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The Crystal and Molecular Structure of Piperazinium Terephthalate, $(H_2NC_4H_8NH_2)^{2+}(O_2C\cdot C_6H_4\cdot CO_2)^{2-}$

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Piperazinium terephthalate has been prepared and examined by X-ray analysis. The compound crystallizes in the monoclinic space group $P2_1/c$ with two formula units in a unit cell. The cell dimensions are: $a=9.45$, $b=8.30$, $c=8.33$ Å, and $\beta=117.3°$. The structure was determined by the Patterson method from the data collected with Cu$K\alpha$ radiation on Weissenberg photographs, and refined by the block-diagonal least-squares method with anisotropic temperature factors for non-hydrogen atoms and fixed isotropic ones for hydrogen atoms. The final R value is 0.108 for 941 non-zero reflections. Acid and base moieties occupy the positions of center of symmetry in the cell. Two N^+–H···O^- hydrogen bonds (2.612 and 2.737 Å) link a nitrogen atom of piperazine with two carboxyl oxygens of the acids related by c glide plane to form a three-dimensional hydrogen bond network, in which each oxygen atom accepts one hydrogen bond. The coordination around the nitrogen atom is nearly tetrahedral. The piperazine ring takes a chair form. The twisting angle between the carboxyl group and the benzene ring plane is 17.3°.

During the course of investigation of the structure of the addition compounds of piperidine with benzoic acids,[1] it was found desirable to extend studies to the addition compounds of bifunctional aromatic acids and bifunctional heterocyclic amines. The present paper reports the formation and the crystal and molecular structure of an addition compound of piperazine with terephthalic acid, showing that the compound is piperazinium terephthalate.

Experimental

Piperazinium terephthalate was prepared by dissolving equimolar quantities of terephthalic acid and piperazine in hot water. After the solution had been left to stand at room temperature, colorless prisms separated out. Mp 307 °C (decomp.); IR: antisymmetric $\nu(CO_2^-)$ 1565 cm^{-1}, symmetric $\nu(CO_2^-)$ 1385 cm^{-1}.

Found: C, 57.19; H, 6.56; N, 10.89%. Calcd for $C_{12}H_{16}N_2O_4$: C, 57.13; H, 6.39; N, 11.10%.

Crystals obtained by slow cooling from aqueous solution were monoclinic prisms elongated along the a axis. Cell constants were determined from Weissenberg and oscillation photographs using Cu$K\alpha$ radiation ($\lambda=1.5418$ Å), and calibrated with sodium chloride.

Crystal data: piperazinium terephthalate, $(H_2NC_4H_8NH_2)^{2+}(OOC\cdot C_6H_4\cdot COO)^{2-}$; formula weight=252.3; monoclinic, $a=9.45(2)$, $b=8.30(1)$, $c=8.33(2)$ Å, $\beta=117.3(2)°$, $V=580.4$ Å^3, $D_m=1.44_2$ (by flotation), $D_c=1.443$ g cm^{-3}, $Z=2$.

Linear absorption coefficient for Cu$K\alpha$; $\mu=9.2$ cm^{-1}, $F(000)=268$.

Absent spectra: $h0l$ when l is odd, $0k0$ when k is odd. Space group is $P2_1/c$.

Three different crystals with approximate dimensions 0.3×0.3×0.9, 0.4×0.3×0.3, and 0.3×0.3×0.3 mm were used for a, b, and c axis photographs, respectively. Using Cu$K\alpha$ radiation, multiple-film equi-inclination Weissenberg photographs were taken for the layers from $0kl$ to $7kl$, from $h0l$ to $h5l$, and $hk0$. In all, 941 independent non-zero reflections were observed out of about 1350 possible reflections within the Cu$K\alpha$ sphere. Intensities were estimated by visual comparison with a calibrated intensity scale. After Lorentz, polarization, and spot-shape corrections were made, the intensities of various layers were put on the same relative scale by making use of all the common reflections. The relative values were put on an absolute scale by Wilson's method. No corrections for absorption and extinction effects were made.

