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Structure of the Chromophore from the Fluorescent Peptide produced by Iron-deficient *Azotobacter Vinelandii*

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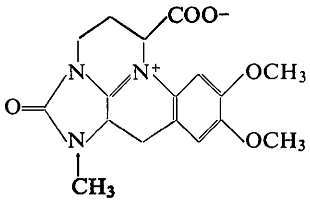
(*Received* 9 *October* 1970)

Iron-deficient cultures of *Azotobacter vinelandii* contain a yellow-green fluorescent peptide which, upon hydrolysis, yields several amino acids and a chromophoric moiety that retains the spectral properties of the parent peptide. Crystal-structure analysis by X-ray diffraction has elucidated the molecular formula of the trimethylated derivative of the chromophore to be the zwitterion:



There appears to be an intramolecular attraction between N^+ and O^- since the plane containing the carboxyl ion is perpendicular to the plane containing the three conjugated rings, thus making the $N^+\cdots O^-$ separation a minimum at 2·64 Å. The compound crystallizes with four molecules of water in the face-centered triclinic space group $F\bar{1}$ with cell parameters: $a=9{\cdot}12\pm0{\cdot}02$, $b=19{\cdot}94\pm0{\cdot}04$, $c=21{\cdot}17\pm0{\cdot}04$ Å, $\alpha=93{\cdot}0\pm0{\cdot}3$, $\beta=92{\cdot}8\pm0{\cdot}3$, and $\gamma=98{\cdot}0\pm0{\cdot}3°$. Visually estimated intensities were obtained from a crystal enclosed in a glass capillary. The final R index for anisotropic refinement was 9·0%. The structure is layered with sheets of hydrogen-bonded water molecules between layers of organic ions. Phases were determined directly from the structure factor magnitudes by the symbolic addition procedure.

Introduction

The presence of yellow-green pigments in cultures of *Azotobacter* was first reported by Beijerinck (1907) in his description of *Azotobacter agile*. The pigment was isolated from iron-deficient cultures of *Azotobacter vinelandii* and the principal component was shown to be a peptide with an attached yellow-green fluorescent chromophore (Bulen & LeComte, 1962). Hydrolysis of the peptide yields the rare amino acids homoserine and β-hydroxyaspartic acid as well as the chromophoric substance which retains the spectral properties of the parent peptide. The chromophore has the formula $C_{14}H_{11}N_3O_5$, which upon prolonged treatment with diazomethane yields the trimethylated derivative $C_{17}H_{17}N_3O_5$ (Corbin, Karle & Karle, 1970). The purpose of this investigation was to establish the molecular formula of the chromophore. Crystals of the trimethylated derivative were provided by Dr J. L. Corbin of the Charles F. Kettering Research Laboratory. Details of the isolation, properties, and methylation of the chromophore, as well as data on degradation products will be published elsewhere (Corbin, 1970).

During the structure determination, it became apparent that a partial structure was obtained which was misplaced with respect to the centers of symmetry. A procedure employing the tangent formula (Karle, 1968) is described wherein the partial structure is used in a noncentrosymmetric triclinic cell to develop the complete structure. The proper placement of the molecules with respect to the center of symmetry is then apparent.

Experimental

Although the trimethylated chromophore crystallizes as transparent, well-formed prisms which are stable in a humid atmosphere, the crystals readily turn to powder when the humidity decreases. Accordingly, the diffraction data were collected from a wet crystal sealed in a capillary. The intensity data were recorded photographically by the multiple-film, equi-inclination Weissenberg technique and were estimated visually by comparison with a calibrated film strip. Layers 0–6 were recorded on the a axis. No cross layers were photographed; however, the individual layers were recorded under controlled conditions of exposure and photographic development. Corrections were made for spot size, Lorentz and polarization factors, and normalized structure factors $|E|$ were derived. The average values of $|E|^2$ and $||E|^2-1|$ indicated that the triclinic cell was centrosymmetric. Cell parameters, derived from precession photographs, and other physical data are listed in Table 1.

Table 1. *Physical data*

M.F.	$C_{17}H_{17}N_3O_5.4H_2O$	
M.W.	415·41 (calc. from formula)	
Color	Very light yellow	
Habit	Prismatic, elongated on a	
Size	~0·8 × 0·3 × 0·3 mm	
Space group	$F\bar{1}$	$P\bar{1}$
a	9·12 ± 0·02 Å	9·12 Å
b	19·94 ± 0·04	11·52
c	21·17 ± 0·04	11·73
α	93·0 ± 0·3°	79·8°
β	92·8 ± 0·3	115·6
γ	98·0 ± 0·3	121·1
V	3802·2	950·5
Z	8	2
Density (calc)	1·451 g.cm^{-3}	
Radiation	Cu $K\alpha$ 1·5418 Å	
No. independent reflections	2758	
$\langle\lvert E\rvert^2\rangle$	0·755	
$\langle\lvert E^2-1\rvert\rangle$	1·046	

For ease in data collection and indexing, a face-centered unit cell, space group $F\bar{1}$, with eight molecular units was chosen. In this cell the angles α, β and γ are between 90 and 100°. All atomic parameters, the Figures, and the subsequent discussion refer to the $F\bar{1}$ cell. Cell parameters for a primitive cell listed in Table 1 are related to the face-centered cell by the matrix

$$\begin{pmatrix} 1 & 0 & 0 \\ -\frac{1}{2} & \frac{1}{2} & 0 \\ -\frac{1}{2} & 0 & \frac{1}{2} \end{pmatrix}.$$

Structure analysis

Phases for the reflections were derived directly from the structure-factor magnitudes by the symbolic addition procedure (Karle & Karle, 1963, 1966). Although the sign determination for centrosymmetric crystals has become quite routine, the triclinic space group $P\bar{1}$ (or $F\bar{1}$, in this case) often presents some difficulty. The nature of the difficulty stems from the fact that there are fewer $\sum_2$ combinations for each hkl than in space groups with more symmetry, and that greater reliance must be placed on indications from single contributors with somewhat lower probabilities of being correct.

