and plane *C* through C(2), O(3), and C(4)] is 43°. Some deviations from the ideal planarity in the areas of the double bonds are found. The ring atoms O(3), C(2), N(1), and C(9a) are coplanar (plane *E*), whereas C(1′) is out of the plane by 0·16 Å, and a twist of about 7° around the double bond C(4)–C(5) is observed. By this twist the $2p_z$ orbital of C(4) is brought nearer to the $2p_z$ orbital of C(2) under the boat (whereas the distances between the orbitals is increased over the boat). The distance C(2)–C(4) is 2·41 Å, and the overlap integral $S_{2·4}$ calculated according to Mulliken, Rieke, Orloff & Orloff (1949) is 0·08, a figure indicating some interaction between C(2) and C(4). The projection of the structure down [001] is shown in Fig. 3. A survey of the bond systems and conformations of some seven-membered rings will be given elsewhere (Jensen, 1972).

No intermolecular contacts significantly shorter than the sum of the respective van der Waals radii of the atoms are found in the structure.

Solutions of 2-phenyl-7-bromo-benz[*d*][1,3]oxazepine show no optical activity (Buchardt, 1967) and an interconversion between the two enantiomorphic conformers of the benzoxazepine ring is assumed to take place as is known for benzcycloheptatrienes (Tochtermann, Schnabel & Mannschreck, 1968) and related heterocyclic compounds (Mannschreck, Rissmann, Vögtle

& Wild, 1967). In the crystal all the molecules have the same chirality, and crystals of each chirality are assumed to co-exist in any batch.

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The Crystal and Molecular Structure
of 2,4,5,7-Tetraphenyl-6-(4-bromophenyl)-1,3-oxazepine

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2,4,5,7-Tetraphenyl-6-(4-bromophenyl)[1,3]oxazepine crystallizes in space group $P\bar{1}$ with $Z=2$ and unit-cell parameters $a=11·403$ (4), $b=6·394$ (5), $c=19·376$ (7) Å, $\alpha=86·52(5)$, $\beta=100·36(1)$, and $\gamma=98·97$ (9)°. The structure was solved by the heavy-atom method and refined by the full-matrix least-squares technique to a final *R*-value of 0·068, using 3077 three-dimensional diffractometer-collected single-crystal X-ray data. A conjugated triene bond system is found in the oxazepine ring, which adopts a boat conformation as usually found in seven-membered carbocyclic and heterocyclic rings with three double bonds. No considerable norcaradiene character of the oxazepine ring is found.

Ultraviolet irradiation of a variety of heteroaromatic *N*-oxides results in ring expansion (Spence, Taylor & Buchardt, 1970). The photoproducts of some quinoline *N*-oxides, isoquinoline *N*-oxides, and quinoxaline *N*-oxides were identified by infrared, ultra-violet, and n.m.r. spectroscopy and by two-dimensional X-ray determinations as benz[*d*][1,3]oxazepines (Buchardt, Jensen & Kjøller Larsen, 1967), benz[*f*][1,3]oxazepines (Simonsen, Lohse & Buchardt, 1970), and benz[*d*][1,3,6]oxazepines (Buchardt & Jensen, 1968) respectively. This paper describes the crystal structure of the main photoproduct of 2,3,5,6-tetraphenyl-4-(4-bromophenyl)-

pyridine *N*-oxide, *i.e.* 2,4,5,7-tetraphenyl-6-(4-bromophenyl)-1,3-oxazepine (I).

I
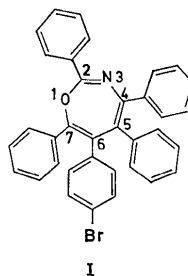
The work on this compound was taken up partly to give an unambiguous identification, and partly to obtain more detailed information about the bond system and the conformation of the 1,3-oxazepine ring.

Experimental

2,4,5,7-Tetraphenyl-6-(4-bromophenyl)-1,3-oxazepine was synthesized by O. Buchardt, C. L. Pedersen, and N. Harrit of the H. C. Ørsted Institute, University of Copenhagen, and they also prepared the single crystals used for the X-ray diffraction study. The compound was dissolved in benzene and crystallized as yellow triclinic needles, when petroleum ether was allowed to diffuse into the solution, m.p. 240–41 °C. The unit-cell dimensions, obtained from Weissenberg and precession photographs (Cu $K\alpha$ radiation, $\lambda = 1.5418$ Å and Mo $K\alpha$ radiation, $\lambda = 0.7107$ Å, respectively) and refined by the least-squares method, using the program *CELSIUS* (Liminga, 1965) are $a = 11.403$ (4), $b = 6.394$ (5), $c = 19.376$ (7) Å, $\alpha = 86.52$ (5), $\beta = 100.36$ (1), and $\gamma = 98.97$ (9)°. With two formula units per unit cell the calculated density is 1.347 g.cm^{-3}, in good agreement with the density of 1.34 (1) g.cm^{-3} measured by flotation in aqueous potassium iodide solution. The linear absorption coefficient, μ(Mo $K\alpha$) is 15.9 cm^{-1}.

All X-ray data were measured from a crystal with the dimensions $0.4 \times 0.45 \times 0.7$ mm with quartz monochromatized Mo $K\alpha$ radiation using a Nonius 3-circle automatic diffractometer. The crystal was mounted with the needle axis (b) parallel to the φ axis of the
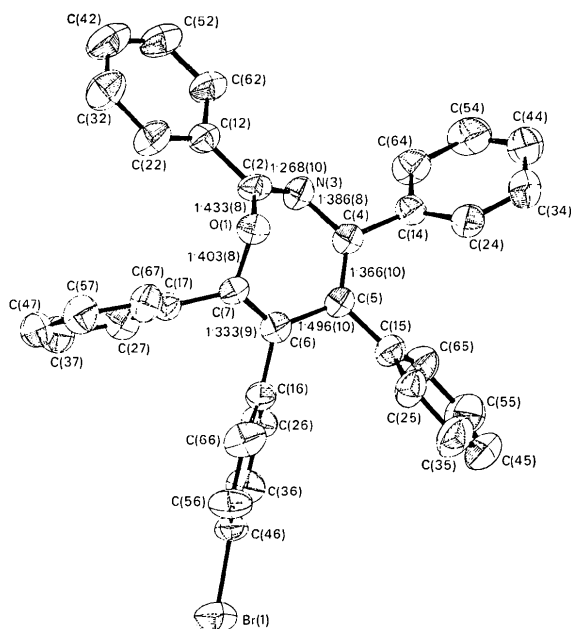