Structure Analysis

Since only two molecular units of acid and base moieties were contained in a unit cell of the space

TABLE 1. FINAL ATOMIC PARAMETERS AND ESTIMATED STANDARD DEVIATIONS (×10^4) FOR NON-HYDROGEN ATOMS
The anisotropic temperature factors are defined as $\exp(-B_{11}h^2-B_{22}k^2-B_{33}l^2-B_{12}hk-B_{13}hl-B_{23}kl)$.

Atom	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
O(1)	6895(4)	6709(4)	768(4)	62(4)	71(5)	58(5)	46(7)	2(8)	3(8)
O(2)	7765(5)	4435(4)	141(4)	117(6)	94(5)	32(5)	71(9)	10(8)	−18(9)
C(1)	7771(5)	5490(5)	1223(5)	28(5)	72(6)	31(6)	3(9)	16(9)	18(11)
C(2)	8928(5)	5238(5)	3179(5)	16(4)	73(6)	39(6)	−8(9)	35(9)	0(10)
C(3)	9347(5)	6513(5)	4414(6)	32(5)	51(6)	54(7)	17(9)	33(10)	11(10)
C(4)	9592(5)	3741(5)	3784(6)	40(5)	62(6)	43(6)	−5(10)	31(10)	−25(11)
C(5)	3480(5)	9221(6)	−614(6)	30(5)	76(7)	72(7)	−23(9)	46(10)	−12(12)
C(6)	4488(5)	9594(6)	1349(6)	55(6)	80(7)	55(7)	−8(10)	81(11)	10(12)
N	6200(4)	9620(5)	1780(4)	35(4)	79(6)	28(5)	13(8)	12(8)	−2(9)

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1) S. Kashino, Y. Sumida, and M. Haisa, *Acta Crystallogr.*, **B28**, 1374 (1972).

TABLE 2. FINAL POSITIONAL PARAMETERS AND ESTIMATED STANDARD DEVIATIONS ($\times 10^3$) FOR HYDROGEN ATOMS

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
H (1)	892 (8)	744 (8)	400 (9)	H (5)	430 (8)	1062 (8)	162 (9)
H (2)	928 (8)	277 (8)	290 (9)	H (6)	417 (8)	869 (8)	200 (10)
H (3)	244 (9)	935 (8)	−79 (10)	H (7)	677 (8)	1002 (8)	311 (9)
H (4)	396 (9)	811 (8)	−81 (10)	H (8)	643 (8)	854 (8)	169 (10)

TABLE 3. OBSERVED AND CALCULATED STRUCTURE FACTORS ($\times 10$)
Unobserved reflections are marked with an asterisk.