In the present investigation, the origin was specified by assigning + signs to $1,17,3$, $0,14,\overline{16}$ and $22\bar{4}$. These reflections are in the *ugu*, *gug*, and *ggu* categories when transformed to a $P\bar{1}$ cell by the matrix given previously and are, therefore, proper for specifying the origin. In the triclinic system, all signs derived from the origin specification are positive, and to obtain negative signs at least one of the assigned symbols must be negative. Unknown symbols were assigned to four reflections in the course of the sign determination, $3,1,15\ c$, $4,2,\bar{8}\ d$, $1,\overline{13},9\ g$, and $5,\bar{7},15\ h$ to implement the $\sum_2$ relationship. It soon became apparent that $c=+$ and there were three indications that $d=h$. With two unknowns left, only three maps needed to be computed since the set containing all + signs was obviously incorrect. Each map contained one very large peak which *a priori* indicated that the phases were in error. Changing the sign of the symbol h from d to $-d$ led to several maps having an anthracene-type structure which appeared in a different location in each map (Fig. 1). The structural formula was not known at this point; however the 14 atoms comprising the anthracene type fragment were used as a basis for a partial

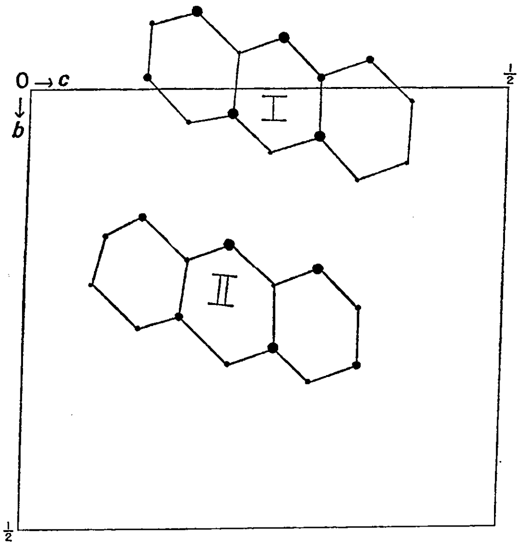


Fig. 1. Positions of maxima showing a probable fragment of the molecule for two different sets of phases.

Table 2. *Observed and calculated structure factors*

Columns represent the index l, $10|F_o|$ and $10F_c$.