Fig. 1. 2,4,5,7-Tetraphenyl-6-(4-bromophenyl)-1,3-oxazepine. The non-hydrogen atoms are represented by their thermal ellipsoids scaled to enclose 50% probability. The atomic numbering is shown together with the bond lengths of the oxazepine ring.

goniometer, and the ω-scanning mode was used with a scan speed of $1.2°$ per minute, each reflexion being scanned over a range of $1.4°$. Of the 4840 independent reflexions within the range $2.5° \leq \theta \leq 25.0°$, 3077 had intensities greater than 2.5 times their corresponding estimated standard deviations and were considered observed. From the distribution of the values of the E's, of all measured $h0l$ reflexions, Table 1, the space group was considered to be $P\bar{1}$, and this was confirmed by the determination of the structure. In the structure determination and refinement no unobserved reflexions were included.

Table 1. *Distribution of normalized structure factors $E(h0l)$*

	Observed	Theoretical	
		Centric	Acentric
$\langle\lvert E\rvert\rangle$	0·81	0·798	0·886
$\langle\lvert E^2-1\rvert\rangle$	0·91	0·968	0·736
$\langle\lvert E\rvert^2\rangle$	1·00	1·00	1·00

The diffraction data were reduced to structure amplitudes by the ALGOL program *OUTDIFF-5*, written by A. M. Sørensen of this laboratory. No absorption corrections were applied.

Determination and refinement of the structure

The structure was solved by the heavy-atom method. The coordinates of the bromine atom were deduced from the three-dimensional Patterson map, and the positions of a further 31 non-hydrogen atoms were postulated from a three-dimensional electron-density map phased only on the contribution of the bromine atom. After four cycles of Fourier refinement a second electron-density map was calculated from which the positions of the remaining 6 non-hydrogen atoms were deduced. The structural parameters were further improved using the full-matrix least-squares method. After one cycle, in which all ring atoms were treated as carbon and in which the positional and individual isotropic thermal parameters were varied, the shifts in the thermal parameters for two atoms clearly proved these to be oxygen and nitrogen. In the difference Fourier map calculated after a further cycle of isotropic refinement, the anisotropy of the thermal movement of several atoms, especially the bromine atom, was indicated. The heights of the peaks corresponding to the 24 hydrogen atoms in the asymmetric unit varied from 0.2 to 0.7 e.A^{-3}, and the peaks of lowest intensity generally corresponded to atoms far away from the oxazepine ring. In the following cycles of full-matrix least-squares refinement the contributions of the hydrogen atoms were included, but their parameters were kept constant. Their thermal parameters were assumed to be the same as those of the carbon atoms to which they were bonded. The temperature factors of all non-hydrogen atoms were changed to anisotropic form and the positional and thermal atomic parameters were

varied in two blocks owing to the limited capacity of the least-squares program. Unit weight was given to each observed reflexion except for very weak reflexions $[F_o \leq 6\sigma(F_o)]$ which were given weights less than 1·0. The form factors for all atoms were taken from *International Tables for X-ray Crystallography* (1962). The final R-value is 0·068. The observed structure amplitudes and the final calculated structure factors are given in Table 2.

Nearly all calculations have been performed using the integrated program system *X-ray* 63 (Stewart, 1964) on the IBM 7094 computer at the Northern Europe University Computing Center, Lyngby, Denmark. The drawings were produced by *ORTEP*, (Johnson, 1965).

Description and discussion of the structure

The final structural parameters, together with their estimated standard deviations, are shown in Tables 3 and 4, and the interatomic distances and angles are shown in Tables 5 and 6. The atomic numbering is shown in Fig. 1. The bond lengths in the oxazepine ring clearly indicate the double bond character of C(2)–N(3), C(4)–C(5), and C(6)–C(7). A number of

Table 2. *Observed structure amplitudes and final calculated structure factors for* 2,4,5,7-*tetraphenyl*-6-(4-*bromophenyl*)-1,3-*oxazepine*

The three columns give H, F_o and F_c.

