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The Crystal and Molecular Structure of the 1:1 Addition Compound of Piperidine with *p*-Toluic Acid, Piperidinium *p*-Toluate

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Crystals of piperidinium *p*-toluate, $[C_5H_{10}NH_2]^+[CH_3C_6H_4CO_2]^-$, are orthorhombic, space group *Pbca*, with eight formula units in the unit cell of dimensions $a=11{\cdot}01$ (1), $b=26{\cdot}45$ (2), $c=8{\cdot}97$ (1) Å. The structure has been determined from the data collected with Cu $K\alpha$ radiation on Weissenberg photographs, and refined by the block-diagonal least-squares method to a final R value of 0·084 for 1053 non-zero reflexions. The structure is ionic and isotypic with the two 1:1 addition compounds of piperidine with *p*-bromo and *p*-chlorobenzoic acids; acid and base moieties are held together by two types of $N^+\text{–}H\cdots O^-$ hydrogen bonds of 2·698 (5) and 2·766 (6) Å to form an infinite chain around the twofold screw axis parallel to the c axis. In the crystal the tetrahedral nature of the angle C–N···O seems to govern the orientation of the hydrogen-bonded molecules, and the molecular packing appears to play a predominant role in determining the hydrogen-bond lengths. In the *p*-toluate ion, the two C–O bond lengths are 1·278 (6) and 1·257 (5) Å, and the C–C–O angles are 116·4 (4) and 120·0 (4)°. The piperidine ring adopts a normal chair form. The average bond lengths for the C–N, C–C and N–H bonds are 1·508 (6), 1·526 (7) and 1·00 (5) Å, respectively. The average bond angle in the ring is 110·6 (4)°.

Introduction

Carboxylic acid–piperidine systems have been known as liquid salts (Prideaux, 1941), and their physicochemical properties such as dielectric polarization (Sobczyk & Syrkin, 1957; Sobczyk, 1959) and infrared spectra (Bruckenstein & Saito, 1965) have been studied in benzene solution. However, the nature of hydrogen bonds between the acid and base components remains an open question (Coates, 1941). The 1:1 adducts of benzoic acid and of several *p*-substituted benzoic acids with piperidine have already been isolated in the solid state (Kashino, 1968; Kashino, Kanei & Hasegawa, 1972), and the crystal structures of the *p*-bromo and *p*-chloro compounds have been determined (Kashino, Sumida & Haisa, 1972). In the present investigation, the structure of the *p*-methyl compound was undertaken in order to elucidate the effect of the *p*-substituents on the crystal structure and the factors determining the orientation and length of hydrogen bond in the crystal.

Experimental

Crystals obtained by slow evaporation from dry benzene solution were orthorhombic plates having well developed {010} faces. As the crystals gradually decomposed, the specimens cut from larger crystals were sealed in glass capillaries. Crystals with approximate cross-sections of 0·48 × 0·41 and 0·49 × 0·35 mm were used for the a axis and c axis photographs, respectively. Using Cu $K\alpha$ radiation, multiple-film equi-inclination Weissenberg photographs were taken for the layers $0kl$ to $6kl$ and $hk0$ to $hk6$. In all, 1053 independent non-zero reflexions were observed out of about 2980 possible reflexions within the Cu $K\alpha$ sphere. The intensities were estimated visually. After Lorentz, polarization, and spot-shape corrections were made the intensities of various layers were put on the same relative scale. The relative values were put on an absolute scale by Wilson's method; $B=4{\cdot}6$ Å^2. No correction for absorption was applied. An extinction correction, $\alpha=9{\cdot}4\times10^{-6}$, was applied for seven strong reflexions with the formula $I_{\text{corr}}=I_{\text{obs}}/(1-\alpha I_{\text{obs}})$ and the primary extinction effect for the reflexions 021, 102 and 202 was

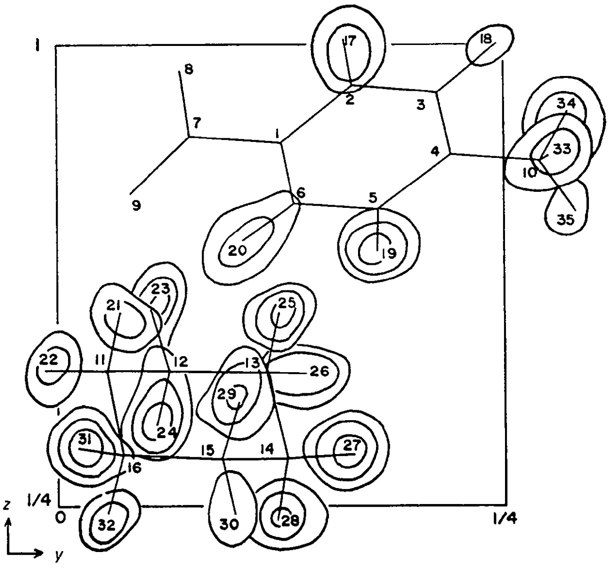

Fig. 1. Composite drawing of the final difference synthesis and numbering of atoms. Contours are at intervals of 0·1 e Å^{-3} starting at 0·2 e Å^{-3}.

Table 1. *Final atomic parameters and e.s.d.'s* ($\times 10^4$) *for non-hydrogen atoms*

Numbering of atoms as in Fig. 1.

The anisotropic temperature factor is defined as $\exp(-\beta_{11}h^2-\beta_{22}k^2-\beta_{33}l^2-\beta_{12}hk-\beta_{13}hl-\beta_{23}kl)$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	4217 (4)	1252 (2)	8389 (5)	113 (5)	15 (1)	113 (5)	4 (3)	−51 (9)	7 (3)
C(2)	3907 (4)	1657 (2)	9307 (5)	120 (5)	18 (1)	139 (7)	4 (3)	7 (11)	7 (4)
C(3)	4487 (5)	2128 (2)	9200 (6)	156 (6)	16 (1)	155 (7)	−9 (4)	−4 (12)	7 (4)
C(4)	5418 (5)	2203 (2)	8191 (6)	154 (6)	20 (1)	178 (8)	−27 (4)	−65 (13)	30 (4)
C(5)	5744 (5)	1797 (2)	7291 (6)	128 (6)	30 (1)	148 (7)	−6 (4)	25 (11)	29 (5)
C(6)	5165 (5)	1326 (2)	7376 (6)	118 (5)	23 (1)	125 (6)	2 (4)	−25 (10)	−6 (5)
C(7)	3583 (5)	746 (2)	8487 (5)	131 (6)	17 (1)	126 (6)	1 (3)	−29 (10)	15 (4)
O(8)	2838 (4)	689 (1)	9567 (4)	189 (5)	17 (1)	173 (5)	−14 (3)	76 (9)	0 (3)
O(9)	3810 (3)	407 (1)	7544 (4)	169 (4)	15 (0)	144 (4)	7 (2)	−26 (8)	−13 (3)
C(10)	6084 (7)	2698 (3)	8063 (8)	242 (10)	29 (1)	266 (12)	−85 (6)	−120 (19)	32 (7)
N(11)	2960 (4)	274 (1)	4669 (4)	132 (4)	14 (1)	120 (5)	−5 (3)	−16 (8)	−5 (3)
C(12)	1877 (5)	623 (2)	4670 (5)	114 (5)	19 (1)	157 (7)	27 (3)	15 (11)	1 (4)
C(13)	2262 (5)	1173 (2)	4618 (5)	147 (6)	14 (1)	142 (7)	23 (3)	18 (11)	2 (4)
C(14)	3051 (5)	1273 (2)	3244 (6)	176 (7)	15 (1)	166 (8)	13 (4)	30 (13)	6 (4)
C(15)	4149 (5)	919 (2)	3251 (6)	128 (6)	22 (1)	165 (8)	10 (4)	71 (12)	5 (4)
C(16)	3742 (5)	367 (2)	3316 (6)	128 (5)	16 (1)	165 (7)	16 (3)	20 (11)	−13 (4)

eliminated by immersing the crystals in liquid nitrogen. The unit-cell dimensions were determined from oscillation and Weissenberg photographs taken with Cu $K\alpha$ radiation ($\lambda = 1{\cdot}5418$ Å). The density was measured at 25 °C using a pycnometer with liquid paraffin as the medium. The crystal data are: piperidinium *p*-toluate, $[C_5H_{10}NH_2]^+[CH_3C_6H_4CO_2]^-$, F.W. 221·3, m.p. 119 °C. Orthorhombic, $a = 11{\cdot}01$ (1),[*] $b = 26{\cdot}45$ (2), $c = 8{\cdot}97$ (1) Å. $U = 2612$ Å^3, $Z = 8$, $D_m = 1{\cdot}11$, $D_x = 1{\cdot}12$ g cm^{-3}. μ(Cu $K\alpha$) = 6·0 cm^{-1}. Space group *Pbca*, from systematic absences *hk*0 with *h* odd, 0*kl* with *k* odd, *h*0*l* with *l* odd.