L	FO	FC
H,K=	0	0
2	308	352
4	264	-259
6	69	62
8	48	-45
H,K=	0	1
1	209	234
2	235	234
3	466	-512
4	92	-67
5	-*	22
6	137	-131
7	71	-67
8	61	-56
9	194	-155
H,K=	0	2
0	434	776
1	38	-22
2	108	-95
3	254	-276
4	75	-55
5	214	-218
6	228	238
7	-*	-7
8	48	37
9	137	98
H,K=	0	3
1	16	-14
2	182	154
3	254	-225
4	197	-186
5	37	35
6	220	-214
7	66	-67
8	18	-21
9	103	-98
H,K=	0	4
0	20	-12
1	110	91
2	236	-199
3	130	111
4	25	17
5	62	58
6	155	160
7	78	69
H,K=	0	5
1	123	-88
2	28	20
3	80	-62
4	118	-111
5	151	134
6	77	-75
7	65	51
8	35	28
H,K=	0	6
0	90	85
1	25	-21
2	33	-27
3	46	-39
4	47	-50
5	51	40
6	49	-45
7	115	98
H,K=	0	7
1	94	82
2	113	112
3	-*	-2
4	22	21
5	29	26
6	53	-45
H,K=	0	8
0	126	-116
1	-*	-12
2	87	-83
3	47	-48
4	20	-20
5	64	-52
H,K=	0	9
1	77	65
2	70	60
3	17	16
H,K=	0	10
0	165	-146
1	61	55
2	59	-43
3	110	87
H,K=	1	0
-8	28	23
-6	71	-77
-4	230	-219
-2	298	-323
0	23	-32
2	343	452
4	259	267
6	34	37
8	22	35
H,K=	1	1
-9	87	77
-8	77	78
-7	105	-111
-6	164	168
-5	55	-52
-4	203	179
-3	289	289
-2	120	95
-1	144	106
0	201	-184
1	245	-239
2	87	-74
3	126	-120
4	64	59
5	38	-28
6	-*	2
7	-*	-18
8	42	44
9	53	-60
H,K=	1	2
-8	54	-51
-7	-*	7
-6	30	-23
-5	246	-276
-4	62	50
-3	191	-200
-2	81	-68
-1	182	205
0	203	-208
1	106	98
2	120	115
3	-*	7
4	103	92
5	195	-198
6	-*	0
7	133	-142
H,K=	1	3
-9	92	82
-8	73	64
-7	-*	-12
-6	31	33
-5	-*	7
-4	31	29
-3	120	-86
-2	378	353
-1	466	-406
0	158	135
1	287	-253
2	251	237
3	147	143
4	240	242
5	186	189
6	53	-45
H,K=	1	4
-8	68	-58
-7	-*	-1
-6	39	42
-5	347	-293
-4	129	119
-3	118	-102
-2	-*	-13
-1	37	23
0	147	-127
1	354	-300
2	69	-45
3	71	-65
4	72	71
5	-*	-13
6	-*	-21
7	-*	6
8	39	-34
H,K=	1	5
-8	21	20
-7	62	-62
-6	141	-146
-5	91	88
-4	45	-47
-3	116	127
-2	347	359
-1	66	67
0	130	127
1	48	-34
2	174	167
3	47	-42
4	265	291
5	-*	-16
6	28	23
7	74	-60
H,K=	1	6
-7	30	-33
-6	29	29
-5	272	-301
-4	-*	8
-3	-*	-1
-2	29	40
-1	121	125
0	58	56
1	163	-172
2	-*	12
3	48	-42
4	-*	19
5	-*	0
6	37	-41
H,K=	1	7
-6	30	34
-5	-*	6
-4	48	59
-3	-*	26
-2	180	199
-1	146	167
0	150	-152
1	118	111
2	119	-133
3	49	-56
4	111	119
5	80	-77
H,K=	1	8
-5	133	-111
-4	-*	-9
-3	29	37
-2	114	124
-1	81	88
0	119	117
1	111	-116
2	96	-108
3	28	-32
4	132	-116
5	79	-60
H,K=	1	9