H,0,-22		
6	59	70
4	80	-96
3	91	-92
1	54	63
0	115	126
-1	51	51
H,0,-21		
-3	122	-123
-1	62	76
0	113	112
2	152	-140
3	141	-124
4	62	-63
6	119	113
7	115	114
H,0,-20		
6	92	84
5	56	67
4	46	34
3	127	-127
2	105	-105
0	64	90
-1	114	112
-4	90	-83
H,0,-19		
-5	51	-27
-4	49	-25
-2	131	127
-1	97	94
1	103	-81
2	63	-71
3	65	-74
4	55	20
5	114	98
6	100	96
7	48	-35
8	99	-90
9	66	-50
H,0,-18		
10	68	40
9	54	-24
8	58	-75
5	88	78
4	82	82
3	44	21
1	143	-124
0	53	-38
-1	156	135
-2	149	130
-4	59	-60
-5	137	-123
-6	58	-34
H,0,-17		
-7	45	-47
-6	61	-66
-4	68	72
-3	122	123
-1	56	-35
0	140	-138
1	127	-125
3	159	145
4	156	191
6	157	-145
7	131	-112
9	46	5
10	60	47
H,0,-16		
11	49	42
10	100	74
9	68	59
7	154	-159
6	66	-50
5	69	69
4	179	173
3	242	231
2	44	32
1	189	-187
0	279	-269
-1	194	-185
-2	93	90
-3	248	243
-4	112	121
-5	44	-44
-6	99	-90
H,0,-15		
-7	113	-106
-6	43	-44
-5	93	90
-4	158	151
-3	159	145
-1	165	-161
0	239	223
1	120	98
3	262	248
4	62	-56
5	165	-152
6	140	-129
7	75	-82
8	54	-76
9	131	111
10	81	63
H,0,-14		
11	61	-49
9	44	11
8	49	23
6	212	-204
5	237	-222
3	70	78
2	311	295
1	265	239
0	44	35
-1	106	-107
-2	261	-245
-3	150	-146
-5	195	195
-8	82	-54
-9	39	-19
H,0,-13		
-8	55	-08
-5	176	160
-4	143	142
-3	75	-72
-2	309	-301
-1	302	-291
0	65	-27
1	51	73
3	69	-58
4	148	-146
5	77	-63
7	215	202
8	290	280
9	140	125
10	68	-41
11	79	-73
H,0,-12		
11	74	-55
10	127	-111
8	65	51
7	307	297
5	138	-145
4	403	-394
3	111	-121
2	45	57
1	258	272
0	405	389
-2	119	-125
-5	61	62
-6	181	184
-7	53	55
-8	75	-63
-9	103	-98
-10	63	-45
H,0,-11		
-9	51	-41
-7	50	23
-6	111	108
-4	177	-178
-3	248	-249
-2	91	58
-1	53	60
0	309	319
1	216	234
2	172	174
3	181	-189
4	192	-201
6	148	126
8	102	-99
9	207	-202
H,0,-10		
10	82	-72
9	119	-113
6	468	452
5	313	304
4	58	31
3	400	-402
2	506	-458
1	163	-150
0	227	247
-1	363	376
-2	42	10
-3	359	-358
-4	262	-271
-5	83	-102
-6	130	133
-7	202	173
-8	123	124
H,0,-9		
-11	114	-106
-10	78	-59
-8	269	281
-7	160	158
-6	62	58
-5	404	-389
-4	342	-340
-2	449	442
-1	562	573
0	441	452
0	443	452
1	188	-184
2	653	-671
3	717	-724
4	68	-61
5	63	66
6	365	348
7	111	119
8	134	-131
10	116	-113
11	74	64
12	102	101
13	87	87
H,0,-8		
9	278	-275
8	109	-116
7	44	51
6	317	319
5	171	174
4	681	654
3	197	-155
2	209	-217
1	238	-257
0	193	178
-1	426	430
-3	107	-88
-4	317	-306
-5	147	-161
-6	185	-166
-7	66	63
-8	137	110
-11	60	-61
H,0,-7		
-9	137	128
-6	241	-241
-5	158	-161
-4	118	-103
-3	581	570
-2	360	385
-1	669	678
0	449	-518
1	479	-515
3	76	-72
4	243	263
5	331	332
6	58	77
7	227	-255
8	155	-209
9	128	-136
10	54	42
H,0,-6		
11	107	97
10	197	190
9	183	194
8	156	-169
7	236	-233
6	232	-230
5	178	167
4	45	59
3	219	228
2	346	-351
1	776	-834
0	214	-231
-1	312	-322
-2	366	376
-3	536	531
-5	100	-111
-6	117	-119
-7	63	-63
-9	134	139
H,0,-5		
-9	90	88
-7	91	-107
-6	249	-244
-5	66	58
-4	50	14
-3	86	110
-1	840	-894
0	846	-953
1	634	659
2	366	420
3	1031	1105
4	152	163
5	50	29
6	227	-225
7	176	-166
8	141	151
10	158	154
11	78	-88
12	58	-90
13	57	-78
H,0,-4		
8	243	242
7	52	-65
6	310	-304
5	169	-186
4	63	-63
3	532	563
2	948	-1018
1	299	321
0	420	-453
-1	525	528
-2	428	-432
-3	297	308
-4	857	894
-5	225	218
-6	215	-205
-7	227	-258
-8	55	-111
-10	58	59
-11	78	67
H,0,-3		
-11	83	79
-10	67	48
-9	79	-68
-8	161	-158
-7	257	-243
-6	176	167
-5	171	-133
-4	224	227
-3	136	-141
-2	293	261
-1	191	-208
2	557	600
3	318	319
4	308	-325
5	327	-342
6	179	-189
8	57	-46
9	194	198
10	83	-72
11	89	-86
12	83	-82
H,0,-2		
11	68	-71
7	290	278
6	154	156
4	201	-220
3	469	-496
2	54	-29
-2	211	-232
-3	487	-504
-4	236	-237
-5	157	174
-6	443	442
-7	146	157
-8	45	30
-9	103	-104
-12	75	38
H,0,-1		
-11	129	-127
-10	76	-60
-9	148	-138
-8	70	79
-7	264	267
-6	458	495
-5	74	80
-4	450	-465
-3	676	-717
-2	533	-552
2	247	292
3	990	-1137
4	707	-751
5	243	228
6	352	306
7	561	567
8	147	154
10	129	-123
H,0,0		
13	86	34
12	84	84
11	98	-101
10	376	-377
9	231	-232
7	339	357
6	162	173
5	152	-151
4	676	-702
3	1226	-1395
2	122	-138
H,1,-22		
4	96	75
2	69	-43
1	117	-105
-1	112	88
H,1,-21		
-2	72	63
1	125	-123
2	98	-88
4	73	68
5	61	52
H,1,-20		
7	124	-106
4	98	102
3	84	83
1	117	-105
0	142	-129
-1	86	-84
-2	61	57
-3	96	103
H,1,-19		
-3	104	104
-1	119	-121
0	165	-150
2	113	96
4	114	98
7	138	-122
8	66	-56
H,1,-18		
9	96	80
8	62	49
7	73	92
6	130	-116
5	145	-132
3	118	115
2	89	77
0	169	-161
-1	67	-59
-3	66	62
-4	134	117
-5	83	65
H,1,-17		
-7	82	-67
-5	129	125
-4	158	150
-2	213	-208
-1	99	-89
1	168	157
2	254	237
3	88	84
4	74	-57
5	170	-167
6	162	-163
7	68	-92
8	100	99
H,1,-16		
10	72	-42
8	64	61
4	85	-63
3	59	46
2	59	69
1	86	68
-1	112	-115
-2	184	-177
H,1,-15		
-6	79	81
-4	60	-56
-3	69	-46
-2	97	89
-1	92	-69
1	62	58
2	85	-84
3	134	-130
4	128	-123
5	84	81
6	106	93
7	171	148
H,1,-14		
9	188	-159
8	82	-80
6	51	42
4	135	-125
3	132	-136
2	112	-118
1	99	67
0	288	291
-1	372	362
-2	141	141
-3	157	-151
-4	72	-72
-5	82	-32
-7	119	105
H,1,-13		
-9	95	96
-8	136	135
-7	145	140
-6	60	10
-5	211	-206
-4	266	-252
-3	209	-214
-2	64	-40
-1	207	216
0	204	210
1	53	-48
2	322	-324
3	253	-255
5	152	134
6	382	372
7	79	80
8	132	-116
9	150	-145
10	108	-104
H,1,-12		
12	66	45
11	62	31
9	74	-71
8	56	-61
7	126	126
6	118	120
5	180	169
3	353	-345
2	437	-431
1	216	-213
0	277	263
-1	275	274
-2	350	342
-3	185	-176
-4	190	-186
-5	179	-170
-6	71	60
-7	126	111
-8	96	96
-10	86	-59
H,1,-11		
-6	122	-109
-5	196	-186
-4	78	-75
-3	245	246
-2	354	347
-1	319	326
0	161	-157
1	267	-266
2	181	-183
3	148	-150
4	161	153
5	214	207
7	182	-172
8	68	-45
9	88	-82
10	75	66
11	104	93
12	91	60
H,1,-10		
9	62	-48
8	244	-233
7	237	-228
5	260	255
4	545	533
3	605	574
2	70	46
1	493	-493
0	233	-230
-2	89	88
-3	357	362
-5	197	-181
-6	246	-250
-7	112	-110
-8	92	90
-9	126	122
-10	72	58
H,1,-9		
-9	94	77
-8	60	72
-7	60	-53
-6	102	-91
-5	58	60
-4	164	162
-3	193	191
-2	447	431
-1	392	-400
1	234	-241
3	113	-79
4	64	-48
5	85	-63
6	122	-132
7	125	-114
8	166	-160
9	156	138
10	148	144
11	93	73
H,1,-8		
10	111	117
7	154	-148
6	336	-333
5	85	-100
4	407	403
3	442	465
2	159	169
1	77	-65
0	524	-537
-1	91	63
-2	208	-202
-3	120	132
-4	216	211
-5	73	73
-6	269	-284
-7	168	-169
-8	87	-81
-10	97	99
H,1,-7		
-10	105	92
-6	119	-132
-5	89	104
-4	261	257
-3	424	409
-2	305	-292
-1	361	-371
0	203	-211
1	138	148
2	385	391
3	181	185
5	119	-121
6	174	-145
8	111	134
9	114	127
10	75	-62
11	63	-76
H,1,-6		
12	76	-96
10	56	-24
9	56	45
8	116	93
7	144	145
6	63	-62
5	263	-355
4	110	-114
2	268	271
1	54	75
0	116	110
-1	573	-587
-2	70	-79
-3	69	-76
-4	214	224
-5	240	238
-6	79	57
-7	69	-60
-8	60	-58
-11	83	69
H,1,-5		
-12	84	63
-11	76	68
-9	175	-179
-8	198	-196
-6	226	228
-5	327	322
-4	248	-225
-3	404	-394
-2	630	-642
-1	386	377
0	89	-64
1	1063	1096
2	851	856
4	580	-567
5	276	-263
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H,1,11		
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H,1,13		
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H,1,16		
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H,1,21		
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H,2,-20		
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H,2,-19		
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6	106	107
4	113	-95
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3	136	-123
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H,2,-16		
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3	192	190
2	124	-117
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7	90	-94
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7	62	-70
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9	107	84
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H,2,-10		
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8	96	81
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H,2,-8		
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7	140	-124
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H,2,-3		
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2	240	-237
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H,2,10		
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2	205	209
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-2	327	-331
-3	120	-117
-4	192	191
-5	386	379
-6	182	187
-7	129	-121
-8	180	-188
-11	75	65
H,2,13		
-12	66	41
-11	65	70
-9	87	-86
-8	87	-98
-7	161	-158
-6	79	67
-5	233	239
-3	118	-110
-2	193	-195
-1	99	-106
0	60	56
1	208	201
3	77	68
4	133	-119
5	174	-181
6	59	-67
7	75	67
H,2,14		
4	117	-97
3	43	-62
2	175	176
1	340	341
0	200	190
-2	117	-120
-3	305	-308
-6	101	93
-7	120	113
-9	108	-107
H,2,15		
-10	98	-97
-9	62	-43
-7	293	287
-6	204	208
-4	126	-132
-3	144	-139
-2	56	-52
-1	120	125
0	279	267
1	119	112
2	154	-155
3	325	-327
4	158	-151
6	138	138
H,2,16		
3	138	-124
2	233	-229
1	146	-136

