	49
2	47	54
3	18*	24
4	0*	10
H= 27, K= 0		
0	47	38
1	29	25
2	43	44
3	40	24
4	40	39
5	0*	7
6	24*	19
H= 28, K= 0		
0	101	104
1	173	184
2	42	45
3	52	52
4	52	38
5	31	32
6	14*	21
H= 29, K= 0		
0	36	42
1	20*	15
2	44	40
3	24*	27
4	53	49
5	28*	25
6	21*	14
H= 30, K= 0		
0	28	28
H= 1, K= 1		
0	90	41
1	101	94
2	34	28
3	64	70
4	40	16
5	77	77
6	35	36
7	26	30
H= 2, K= 1		
0	167	156
1	52	49
2	144	137
3	58	43
4	158	152
5	36	34
6	63	66
7	22*	32
8	44	47
H= 3, K= 1		
0	79	99
1	176	193
2	144	136
3	23	32
4	31	44
5	49	44
6	13*	10
7	44	50
8	20*	20
H= 4, K= 1		
0	40	37
1	20*	16
2	34	36
3	53	50
4	24*	27
5	24*	19
6	0*	17
H= 5, K= 1		
0	176	184
1	54	42
2	17*	16
3	47	34
4	79	24
H= 6, K= 1		
0	26	31
1	77	64
2	20*	30
3	68	61
4	57	52
5	32	37
6	10*	2
H= 7, K= 1		
0	176	184
1	155	173
2	181	185
3	77	77
4	29	35
5	24*	30
6	21*	14
H= 8, K= 1		
0	155	155
1	158	180
2	255	253
3	276	253
4	117	121
5	156	199
6	135	105
7	79	84
8	28	25
H= 9, K= 1		
0	140	136
1	185	179
2	21*	20
3	40	45
4	12*	12
H= 10, K= 1		
0	192	152
1	42	43
2	126	119
3	40	37
4	30	21
H= 11, K= 1		
0	29	27
1	278	319
2	112	117
3	145	145
4	76	73
5	131	147
6	32	37
7	102	103
8	34	45
H= 12, K= 1		
0	102	104
1	52	52
2	37	38
3	40	47
4	0*	12
5	31	38
H= 13, K= 1		
0	47	38
1	29	25
2	43	44
3	40	24
4	40	39
5	0*	7
6	24*	19
H= 14, K= 1		
0	101	104
1	173	184
2	42	45
3	52	52
4	52	38
5	31	32
6	14*	21
H= 15, K= 1		
0	67	67
1	116	120
2	45	51
3	93	89
4	58	62
5	26	26
6	48	42
7	40	53
H= 16, K= 1		
0	104	106
1	111	106
2	137	138
3	102	106
4	126	126
5	40	44
6	92	94
7	25	30
8	0*	22
H= 17, K= 1		
0	109	106
1	111	106
2	137	138
3	102	106
4	126	126
5	40	44
6	92	94
7	25	30
8	15*	16
H= 18, K= 1		
0	33	30
1	68	58
2	106	101
3	61	58
4	100	100
5	26	11
6	15*	16
7	10	10
H= 19, K= 1		
0	0*	25
1	17*	9
2	19*	4
3	35	31
H= 20, K= 1		
0	47	38
1	29	25
2	43	44
3	40	24
4	40	39
5	0*	7
6	24*	19
H= 21, K= 1		
0	47	38
1	29	25
2	43	44
3	40	24
4	0*	10
H= 22, K= 1		
0	36	42
1	20*	15
2	44	40
3	24*	27
4	53	49
5	28*	25
6	21*	14
H= 23, K= 1		
0	47	38
1	29	25
2	43	44
3	40	24
4	40	39
5	0*	7
6	24*	19
H= 24, K= 1		
0	101	104