0	0	L
2	2250	-2304
4	570	-530
6	471	-294
8	1075	1107
10	395	317
12	479	-483
14	585	-605
16	145	-96
18	101	62
20	579	-547
22	39	59
24	144	-113
26	76	61
0	2	L
-26	132	-139
-24	144	-94
-22	430	-448
-20	203	167
-18	304	-348
-16	78	-138
-14	142	106
-12	359	-372
-10	364	-320
-8	119	139
-6	892	856
-4	1123	-1230
-2	2615	-2692
0	1898	2077
2	1849	1970
4	1039	-1130
6	235	-345
8	257	-293
10	337	353
12	608	595
14	161	166
16	669	669
18	117	95
20	155	-189
22	205	181
24	0	-35
26	117	-146
0	4	L
-26	135	105
-24	153	113
-22	67	98
-20	286	-285
-18	314	339
-16	271	-249
-14	881	-857
-12	794	702
-10	1409	-1313
-8	2119	-2140
-6	1783	-1952
-4	233	215
-2	1294	-1398
0	905	896
2	1170	-1064
4	457	593
6	1618	1753
8	1595	1690
10	227	-156
12	366	404
14	808	797
16	264	-303
18	0	27
20	323	-321
22	241	285
24	102	117
26	127	-118
0	6	L
-24	211	212
-22	243	270
-20	312	361
-18	167	-164
-16	0	21
-14	815	-872
-12	997	871
-10	414	-360
-8	328	419
-6	87	116
-4	1049	-1165
-2	753	795
0	325	-347
2	978	-972
4	0	-71
6	1118	-1069
8	312	-366
10	346	-350
12	86	81
14	253	-261
16	82	113
18	317	-318
20	90	-70
22	216	221
24	107	99
0	8	L
-24	220	-208
-22	252	265
-20	299	274
-18	549	557
-16	183	170
-14	442	-403
-12	272	263
-10	850	746
-8	574	460
-6	89	-69
-4	925	-975
-2	889	826
0	2252	-2324
2	526	-476
4	1246	-1222
6	91	-50
8	402	432
10	49	68
12	388	361
14	443	438
16	0	-14
18	257	-256
20	276	285
22	0	-20
0	10	L
-24	176	-189
-22	0	-3
-20	166	152
-18	425	484
-16	72	-58
-14	339	-314
-12	221	-174
-10	228	219
-8	705	709
-6	495	549
-4	1757	-1652
-2	1546	1624
0	1418	1437
2	871	-775
4	44	45
6	0	70
8	110	118
10	238	201
12	56	65
14	155	121
16	0	29
18	439	-474
20	0	17
22	97	114
0	12	L
-24	225	-277
-22	192	-179
-20	270	309
-18	0	30
-16	472	-522
-14	372	362
-12	477	-527
-10	0	53
-8	773	799
-6	149	112
-4	0	-38
-2	298	-299
0	0	23
2	67	57
4	257	-189
6	162	-164
8	436	-426
10	254	-291
12	216	-221
14	288	275
16	590	601
18	337	-405
20	97	105
22	120	99
0	14	L
-22	154	-159
-20	0	-46
-18	535	577
-16	1218	-1275
-14	912	1003
-12	72	-44
-10	0	58
-8	469	-451
-6	302	304
-4	0	5
-2	189	-234
0	573	-513
2	159	-167
4	394	415
6	326	-294
8	481	463
10	527	-542
12	102	102
14	58	-43
16	76	115
18	71	102
20	80	-76
0	16	L
-20	143	149
-18	164	141
-16	744	-779
-14	80	89
-12	642	706
-10	218	-212
-8	155	127
-6	82	-98
-4	0	-28
-2	140	131
0	418	-434
2	218	280
4	840	868
6	492	-492
8	544	-524
10	210	220
12	240	-226
14	0	16
16	366	-338
18	168	-184
0	18	L
-18	348	330
-16	439	-415
-14	0	7
-12	146	-138
-10	528	571
-8	41	-22
-6	266	280
-4	250	255
-2	428	-453
0	145	187
2	266	-278
4	878	902
6	294	-318
8	0	2
10	326	-388
12	238	247
14	136	-96
16	86	64
0	20	L
-16	162	182
-14	112	-115
-12	48	-49
-10	173	-185
-8	213	230
-6	148	140
-4	170	-183
-2	114	91
0	161	-146
2	409	399
4	78	-90
6	161	186
8	0	-13
10	259	245
12	124	87
14	259	-203
0	22	L
-12	85	-112
-10	73	-75
-8	177	-165
-6	0	-14
-4	131	134
-2	142	-125
0	50	-49
2	229	238
4	71	78
6	54	55
8	78	-61
10	0	-20
0	24	L
-8	102	-90
-6	68	-76
-4	86	80
-2	57	-83
0	114	-118
2	201	186
4	344	-372
6	157	171
1	-25	L
-3	145	-143
-1	142	-156
1	0	-59
3	137	166
5	127	-121
1	-23	L
-7	245	-209
-5	244	207
-3	75	-71
-1	55	-62
1	147	104
3	307	-290
5	420	424
7	223	-241
9	179	179
11	91	91
1	-21	L
-11	59	46
-9	338	269
-7	206	-208
-5	145	113
-3	0	2
-1	205	208
1	0	-59
3	162	-146
5	0	54
7	97	-89
9	0	-19
11	0	-5
13	185	-174
15	193	160
1	-19	L
-15	0	-47
-13	194	170
-11	0	11
-9	151	-116
-7	187	134
-5	90	-80
-3	92	-84
-1	130	139
1	124	123
3	586	-650
5	369	405
7	550	-590
9	137	137
11	66	62
13	35	16
15	123	-120
17	0	-44
19	151	178
1	-17	L
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-15	302	280
-13	98	-111
-11	0	-11
-9	346	-353
-7	713	697
-5	628	-654
-3	71	34
-1	490	449
1	687	663
3	215	191
5	202	-186
7	286	-287
9	373	-361
11	220	245
13	137	92
15	256	-273
17	81	-98
19	285	-259
1	-15	L
-19	236	-250
-17	117	96
-15	54	-82
-13	497	466
-11	494	-477
-9	604	-579
-7	1284	1309
-5	89	44
-3	572	-588
-1	134	-76
1	1035	1079
3	541	538
5	271	-262
7	511	-516
9	71	95
11	306	-310
13	403	502
15	391	-401
17	112	153
19	187	88
21	275	-267
1	-13	L
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-17	262	-237
-15	0	-2
-13	0	86
-11	705	744
-9	1607	-1688
-7	789	819
-5	538	-592
-3	247	-233
-1	618	652
1	241	-191
3	574	604
5	266	286
7	335	319
9	374	394
11	527	594
13	0	43
15	155	180
17	80	-63
19	74	99
21	55	74
23	155	-172
1	-11	L
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-9	282	201
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-3	374	-350
-1	187	152
1	1860	1935
3	1835	-1810
5	56	59
7	312	349
9	741	772
11	161	-100
13	196	201
15	284	283
17	0	8
19	263	-281
21	93	117
23	287	283
1	-9	L
-23	287	152
-21	224	-254
-19	367	353
-17	131	133
-15	71	-61
-13	176	-134
-11	760	-731
-9	571	500
-7	557	478
-5	160	-184
-3	1718	-1771
-1	454	-499
1	0	-96
3	1487	-1347
5	1344	-1311
7	161	115
9	0	-1
11	484	461
13	265	284
15	40	85
17	166	193
19	41	-74
21	158	-202
23	605	607
1	-7	L
-23	226	207
-21	38	30
-19	244	245
-17	176	200
-15	512	509
-13	196	217
-11	412	-383
-9	872	815
-7	259	173
-5	409	-341
-3	965	1099
-1	1542	-1453
1	648	-458
3	915	-856
5	977	-979
7	524	-492
9	0	-16
11	106	-102
13	155	138
15	391	422
17	602	-688
19	305	-321
21	190	-230
23	376	455
1	-5	L
-23	34	53
-21	0	0
-19	98	47
-17	245	226
-15	39	64
-13	389	342
-11	1279	-1256
-9	1625	1625
-7	773	708
-5	827	676
-3	745	-1025
-1	335	164
1	2036	2271
3	1310	-1350
5	227	-140
7	656	-697
9	235	225
11	1210	-1307
13	420	454
15	324	-364
17	281	293
19	196	-211
21	474	-490
23	184	205
25	90	88
1	-3	L
-23	552	-552
-21	169	142
-19	0	-32
-17	403	-361
-15	131	-135
-13	808	795
-11	235	-225
-9	888	767
-7	1796	1910
-5	36	-67
-3	617	719
-1	1400	1460
1	931	-450
3	2200	2266
5	1255	-1188
7	124	170
9	424	402
11	81	-41
13	515	-533
15	392	407
17	0	3
19	258	314
21	196	210
23	193	-205
25	106	-104
1	-1	L
-25	249	223
-23	726	-715
-21	332	286
-19	144	125
-17	0	46
-15	913	-903
-13	695	-666
-11	1050	1120
-9	896	978
-7	1394	-1625
-5	891	-938
-3	2200	-2252
3	107	-364
5	1493	1318
7	365	162
9	318	279
11	1058	-1120
13	627	619
15	196	123
17	0	-58
19	645	-765
21	723	848
23	36	-101
25	50	69
1	1	L
-25	697	639
-23	698	-747
-21	151	138
-19	211	223
-17	386	-393
-15	595	-581
-13	787	-835
-11	179	-180
-9	53	-16
-7	1391	1409
-5	1173	-1193
-3	588	479
1	208	154
3	435	473
5	2750	2832
7	860	975
9	2021	-1971
11	620	-615
13	533	-562
15	482	470
17	358	345
19	1113	-1228
21	585	642
23	186	226
25	119	-82
1	3	L
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-23	0	13
-21	0	-9
-19	59	35
-17	161	152
-15	337	-335
-13	842	859
-11	275	-233
-9	1321	1381
-7	908	-733
-5	1271	1363
-3	448	575
-1	1195	-1141
1	2400	-2482
3	1080	834
5	338	-433
7	497	365
9	485	396
11	1472	-1552
13	167	186
15	172	157
17	302	223
19	914	-989
21	272	306
23	60	55
25	113	-116
1	5	L
-25	0	14
-23	142	129
-21	209	185
-19	144	142
-17	122	115
-15	417	-369
-13	93	-108
-11	308	316
-9	1757	-1701
-7	839	814
-5	693	-667
-3	637	-658
-1	291	-425
1	1639	1496
3	1357	1132
5	2019	2121
7	1060	-1054
9	1072	1021
11	737	801
13	253	-227
15	39	-14
17	58	72
19	272	-316
21	264	-282
23	160	-145
25	0	-6
1	7	L
-25	383	-365
-23	211	-193
-21	78	-74
-19	143	164
-17	101	98
-15	299	-305
-13	164	215
-11	697	-695
-9	370	338
-7	628	-567
-5	924	1037
-3	670	759
-1	91	126
1	359	342
3	634	741
5	1471	1543
7	1826	-1968
9	613	559
11	207	212
13	284	318
15	192	219
17	0	13
19	278	311
21	63	88
23	164	-157
25	160	-189
1	9	L
-25	166	-183
-23	77	-110
-21	200	-225
-19	115	109
-17	432	439
-15	122	68
-13	144	66
-11	135	106
-9	695	-712
-7	1200	-1228
-5	435	375
-3	1891	-1991
-1	98	-97
1	943	-1000
3	158	-28
5	44	-57
7	338	-367
9	185	-145
11	321	326
13	763	765
15	494	532
17	0	-102
19	302	308
21	0	-9
1	11	L
-23	214	-185
-21	120	140
-19	117	143
-17	154	-111
-15	295	295
-13	121	115
-11	54	15
-9	808	-847
-7	457	-432
-5	399	351
-3	287	313
-1	1222	-1196
1	274	-229
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Table 2 (*cont.*)