-3	152	-140
-2	73	66
-1	-*	-10
0	82	-75
1	47	47
2	66	-64
H,K=	1	10
1	96	-78
H,K=	2	0
-10	308	-239
-8	35	-33
-6	225	204
-4	145	-124
-2	263	224
0	220	-175
2	555	-733
4	183	-170
6	125	-140
8	24	-19
H,K=	2	1
-9	24	22
-8	-*	-11
-7	292	305
-6	74	62
-5	46	-41
-4	121	98
-3	46	-48
-2	-*	2
-1	620	1083
0	38	21
1	235	188
2	119	-97
3	122	-91
4	137	-120
5	-*	-2
6	36	-37
7	-*	-29
8	63	49
H,K=	2	2
-9	77	65
-8	28	-28
-7	246	250
-6	83	69
-5	183	172
-4	341	-360
-3	367	-412
-2	194	-182
-1	434	-564
0	150	-142
1	79	-71
2	172	-162
3	-*	-2
4	98	83
5	52	-46
6	116	-112
7	-*	-13
8	108	-83
H,K=	2	3
-9	46	-40
-8	-*	-9
-7	237	235
-6	69	61
-5	103	95
-4	57	-37
-3	127	-99
-2	212	-165
-1	156	113
0	83	-71
1	267	-237
2	41	29
3	-*	-16
4	77	75
5	122	122
6	89	86
7	41	35
8	75	63
H,K=	2	4
-9	74	-62
-8	25	-26
-7	-*	15
-6	63	58
-5	71	66
-4	214	-186
-3	136	-102
-2	144	-117
-1	52	-43
0	107	-77
1	100	86
2	25	20
3	32	-29
4	210	199
5	118	-121
6	-*	-23
7	90	-84
H,K=	2	5
-9	61	-64
-8	91	-82
-7	-*	4
-6	48	-50
-5	91	-90
-4	-*	0
-3	167	-136
-2	84	-71
-1	82	68
0	102	-73
1	26	10
2	33	33
3	116	108
4	211	204
5	42	45
6	175	165
7	119	-98
H,K=	2	6
-6	60	62
-5	42	43
-4	47	41
-3	61	-62
-2	131	133
-1	84	-84
0	66	60
1	-*	5
2	35	-32
3	36	37
4	35	32
H,K=	2	7
-7	77	-66
-6	30	-28
-5	90	-93
-4	94	99
-3	36	-43
-2	125	124
-1	30	31
0	27	22
1	-*	0
2	36	-48
H,K=	2	8
-6	53	-52
-5	65	62
-4	65	-53
-3	35	-40
-2	93	90
-1	72	-79
0	153	152
1	-*	-16
2	59	60
H,K=	2	9
-1	113	-91
0	-*	-2
1	107	-96
2	27	22
3	34	-34
H,K=	2	10
-1	40	38
0	-*	11
1	76	60
H,K=	3	0
-10	70	72
-8	137	-139
-6	241	-243
-4	69	73
-2	574	720
0	351	339
2	297	-311
4	183	-181
6	77	-78
8	188	-135
H,K=	3	1
-8	90	96
-7	-*	1
-6	51	-50
-5	34	-30
-4	207	-176
-3	54	47
-2	250	-236
-1	332	308
0	18	20
1	154	144
2	67	66
3	64	57
4	87	-82
5	65	60
6	59	-57
H,K=	3	2
-10	84	76
-9	66	62
-8	22	-29
-7	153	158
-6	99	-83
-5	239	264
-4	-*	-2
-3	295	302
-2	80	21
-1	34	-33
0	194	-182
1	22	-15
2	168	-172
3	92	-80
4	81	65
5	121	-128
6	66	66
7	67	55
H,K=	3	3
-10	36	-38
-9	50	-47
-8	63	80
-7	56	-60
-6	139	-118
-5	55	-57
-4	105	-91
-3	37	26
-2	24	-15
-1	91	84
0	113	-84
1	136	127
2	81	-76
3	107	110
4	214	-244
5	27	20
6	76	-70
7	48	-39
H,K=	3	4
-9	76	77