Structure analysis

The space group and unit-cell dimensions showed that the present compound was isotypic with the 1:1 addition compounds of piperidine with *p*-bromo and *p*-chlorobenzoic acids (Kashino, Sumida & Haisa, 1972), and the same molecular arrangement adequately explained the (0*kl*) Patterson projection of the present compound. Thus the positional parameters of the *p*-chloro compound were used as starting values, while the bond length C–CH$_3$ was taken to be 1·514 Å (Takwale & Pant, 1971). The discrepancy index R was 0·282 for all the observed reflexions. The structure was refined by the block-diagonal least-squares method with anisotropic thermal parameters to an R index of 0·132. A difference Fourier synthesis revealed sixteen hydrogen atoms, but the two hydrogen atoms of the methyl group and one of the two expected to belong to the nitrogen atom could not be located. The subsequent refinement, carried out by introducing the positional parameters of the sixteen hydrogen atoms and the isotropic temperature factor, $B = 4{\cdot}6$ Å^2, as fixed parameters, reduced the R index to 0·103. A difference synthesis revealed all the peaks corresponding to nineteen hydrogen atoms. After correction for extinction, the positional parameters of the hydrogen atoms were also refined, but the isotropic thermal parameters were kept constant with the values 7·0 Å^2 for the hydrogen atoms of the methyl group and 3·8 Å^2 for others. The final R index is 0·084 for 1053 non-zero reflexions, and the magnitude of the shifts in the parameters is approximately the same as the errors. The weighting scheme adopted was:

$$\sqrt{w} = 0{\cdot}0, \quad \text{if } F_o < F_{\min} \ (=3{\cdot}0),$$
$$\sqrt{w} = 1{\cdot}0, \quad \text{if } F_{\min} \le F_o \le F_{\max} \ (=21{\cdot}0)$$

and

$$\sqrt{w} = F_{\max}/F_o, \ \text{if } F_o > F_{\max}\,.$$

The final atomic parameters and their standard deviations for non-hydrogen atoms are given in Table 1 and the final positional parameters for the hydrogen atoms in Table 2. A composite drawing of the final

Table 2. *Final positional parameters for hydrogen atoms with their e.s.d.'s in parentheses*

	x	y	z
H(17)	0·320 (4)	0·162 (2)	1·005 (5)
H(18)	0·418 (4)	0·246 (2)	1·000 (6)
H(19)	0·639 (4)	0·179 (2)	0·661 (5)
H(20)	0·533 (4)	0·104 (2)	0·677 (5)
H(21)	0·339 (4)	0·035 (2)	0·562 (5)
H(22)	0·257 (4)	−0·007 (2)	0·468 (5)
H(23)	0·137 (4)	0·052 (2)	0·565 (5)
H(24)	0·142 (4)	0·055 (2)	0·382 (5)
H(25)	0·279 (4)	0·124 (2)	0·562 (5)
H(26)	0·147 (4)	0·140 (2)	0·461 (5)
H(27)	0·339 (4)	0·165 (2)	0·330 (5)
H(28)	0·251 (4)	0·122 (2)	0·224 (5)
H(29)	0·474 (4)	0·101 (2)	0·416 (5)
H(30)	0·464 (4)	0·098 (2)	0·234 (5)
H(31)	0·447 (4)	0·011 (2)	0·343 (5)
H(32)	0·317 (4)	0·028 (2)	0·236 (6)
H(33)	0·690 (5)	0·274 (2)	0·814 (7)
H(34)	0·620 (5)	0·285 (2)	0·889 (7)
H(35)	0·576 (5)	0·290 (2)	0·724 (7)

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[*] Numbers in parentheses here and throughout this paper are the estimated standard deviations in the least significant digits.

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

Unobserved reflexions are marked with an asterisk.