1	173	184
2	42	45
3	52	52
4	52	38
5	31	32
6	14*	21
H= 25, K= 1		
0	67	67
1	116	120
2	45	51
3	93	89
4	58	62
5	26	26
6	48	42
7	40	53
H= 26, K= 1		
0	33	30
1	68	58
2	106	101
3	61	58
4	100	100
5	26	11
6	15*	16
7	10	10
H= 27, K= 1		
0	0*	25
1	17*	9
2	19*	4
3	35	31
H= 28, K= 1		
0	47	38
1	29	25
2	43	44
3	40	24
4	40	39
5	0*	7
6	24*	19
H= 29, K= 1		
0	36	42
1	20*	15
2	44	40
3	24*	27
4	53	49
5	28*	25
6	21*	14
H= 30, K= 1		
0	28	28
H= 1, K= 2		
0	41	36
1	90	90
2	64	63
3	49	43
4	78	74
5	18*	24
6	31	34
7	21*	26
H= 2, K= 2		
0	30	42
1	49	49
2	47	54
3	18*	24
4	0*	10
H= 3, K= 2		
0	47	38
1	29	25
2	43	44
3	40	24
4	40	39
5	0*	7
6	24*	19
H= 4, K= 2		
0	101	104
1	173	184
2	42	45
3	52	52
4	52	38
5	31	32
6	14*	21
H= 5, K= 2		
0	67	67
1	116	120
2	45	51
3	93	89
4	58	62
5	26	26
6	48	42
7	40	53
H= 6, K= 2		
0	33	30
1	68	58
2	106	101
3	61	58
4	100	100
5	26	11
6	15*	16
7	10	10
H= 7, K= 2		
0	0*	25
1	17*	9
2	19*	4
3	35	31
H= 8, K= 2		
0	47	38
1	29	25
2	43	44
3	40	24
4	40	39
5	0*	7
6	24*	19
H= 9, K= 2		
0	36	42
1	20*	15
2	44	40
3	24*	27
4	53	49
5	28*	25
6	21*	14
H= 10, K= 2		
0	47	38
1	29	25
2	43	44
3	40	24
4	40	39
5	0*	7
6	24*	19
H= 11, K= 2		
0	101	104
1	173	184
2	42	45
3	52	52
4	52	38
5	31	32
6	14*	21
H= 12, K= 2		
0	67	67
1	116	120
2	45	51
3	93	89
4	58	62
5	26	26
6	48	42
7	40	53
H= 13, K= 2		
0	33	30
1	68	58
2	106	101
3	61	58
4	100	100
5	26	11
6	15*	16
7	10	10
H= 14, K= 2		
0	0*	25
1	17*	9
2	19*	4
3	35	31
H= 15, K= 2		
0	47	38
1	29	25
2	43	44
3	40	24
4	40	39
5	0*	7
6	24*	19
H= 16, K= 2		
0	101	104
1	173	184
2	42	45
3	52	52
4	52	38
5	31	32
6	14*	21
H= 17, K= 2		
0	67	67
1	116	120
2	45	51
3	93	89
4	58	62
5	26	26
6	48	42
7	40	53
H= 18, K= 2		
0	33	30
1	68	58
2	106	101
3	61	58
4	100	100
5	26	11
6	15*	16
7	10	10
H= 19, K= 2		
0	0*	25
1	17*	9
2	19*	4
3	35	31
H= 20, K= 2		
0	47	38
1	29	25
2	43	44
3	40	24
4	40	39
5	0*	7
6	24*	19
H= 21, K= 2		
0	36	42
1	20*	15
2	44	40
3	24*	27
4	53	49
5	28*	25
6	21*	14
H= 22, K= 2		
0	47	38
1	29	25
2	43	44
3	40	24
4	40	39
5	0*	7
6	24*	19
H= 23, K= 2		
0	101	104
1	173	184
2	42	45
3	52	52