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6	72	39	-10	303	291	9	257	-255	-17	508	-458	17	77	-119	3	1453	-1528	-9	271	-242	-7	154	113	-11	160	176	8	93	-60	8	519	538	-10	1235	-1256	-2	230	-203	-2	0	-21
8	0	54	-8	0	-24	5	-21	L	-15	593	693	19	84	-93	5	395	360	-7	197	-153	-5	437	385	-9	215	-190	10	0	-41	10	372	-292	-8	296	-313	0	246	234	0	197	-258
10	434	-421	-6	762	823	-5	268	-229	-13	394	-421	21	119	-100	7	689	-709	-5	782	783	-3	181	125	-7	0	-15	12	232	-210	12	321	-315	-6	287	241	2	330	406	2	237	273
12	82	-116	-4	359	-374	-3	243	223	-11	0	9	5	-7	L	9	339	-342	-3	474	484	-1	955	-936	-5	523	596	14	81	24	14	0	-20	-4	361	291	4	180	-106	4	185	117
14	655	714	-2	305	335	-1	107	-108	-9	0	-13	-17	226	239	11	539	-564	-1	1213	1152	1	481	418	-3	651	-765	16	0	28	16	0	-61	-2	910	833	6	260	-235	6	0	69
16	208	222	0	284	-266	1	166	143	-7	521	616	-15	307	345	13	1082	-1010	1	1358	-1347	3	415	382	-1	146	142	6	-12	L	6	-4	L	0	306	-242	8	618	573	8	270	-287
18	50	65	2	247	-222	3	82	46	-5	0	16	-13	277	-291	15	496	500	3	328	-324	5	0	-54	1	312	383	-4	269	-266	-12	376	366	2	438	-372	10	691	641	6	18	L
20	126	-113	4	286	-279	5	345	-296	-3	0	-36	-11	201	-184	17	0	11	5	224	-4	7	542	466	3	0	-1	-2	198	186	-10	0	-34	4	458	432	12	0	27	-8	405	395
22	214	240	6	142	174	7	186	135	-1	379	-359	-9	293	-290	19	182	119	7	1179	1152	9	286	-270	5	346	-419	0	445	443	-8	0	112	6	498	-493	14	118	-152	-6	527	-500
4	10	L	8	500	477	9	264	-205	1	76	95	-7	385	445	21	0	-71	9	537	464	11	448	432	7	0	-10	2	804	722	-6	222	-180	8	473	-397	16	110	-97	-4	323	335
-22	169	-202	10	673	-706	11	304	312	3	331	-253	-5	900	-1178	5	-1	L	11	1822	-1833	13	307	-246	9	219	-223	4	1426	-1563	-4	388	330	10	355	-330	18	225	232	-2	151	-137
-20	197	177	12	154	-141	5	-19	L	5	442	440	-3	152	-199	-19	0	-18	13	1150	1116	15	208	-168	5	19	L	6	715	699	-2	0	-193	12	550	-581	8	10	L			

structure (Karle, 1968) in the *noncentrosymmetric* space group $F1$.

For convenience, in order to contain the coordinates of one molecule within the bounds of the unit cell, the y coordinates of the atoms in the partial structure I, Fig. 1, were arbitrarily shifted by $\frac{1}{2}$. The change in origin from that originally specified in the phase determination had the effect of changing the signs of all reflections which obey the condition: $(-h+k)/2$ is odd. All further discussion of signs as well as the signs in Table 2 refer to the new origin.