K	FO	FC
H,L=	0	0
2	869	909
4	527	-600
6	798	-810
8	245	-239
10	584	-580
12	1113	-981
14	-*	-2
16	-*	-29
18	97	79
20	665	-636
22	-*	-61
24	251	228
26	-*	39
28	52	67
30	94	86
32	140	110
H,L=	2	0
0	159	-179
1	506	518
2	1722	-1757
3	2245	2059
4	150	133
5	435	498
6	290	258
7	574	639
8	217	211
9	537	516
10	520	465
11	244	236
12	116	-91
13	188	183
14	78	71
15	107	94
16	397	-386
17	48	-59
18	65	92
19	220	-210
20	186	179
21	255	-248
22	361	331
23	389	-358
24	73	96
25	54	66
26	112	-111
27	-*	21
28	-*	-5
29	-*	-13
30	-*	-36
31	68	59
32	-*	-19
33	119	87
H,L=	4	0
0	601	-616
1	154	-156
2	249	-201
3	161	140
4	493	-479
5	63	-83
6	136	-114
7	537	-480
8	608	607
9	208	-194
10	494	473
11	-*	-25
12	181	-146
13	36	-43
14	411	383
15	176	-172
16	315	286
17	218	-183
18	-*	22
19	52	-78
20	71	-94
21	203	187
22	150	-148
23	-*	18
24	122	-130
25	172	131
26	67	-78
27	63	66
28	-*	-12
29	-*	23
30	50	-43
H,L=	6	0
0	363	-331
1	150	-129
2	219	215
3	224	-204
4	139	111
5	-*	-16
6	-*	-12
7	222	-200
8	-*	-27
9	-*	0
10	291	-241
11	95	91
12	-*	-14
13	-*	-5
14	148	122
15	145	118
16	48	53
17	236	198
18	96	-99
19	60	40
20	-*	50
21	-*	65
22	-*	-36
23	-*	37
24	83	-98
25	-*	10
26	-*	-26
27	62	-56
28	-*	21
29	95	-80
30	40	39
H,L=	8	0
0	89	70
1	140	-131
2	101	105
3	222	-187
4	-*	14
5	-*	-30
6	-*	26
7	-*	-15
8	-*	11
9	113	-138
10	165	-161
11	-*	19
12	-*	35
13	-*	31
14	136	-109
15	-*	3
16	55	-57
17	-*	-9
18	-*	-39
19	-*	19
20	-*	35
21	51	51
22	-*	45
23	-*	-7
24	74	62
25	-*	-50
26	150	105
H,L=	10	0
0	136	113
1	-*	-29
2	96	84
3	-*	28
4	68	-63
5	171	146
6	-*	23
7	349	243
8	-*	14
9	55	-62
10	77	-72
11	94	-87
12	-*	6
13	-*	31
14	73	-56
H,L=	12	0
0	49	-45
1	-*	-3
2	-*	-36
3	-*	-27
4	109	-76
H,L=	0	1
2	971	807
4	472	-539
6	406	404
8	328	341
10	312	-321
12	305	-284
14	384	-339
16	-*	34
18	55	60
20	52	63
22	208	-190
24	-*	49
26	-*	-25
28	-*	60
30	105	82
32	51	39
H,L=	1	1
1	300	-266
2	275	282
3	578	653
4	571	652
5	91	-99
6	166	-148
7	430	412
8	488	482
9	141	140
10	963	929
11	208	181
12	491	502
13	256	-234
14	236	-209
15	256	-246
16	128	-142
17	160	-148
18	71	-77
19	131	-139
20	85	-86
21	214	197
22	-*	-6
23	-*	-26
24	-*	-25
25	-*	-5
26	-*	-19
27	-*	9
28	-*	-15
29	-*	-3
30	105	-84
31	-*	11
32	122	-73
H,L=	2	1
1	197	-155
2	1042	1014
3	281	-234
4	606	-674
5	-*	16
6	293	-274
7	331	347
8	222	193
9	140	132
10	763	730
11	520	507
12	85	-81
13	157	-147
14	345	-314
15	67	-66
16	-*	-29
17	143	-134
18	154	152
19	-*	-47
20	-*	-7
21	53	66
22	204	-174
23	-*	29
24	67	66
25	127	-123
H,L=	3	1
1	413	376
2	579	-616
3	143	-106
4	574	549
5	744	-770
6	232	203
7	387	-355
8	183	-158
9	593	-571
10	554	-494
11	280	240
12	168	-154
13	324	298
14	67	70
15	301	288
16	99	117
17	312	291
18	80	-93
19	103	116
20	106	-118
21	-*	-29
22	157	161
23	128	-109
H,L=	4	1
1	160	145
2	103	-80
3	-*	-33
4	240	-230
5	88	-81
6	-*	-35
7	427	-418
8	351	-323
9	165	-151
10	299	262
11	391	375
12	199	-181
13	223	201
14	143	138
15	55	-63
16	73	85
17	-*	0
18	-*	6
19	-*	35
20	52	-55
21	67	86
22	61	70
23	-*	-48
24	43	62
25	58	-77
26	47	-43
27	55	56
H,L=	5	1
1	98	-83
2	33	-28
3	113	-108
4	53	-59
5	327	309
6	267	-251
7	531	558
8	-*	-67
9	95	94
10	-*	-23
11	-*	-24
12	121	121
13	164	-154
14	135	121
15	191	-180
16	52	-66
17	143	-148
18	-*	40
19	102	-94
20	-*	-17
21	-*	-45
22	-*	-7
23	70	78
24	-*	-49
25	-*	27
26	-*	20
27	66	-73
H,L=	6	1
1	271	299
2	70	-51
3	160	-126
4	196	168
5	51	40
6	69	-80
7	-*	4
8	248	-232
9	39	48
10	-*	7
11	183	-151
12	56	-66
13	-*	33
14	127	121
15	55	-63
16	82	74
17	-*	40
18	-*	-55
19	74	-77
20	-*	-41
21	-*	12
22	39	43
23	45	55
H,L=	7	1
1	-*	38
2	160	126
3	160	-117
4	-*	31
5	128	-101
6	85	76
7	99	-108
8	101	107
9	-*	33
10	63	-60
11	65	-68
12	66	-70
13	-*	-4
14	-*	66
15	124	118
16	-*	-32
17	125	115
H,L=	8	1
1	-*	40
2	90	78
3	73	-84
4	211	165
5	-*	26
6	65	-58
7	66	74
8	66	64
9	67	84
10	-*	-55
11	207	-172
H,L=	9	1
1	-*	-9
2	55	-40
3	67	73
4	110	-108
5	111	88
H,L=	10	1
1	-*	-13
2	-*	-34
3	-*	-4
4	-*	-15
5	-*	-22
6	-*	-57
7	55	61
8	147	98
9	55	67
10	-*	-5
11	143	-100
H,L=	11	1
1	-*	9
2	-*	13
3	-*	-28
4	54	44
5	-*	-17
6	-*	28
7	-*	-33
8	-*	-2
9	63	55
10	87	56
H,L=	12	1
1	-*	29
2	-*	13
3	-*	-13
4	-*	-11
5	82	-55
6	47	-29
H,L=	0	2
0	601	-697
2	610	639
4	132	134
6	120	-106
8	443	-422
10	-*	12
12	459	479
14	339	306
16	152	118
18	190	159
20	-*	43
22	555	-486
24	215	-181
H,L=	1	2
0	1947	1913
1	1311	-1319
2	853	860
3	223	-197
4	731	-708
5	475	-460
6	146	-132
7	168	173
8	254	-232
9	-*	-22
10	112	-138
11	258	-225
12	62	-68
13	160	150
14	-*	34
15	289	-268
16	138	142
17	134	125
18	70	-67
19	92	-105
20	262	-231
21	179	168
22	127	-128
23	128	124
24	107	101
H,L=	2	2
0	1764	-1788
1	479	463
2	638	-606
3	1257	-1298
4	334	316
5	454	-426
6	253	208
7	-*	20
8	103	89
9	299	-262
10	95	88
11	189	-173
12	178	153
13	275	240
14	78	-70
15	289	269
16	160	-146
17	-*	72
18	-*	2
19	253	230
20	236	208
21	-*	60
22	-*	76
23	-*	32
24	79	83
25	-*	-32
26	-*	-16
27	95	-92
H,L=	3	2
0	517	521
1	170	173
2	54	61
3	564	530
4	391	-404
5	80	85
6	229	213
7	172	157
8	70	-82
9	181	173
10	68	87
11	205	-165
12	61	60
13	133	115
14	150	-140
15	-*	1
16	129	-114
17	166	152
18	-*	-54
19	-*	-29
20	-*	38
21	135	-117
22	46	46
23	135	-117
24	155	146
25	53	-41
H,L=	4	2
0	667	752
1	545	535
2	584	586
3	353	-351
4	380	381
5	343	-299
6	358	-318
7	63	-62
8	267	-275
9	167	-135
10	56	-74
11	-*	11
12	148	-153
13	250	-237
14	220	-203
15	107	-95
16	73	-63
17	69	-63
18	50	-56
19	180	150
20	-*	-57
21	-*	-3
22	-*	-27
23	-*	41
24	-*	39
25	41	54
26	162	129
27	-*	-8
28	63	65
H,L=	5	2
0	-*	36
1	277	248
2	123	-103
3	179	177
4	168	-127
5	-*	-23
6	-*	-18
7	70	-69
8	228	190
9	-*	-8
10	195	176
11	-*	-12
12	60	-67
13	49	49
14	-*	-17
15	-*	-25
16	67	76
17	137	109
H,L=	6	2
0	135	99
1	175	151
2	52	53