4	52	38
5	31	32
6	14*	21
H= 24, K= 2		
0	67	67
1	116	120
2	45	51
3	93	89
4	58	62
5	26	26
6	48	42
7	40	53
H= 25, K= 2		
0	33	30
1	68	58
2	106	101
3	61	58
4	100	100
5	26	11
6	15*	16
7	10	10
H= 26, K= 2		
0	0*	25
1	17*	9
2	19*	4
3	35	31
H= 27, K= 2		
0	47	38
1	29	25
2	43	44
3	40	24
4	40	39
5	0*	7
6	24*	19
H= 28, K= 2		
0	36	42
1	20*	15
2	44	40
3	24*	27
4	53	49
5	28*	25
6	21*	14
H= 29, K= 2		
0	47	38
1	29	25
2	43	44
3	40	24
4	40	39
5	0*	7
6	24*	19
H= 30, K= 2		
0	28	28
H= 1, K= 3		
0	31	23
1	101	94
2	34	28
3	64	70
4	40	16
5	77	77
6	35	36
7	26	30
H= 2, K= 3		
0	45	52
1	7*	5
H= 3, K= 3		
0	57	59
1	40	38
2	60	56
3	59	52
4	51	41
5	14*	9
6	31	31
7	18*	13
H= 4, K= 3		
0	57	48
1	96	91
2	44	48
3	40	44
4	34	38
5	31	32
6	30	28
H= 5, K= 3		
0	125	116
1	94	98
2	156	157
3	76	79
4	93	98
5	31	32
6	56	56
7	39	23
8	30	28
H= 6, K= 3		
0	83	94
1	129	124
2	24	4
3	147	154
4	26	28
5	62	51
6	52	41
7	27	26
8	21*	16
H= 7, K= 3		
0	97	48
1	61	56
2	112	112
3	41	35
4	54	62
5	0*	8
6	0*	13
7	2*	15
H= 8, K= 3		
0	37	48
1	96	91
2	40	44
3	10*	23
4	51	52
5	26*	30
6	40	48
H= 9, K= 3		
0	43	61
1	71	70
2	64	63
3	49	43
4	78	74
5	18*	24
6	31	34
7	21*	26
H= 10, K= 3		
0	30	42
1	49	49
2	47	54
3	18*	24
4	0*	10
H= 11, K= 3		
0	47	38
1	29	25
2	43	44
3	40	24
4	40	39
5	0*	7
6	24*	19
H= 12, K= 3		
0	101	104
1	173	184
2	42	45
3	52	52
4	52	38
5	31	32
6	14*	21
H= 13, K= 3		
0	67	67
1	116	120
2	45	51
3	93	89
4	58	62
5	26	26
6	48	42
7	40	53
H= 14, K= 3		
0	33	30
1	68	58
2	106	101
3	61	58
4	100	100
5	26	11
6	15*	16
7	10	10
H= 15, K= 3		
0	0*	25
1	17*	9
2	19*	4
3	35	31
H= 16, K= 3		
0	47	38
1	29	25
2	43	44
3	40	24
4	40	39
5	0*	7
6	24*	19
H= 17, K= 3		
0	101	104
1	173	184
2	42	45
3	52	52
4	52	38
5	31	32
6	14*	21
H= 18, K= 3		
0	67	67
1	116	120
2	45	51
3	93	89
4	58	62
5	26	26
6	48	42
7	40	53
H= 19, K= 3		
0	33	30
1	68	58
2	106	101
3	61	58
4	100	100
5	26	11
6	15*	16
7	10	10
H= 20, K= 3		
0	0*	25
1	17*	9
2	19*	4
3	35	31
H= 21, K= 3		
0	47	38
1	29	25
2	43	44
3	40	24
4	40	39
5	0*	7
6	24*	19
H= 22, K= 3		
0	36	42
1	20*	15
2	44	40
3	24*	27
4	53	49
5	28*	25