Phases based on the partial structure were accepted if $|F_c| > 0{\cdot}25|F_o|$ for $|E_o| > 1{\cdot}5$, and they were used as a starting set in the tangent formula (Karle & Hauptman, 1956). The resulting E map showed that two of the atoms assumed for the partial structure had disappeared. The 12 meaningful atoms (peak values of 200–400 on an arbitrary scale) were eventually identified as (1), (5), (6), (7), (8), (9), (10), (11), (12), N(13), O(20), and O(22), (see Fig. 2). Eight new peaks (peak values 170–250), which appeared in positions that could be part of the molecule, were used in a subsequent partial structure-tangent formula cycle; six additional peaks that could have been part of another molecule related by a center of symmetry were not used. The E map based on the partial structure of 20 atoms now revealed the 25 atoms of another molecule, related by a center of symmetry that did not correspond to an origin in the $F1$ cell (Fig. 3). At this point, two water molecules were also found. Coordinates of the molecules were translated so as to place them in an $F\bar{1}$ cell, and a difference map revealed that each asymmetric unit had a total of four water molecules. Chemical information available to us indicated that the crystal contained at least two, and probably more, molecules of water crystallization for each chromophore molecule.

After refining the coordinates, the original phase determination was re-examined to determine the points of difficulty. The following exceptions to the $\sum_2$ relationship were noted:

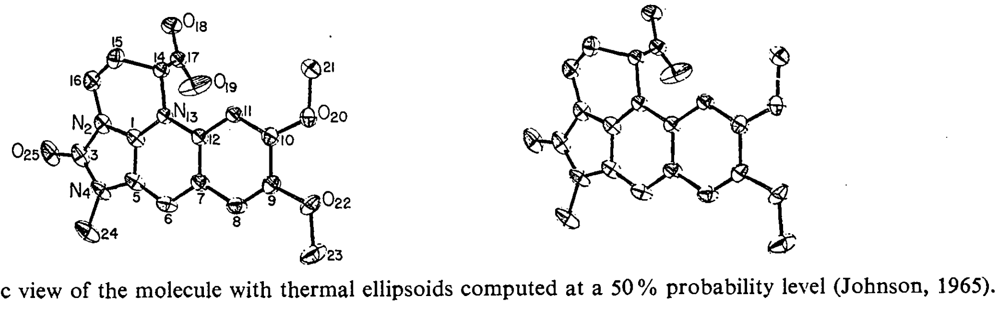


Fig. 2. A stereoscopic view of the molecule with thermal ellipsoids computed at a 50% probability level (Johnson, 1965).

$$(1)\quad \begin{array}{rrrc} 0 & 8 & 0 & - \\ 1 & \overline{19} & 3 & - \\ \hline 1 & \overline{11} & 3 & - \end{array} \qquad (4)\quad \begin{array}{rrrc} 0 & \overline{18} & 16 & - \\ 1 & 13 & 5 & - \\ \hline 1 & \overline{5} & 21 & - \end{array}$$

$$(2)\quad \begin{array}{rrrc} 0 & \overline{18} & 16 & - \\ 5 & 15 & \overline{3} & - \\ \hline 5 & \overline{3} & 13 & - \end{array} \qquad (5)\quad \begin{array}{rrrc} \overline{1} & 19 & \overline{7} & - \\ 1 & \overline{7} & 23 & \pm \\ \hline 0 & 12 & 16 & + \end{array}$$

$$(3)\quad \begin{array}{rrrc} \overline{4} & \overline{4} & 8 & + \\ 5 & 15 & \overline{3} & - \\ \hline 1 & 11 & 5 & + \end{array} \qquad (6)\quad \begin{array}{rrrc} \overline{1} & 5 & 9 & + \\ 1 & 7 & 7 & = \\ \hline 0 & 12 & 16 & + \end{array}$$

Each reflection had an $|E|$ value greater than 2·0, and the probability for each sign indication was in the range 0·94–0·97. Relationships (2)–(4) gave the three indications, each one incorrect, that symbol $d=h$. These were not the major sources of difficulty, however. Relationships (5) and (6) led to an incorrect sign for 0,12,16, which in turn caused a large subset of signs to be reversed. In spite of faulty sign indications, a sufficient fragment of the molecule appeared in an E map which could be used for a partial structure in a space group with less symmetry.

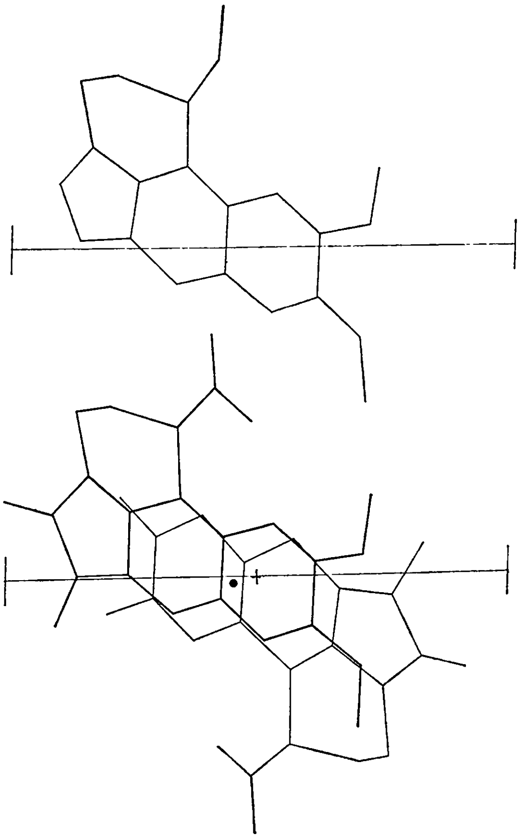


Fig. 3. Progress in obtaining positions of the atoms, assuming that the cell is noncentrosymmetric. Molecules were related by a center of symmetry, indicated by ●, and required translation in order that a center of symmetry in the cell, indicated by +, coincided with the center of symmetry between the two molecules.

Identification of the N and O atoms, aside from chemical considerations, was made from the weight of the Fourier peaks. It was independently confirmed by the behavior of the thermal parameters in the least-squares refinement in the case where all the nonhydrogen atoms of the molecule were labeled as carbon atoms. Furthermore, a difference map computed after the first cycle of full-matrix refinement with anisotropic thermal factors was essentially featureless, except for the maxima ($\sim$0·5 to 0·75 e.Å^{-3}) associated with the hydrogen atoms.