3	211	186
4	138	100
5	462	421
6	-*	-25
7	389	362
8	261	-226
9	83	99
10	-*	32
11	149	125
12	-*	8
13	53	-70
14	86	-71
15	130	117
16	-*	-39
17	-*	-11
18	-*	39
19	140	-121
20	61	47
21	136	-113
22	56	47
23	-*	-38
24	-*	-44
25	-*	-28
26	-*	-21
27	74	-61
28	-*	-12
29	44	39
H,L=	7	2
0	94	-68
1	133	104
2	-*	-21
3	-*	23
4	-*	34
5	56	-60
6	-*	-32
7	98	-96
8	-*	40
9	-*	31
10	-*	23
11	157	123
12	60	-61
13	86	-88
14	61	70
H,L=	8	2
0	169	-148
1	-*	34
2	242	-214
3	-*	37
4	160	-154
5	83	-91
6	84	102
7	224	-199
8	74	74
9	-*	38
10	162	158
11	137	116
12	87	87
13	87	-83
14	-*	2
15	61	-39
H,L=	9	2
0	106	-80
1	-*	3
2	-*	25
3	51	-53
4	51	70
5	-*	-38
6	-*	12
7	107	-100
8	107	-78
9	-*	-27
10	-*	-15
11	87	84
12	-*	29
13	60	-63
H,L=	10	2
0	-*	46
1	-*	22
2	-*	42
3	-*	38
4	61	44
5	-*	-18
6	-*	5
7	61	-66
8	60	-67
H,L=	11	2
0	-*	8
1	-*	3
2	-*	32
3	-*	-15
4	-*	8
5	99	85
H,L=	0	3
2	231	-199
4	383	-353
6	-*	-7
8	674	-661
10	503	-469
12	340	-346
14	375	315
16	181	182
18	48	60
20	248	230
H,L=	1	3
1	437	-346
2	141	135
3	87	79
4	116	112
5	26	35
6	88	99
7	-*	14
8	-*	9
9	228	203
10	231	221
11	164	-137
12	109	94
13	-*	3
14	-*	-7
15	178	175
16	-*	-34
17	-*	-10
18	149	138
19	-*	-41
20	-*	56
21	149	-133
22	-*	9
23	-*	-5
24	93	-95
25	-*	11
26	40	-47
27	39	30
28	-*	9
29	-*	-38
30	-*	-18
31	-*	-5
32	64	-57
H,L=	2	3
1	230	-220
2	301	-260
3	877	840
4	88	-88
5	82	83
6	229	218
7	96	94
8	81	-78
9	72	69
10	222	210
11	336	-314
12	179	159
13	268	-264
14	99	102
15	220	-220
16	67	-73
17	159	-137
18	192	-151
19	-*	-54
20	109	107
21	221	183
22	-*	-19
23	-*	-1
24	-*	-38
25	41	61
26	-*	2
27	38	51
28	-*	-3
29	-*	-2
30	-*	-20
31	-*	-1
32	83	-52
H,L=	3	3
1	276	250
2	88	61
3	359	-334
4	221	-193
5	62	-48
6	308	-290
7	137	-139
8	72	-56
9	-*	23
10	149	-140
11	291	-294
12	249	-262
13	-*	12
14	212	-195
15	40	50
16	72	80
17	208	205
18	264	266
19	58	52
H,L=	4	3
1	51	63
2	176	-166
3	325	343
4	319	306
5	494	-461
6	432	435
7	122	-114
8	35	37
9	151	-130
10	64	-70
11	46	-57
12	-*	-6
13	49	54
14	137	-123
15	136	130
16	-*	-11
17	149	141
18	121	-111
19	-*	17
20	-*	-40
21	-*	28
22	-*	23
23	102	-90
24	-*	4
25	-*	41
26	-*	-35
27	-*	31
28	-*	30
29	-*	-12
30	48	44
H,L=	5	3
1	122	-94
2	39	39
3	233	216
4	140	-124
5	444	442
6	317	-279
7	53	-53
8	312	296
9	-*	29
10	221	220
11	99	96
12	189	187
13	-*	15
14	155	-161
15	407	-417
16	99	-95
17	221	-224
18	-*	-3
19	-*	-4
20	-*	-40
21	115	108
22	37	-59
23	-*	28
24	-*	-22
25	-*	-32
26	37	46
H,L=	6	3
1	277	-239
2	148	-120
3	31	27
4	-*	-28
5	32	41
6	81	73
7	242	217
8	-*	22
9	60	-36
10	46	-43
11	226	212
12	135	130
13	72	77
14	-*	-12
15	119	-118
16	52	-63
H,L=	7	3
1	106	88
2	-*	4
3	57	-60
4	212	196
5	214	-210
6	101	101
7	249	-232
8	132	121
9	51	-50
10	171	-144
11	173	156
12	53	72
13	178	159
14	-*	25
15	98	87
16	-*	15
17	75	76
18	85	-75
H,L=	8	3
1	-*	9
2	-*	20
3	95	-85
4	-*	-36
5	61	-66
6	-*	29
7	-*	9
8	-*	12
9	62	-57
10	175	-151
11	150	112
12	-*	20
13	-*	23
14	75	82
15	-*	-8
16	-*	-22
17	84	88
18	58	59
H,L=	9	3
1	76	-55
2	-*	24
3	44	44
4	-*	27
5	36	41
6	115	-105
7	-*	42
8	98	-83
9	-*	-42
10	143	-109
H,L=	10	3
1	-*	2
2	-*	-12
3	52	55
4	52	-50
5	60	69
H,L=	11	3
1	-*	23
2	-*	-33
3	-*	6
4	40	16
5	-*	8
6	-*	20
7	76	74
H,L=	0	4
0	674	724
2	484	411
4	156	131
6	226	188
8	125	-121
10	381	-328
12	235	-212
14	275	-251
16	75	88
18	-*	-29
20	-*	4
22	-*	-5
24	59	-56
26	-*	11
28	48	36
H,L=	1	4
0	503	406
1	214	160
2	-*	1
3	325	265
4	351	305
5	422	363
6	160	-155
7	454	-378
8	238	-192
9	184	147
10	85	-76
11	153	120
12	123	106
13	133	-123
14	138	132
15	-*	-8
16	-*	-7
17	-*	21
18	181	163
19	-*	-7
20	66	-62
21	124	-129
22	237	-187
23	-*	20
24	136	-120
H,L=	2	4
0	381	-330
1	363	-325
2	301	-287
3	62	-63
4	205	-177
5	424	366
6	210	185
7	305	281
8	-*	34
9	260	243
10	43	-51
11	84	77
12	-*	39
13	-*	54
14	-*	-14
15	-*	29
16	49	53
17	203	-176
18	59	-68
19	147	-134
20	-*	61
21	-*	10
22	137	131
H,L=	3	4
0	483	-496
1	227	-228
2	767	-773
3	290	-249
4	367	310
5	-*	10
6	220	215
7	191	178
8	80	83
9	66	-67
10	-*	6
11	59	-60
12	-*	-3
13	144	149
14	149	146
15	112	122
16	171	-178
17	-*	-52
18	192	172
19	-*	35
20	54	68
21	-*	29
22	-*	54
23	-*	28
24	-*	9
25	-*	-24
26	44	-65
H,L=	4	4
0	289	263
1	234	-192
2	84	90
3	-*	-14
4	344	-335
5	91	99
6	55	-58
7	182	-162
8	151	141
9	44	-31
10	49	65
11	142	-143
12	-*	34
13	56	-71
14	166	145
15	-*	-52
16	109	109
17	-*	-46
18	55	-66
19	-*	7
20	137	-141
21	55	58
22	69	-85
H,L=	5	4
0	331	268
1	-*	24
2	-*	38
3	182	-184
4	208	195
5	381	-353
6	154	-137
7	-*	13
8	114	-123
9	-*	-29
10	41	45
11	75	-91
12	131	-148
13	-*	-39
14	127	126
15	120	-119
16	107	-109
17	48	-47
18	-*	22
19	129	122
20	71	-80
21	76	70
22	-*	-49
23	-*	4
24	-*	26
25	51	53
26	42	43
27	-*	22
28	100	82
H,L=	6	4
0	-*	20
1	74	-72
2	40	41
3	-*	-23
4	75	-81
5	81	83
6	-*	-15
7	-*	10
8	120	118
9	42	-33
10	-*	-46
11	61	-74
12	74	-75
13	126	117
14	-*	61
15	127	122
16	-*	4
17	43	47
H,L=	7	4
0	60	73
1	-*	-36
2	94	87
3	-*	-38
4	176	156
5	231	230
6	113	-127
7	246	252
8	97	-105
9	-*	-12
10	-*	46
11	99	-102
12	76	-85
13	62	57
14	-*	29
15	61	66
16	86	-82
H,L=	8	4
0	-*	-7
1	-*	9
2	-*	-30
3	43	-46
4	76	-68
5	87	-95
6	-*	0
7	-*	-47
8	160	146
9	-*	-32
10	-*	5
11	-*	30
12	97	-105
13	-*	26
14	-*	1
15	59	-54
H,L=	9	4
0	-*	4
1	-*	-16
2	116	-111
3	-*	-34
4	98	-100
5	-*	15
6	-*	-11
7	43	-56
8	96	101
9	-*	-2
10	-*	72
11	83	72
H,L=	10	4
0	93	89
1	-*	25
2	51	52
H,L=	11	4
0	65	69
H,L=	0	5
2	330	296
4	88	-80
6	357	311
8	349	278
10	155	-141
12	62	-67
14	-*	-22
16	86	-90
18	209	-194
20	140	-139
22	60	-50
24	130	102
26	51	46
28	-*	-21
30	99	69
H,L=	1	5
1	216	180
2	248	210
3	225	-177
4	101	89
5	113	97
6	-*	2
7	-*	20
8	56	53
9	45	-34
10	136	123
11	53	42
12	39	69
13	-*	9
14	-*	-21
15	101	-91
H,L=	2	5
1	407	-323
2	257	195
3	140	-115
4	-*	-35
5	81	-74