6	21*	14
H= 23, K= 3		
0	47	38
1	29	25
2	43	44
3	40	24
4	40	39
5	0*	7
6	24*	19
H= 24, K= 3		
0	101	104
1	173	184
2	42	45
3	52	52
4	52	38
5	31	32
6	14*	21
H= 25, K= 3		
0	67	67
1	116	120
2	45	51
3	93	89
4	58	62
5	26	26
6	48	42
7	40	53
H= 26, K= 3		
0	33	30
1	68	58
2	106	101
3	61	58
4	100	100
5	26	11
6	15*	16
7	10	10
H= 27, K= 3		
0	0*	25
1	17*	9
2	19*	4
3	35	31
H= 28, K= 3		
0	47	38
1	29	25
2	43	44
3	40	24
4	40	39
5	0*	7
6	24*	19
H= 29, K= 3		
0	36	42
1	20*	15
2	44	40
3	24*	27
4	53	49
5	28*	25
6	21*	14
H= 30, K= 3		
0	28	28
H= 1, K= 4		
0	0*	25
1	17*	9
2	19*	4
3	35	31
H= 2, K= 4		
0	47	38
1	29	25
2	43	44
3	40	24
4	40	39
5	0*	7
6	24*	19
H= 3, K= 4		
0	101	104
1	173	184
2	42	45
3	52	52
4	52	38
5	31	32
6	14*	21
H= 4, K= 4		
0	67	67
1	116	120
2	45	51
3	93	89
4	58	62
5	26	26
6	48	42
7	40	53
H= 5, K= 4		
0	33	30
1	68	58
2	106	101
3	61	58
4	100	100
5	26	11
6	15*	16
7	10	10
H= 6, K= 4		
0	0*	25
1	17*	9
2	19*	4
3	35	31
H= 7, K= 4		
0	47	38
1	29	25
2	43	44
3	40	24
4	40	39
5	0*	7
6	24*	19
H= 8, K= 4		
0	101	104
1	173	184
2	42	45
3	52	52
4	52	38
5	31	32
6	14*	21
H= 9, K= 4		
0	67	67
1	116	120
2	45	51
3	93	89
4	58	62
5	26	26
6	48	42
7	40	53
H= 10, K= 4		
0	33	30
1	68	58
2	106	101
3	61	58
4	100	100
5	26	11
6	15*	16
7	10	10
H= 11, K= 4		
0	0*	25
1	17*	9
2	19*	4
3	35	31
H= 12, K= 4		
0	47	38
1	29	25
2	43	44
3	40	24
4	40	39
5	0*	7
6	24*	19
H= 13, K= 4		
0	101	104
1	173	184
2	42	45
3	52	52
4	52	38
5	31	32
6	14*	21
H= 14, K= 4		
0	67	67
1	116	120
2	45	51
3	93	89
4	58	62
5	26	26
6	48	42
7	40	53
H= 15, K= 4		
0	33	30
1	68	58
2	106	101
3	61	58
4	100	100
5	26	11
6	15*	16
7	10	10
H= 16, K= 4		
0	0*	25
1	17*	9
2	19*	4
3	35	31
H= 17, K= 4		
0	47	38
1	29	25
2	43	44
3	40	24
4	40	39
5	0*	7
6	24*	19
H= 18, K= 4		
0	101	104
1	173	184
2	42	45
3	52	52
4	52	38
5	31	32
6	14*	21
H= 19, K= 4		
0	67	67
1	116	120
2	45	51
3	93	89
4	58	62
5	26	26
6	48	42
7	40	53
H= 20, K= 4		
0	33	30
1	68	58
2	106	101
3	61	58
4	100	100
5	26	11
6	15*	16
7	10	10
H= 21, K= 4		
0	0*	25
1	17*	9
2	19*	4
3	35	31
H= 22, K= 4		
0	47	38
1	29	25
2	43	44