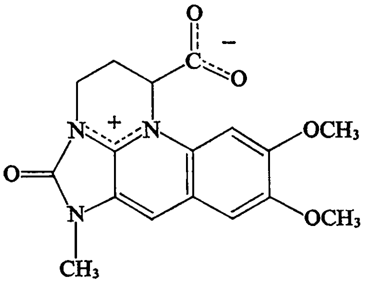
Isotropic refinement with individual scale factors for each layer and without hydrogen atoms led to an R index of 16·4%. The values of the individual scale factors were similar in magnitude, but they varied from each other in a random fashion. The data were adjusted to one scale by the values for the scale factors for the separate layers; subsequently, only one scale factor was varied in the anisotropic refinement. The weighting function used in the expression $\sum w(|F_o|^2-|F_c|^2)$ was: $w=0·5$ for $F_o=0$, $w=1·0$ for $|F_o|<40$ and $w=\frac{40}{|F_o|}$ for $|F_o|\geq 40$. Sixteen hydrogen atoms were included with constant parameters in the final cycles of the anisotropic refinement. Their approximate coordinates as found in a difference map are listed in Table 3, and the thermal parameters used were the same as those of the atom to which each hydrogen atom is attached. The three hydrogen atoms on the methyl C(24) atom were not found, as well as the hydrogen atoms belonging to $W(2)$, $W(3)$, and $W(4)$. The final R index for the observed data is 9·0%. Observed and calculated structure factors are listed in Table 2. Fractional coordinates and thermal parameters are shown in Table 4. Thermal parameter values should be considered as only approximate descriptions of the motions of the atoms, because of the way in which the data had to be collected.

Table 3. *Approximate coordinates for hydrogen atoms as found in a difference map*

	x	y	z
H(6)	0·338	0·578	0·188
H(8)	0·512	0·610	0·280
H(11)	0·608	0·388	0·283
H(14)	0·533	0·318	0·213
H(15-1)	0·503	0·322	0·100
H(15-2)	0·442	0·253	0·122
H(16-1)	0·292	0·310	0·038
H(16-2)	0·193	0·278	0·102
H(21-1)	0·840	0·388	0·345
H(21-2)	0·695	0·370	0·395
H(21-3)	0·817	0·397	0·428
H(23-1)	0·540	0·657	0·377
H(23-2)	0·733	0·682	0·410
H(23-3)	0·693	0·688	0·338
HW(1-1)	0·092	0·295	0·313
HW(1-2)	−0·105	0·288	0·307

Discussion

The structural formula of the trimethylated derivative of the chromophore in the fluorescent peptide isolated from iron-deficient cultures of *Azotobacter vinelandii* has been established by X-ray analysis to be:



The molecule is shown in the stereodiagram in Fig. 2. The unusual heterocyclic structure of the chromophore does not appear to fit any naturally occurring system (Corbin, Karle & Karle, 1970). The molecule exists as a zwitterion, where the negative charge is divided between the two oxygen atoms in the carboxyl group with the two C⩵O distances differing by 0·02 Å (Fig. 4); the positive charge is divided between the two nitrogen atoms, N(2) and N(13), with N(13) probably possessing most of the charge since the C(1)–N(13) bond length is more than 0·04 Å shorter than the C(1)–N(2) bond length. All four C–N bonds in the five-membered ring are adjacent to double bonds. They assume a definite double-bond character, evidenced by their foreshortened bond lengths, 1·34 to 1·38 Å, as compared to 1·47 to 1·50 Å for the single bonds N(4)–C(24), N(2)–C(16), and N(13)–C(14). The molecule is characterized by two planes whose equations are:

$$7{\cdot}07485x+2{\cdot}67101y-13{\cdot}3834z=1{\cdot}53679 \qquad (A)$$

$$5{\cdot}61748x-2{\cdot}52317y+16{\cdot}0298z=4{\cdot}70301 \qquad (B)$$

All atoms (excluding H atoms), except the carboxyl ion and C(15), lie essentially in plane *A*, the greatest deviations being −0·068 Å for C(23) in one of the methoxy groups and +0·127 Å and −0·120 Å for C(16) and C(14), respectively. Atom C(15) is 0·66 Å above this plane. The greatest deviation for any of the atoms comprising the three collinear rings is +0·034 Å for C(3). The carboxyl ion and the bonded C(14) atom, coplanar to within 0·003 Å, lie in plane *B* which

Table 4. *Fractional coordinates and thermal parameters*

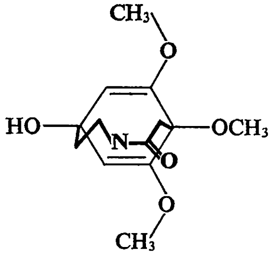
Thermal parameters are of the form $T=\exp\left[-\tfrac{1}{4}(B_{11}h^2a^{*2}+B_{22}k^2b^{*2}+B_{33}l^2c^{*2}+2B_{12}hka^*b^*+2B_{13}hla^*c^*+2B_{23}klb^*c^*)\right]$.
The B_{ij} values are in Å² units.