-8	-*	-11
-7	-*	8
-6	22	25
-5	-*	17
-4	-*	1
-3	260	223
-2	160	-132
-1	47	57
0	251	-217
1	241	220
2	61	-51
3	204	212
4	113	122
5	35	-37
6	43	49
H,K=	3	5
-7	85	88
-6	202	-214
-5	65	65
-4	25	22
-3	36	-30
-2	157	140
-1	151	-133
0	98	-81
1	122	-120
2	93	-90
3	46	41
4	150	-172
5	39	44
6	17	-14
H,K=	3	6
-7	46	-41
-6	-*	19
-5	22	30
-4	-*	22
-3	238	240
-2	86	98
-1	22	-14
0	72	67
1	-*	11
2	-*	25
3	83	97
4	46	-58
H,K=	3	7
-7	64	65
-6	191	-177
-5	-*	13
-4	68	-81
-3	48	52
-2	23	-2
-1	23	20
0	50	-55
1	113	-125
2	39	43
3	85	-97
4	56	-49
5	62	-33
H,K=	3	8
-6	55	50
-5	-*	10
-4	44	-57
-3	76	78
-2	22	-12
-1	94	-98
0	-*	6
1	43	-55
H,K=	3	9
-2	36	-34
-1	46	45
0	53	-47
1	40	-41
2	60	40
H,K=	4	0
-10	94	82
-8	289	320
-6	26	-26
-4	113	-93
-2	308	292
0	97	-76
2	162	162
4	55	47
6	35	-33
H,K=	4	1
-9	42	-50
-8	109	114
-7	-*	16
-6	138	126
-5	155	-130
-4	127	-109
-3	124	99
-2	326	-287
-1	365	-356
0	214	-191
1	266	-266
2	43	-50
3	75	70
4	-*	11
5	129	-148
H,K=	4	2
-8	164	171
-7	55	-39
-6	21	-16
-5	144	-130
-4	18	12
-3	63	-52
-2	227	240
-1	138	129
0	80	-62
1	141	122
2	117	104
3	103	102
4	-*	16
5	-*	25
6	68	-55
H,K=	4	3
-10	22	-24
-9	21	-24
-8	26	24
-7	28	24
-6	-*	-2
-5	198	-177
-4	174	-157
-3	210	-208
-2	114	-102
-1	309	-330
0	-*	12
1	34	33
2	61	56
3	296	338
4	32	-33
5	-*	-1
6	111	-104
H,K=	4	4
-9	54	-56
-8	20	25
-7	68	-72
-6	-*	-7
-5	32	27
-4	-*	-1
-3	150	134
-2	76	63
-1	-*	14
0	108	-83
1	57	-43
2	109	111
3	136	150
4	41	49
5	159	164
6	102	-99
H,K=	4	5
-9	52	-53
-8	103	-104
-7	38	37
-6	76	-93
-5	63	63
-4	32	-29
-3	164	156
-2	29	34
-1	25	25
0	71	66
1	22	-22
2	86	82
3	63	59
4	-*	8
5	78	-77
6	131	-138
H,K=	4	6
-7	108	-124
-6	21	-28
-5	41	34
-4	-*	-15
-3	187	193
-2	-*	16
-1	55	50
0	46	-45
1	52	-58
2	27	28
3	78	90
4	-*	-6
5	103	104
H,K=	4	7
-7	26	22
-6	52	43
-5	20	23
-4	27	37
-3	169	175
-2	72	-72
-1	160	170
0	148	-163
1	-*	5
2	48	-53
3	88	-80
4	27	25
H,K=	4	8
-6	52	-42
-5	-*	19
-4	30	23
-3	69	67
-2	46	58
-1	29	-25
0	34	-32
1	56	-58
2	94	-92
H,K=	4	9
-5	65	-68
-4	-*	4
-3	-*	-14
-2	36	-31
-1	88	78
0	50	-49
1	46	35
H,K=	5	0
-8	178	182
-6	173	160
-4	120	104
-2	365	336
0	28	15
2	225	-235
4	56	-63
6	85	79
H,K=	5	1
-10	26	28
-9	50	46
-8	50	54
-7	58	-50
-6	99	87