Table 2 (cont.)

least-squares planes through parts of the molecule has been calculated and the parameters for some of them are given in Table 7. As expected from models and from known structures of seven-membered rings (cf. Table 8) the oxazepine ring adopts a boat conformation with the oxygen atom as bow atom. The bow angle (the angle between plane I through C(7), O(1), and C(2) and the least squares plane through C(2), N(3), C(6), and C(7), plane II,) is 60°, and the stern angle (the angle between plane II and the least-squares plane through N(3), C(4), C(5), and C(6), plane III) is 31°. The areas around the three double bonds are only approximately planar, (cf. Table 7): the deviation of C(12) from the least squares plane through O(1), C(2), N(3), and C(4) is 0·05 Å. The deviations of N(3), C(14), and C(15) from the plane through C(4), C(5), and C(6)

are −0·16, 0·06, and −0·07 Å respectively. These deviations do not describe a real twist, and they are probably caused by lack of space. About the bond C(6)–C(7), however, a real torsion of 10° is observed. This deviation from planarity may also be caused by overcrowding. As a result of this twist the distance between the $2p_z$ orbitals of C(2) and C(7) is diminished under the boat. This has been observed as well in a benz[d][1,3]oxazepine (Jensen, 1972) as in thujic acid (Davis & Tulinsky, 1966). The distance C(2)–C(7) is 2·28 Å, and the overlap integral $S_{2.7}$ calculated according to Mulliken, Rieke, Orloff & Orloff (1949) is 0·14, a figure which indicates a not quite negligible interaction between the two carbon atoms. Nevertheless, one would not describe the oxazepine ring as having a considerable degree of norcaradiene character.