6	47	47
7	137	116
8	174	150
9	206	192
10	154	142
11	213	191
12	198	180
13	105	93
14	-*	8
15	206	184
16	-*	-21
17	-*	25
18	-*	-52
19	190	-163
20	-*	-9
21	84	-48
H,L=	3	5
1	42	-37
2	48	-43
3	-*	-1
4	61	-55
5	57	-64
6	160	133
7	59	-73
8	144	-134
9	67	-87
10	101	-92
11	-*	51
12	-*	-43
13	-*	18
14	85	93
15	134	128
16	-*	53
17	-*	17
18	195	-179
19	52	59
H,L=	4	5
1	141	122
2	-*	-40
3	289	-242
4	-*	-13
5	297	-272
6	283	-259
7	87	90
8	283	-252
9	-*	-54
10	195	-178
11	65	-79
12	220	-200
13	67	-78
14	67	-81
15	269	256
16	296	267
17	258	242
18	213	189
H,L=	5	5
1	60	-72
2	-*	-31
3	48	59
4	-*	-31
5	-*	2
6	145	139
7	190	175
8	161	-154
9	106	98
10	85	83
11	61	-76
12	-*	-48
13	147	-114
14	-*	35
15	75	83
16	-*	25
17	41	-55
18	48	-43
19	47	-64
20	46	50
H,L=	6	5
1	42	42
2	-*	-39
3	127	105
4	76	-79
5	215	217
6	318	-290
7	246	241
8	-*	45
9	105	-117
10	267	251
11	49	-70
12	-*	8
13	222	-189
14	137	-150
15	238	-217
16	-*	22
17	136	128
18	50	48
19	-*	-36
20	-*	-16
21	59	77
22	-*	-40
23	46	56
24	-*	-4
25	-*	29
26	39	46
H,L=	7	5
1	-*	-8
2	-*	-35
3	-*	4
4	44	-40
5	54	-60
6	99	102
7	-*	3
8	63	-67
9	-*	-8
10	77	85
11	54	-48
12	54	-55
H,L=	8	5
1	100	89
2	44	57
3	-*	-16
4	89	97
5	142	-150
6	54	71
7	44	-43
8	159	162
9	53	-59
10	74	87
H,L=	9	5
1	43	40
2	-*	-27
3	-*	-1
4	52	-60
H,L=	10	5
1	-*	-38
2	39	48
H,L=	0	6
0	192	164
2	163	140
4	122	-97
6	332	-303
8	229	213
10	90	85
12	-*	21
14	77	83
16	-*	61
18	-*	-56
20	188	-150
22	-*	-17
24	-*	-25
26	-*	32
28	49	-43
H,L=	1	6
0	512	490
1	-*	-11
2	314	291
3	133	104
4	68	-81
5	180	-151
6	-*	-6
7	-*	-29
8	102	-94
9	-*	-28
10	71	-65
11	-*	-33
12	-*	-61
13	-*	-28
14	44	-45
15	82	-73
16	80	65
17	114	96
18	-*	24
19	-*	1
20	110	-97
21	-*	4
22	128	-110
H,L=	2	6
0	210	-189
1	40	45
2	-*	3
3	327	278
4	91	80
5	134	-106
6	148	-132
7	237	-180
8	-*	16
9	-*	-30
10	34	38
11	-*	34
12	69	85
13	-*	25
14	-*	-20
15	-*	-32
16	37	-53
17	246	232
18	-*	44
19	-*	0
20	-*	26
21	81	-66
H,L=	3	6
0	272	-238
1	-*	49
2	207	-170
3	-*	23
4	-*	-39
5	-*	22
6	215	196
7	108	100
8	49	-52
9	129	134
10	-*	9
11	-*	34
12	104	102
13	67	81
14	88	-90
15	-*	11
16	60	-65
17	-*	22
18	-*	3
19	-*	-42
20	97	88
21	-*	-50
22	104	88
H,L=	4	6
0	86	-70
1	52	-53
2	33	-31
3	144	134
4	145	130
5	104	-106
6	151	144
7	-*	-59
8	63	-64
9	-*	-19
10	53	-56
11	-*	-24
12	-*	5
13	64	69
14	118	-111
15	112	-117
16	-*	-65
17	65	83
18	99	90
H,L=	5	6
0	123	131
1	-*	43
2	-*	22
3	-*	-16
4	71	-76
5	50	-56
6	-*	-40
7	114	-100
H,L=	6	6
0	-*	-3
1	-*	3
2	-*	-25
3	49	67
4	84	94
5	149	-146
6	-*	61
7	-*	46
8	164	-173
9	148	137
10	-*	-43
11	-*	2
12	64	67
13	-*	48
14	-*	3
15	91	-86
H,L=	7	6
0	-*	28
1	-*	-1
2	-*	39
3	-*	48
4	-*	22
5	90	85
H,L=	8	6
0	115	-99
1	-*	-35
2	-*	-27
3	-*	18
4	102	98
H,L=	9	6
0	90	-76
H,L=	0	7
2	355	-302
4	161	-152
6	102	-92
8	264	-240
10	294	-266
12	211	-161
14	62	66
16	73	79
18	82	80
20	188	129
22	49	52
H,L=	1	7
1	-*	-31
2	-*	41
3	-*	43
4	62	-64
5	166	145
6	91	95
7	-*	-51
8	107	89
9	-*	1
10	-*	8
11	-*	4
12	-*	12
13	-*	-12
14	-*	51
15	93	-84
16	-*	-50
17	104	-86
18	-*	-24
19	121	116
H,L=	2	7
1	133	118
2	-*	54
3	198	168
4	-*	18
5	117	113
6	-*	-29
7	-*	22
8	-*	38
9	-*	10
10	242	212
11	73	-92
12	73	68
13	149	-127
14	-*	-20
15	229	-181
16	57	-65
17	225	-180
18	-*	38
19	-*	12
20	-*	43
21	69	53
22	-*	-54
23	103	85
H,L=	3	7
1	-*	-18
2	-*	42
3	-*	31
4	205	-165
5	-*	-30
6	83	82
7	206	-150
8	71	65
9	-*	38
10	-*	-16
11	-*	38
12	-*	45
13	48	69
14	57	82
15	-*	49
16	78	-83
H,L=	4	7
1	-*	23
2	-*	-8
3	-*	54
4	81	96
5	70	-75
6	226	220
7	264	-257
8	-*	18
9	-*	-47
10	-*	-44
11	-*	37
12	-*	-24
13	112	124
14	-*	64
15	-*	27
16	53	-68
17	-*	23
18	84	-103
19	162	123
20	76	-66
H,L=	5	7
1	-*	-5
2	84	82
3	-*	7
4	-*	22
5	-*	-42
6	-*	53
7	-*	-21
8	83	-78
9	47	53
10	95	-82
11	-*	7
12	-*	-28
13	-*	-17
14	-*	14
15	-*	50
16	60	54
H,L=	6	7
1	118	-106
2	-*	-26
3	-*	-32
4	-*	-11
5	104	103
6	43	58
7	-*	25
8	-*	-66
9	101	101
10	42	-53
11	-*	26
12	48	55
13	47	58
14	56	60
H,L=	0	8
0	204	-185
2	102	93
4	-*	34
6	-*	73
8	-*	-23
10	58	-57
12	-*	-15
14	-*	-59
16	74	48
18	85	-94
20	77	63
22	37	47
H,L=	1	8
0	365	337
1	105	-106
2	229	219
3	165	-151
4	-*	-60
5	-*	32
6	148	-122
7	-*	22
8	-*	12
9	-*	-51
10	-*	-39
11	-*	-15
12	72	-64
13	-*	-8
14	-*	20
15	-*	20
16	57	74
17	66	-80
18	-*	-38
19	-*	-19
20	133	-102
21	123	87
22	112	-76
H,L=	2	8
0	-*	53
1	58	-65
2	58	75
3	-*	-36
4	90	-101
5	138	134
H,L=	3	8
0	138	-121
1	-*	-15
2	-*	19
3	56	33
4	-*	-39
5	112	95
6	56	-58
7	55	60
8	46	50
9	-*	-13
10	-*	7
11	-*	27
12	-*	10
13	-*	22
14	-*	8
15	97	66
H,L=	4	8
0	-*	-4
1	54	-34
2	54	-50
H,L=	5	8
0	-*	-57
1	-*	20
2	-*	38
3	-*	43
4	-*	-61
5	-*	-28
6	-*	6
7	-*	-52
8	74	87
9	60	-63
10	-*	25
11	-*	-6
12	-*	-21
13	-*	-17
14	52	-45
15	62	-68
H,L=	6	8
0	81	76
1	-*	-15
2	-*	-6
3	47	-47
H,L=	0	9
2	57	45
4	98	85
6	-*	-58
8	-*	-8
10	53	-53
12	72	-46
14	-*	-54
16	-*	11
18	-*	35
20	174	-112
H,L=	1	9
1	-*	37
2	-*	-33
3	177	-135
4	-*	-6
5	-*	1
6	-*	2
7	-*	23
8	58	-44
9	-*	-2
10	114	-101
11	-*	-26
12	53	66
13	-*	32
14	-*	10
15	45	57
16	42	35
17	69	79
H,L=	2	9
1	122	-100
2	-*	54
3	67	-59
4	-*	57
5	142	120
6	53	-46
7	75	74
8	74	82
9	51	39
10	61	60
H,L=	3	9
1	-*	33
2	53	21
3	-*	-17
4	-*	-31
5	-*	42
6	102	-94
7	50	65
8	-*	6
9	48	43
10	47	61
11	80	-78
H,L=	4	9
1	-*	38
2	-*	-48
3	-*	-62
4	69	-76
5	-*	43
6	58	-72
H,L=	5	9
1	-*	6
2	-*	-17
3	47	55
4	-*	36
5	-*	-23
6	-*	14
7	37	-57
8	36	35
H,L=	6	9
1	-*	40
2	-*	18
3	47	53
H,L=	0	10
0	250	-223
2	137	-124
4	59	69
6	-*	22
8	-*	17
10	65	57
12	43	50
14	-*	17
16	43	-50
H,L=	1	10
0	-*	29
1	188	146
H,L=	2	10
0	-*	37
1	56	-49
2	-*	33
3	56	-73
4	-*	32
5	68	-59
6	-*	37
7	54	-34
H,L=	3	10
0	84	-93
1	-*	20
2	53	-53
H,L=	0	11
2	150	-113
H,L=	1	11
1	-*	8
2	-*	23
3	54	50
4	-*	10
5	36	-47
H,L=	2	11
1	40	45
H,L=	3	11
1	61	-59