tions estimated from the least-squares residuals (Cruickshank, 1965) are listed in Tables 2 and 3.

The observed and calculated structure factors are given in Table 4. Atomic scattering factors were taken from the *International Tables for X-ray Crystallography* (1962).

Discussion

The crystal packing is illustrated in Fig. 1. The polymethinium chains pack in sheets normal to **b**, stabilized by ionic interactions with the perchlorate ions. The occurrence of these sheets is fully consistent with the pronounced crystal cleavage parallel to (010). None of the intermolecular contacts are abnormal. Excluding hydrogen atoms, the closest approaches involving the perchlorate group are 3·25 [O(3)–C(1)] and 3·42 Å [O(2)–N(2)], and for the organic ions 3·49 [N(2)–C(1)] and 3·56 Å [C(1)–C(5)].

Table 5. *Bond distances and angles*

N(1)–C(2)	1·451 (10) Å	C(2)–N(1)–C(3)	116·4 (6)°
N(1)–C(3)	1·452 (10)	C(6)–N(2)–C(7)	117·5 (7)
N(2)–C(7)	1·449 (10)	C(1)–N(1)–C(2)	121·2 (6)
N(2)–C(6)	1·446 (11)	C(5)–N(2)–C(7)	120·7 (7)
N(1)–C(1)	1·306 (8)	C(1)–N(1)–C(3)	122·3 (6)
N(2)–C(5)	1·309 (9)	C(5)–N(2)–C(6)	121·4 (6)
C(1)–C(4)	1·395 (8)	N(1)–C(2)–C(4)	120·1 (4)
C(4)–C(5)	1·366 (8)	N(2)–C(5)–C(4)	126·3 (6)
Cl—O(1)	1·431 (11)	C(1)–C(4)–C(5)	118·0 (5)
Cl—O(2)	1·387 (16)	O(1)–Cl—O(2)	115·5 (8)
Cl—O(3)	1·420 (10)	O(1)–Cl—O(3)	112·6 (6)
Cl—O(4)	1·477 (11)	O(1)–Cl—O(4)	98·8 (7)
C(1)–H(1)	1·26 (17)	O(2)–Cl—O(3)	116·6 (8)
C(5)–H(5)	0·69 (9)	O(2)–Cl—O(4)	106·9 (8)
C(4)–H(4)	0·91 (12)	O(3)–Cl—O(4)	103·9 (7)
C(2)–H(21)	0·76 (6)		
C(2)–H(22)	0·93 (12)		
C(2)–H(23)	1·08 (9)		
C(3)–H(31)	1·28 (16)		
C(3)–H(32)	0·98 (32)		
C(3)–H(33)	1·06 (21)		
C(6)–H(61)	0·85 (17)		
C(6)–H(62)	0·92 (10)		
C(6)–H(63)	1·02 (17)		
C(7)–H(71)	1·02 (17)		
C(7)–H(72)	1·09 (23)		
C(7)–H(73)	1·27 (28)		

The intramolecular bond lengths and angles are listed in Table 5.

The chemically equivalent bonds within the polymethinium chain are all very similar. The four nitrogen–methyl carbon bonds are almost equal in length with an average value of 1·450 Å, which is marginally less than the value of 1·475 Å expected for a carbon–nitrogen single bond. The two conjugated nitrogen–carbon bonds are also very similar in length, with an average value of 1·308 Å.

The plane which gives the best fit to the nine non-hydrogen atoms of the polymethinium chain was determined by least-squares calculations to be

$$0{\cdot}6895\ x - 0{\cdot}0539\ y - 0{\cdot}7223\ z = 1{\cdot}920\ \text{Å}\ .$$

A χ^2 test (Wheatley, 1953) showed that with high probability the polymethinium chain is nonplanar, although the departures of the nine heavy atoms and of H(1), H(4) and H(5) from the plane are relatively small (Table 6).

Table 6. *Planarity of the molecule*

	Deviation from planarity
C(2)	0·075 (8) Å
N(1)	0·025 (5)
C(3)	−0·070 (9)
C(1)	−0·010 (5)
C(4)	−0·045 (6)
C(5)	−0·035 (6)
N(2)	−0·014 (6)
C(6)	0·128 (9)
C(7)	0·035 (12)
H(1)	0·36 (18)
H(4)	0·12 (12)
H(5)	−0·01 (9)