Table 3. *Final heavy-atom parameters of* 2,4,5,7-*tetraphenyl*-6-(4-*bromophenyl*)-1,3-*oxazepine*
and their estimated standard deviations in parentheses

The positional parameters are multiplied by 10^4. The temperature factors are in the form

$$T_j = \exp\left[-\tfrac{1}{4}(h^2a^{*2}B_{11} + k^2b^{*2}B_{22} + l^2c^{*2}B_{33} + 2hka^*b^*B_{12} + 2hla^*c^*B_{13} + 2klb^*c^*B_{23})\right]$$

|	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
O(1)	822 (4)	2560 (7)	6607 (2)	3·82 (23)	2·35 (20)	3·69 (21)	0·40 (22)	0·67 (25)	−0·13 (16)
C(2)	592 (6)	413 (11)	6387 (3)	3·70 (35)	2·99 (33)	2·91 (28)	−0·90 (36)	0·72 (36)	−0·59 (24)
N(3)	1356 (5)	−830 (9)	6601 (3)	3·17 (28)	2·45 (26)	4·27 (28)	0·40 (28)	0·09 (32)	−0·40 (21)
C(4)	2435 (6)	−251 (10)	7050 (4)	3·26 (34)	2·16 (27)	3·79 (32)	0·14 (31)	0·40 (37)	−0·05 (23)
C(5)	2562 (6)	890 (10)	7640 (3)	3·04 (31)	2·08 (27)	3·69 (30)	0·13 (30)	0·21 (34)	0·04 (23)
C(6)	1543 (6)	1868 (9)	7809 (3)	3·51 (33)	1·52 (26)	3·68 (30)	0·04 (30)	0·69 (37)	−0·17 (22)
C(7)	686 (6)	2498 (9)	7314 (3)	3·20 (32)	1·96 (27)	3·09 (29)	0·00 (30)	0·34 (35)	−0·11 (22)
C(12)	−529 (6)	−128 (11)	5895 (3)	3·29 (32)	3·60 (36)	2·86 (27)	−0·16 (30)	0·41 (40)	0·21 (25)
C(22)	−1392 (7)	1225 (13)	5738 (4)	4·34 (39)	4·50 (40)	4·25 (35)	0·75 (41)	−0·47 (42)	−0·18 (29)
C(32)	−2435 (8)	666 (16)	5263 (5)	5·01 (47)	6·60 (56)	4·98 (44)	1·76 (52)	−0·58 (50)	0·50 (39)
C(42)	−2643 (9)	−1265 (17)	4939 (5)	5·69 (52)	6·86 (57)	5·18 (45)	−0·89 (59)	−0·93 (54)	−1·01 (41)
C(52)	−1765 (8)	−2601 (14)	5092 (4)	5·80 (50)	4·66 (43)	4·59 (40)	−0·68 (50)	−0·35 (51)	−1·11 (33)
C(62)	−718 (7)	−2080 (12)	5557 (4)	4·57 (41)	3·90 (37)	3·62 (32)	−0·32 (40)	0·10 (41)	−0·53 (27)
C(14)	3429 (6)	−1180 (11)	6838 (3)	3·60 (35)	2·76 (32)	3·58 (30)	0·83 (34)	0·74 (36)	−0·43 (23)
C(24)	4554 (7)	−26 (11)	6822 (4)	3·88 (38)	3·07 (34)	4·84 (37)	0·61 (37)	0·66 (42)	−0·75 (27)
C(34)	5446 (8)	−838 (15)	6561 (5)	4·00 (43)	6·74 (54)	5·90 (44)	1·49 (50)	0·73 (49)	−1·22 (38)
C(44)	5203 (9)	−2885 (17)	6317 (5)	5·27 (52)	7·82 (62)	6·19 (49)	4·03 (63)	−0·21 (57)	−2·18 (43)
C(54)	4096 (10)	−4064 (14)	6349 (5)	7·24 (60)	4·16 (42)	6·03 (46)	3·22 (55)	−0·53 (59)	−1·60 (34)
C(64)	3182 (7)	−3272 (12)	6594 (4)	5·15 (44)	3·00 (36)	5·28 (39)	0·99 (41)	0·03 (46)	−1·16 (29)
C(15)	3677 (6)	1146 (11)	8161 (4)	3·25 (34)	3·35 (34)	3·80 (31)	0·87 (35)	0·21 (37)	−0·53 (25)
C(25)	4268 (6)	3157 (11)	8346 (4)	3·24 (34)	3·39 (34)	6·33 (42)	0·18 (35)	0·16 (43)	−1·30 (30)
C(35)	5256 (8)	3426 (15)	8857 (5)	4·06 (45)	5·52 (51)	7·77 (57)	−0·27 (49)	−0·37 (57)	−2·54 (43)
C(45)	5723 (8)	1762 (20)	9224 (5)	4·23 (47)	9·40 (74)	6·14 (52)	1·21 (63)	−0·89 (54)	−2·52 (50)
C(55)	5164 (9)	−267 (17)	9051 (5)	6·44 (56)	7·11 (59)	5·80 (48)	4·05 (63)	−0·56 (60)	0·36 (42)
C(65)	4156 (8)	−593 (13)	8525 (4)	4·89 (44)	3·99 (40)	5·35 (42)	1·31 (44)	0·02 (49)	−0·06 (32)
C(16)	1512 (6)	2103 (10)	8555 (3)	3·08 (33)	2·59 (31)	3·37 (30)	0·34 (31)	0·50 (35)	−0·66 (24)
C(26)	1507 (7)	433 (11)	9048 (4)	5·08 (41)	2·56 (32)	3·66 (33)	1·11 (36)	0·90 (40)	−0·09 (25)
C(36)	1489 (7)	675 (11)	9742 (4)	5·61 (44)	2·53 (33)	4·11 (35)	1·09 (38)	1·06 (44)	0·31 (26)
C(46)	1484 (6)	2724 (11)	9974 (3)	4·01 (36)	3·78 (35)	2·74 (28)	0·19 (36)	0·37 (36)	−0·99 (26)
C(56)	1470 (8)	4381 (11)	9500 (4)	6·81 (49)	2·55 (34)	3·76 (34)	1·08 (40)	0·26 (45)	−0·77 (27)
C(66)	1482 (7)	4129 (11)	8810 (4)	5·83 (45)	2·19 (32)	4·45 (37)	0·62 (38)	−0·05 (45)	0·12 (26)
C(17)	−444 (6)	3152 (10)	7420 (3)	2·99 (32)	2·80 (30)	2·91 (27)	0·56 (31)	0·18 (33)	−0·18 (23)
C(27)	−1260 (7)	1851 (11)	7759 (4)	4·54 (40)	2·89 (33)	4·21 (35)	0·52 (36)	0·99 (42)	−0·06 (26)
C(37)	−2364 (8)	2430 (14)	7827 (4)	4·24 (43)	5·62 (49)	5·10 (44)	−0·27 (46)	1·18 (46)	−0·67 (35)
C(47)	−2663 (7)	4380 (15)	7536 (4)	4·33 (43)	5·71 (49)	4·86 (40)	1·85 (47)	0·32 (47)	−1·21 (35)
C(57)	−1839 (8)	5692 (13)	7207 (4)	4·95 (44)	3·74 (39)	5·56 (43)	1·97 (43)	0·23 (48)	−0·18 (32)
C(67)	−744 (7)	5133 (11)	7137 (4)	3·73 (39)	3·27 (36)	4·89 (37)	0·81 (36)	0·34 (41)	0·47 (28)
Br(1)	1523 (1)	3143 (2)	10929 (5)	6·20 (5)	5·03 (5)	3·94 (4)	0·09 (5)	0·75 (5)	−1·11 (3)
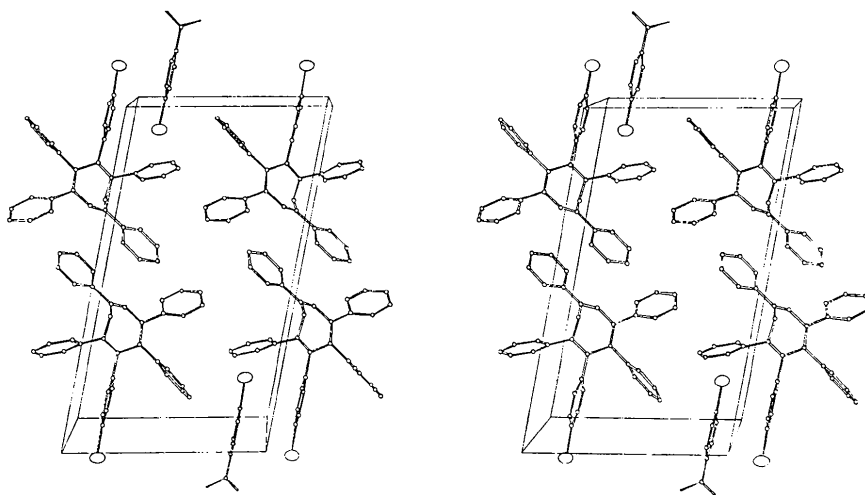
Fig. 2. Stereo diagram illustrating the molecular packing of 2,4,5,7-tetraphenyl-6-(4-bromophenyl)-1,3-oxazepine. The *a* axis is →, the *c* axis is ↓ and the *b* axis is directed upward.