difference synthesis is shown in Fig. 1. The observed and calculated structure factors are listed in Table 3.

The atomic scattering factors used were those of Hanson, Herman, Lea & Skillman (1964). The computations were performed on the HITAC 5020E computer of the Computer Center of the University of Tokyo using the programs in the Universal Crystallographic Computation Program System (1967).

Description and discussion of the structure

Hydrogen bonding and molecular packing

The difference electron density map in Fig. 1 shows that two hydrogen atoms belong to the nitrogen atom of the piperidine ring. Therefore it can be concluded that the present compound is composed of a piperidinium cation and a *p*-toluate anion. The projections of the crystal structure along the *c* and *a* axes are shown in Fig. 2. Two kinds of N^+–H···O^- hydrogen bonds of nearly equal length link the nitrogen atom of the piperidinium ion with the carboxylate oxygen atoms of the *p*-toluate ions to form a hydrogen-bonded chain, which arranges the molecules around the twofold screw axis along the *c* axis. The molecular geometry of the hydrogen bond system is shown in Fig. 3, and is compared in Table 4 with that of related compounds. The geometries of the hydrogen bonds in the three isomorphous compounds are essentially the same. It may be seen that the C–N···O angles are tetrahedral in nature, as found in other N^+–H···O^- hydrogen bond systems, for example ammonium trifluoroacetate (Cruickshank, Jones & Walker, 1964), ammonium acetate (Nahringbauer, 1967), hexamethylenediammonium adipate (Hirokawa, Ohashi & Nitta, 1954), α-glycine (Jönsson & Kvick, 1972) and nicotinyl salicylate (Kim & Jeffrey, 1971). The deviations from the regular tetrahedral angle in these compounds range within 15°. The N···O(8′) bond length, 2·698 Å, with nearly tetrahedral C–N···O angles, 108·7 and 108·1°, is significantly shorter than the N···O(9) bond length, 2·766 Å, with C–N···O angles of 101·0 and 122·2°. This is also the case for piperazinium terephthalate (Kashino, Sasaki & Haisa, 1973), as seen in Table 4.

Recently Kim & Jeffrey (1971) have found a short N^+–H···O^- separation of 2·627 Å in nicotinyl salicylate. The C–N···O angles are calculated to be 109·0, 108·8 and 104·7° from their data. Thus the condition that the C–N···O angle be near tetrahedral seems necessary for the formation of the N^+–H···O^- hydrogen bond. Chain-like arrangement of the piperidinium and benzoate ions around the twofold screw axis, as found in the present system, satisfies this condition and moreover the principle of maximum hydrogen bonding. This may be an important factor making the *p*-methyl compound isotypic with the *p*-bromo and *p*-chloro compounds. The packing coefficients of the *p*-methyl, *p*-bromo and *p*-chloro compounds are calculated to be 0·69, 0·72 and 0·73, respectively, using the intermolecular radii given by Kitaigorodskii (1955) and the observed bond lengths. Thus the packing condition of Kitaigorodskii (1955) is also satisfied in this series of compounds.

As shown in Table 4, the hydrogen bond lengths of these compounds are substantially identical and no effect due to the electron withdrawing properties of the substituents, such as has been observed in the case of ammonium trifluoroacetate and ammonium acetate (Nahringbauer, 1967), is discernible. This is probably because the intermolecular contacts are so close that more short hydrogen bonds cannot be allowed. The intermolecular distances are listed in Table 5, and some of these are shown in Fig. 2. The distances C(7)···H(21^{i}) and C(7)···H(22^{iv}) are significantly shorter than those estimated from the intermolecular radii, and the distances C(1)···H(25^{i}), H(20)···H(29^{i}), C(2)···H(19^{iii}), C(7)···N(11^{iv}), O(9)···H(31^{v}), C(6)···C(13^{viii}), C(5)···C(13^{vii}) and H(17)···H(28^{viii}) are almost the same as the estimated values. It can be shown that the shortening of the hydrogen bond lengths should cause all these intermolecular distances except C(2)···H(19^{iii}) and H(17)···H(28^{viii}) to become unexpectedly close.

Effect of the bulkiness of the substituents on the crystal structure

In the three isomorphous compounds the long axes of the acid anions make angles of about 4° with the (001) plane (*cf.* Fig. 2). The angles here are determined only by the geometry of the hydrogen-bond system and no influence of the substituents is discernible. The

Table 4. C–N···O *angles* (°) *and* N^+–H···O^- *hydrogen bond lengths* (Å) *in the* 1:1 *addition compounds of benzoic acids with amines*

Compound	Piperidinium *p*-toluate	Piperidinium *p*-bromobenzoate	Piperidinium *p*-chlorobenzoate	Piperazinium terephthalate
C(12)–N···O(8′)	108·7 (4)	109	108	106·4
C(16)–N···O(8′)	108·1 (4)	108	106	108·6
C(12)–N···O(9)	101·0 (4)	101	102	107·5
C(16)–N···O(9)	122·2 (4)	123	124	102·7
N^+–H···$O(8')^-$	2·698 (5)	2·687 (8)	2·674 (10)	2·616 (7)
N^+–H···$O(9)^-$	2·766 (6)	2·762 (9)	2·722 (11)	2·737 (7)
Reference	Present work	Kashino, Sumida & Haisa (1972)		Kashino, Sasaki & Haisa (1973)