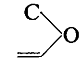
	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	B†
C(1)	0·3386	0·4202	0·1486	1·13	2·48	2·85	−0·28	−0·15	0·66	2·0
N(2)	0·2614	0·3806	0·1014	1·36	2·79	2·67	−0·71	−0·76	0·33	2·3
C(3)	0·1844	0·4200	0·0639	1·98	4·19	3·20	−0·71	−0·91	1·16	3·1
N(4)	0·2093	0·4845	0·0923	2·34	3·26	3·56	−0·05	−1·06	1·49	2·8
C(5)	0·3036	0·4869	0·1442	1·33	2·64	3·38	−0·07	−0·30	1·16	2·5
C(6)	0·3681	0·5356	0·1882	2·37	2·02	4·10	0·14	−0·15	0·99	2·6
C(7)	0·4637	0·5169	0·2357	2·37	1·86	3·03	−0·21	−0·22	0·33	2·2
C(8)	0·5371	0·5661	0·2822	2·66	1·86	3·56	0·07	−0·15	0·16	2·5
C(9)	0·6297	0·5496	0·3277	2·43	2·02	3·03	−0·49	−0·53	−0·11	2·3
C(10)	0·6629	0·4812	0·3295	2·53	2·17	2·49	−0·02	−0·38	0·14	2·2
C(11)	0·5915	0·4323	0·2858	2·27	1·70	2·49	−0·02	−0·45	0·16	1·9
C(12)	0·4977	0·4493	0·2386	2·01	1·70	2·49	−0·35	−0·38	0·16	1·9
N(13)	0·4264	0·4011	0·1924	1·65	1·70	2·49	−0·35	−0·53	0·33	1·7
C(14)	0·4380	0·3270	0·1913	2·24	1·70	2·49	−0·07	−0·60	0·08	1·9
C(15)	0·4269	0·2999	0·1214	2·73	2·64	2·67	−0·35	0·02	0·16	2·4
C(16)	0·2842	0·3101	0·0878	3·28	2·95	3·03	−0·49	−0·91	−0·09	2·7
C(17)	0·3129	0·2903	0·2297	2·50	2·02	2·67	−0·14	−0·45	0·33	1·9
O(18)	0·2988	0·2283	0·2245	2·95	1·70	4·27	−0·56	−0·03	0·49	2·5
O(19)	0·2392	0·3266	0·2609	6·66	2·64	9·62	−0·35	5·70	0·16	4·9
O(20)	0·7559	0·4711	0·3774	2·89	2·48	3·03	0·21	−1·52	−0·16	2·4
C(21)	0·7865	0·4031	0·3848	5·39	2·79	3·56	1·20	−1·52	0·14	3·2
O(22)	0·7049	0·5931	0·3738	4·29	2·02	4·10	−0·28	−1·29	−0·83	3·0
C(23)	0·6677	0·6615	0·3752	3·99	2·17	6·06	−0·14	−0·53	−0·99	3·8
C(24)	0·1409	0·5427	0·0688	3·31	4·81	5·34	1·06	−1·06	2·49	4·0
O(25)	0·1053	0·4006	0·0166	3·73	5·28	3·38	−0·85	−2·13	1·16	3·7
W(1)	0·0085	0·2901	0·3328	2·99	4·81	3·74	−0·28	0·07	0·33	3·7
W(2)	−0·0439	0·5571	0·4722	3·93	3·88	4·10	−0·71	−0·91	0·06	3·6
W(3)	0·0635	0·3183	0·4629	9·45	4·97	4·63	0·78	−1·59	−0·49	5·1
W(4)	0·3869	0·2918	0·4738	14·52	9·47	10·87	0·49	−1·67	−0·83	9·4
Standard deviations										
C	0·0006	0·0002	0·0002	0·32	0·22	0·20	0·16	0·16	0·16	
N	0·0005	0·0002	0·0002	0·26	0·16	0·16	0·14	0·14	0·13	
O	0·0004	0·0002	0·0002	0·26	0·14	0·14	0·14	0·14	0·11	
W(1–3)	0·0005	0·0002	0·0002	0·25	0·16	0·16	0·14	0·14	0·13	
W(4)	0·0010	0·0004	0·0004	0·65	0·48	0·48	0·42	0·42	0·32	

† Thermal factors for the isotropic refinement.

is perpendicular to the plane of the rings. This configuration results in a minimum intramolecular distance between $N^+(13)$ and $O^-(19)$ of only 2·64 Å.

This investigation affords a further insight into the preferred orientation of OCH_3 groups in enol or phenol ethers. The two OCH_3 are *ortho* to each other, in the plane of the adjacent aromatic ring, and are disposed in opposite directions. The C(11)···C(21) and C(8)···C(23) separations are only 2·82 and 2·77 Å, respectively. Hydrogen atoms on the CH_3 groups are oriented so that one H atom is in the plane of the heavy atoms and directed away from the ring, whereas the other two H atoms are symmetrically disposed above and below the plane maximizing the distance of closest approach between an H atom and C(8) or C(11) on the ring. In a photoproduct from a mescaline derivative (Yonemitsu, Nakai, Kanaoka, Karle & Witkop, 1969; Karle & Karle, 1970),



the two OCH_3 groups adjacent to the double bonds lie so that each  group is planar, and the CH_3 groups are *cis* to the double bonds. In the present investigation, this type of preferred orientation is reflected in the value of C–C bond lengths in the adjacent aromatic ring where C(8)–C(9) and C(10)–C(11), the bonds *cis* to the O–CH_3 bonds, are 0·10 and 0·06 Å shorter than the C(9)–C(10) bond. A similar observation has been made in the

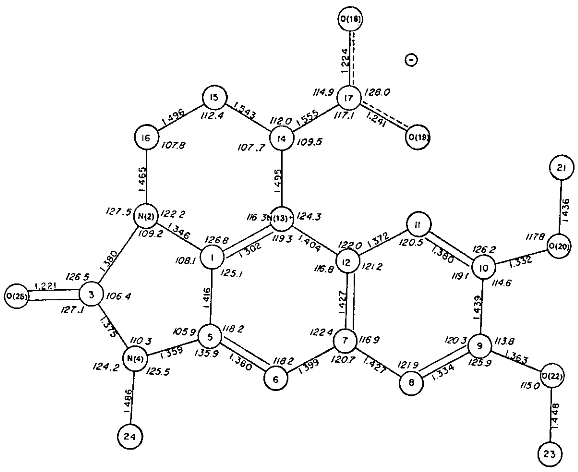


Fig. 4. Bond lengths and angles. Standard deviations based on the least-squares fit alone are 0·007 Å for the bond lengths and 0·4° for the angles.

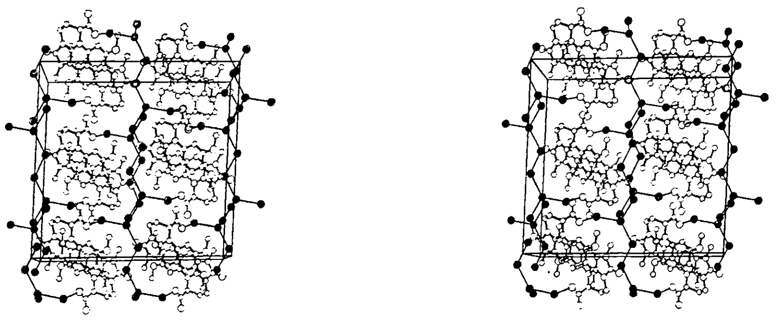


Fig. 5. Packing in the $C_{17}H_{17}N_3O_5.4H_2O$ crystal. Shaded atoms represent the O atoms of the H_2O molecules, and the lines radiating from them indicate possible hydrogen bonds. Axial directions are *b*↓, *c*→ and *a* out from the plane of the paper.