Table 4. *Hydrogen atom parameters of 2,4,5,7-tetraphenyl-6-(4-bromophenyl)-1,3-oxazepine*

The positional parameters are multiplied by 10³.

	x/a	y/b	z/c	B
H(22)	−125	262	597	4·2
H(32)	−303	170	515	5·5
H(42)	−340	−170	461	5·6
H(52)	−190	−402	486	4·8
H(62)	−9	−305	566	4·0
H(24)	472	146	700	3·7
H(34)	625	4	656	5·3
H(44)	581	−353	613	6·0
H(54)	393	−555	618	5·3
H(64)	237	−414	660	4·4
H(25)	395	443	810	4·0
H(35)	567	491	897	5·3
H(45)	644	197	961	6·3
H(55)	547	−153	930	5·9
H(65)	376	−207	843	4·7
H(26)	151	−104	889	3·6
H(36)	149	−56	1008	4·0
H(56)	143	582	966	4·0
H(66)	148	538	848	3·9
H(27)	−105	47	797	3·8
H(37)	−294	148	808	4·8
H(47)	−347	481	756	4·8
H(57)	−204	710	701	4·3
H(67)	−17	613	690	3·8

In the norcaradiene ring system (Fritchie, 1966) six carbon atoms are almost coplanar ('stern' angle 4·2° compared to 31° in this compound), and the positions of the double bonds differ from those of the oxazepine ring. A possible delocalization of the double bond character in some seven-membered carbocyclic and heterocyclic rings containing the conjugated triene

bond system has been the subject of some considerations and molecular orbital calculations (Smid, 1962; Meier, Meuche & Heilbronner, 1962). The calculations predicted little, if any, delocalization, even when a ring for simplicity was assumed to be planar, and in full agreement with the predictions no evidence for delocalization of the double-bond character has been given in any of the solid-state structures of uncomplexed rings listed in Table 8. Evidence against a greater degree of delocalization of the double bond character