Table 5. *Intermolecular distances* (Å) *with their e.s.d.'s in parentheses*

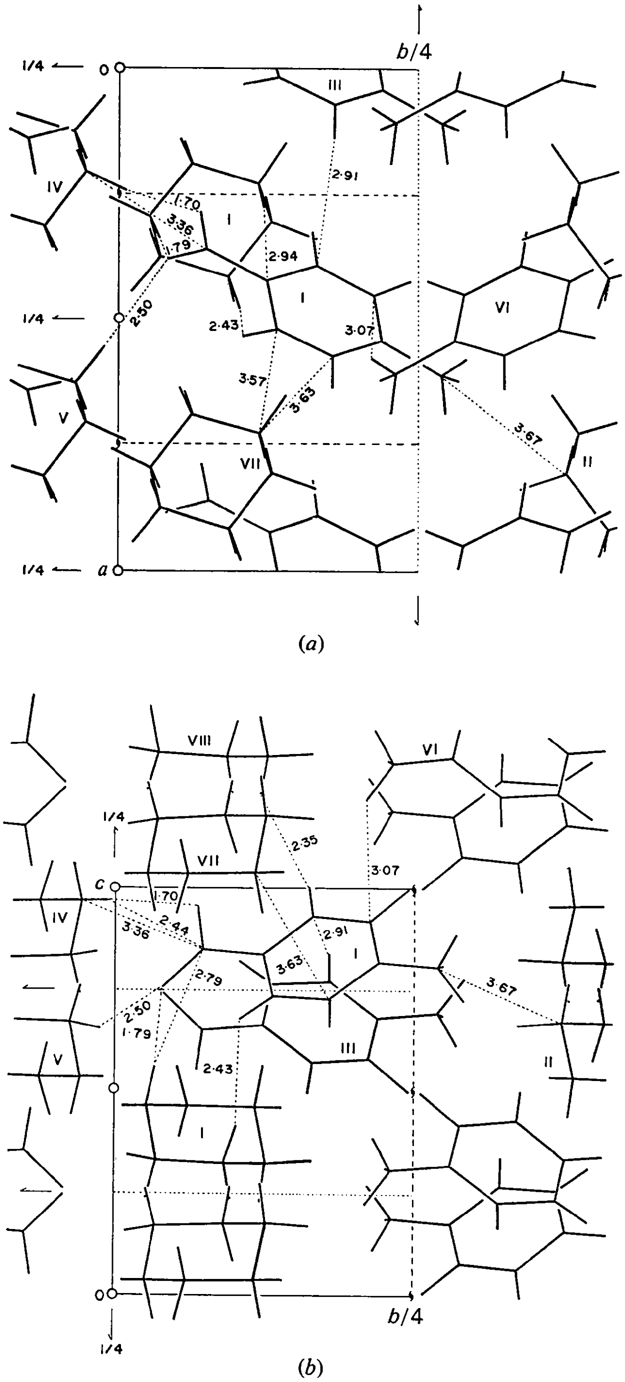
$O(8^{i})$	$H(22^{iv})$	1·70 (5)	$C(3^{i})$	$H(35^{vi})$	3·07 (6)
$O(9^{i})$	$H(21^{i})$	1·79 (5)	$C(5^{i})$	$C(13^{vii})$	3·633 (7)
$O(9^{i})$	$H(22^{iv})$	2·60 (5)	$C(5^{i})$	$H(26^{vii})$	3·08 (5)
$O(9^{i})$	$H(31^{v})$	2·50 (5)	$C(6^{i})$	$H(26^{vii})$	3·07 (5)
$C(7^{i})$	$H(22^{iv})$	2·44 (5)	$C(6^{i})$	$C(13^{vii})$	3·573 (7)
$C(7^{i})$	$N(11^{iv})$	3·360 (6)	$C(6^{i})$	$H(23^{vii})$	3·08 (5)
$C(7^{i})$	$H(21^{i})$	2·79 (5)	$C(6^{i})$	$H(29^{i})$	3·04 (5)
$C(7^{i})$	$H(25^{i})$	3·01 (5)	$C(10^{i})$	$C(14^{ii})$	3·671 (9)
$C(1^{i})$	$H(25^{i})$	2·94 (5)	$H(17^{i})$	$H(28^{viii})$	2·35 (7)
$C(2^{i})$	$H(19^{iii})$	2·91 (5)	$H(20^{i})$	$H(29^{i})$	2·43 (7)
$C(2^{i})$	$C(5^{iii})$	3·784 (8)	$H(33^{i})$	$C(14^{ii})$	3·15 (6)
$C(2^{i})$	$H(26^{vii})$	3·07 (5)			

Symmetry code: i x, y, z (as given in Table 1); ii $\frac{1}{2}+x, \frac{1}{2}-y, 1-z$; iii $-\frac{1}{2}+x, y, \frac{3}{2}-z$; iv $\frac{1}{2}-x, -y, \frac{1}{2}+z$; v $1-x, -y, 1-z$; vi $x, \frac{1}{2}-y, \frac{1}{2}+z$; vii $1+x, y, z$; viii $x, y, 1+z$.

corresponding angles with respect to the (100) plane are about 29, 26 and 26° for the *p*-methyl, *p*-bromo and *p*-chloro compounds, respectively. These angles are also very similar and are determined mainly by the contact between the hydrogen-bonded chains which are related by a centre of symmetry. The contact between the atoms C(3) and $H(35^{vi})$ of the methyl group is 3·07 Å and is normal, but the corresponding contacts in the *p*-bromo and *p*-chloro compounds (3·98 and 3·89 Å, respectively) are rather loose. This shows that the hydrogen-bonded chains related by the *c* glide plane are not in direct contact. The packing is determined by two factors: (1) the contact between the *p*-substituent and the atom $C(14^{ii})$, (2) the bond length between the atom C(4) and the *p*-substituent. In fact, the differences in the cell constants *b* of the three compounds (26·45, 27·30 and 26·37 Å for *p*-methyl, *p*-bromo and *p*-chloro compounds, respectively) correspond to the difference in both factors for these compounds. Such a situation is caused by the fact that the piperidine and acid moieties connected by the hydrogen bonds cannot alter their relative positions to allow a more intimate packing between the hydrogen-bonded chains related by the *c* glide plane. Thus the rather loose contact around the *p*-substituents results. This packing scheme explains the similarity of the melting points of the three compounds (119, 120 and 121 °C for the *p*-methyl, *p*-bromo and *p*-chloro compounds, respectively).

The structure of the p-toluate and piperidinium ions

The bond lengths and angles of the *p*-toluate and piperidinium ions are shown in Table 6. The two C–O bond lengths are 1·278 and 1·257 Å, and the C–C–O angles are 116·4 and 120·0°. The bond length C(1)–C(7) is 1·512 Å. These values are very similar to those of the *p*-bromobenzoate ion in the 1:1 addition compound. The average C–C bond length in the benzene ring is 1·395 Å. The dihedral angle between the plane of the benzene ring and that through C(7), O(8) and O(9) is 8·0°. The deviation of the atom C(10) of the methyl group from the benzene ring plane is only 0·015 Å. The bond length C(4)–C(10) (1·505 Å) agrees with the corresponding length (1·499 Å) in *p*-toluic acid (Takwale & Pant, 1971). The average C–H bond length in the benzene ring, 1·03 (5) Å, is normal. In the methyl group, the average C–H bond length is 0·91 (9) Å.



(*a*)

(*b*)

Fig. 2. (*a*) The projection of the crystal structure along the *c* axis. (*b*) The projection of the crystal structure along the *a* axis. The intermolecular contacts are shown by dotted lines.

This is comparable with the value of 1·0 Å found in *p*-cresol at −150°C (Bois, 1970). However, the intramolecular contact H(33)···H(34) is extraordinarily short (1·1 Å), as found in *p*-toluic acid (1·2 Å, calculated from the data of Takwale & Pant, 1971). This is probably because of the poor resolution of the positions of the hydrogen atoms, caused by large thermal vibration of the methyl group. In the piperidinium ion, atoms C(12), C(13), C(15) and C(16) form a plane within 0·0002 Å. The atom N(11) deviates from this plane by 0·672 Å, while the atom C(14) deviates by −0·688 Å; the piperidine ring takes a chair form. The average N–H bond length is 1·00 (5) Å and the average C–N–H angle is 108 (3)°. Therefore, the orbital of the nitrogen atom is an sp^3 hybrid. The average C–C bond length in the ring is 1·526 Å in agreement with that found in the *p*-bromo and *p*-chloro compounds. The average C–N and C–H bond lengths are 1·508 and 1·05 (5) Å, respectively. The average bond angle between non-hydrogen atoms in the ring is 110·6 (4)°, being slightly greater than the regular tetrahedral angle. The difference in the bond angles, C–C–C, C–N–C and C–C–N is not significant.