-5	145	-123
-4	67	49
-3	204	170
-2	68	-53
-1	231	185
0	71	61
1	283	-282
2	42	-39
3	182	-195
4	91	-98
H,K=	5	2
-9	138	147
-8	83	78
-7	73	73
-6	49	-41
-5	143	-125
-4	110	-91
-3	368	-403
-2	194	173
-1	219	-221
0	205	194
1	30	24
2	75	63
3	107	-100
4	24	23
H,K=	5	3
-10	73	71
-9	-*	-18
-8	92	100
-7	-*	5
-6	144	151
-5	31	-27
-4	71	59
-3	-*	-1
-2	196	-180
-1	133	-112
0	91	74
1	169	-172
2	82	82
3	-*	10
4	53	-58
5	79	75
6	61	58
H,K=	5	4
-8	21	29
-7	87	-92
-6	43	-45
-5	30	-20
-4	104	-106
-3	39	-39
-2	37	-28
-1	-*	19
0	44	43
1	43	39
2	143	150
3	194	-229
4	80	84
5	89	-80
H,K=	5	5
-7	22	-25
-6	97	119
-5	88	-87
-4	140	138
-3	27	-33
-2	117	-126
-1	-*	6
0	54	51
1	52	55
2	104	115
3	80	86
H,K=	5	6
-8	65	54
-7	114	-111
-6	-*	21
-5	-*	0
-4	45	41
-3	42	-41
-2	-*	-12
-1	-*	-14
0	123	-128
1	63	69
2	60	-65
3	118	-107
H,K=	5	7
-6	43	46
-5	45	-42
-4	113	127
-3	-*	6
-2	52	-49
-1	-*	18
0	41	43
1	38	35
2	20	22
3	20	25
H,K=	5	8
-6	99	-96
-5	-*	-6
-4	-*	-11
-3	97	-96
-2	29	31
-1	52	-51
0	34	-34
1	92	87
2	15	-15
H,K=	5	9
-4	25	-25
-3	-*	-4
-2	113	-99
-1	-*	-14
0	67	63
H,K=	6	0
-10	25	-21
-8	161	-167
-6	166	-156
-4	272	248
-2	144	-115
0	136	-121
2	132	137
4	147	-140
H,K=	6	1
-10	63	61
-9	147	159
-8	26	19
-7	91	-95
-6	104	-95
-5	57	55
-4	141	-113
-3	223	188
-2	-*	7
-1	148	-127
0	101	89
1	132	116
2	96	92
3	-*	26
4	50	38
5	48	-55
H,K=	6	2
-9	54	53
-8	91	-94
-7	61	47
-6	107	-96
-5	25	-24
-4	131	112
-3	46	-35
-2	268	-279
-1	60	-47
0	121	-114
1	64	-64
2	209	246
3	96	-89
4	-*	-2
5	99	-78
H,K=	6	3
-10	23	25
-9	-*	-1
-8	-*	-18
-7	130	-146
-6	36	-39
-5	37	29
-4	157	143
-3	161	140
-2	149	148
-1	-*	-14
0	-*	-5
1	186	196
2	28	23
3	45	45
4	38	45
5	121	-129
H,K=	6	4
-7	59	-64
-6	33	20
-5	59	-57
-4	97	90
-3	35	39
-2	183	-177
-1	26	30
0	64	-64
1	59	49
2	180	186
3	-*	-14
4	-*	1
5	112	-131
H,K=	6	5
-9	35	40
-8	102	-100
-7	-*	19
-6	-*	5
-5	51	55
-4	260	306
-3	40	-32
-2	188	197
-1	160	-178
0	80	-87
1	-*	8
2	33	-34
3	-*	28
4	40	59
H,K=	6	6
-8	51	47
-7	54	-59
-6	34	36
-5	32	26
-4	122	130
-3	59	57
-2	72	66
-1	74	-78
0	-*	-18
1	57	-60
2	51	-52
H,K=	6	7
-7	20	23
-6	81	-79
-5	28	30
-4	83	77
-3	-*	14
-2	-*	23
-1	95	-96
0	68	-64
1	140	-113
2	47	48
H,K=	6	8
-5	25	-25
-4	-*	2