One of the motivations for this crystal structure determination was to check the usefulness of spectroscopic techniques in determining the orientations of dye molecules in the crystal phase (Anex & Simpson, 1960; Gramaccioni & Simpson, 1972). It is therefore of interest to compare the optical and X-ray results. We may note in passing that the optical studies of Gramaccioni & Simpson were completed before, and independently of, the X-ray work. Conversely the crystal structure determination was achieved without reference to the detailed spectroscopic data. The results of Gramaccioni & Simpson, expressed relative to the unit cell defined in Table 1, may be summarized as follows. R_{max}, the plane of polarization of incident light for which maximum reflectivity is observed from the (010) face is approximately parallel to the $(10\bar{1})$ face. Its exact orientation, as determined spectroscopically is illustrated in Fig. 2. Reflection spectra from the (010) and other prominent crystal faces are consistent with at least two optically non-equivalent molecules in the unit cell. The transition moments of these molecules lie approximately in planes parallel to the $(10\bar{1})$ crystal face. More precisely, the optical data of Gramaccioni & Simpson (1972) predict that the transition moments are oriented so that their projection on the (010) crystal face is parallel to R_{max}. The angles of the transition moments out of the (010) plane, *i.e.*, the angles they make with R_{max} (Fig. 2) are estimated from reflection spectra to be about $\pm 55°$, and from absorption spectra to be about $\pm 60°$.

Physically, the transition moment is expected to be parallel to the long axis of the polymethinium chain. We have therefore assumed this direction to be defined by the vector from N(1) to N(2). From the refined coordinates of N(1) and N(2), the transition moments of the two non-parallel molecules in the unit cell are calculated to have direction cosines of 0·431, 0·879, 0·205 and 0·431, −0·879, 0·205 relative to orthogonal axes parallel to **a***, **b** and **c**. The projection of N(1)–N(2) on to (010) (Fig. 2) for all molecules in the

unit cell makes an angle of 65° with **c**. This may be compared with the angle of 65° between R_{max} and **c** (Gramaccioni & Simpson, 1972). Furthermore, the N(1)–N(2) vector for two molecules in the unit cell is calculated to make an angle of +61·5° with R_{max}, while the angle for the other two glide-related molecules is −61·5°. As discussed above, Gramaccioni & Simpson (1972) predict about ±55° or ±60°. The agreement between the optical and X-ray data is therefore excellent, and within the expected error of the spectroscopic analysis.

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The Crystal Structure of Methyl Orange Monohydrate Monoethanolate

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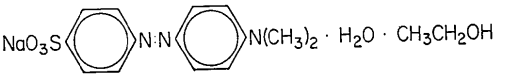
Crystals of the title compound (sodium 4′-dimethylaminoazobenzene-4-sulphonate monohydrate monoethanolate, $C_{14}H_{14}NaN_3O_3S.H_2O.C_2H_6O$) are monoclinic, $P2_1/c$, with $a=22{\cdot}11$ (2), $b=10{\cdot}34$ (1), $c=8{\cdot}30$ (1) Å, $\beta=91{\cdot}58$ (5)°, $Z=4$. 2952 of a possible 3221 independent reflexions in the range $\sin\theta/\lambda \leq 0{\cdot}59$ were observed and measured diffractometrically. The crystal structure was determined by symbolic addition procedures and refined by block-diagonal least-squares methods to a final R index of 0·049. The two phenyl rings of the azobenzene nucleus are inclined to each other at 10°. The coordination of the sodium ion is distorted octahedral; two water molecules lie at opposite corners, and the remaining positions are occupied by an oxygen atom from each of three different sulphonate groups and by an ethanol hydroxyl group. The water and ethanol molecules each donate one hydrogen bond, and the sulphonate group accepts two.

Introduction

Methyl orange has long been used as an acid-base indicator, and its protein-binding properties have been of interest for nearly as long. Recent spectroscopic work by Carey, Schneider & Bernstein (1972) suggests that, when bound to bovine serum albumin, the conformation of the organic moiety is such that the phenyl rings are effectively parallel. Similar indications are obtained for solid material, including the monohydrate monoethanolate (I). It was considered to be of interest to check the interpretation of the spectroscopic results by means of an X-ray analysis of I. It was found that the rings were indeed nearly parallel, the angle between them being only 10°.



(I)

Experimental

Crystal data: F.W. 391·4, $V=1900$ Å^3, $D_m=1{\cdot}39$ (flotation in ether–chloroform), $D_x=1{\cdot}37$ g cm^{-3},