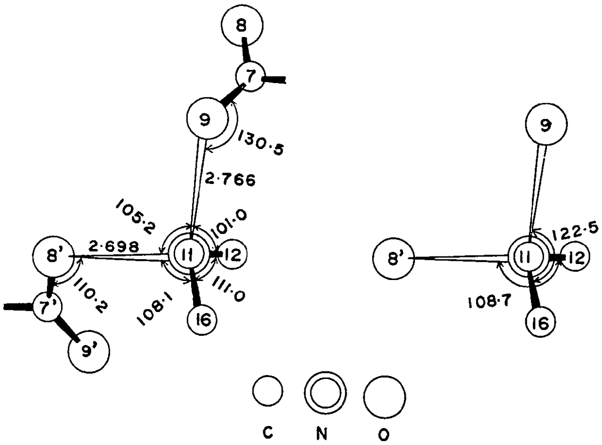


Fig. 3. Molecular geometries of the hydrogen-bond system. Covalent bonds are filled and open bonds represent hydrogen bonds.

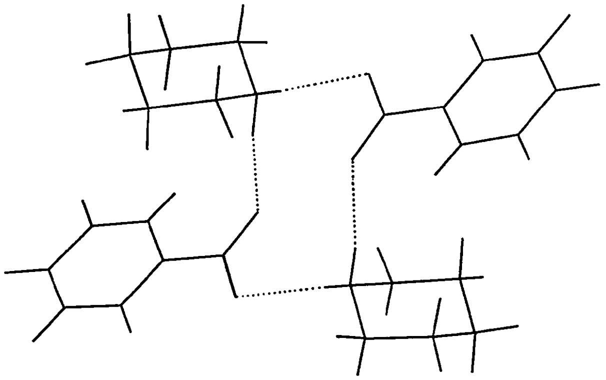


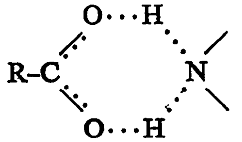
Fig. 4. A model of the 1:1 addition compounds of benzoic acids and piperidine in benzene solution.

Table 6. *Bond lengths and angles along with their e.s.d.'s in parentheses*

C(1)—C(2)	1·395 (6) Å	C(1)—C(2)—C(3)	122·1 (5)°
C(2)—C(3)	1·403 (7)	C(2)—C(3)—C(4)	120·6 (5)
C(3)—C(4)	1·382 (8)	C(3)—C(4)—C(5)	117·5 (5)
C(4)—C(5)	1·390 (8)	C(4)—C(5)—C(6)	122·5 (5)
C(5)—C(6)	1·401 (8)	C(5)—C(6)—C(1)	120·0 (5)
C(6)—C(1)	1·398 (7)	C(6)—C(1)—C(2)	117·3 (4)
C(1)—C(7)	1·512 (6)	C(3)—C(4)—C(10)	122·4 (5)
C(7)—O(8)	1·278 (6)	C(5)—C(4)—C(10)	120·2 (9)
C(7)—O(9)	1·257 (5)	C(2)—C(1)—C(7)	122·2 (4)
C(4)—C(10)	1·505 (9)	C(6)—C(1)—C(7)	120·5 (4)
N(11)–C(12)	1·507 (6)	C(1)—C(7)—O(8)	116·4 (4)
N(11)–C(16)	1·508 (6)	C(1)—C(7)—O(9)	120·0 (4)
C(12)–C(13)	1·514 (7)	O(8)—C(7)—O(9)	123·7 (5)
C(13)–C(14)	1·532 (7)	N(11)–C(12)–C(13)	111·5 (4)
C(14)–C(15)	1·529 (8)	C(12)–C(13)–C(14)	110·5 (4)
C(15)–C(16)	1·530 (7)	C(13)–C(14)–C(15)	109·8 (5)
N(11)–H(21)	1·00 (5)	C(14)–C(15)–C(16)	110·7 (4)
N(11)–H(22)	1·01 (5)	C(15)–C(16)–N(11)	110·6 (4)
		C(16)–N(11)–C(12)	110·7 (4)
		H(21)–N(11)–C(12)	105 (3)
		H(22)–N(11)–C(12)	102 (3)
		H(21)–N(11)–C(16)	113 (3)
		H(22)–N(11)–C(16)	113 (3)

A structural model of the 1:1 addition compounds of benzoic acid and piperidine in benzene solution

Although a thorough discussion of the structure in solution is beyond the scope of this paper, a comment on this problem will be given. Sobczyk & Syrkin (1957) have proposed the structure as



based on the fact that the dielectric polarization of the addition compounds of piperidine with a series of carboxylic acids does not depend on the strength of the acids, and the dipole moment is not significantly larger than that of the parent acids. On the other hand, Bruckenstein & Saito (1965) have proposed, on the basis of the infrared spectra, that the monomeric 1:1 adducts of carboxylic acids and amines are ion pairs and their oligomers are formed by long-range electrostatic forces rather than by hydrogen bonds. The ν-CO_2^- absorptions of the solid 1:1 addition compounds are substantially the same as those in benzene solution (Kashino, 1968; Kashino, Kanei & Hasegawa, 1972). This suggests that the environment around the CO_2^- group in benzene solution is similar to that in the solid state. It has been found that the 1:1 addition compounds of piperidine with benzoic acid, *p*-toluic acid and *p*-bromobenzoic acid exist as dimers, $(p\text{-}XC_6H_4CO_2H.C_5H_{10}NH)_2$, in benzene (Kashino, Kusunoki & Hasegawa, unpublished). If we consider the hydrogen-bonded chain mentioned before and assume about a 180° rotation of the acid moiety around the hydrogen bond, $N(11)^+\text{–}H(22)\cdots O(8)^-$, the hydrogen-bonded dimer illustrated in Fig. 4 can be formed without serious change to the tetrahedral arrangement of the hydrogen bond around the nitrogen atom. In this model there are no unreasonable intermolecular contacts. Thus this may be a plausible model of the molecular structure in benzene solution, consistent with dimer formation, infrared spectra and, qualitatively, with the dipole moment in solution.

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The Crystal Structure of Strophanthidin, a Cardioactive Steroid, $C_{23}H_{32}O_6.\frac{1}{2}H_2O$

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Strophanthidin, $C_{23}H_{32}O_6.\frac{1}{2}H_2O$, is the aglycone of the strophanthus group of active cardiac glycosides which have a digitalis-like action on the heart. A partial structure was obtained using the symbolic addition procedure for non-centrosymmetric crystals and the complete structure was then developed using the tangent formula. The space group is $P2_1$ with $a=13{\cdot}608$ (8), $b=12{\cdot}068$ (8), $c=13{\cdot}693$ (8) Å, $\beta=109{\cdot}4$ (2)° and $Z=4$. The X-ray analysis confirmed the expected configuration. As in other cardioactive steroids, the A/B and C/D ring junctions are *cis*. The two molecules in the asymmetric unit differ in the vicinity of the lactone rings, in such a way as to indicate a disorder in one of the molecules.

Introduction

Symptoms of congestive heart failure can be relieved with proper dosages of specific cardiotonic agents. These drugs allow the heart to empty more completely with each beat with no increase in oxygen consumption. The heart becomes a better mechanical pump, more able to meet the needs of the circulatory system. The drugs usually contain a mixture of compounds called cardiac glycosides. Removal of the glycoside by hydrolytic cleavage leaves the aglycone or genin which also exhibits cardiac activity but usually to a lesser degree. The best known and most widely used drug of this type is digitalis. Strophanthidin, the aglycone of the strophanthus group of active cardiac glycosides, is a naturally occurring steroid which is obtained from the seeds of the *Strophanthus kombe* (dogbane) tree found in Africa and Asia. The determination of its structure is part of a series of studies on steroids exhibiting cardiac activity. Prior structures which relate to this study are digitoxigenin (DTG, Karle & Karle, 1969*b*); Δ-8,14-anhydrodigitoxigenin (ADTG, Gilardi & Karle, 1970) and batrachotoxinin A (Karle & Karle, 1969*a*). The first two are illustrated in Fig. 1, along with the two molecules of strophanthidin found in the asymmetric unit.

Experimental

Single crystals were selected from a commercial sample of strophanthidin (Sandoz Ltd., Basle, Switzerland).