Table 5. *Bond lengths and their estimated standard deviations in parentheses*

O(1)—C(2)	1·433 (8) Å	C(5)—C(15)	1·469 (9) Å
C(2)—N(3)	1·268 (10)	C(15)-C(25)	1·391 (10)
N(3)—C(4)	1·386 (8)	C(25)-C(35)	1·357 (11)
C(4)—C(5)	1·366 (10)	C(35)-C(45)	1·367 (15)
C(5)—C(6)	1·496 (10)	C(45)-C(55)	1·386 (16)
C(6)—C(7)	1·333 (9)	C(55)-C(65)	1·390 (12)
C(7)—O(1)	1·403 (8)	C(65)-C(15)	1·409 (11)
C(2)—C(12)	1·459 (9)	C(6)—C(16)	1·469 (10)
C(12)-C(22)	1·391 (11)	C(16)-C(26)	1·390 (9)
C(22)-C(32)	1·380 (11)	C(26)-C(36)	1·366 (11)
C(32)-C(42)	1·387 (15)	C(36)-C(46)	1·412 (11)
C(42)-C(52)	1·396 (15)	C(46)-Br(1)	1·878 (7)
C(52)-C(62)	1·369 (11)	C(46)-C(56)	1·358 (10)
C(62)-C(12)	1·412 (11)	C(56)-C(66)	1·360 (11)
C(4)—C(14)	1·488 (11)	C(66)-C(16)	1·421 (10)
C(14)-C(24)	1·381 (10)	C(7)—C(17)	1·467 (10)
C(24)-C(34)	1·394 (13)	C(17)-C(27)	1·379 (10)
C(34)-C(44)	1·389 (15)	C(27)-C(37)	1·396 (13)
C(44)-C(54)	1·375 (14)	C(37)-C(47)	1·402 (13)
C(54)-C(64)	1·393 (15)	C(47)-C(57)	1·378 (12)
C(64)-C(14)	1·416 (10)	C(57)-C(67)	1·382 (13)
		C(67)-C(17)	1·415 (10)

Table 6. *Bond angles and their estimated standard deviations in parentheses*

C(7)—O(1)—C(2)	106·8 (5)°	C(15)-C(25)-C(35)	121·3 (7)°
O(1)—C(2)—N(3)	120·1 (6)	C(25)-C(35)-C(45)	122·5 (9)
O(1)—C(2)—C(12)	114·7 (6)	C(35)-C(45)-C(55)	117·8 (8)
C(12)-C(2)—N(3)	125·1 (7)	C(45)-C(55)-C(65)	120·9 (9)
C(2)—C(12)-C(22)	122·3 (7)	C(55)-C(65)-C(15)	120·4 (8)
C(2)—C(12)-C(62)	118·1 (7)	C(5)—C(6)—C(7)	122·4 (6)
C(62)-C(12)-C(22)	119·6 (6)	C(5)—C(6)—C(16)	117·1 (6)
C(12)-C(22)-C(32)	120·6 (8)	C(16)-C(6)—C(7)	120·5 (7)
C(22)-C(32)-C(42)	120·4 (9)	C(6)—C(16)-C(26)	123·9 (6)
C(32)-C(42)-C(52)	118·7 (8)	C(6)—C(16)-C(66)	120·1 (6)
C(42)-C(52)-C(62)	122·1 (8)	C(66)-C(16)-C(26)	116·0 (6)
C(52)-C(62)-C(12)	118·6 (8)	C(16)-C(26)-C(36)	123·3 (7)
C(2)—N(3)—C(4)	123·9 (6)	C(26)-C(36)-C(46)	118·7 (6)
N(3)—C(4)—C(5)	124·9 (7)	C(36)-C(46)-C(56)	119·2 (7)
N(3)—C(4)—C(14)	111·0 (6)	C(36)-C(46)-Br(1)	120·0 (5)
C(14)-C(4)—C(5)	124·0 (6)	Br(1)-C(46)-C(56)	120·8 (6)
C(4)—C(14)-C(24)	122·4 (6)	C(46)-C(56)-C(66)	121·9 (7)
C(4)—C(14)-C(64)	118·5 (6)	C(56)-C(66)-C(16)	120·9 (6)
C(64)-C(14)-C(24)	118·9 (7)	C(6)—C(7)—O(1)	119·6 (7)
C(14)-C(24)-C(34)	122·2 (7)	C(6)—C(7)—C(17)	126·7 (6)
C(24)-C(34)-C(44)	119·0 (8)	C(17)-C(7)—O(1)	113·6 (5)
C(34)-C(44)-C(54)	119·1 (10)	C(7)—C(17)-C(27)	122·0 (6)
C(44)-C(54)-C(64)	122·9 (9)	C(7)—C(17)-C(67)	119·5 (6)
C(54)-C(64)-C(14)	117·9 (7)	C(67)-C(17)-C(27)	118·5 (7)
C(4)—C(5)—C(6)	121·6 (6)	C(17)-C(27)-C(37)	121·9 (7)
C(4)—C(5)—C(15)	122·5 (7)	C(27)-C(37)-C(47)	119·3 (8)
C(15)-C(5)—C(6)	115·9 (6)	C(37)-C(47)-C(57)	118·7 (8)
C(5)—C(15)-C(25)	120·5 (6)	C(47)-C(57)-C(67)	122·4 (8)
C(5)—C(15)-C(65)	122·4 (6)	C(57)-C(67)-C(17)	119·2 (7)
C(65)-C(15)-C(25)	117·0 (6)		

is, besides the lengths of bonds in the rings, the fact that all the rings adopt a boat conformation, in which three almost planar areas are found (corresponding to the three double bonds), whereas the torsional angles around the single bonds have a considerable magnitude (30–50°).