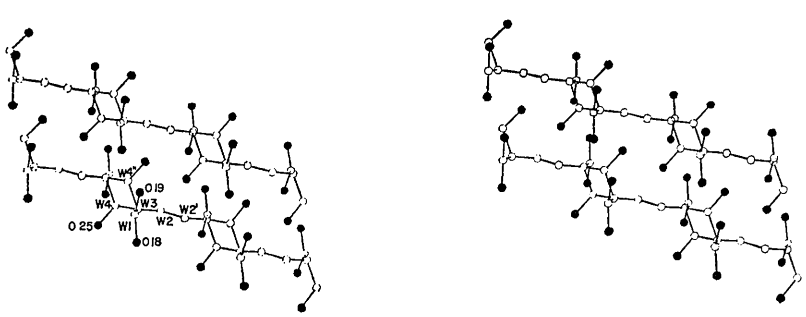
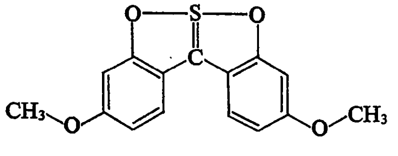
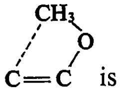


Fig. 6. A layer of H_2O molecules parallel to the *ab* plane. Shaded atoms represent O(18), O(19), and O(25) from the organic moiety. The lines indicate possible hydrogen bonds. Axial directions are *a*↑, *b*→ and *c* into the plane of the paper.



molecule (Gilardi & Karle, 1971), where the C–C bonds *cis* to the O–CH_3 bonds are 0·04–0·05 Å shorter than the C–C bonds *trans* to the O–CH_3 bonds. In each of the aforementioned molecules, as well as in reserpine (Karle & Karle, 1968), the *C*···*C* distance in  is only 2·77 to 2·82 Å. Observations of preferred orientation, by means of the nuclear Overhauser effect, have also been made on enol and phenol ethers in solution; the methoxy and vinyl protons *cis* to the ethylenic bond show long-range coupling (Woods, Miura, Ogiso, Kurabayashi & Mishima, 1968). If a methoxy group is not coplanar with an attached unsaturated ring, such as the central OCH_3 group in 3,4,5-trimethoxyphenyl derivatives, the chemical reactivity of the nonplanar OCH_3 is enhanced (Brossi & Teitel, 1969).

The high-water content in this crystal, four H_2O molecules per organic molecule, is interesting considering that the organic moiety participates in only three hydrogen bonds, O(25)···H*W*(4), O(18)···H*W*(1), and O(19)···H*W*(1). Fig. 5 (stereodiagram) illustrates the packing of the molecules and shows the layered structure in which layers of organic molecules are interleaved with layers of H_2O molecules, hydrogen-bonded to each other. The H_2O molecules are easily lost from the lattice, destroying the crystal in the process. The depiction in Fig. 6 is at right-angles to that in Fig. 5 and it shows a portion of the layer of H_2O molecules parallel to the *ab* plane. Thermal parameters for *W*(4) are rather large, probably an indication of a reduced occupancy. Occupancy parameters were not refined. It may be at this site that the lattice begins to lose its water content.

Lengths for the hydrogen bonds are shown in Table 5. Hydrogen atoms on three water molecules were not located, and there are several different ways in which they could be directed. A difficulty arises in presuming that a hydrogen bond exists between *W*(2) and *W*(2′), formed across a crystallographic center of symmetry. Since a hydrogen bond requires one H atom between two O atoms, and a center of symmetry implies either two H atoms or none, there may be a small deviation from a centrosymmetric space group. Another question arises as to whether there is hydrogen bonding between *W*(3) and *W*(4) (see Figs. 5, 6 & 7). There are a sufficient number of protons for one to exist between *W*(3) and *W*(4); the *W*(3)···*W*(4) distance of 3·05 Å, although somewhat long for an OH···O bond, has been observed in other hydrates; and the coordination about *W*(3) is unusual, being a distorted trigonal bipyramid with one position vacant. However, a trigonal bipyramid type of coordination about a water molecule has been established in at least one inorganic crystal, $Na_4XeO_6.8H_2O$ (Ibers, Hamilton & MacKenzie, 1964).

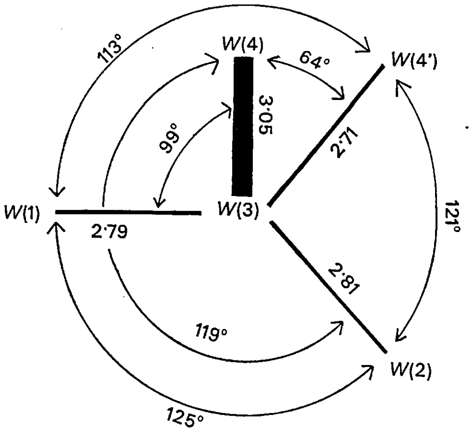


Fig. 7. Geometry about the *W*(3) atom.

Table 5. *Possible hydrogen bonds*

	Lengths (Å)	Symmetry operation on primed atoms
O(18)···*W*(1′)	2·97	$\bar{x}, \frac{1}{2}-y, \frac{1}{2}-z$
O(19)···*W*(1)	2·70	
W(1)···*W*(3)	2·79	
W(2)···*W*(2′)	2·81	$\bar{x}, 1-y, 1-z$
W(2)···*W*(3′)	2·81	$\bar{x}, 1-y, 1-z$
W(3)···*W*(4′)	2·71	$\frac{1}{2}-x, \frac{1}{2}-y, 1-z$
W(3)···*W*(4)	3·05	
W(4′)···O(25)	2·81	$-\frac{1}{2}+x, y, -\frac{1}{2}+z$

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