Table 7. Least-squares planes and some angles between them

The equations of the planes are in direct (unit cell) space. Distances (Å) of atoms defining the plane are marked with an asterisk.

$$\text{I} \quad 10 \cdot 914x - 1 \cdot 3733y + 1 \cdot 9915z - 1 \cdot 8617 = 0$$
$$\text{II} \quad -7 \cdot 7199x - 3 \cdot 4050y + 8 \cdot 6657z - 4 \cdot 9478 = 0$$
$$\text{III} \quad -2 \cdot 3919x - 4 \cdot 8406y + 10 \cdot 940z - 7 \cdot 2839 = 0$$
$$\text{IV} \quad -6 \cdot 4148x - 1 \cdot 0369y + 16 \cdot 792z - 10 \cdot 302 = 0$$
$$\text{V} \quad 4 \cdot 8205x + 5 \cdot 2977y - 1 \cdot 6095z - 0 \cdot 47643 = 0$$
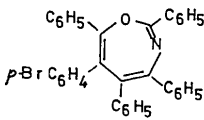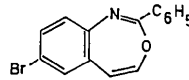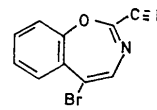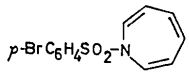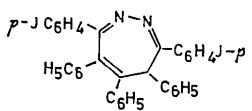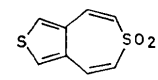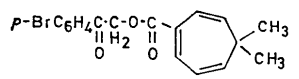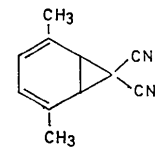
Table 7 (cont.)

	I	II	III	IV	V
O(1)	0·00*	0·729		0·000*	−0·213
C(2)	0·00*	0·011*		−0·001*	
N(3)		−0·008*	−0·015*	0·001*	
C(4)		0·633	0·032*	−0·001*	
C(5)		0·608	−0·031*		0·00*
C(6)		0·008*	0·014*		0·00*
C(7)	0·00*	−0·010*			0·00*
C(12)				0·051	
C(14)		0·052			
C(15)		−0·210			
C(16)					0·010
C(17)					0·215

∠ Plane I –Plane II   60°
∠ Plane II–Plane III   31

The five phenyl groups are planar within the experimental error, but deviations as big as 0·13 Å from these

Table 8. Seven-membered carbocyclic and heterocyclic rings containing a conjugated triene-bond system

Compound	Name	'Boat'-angles 'stern' 'bow'		Reference
C6H5, O, C6H5, N; p-BrC6H4, C6H5, C6H5	2,4,5,7-Tetraphenyl-6-(4-bromophenyl)-1,3-oxazepine	31°\	O /60°	This work
Br; N–C6H5, O	2-Phenyl-7-bromobenz[d]-[1,3]oxazepine	18°\	O /43°	Jensen (1972)
O, C≡N, N; Br	2-Cyano-5-bromobenz[f]-[1,3]oxazepine	26°\	O /56°	Simonsen (1971)
p-BrC6H4SO2–N	N-p-Bromobenzenesulphonylderivative of 1H-azepine	0·58-0·54 Å ↕\	C(4)–C(5) N / ↕ 0·60 Å	Paul, Johnson, Paquette, Barrett & Haluska (1968)
p-JC6H4, N–N, C6H4J-p, H5C6, C6H5, C6H5	3,7-Bis(p-iodophenyl)-4,5,6-triphenyl-4H-1,2-diazepine	48°\	C(4) /51°*	Brown, Towns & Trefonas (1970)
SO2	Thiepin 1,1-dioxide	22·8°\	O–S–O /44·6°	Ammon, Watts & Stewart (1970)
S, SO2	Thieno[3,4-d]thiepin 6,6-dioxide	19·8°\	O–S–O /45·2°	Sakore, Schlessinger & Sobell (1969)
p-BrC6H4C-C-O-C, O, H2, O, CH3, CH3	p-Bromophenacylester of 7,7-dimethylcyclo-heptatriene-3-carboxylic acid	24·4°\	CH3–CH3 /47·9°	Davis & Tulinsky (1966)
CH3, CN, CN, CH3	2,5-Dimethyl-7,7-dicyanonorcaradiene	4·2°\	NC–CN /72°	Fritchie (1966)

*_Calculated from the data given in the paper indicated.

planes are found for atoms bonded directly to the phenyl groups. Phenyl group C(12) to C(62) is nearly coplanar with the plane IV of the double bond C(2)–N(3), while the remaining four phenyl groups form angles of 45–65° with the planes III and V of the double bonds involving the ring atom, to which they are bonded.

The conformation of the oxazepine ring gives rise to the existence of two enantiomers of the molecule, and a rapid interconversion between these forms is assumed to take place in solution, a process analogous to that found for cycloheptatrienes (Anet, 1964), azepines (Mannschreck, Rissmann, Vögtle & Wild, 1967) and oxepines (Günther, 1965). As visualized in Fig. 1, no tendency to inversion is observed in the crystal, in which the atoms in the oxazepine ring and those bonded directly to this ring move less than the atoms in the outer parts of the molecule. In Fig. 2 a stereo view of the structure is given.

Several intermolecular van der Waals contacts have been observed, but the crystal packing is in general not very compact.

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La Structure Cristalline de l'Acide Ethylènediamine Tétra-acétique, EDTA

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Ethylenediaminetetra-acetic acid, EDTA, $C_{10}H_{16}O_8N_2$, crystallizes in the monoclinic system, space group $C2/c$, with cell dimensions: $a = 13·286$, $b = 5·578$, $c = 16·120$ Å, $\beta = 96·30°$ and 4 molecules per unit cell. The structure was solved by the symbolic addition procedure and refined by least-squares techniques. The final R index was 0·053. The molecule of EDTA exists in the crystal as the zwitterion $-CH_2(HOOCC\overset{+}{H}_2NHCH_2COO^-)_2]$. The hydrogen atom of the charged amino group $\overset{+}{N}H$ is involved in a trifurcated and chelated hydrogen bond. Neighbouring molecules of EDTA are bound by two very strong hydrogen bonds as short as 2·46 Å between COOH and COO^- groups. These nearly symmetrical hydrogen bonds, with the hydrogen atom clearly located at 1·19 Å from the oxygen, explain the high density and very low solubility of EDTA crystals. The ability of EDTA molecules and ions to adopt very different conformations is considered.

Généralités

L'acide éthylènediamine tétra-acétique EDTA, de formule brute $C_{10}H_{16}O_8N_2$, est un réactif largement utilisé en analyse complexométrique.

La structure a été déterminée dans le cadre d'une étude générale des sites de protonation et des liaisons hydrogène dans les acides α-amino-polycarboxyliques. A partir d'une étude approfondie par spectroscopie infrarouge de certains de ces acides et de leurs sels et plus