-3	36	-34
-2	71	63
-1	105	-97
0	-*	-11
1	46	-47
H,K=	6	9
-2	61	-52
H,K=	7	0
-10	136	138
-8	83	98
-6	160	-161
-4	116	-105
-2	54	-38
0	222	-225
2	134	-145
4	39	31
H,K=	7	1
-10	42	40
-9	166	176
-8	49	49
-7	109	109
-6	33	-22
-5	46	-51
-4	203	-201
-3	88	67
-2	155	-135
-1	54	52
0	-*	6
1	52	-43
2	-*	-9
3	50	-55
4	44	43
H,K=	7	2
-6	105	-86
-5	94	-85
-4	-*	6
-3	174	-168
-2	29	23
-1	120	117
0	128	-128
1	148	156
2	105	-98
H,K=	7	3
-9	71	72
-8	39	-36
-7	-*	21
-6	57	-55
-5	126	-128
-4	211	-223
-3	78	-75
-2	70	-59
-1	78	74
0	135	142
1	174	190
2	52	-47
3	104	104
H,K=	7	4
-9	52	-62
-8	28	-25
-7	121	135
-6	43	-38
-5	129	130
-4	-*	8
-3	157	-160
-2	28	26
-1	-*	-2
0	31	34
1	83	78
2	54	57
3	-*	22
4	20	-23
H,K=	7	5
-8	103	-117
-7	-*	7
-6	25	27
-5	45	37
-4	64	-62
-3	46	46
-2	28	29
-1	28	-4
0	128	151
1	25	29
2	75	-73
H,K=	7	6
-7	81	77
-6	-*	-23
-5	146	167
-4	-*	2
-3	76	-76
-2	-*	-9
-1	-*	18
0	44	43
1	47	37
2	73	60
H,K=	7	7
-7	60	-63
-6	97	91
-5	52	39
-4	64	-57
-3	86	73
-2	86	-78
-1	-*	-33
0	41	36
1	69	-55
H,K=	7	8
-5	36	36
-4	63	66
-3	118	-112
-2	40	32
-1	41	26
0	40	26
H,K=	8	0
-10	173	172
-8	71	-74
-6	103	103
-4	224	217
-2	42	-54
0	57	-52
2	151	-157
H,K=	8	1
-9	108	-109
-8	-*	10
-7	127	-118
-6	-*	-43
-5	207	207
-4	-*	-38
-3	-*	-44
-2	-*	13
-1	76	-84
0	-*	9
1	72	65
2	57	-60
3	55	-61
H,K=	8	2
-10	91	87
-9	118	102
-8	142	-147
-7	-*	-27
-6	-*	11
-5	67	-66
-4	165	143
-3	67	-49
-2	-*	2
-1	-*	-17
0	139	122
1	-*	18
2	-*	-23
3	51	47
H,K=	8	3
-9	90	-89
-8	47	58
-7	-*	-25
-6	46	-46
-5	194	192
-4	85	-76
-3	99	-86
-2	62	-60
-1	92	-91
0	-*	-12
1	107	108
2	66	-63
H,K=	8	4
-8	101	-91
-7	-*	-14
-6	-*	1
-5	162	156
-4	-*	7
-3	166	174
-2	91	-88
-1	-*	-17
0	113	108
1	92	-94
2	60	66
3	29	-42
H,K=	8	5
-5	52	40
-4	-*	2
-3	54	-67
-2	68	-70
-1	-*	-14
0	65	-60
1	97	94
2	37	-44
H,K=	8	6
0	93	-78
H,K=	9	0
-8	25	25
-6	61	-64
-4	19	-18
-2	30	28
0	114	110
H,K=	9	1
-7	106	-106
-6	64	-66
-5	58	-49
-4	100	-87
-3	75	-66
-2	57	61
-1	101	-100
0	104	106
1	-*	-18
2	50	59
H,K=	9	2
-8	73	51
-7	-*	-13
-6	-*	-14
-5	102	-94
-4	80	-60
-3	-*	17
-2	-*	-21
-1	116	103
0	146	140
1	-*	-26
2	100	77
H,K=	9	3
-9	59	-64
-8	-*	27
-7	47	-49
-6	65	71
-5	38	41
-4	38	-41
-3	38	29
-2	48	56
-1	46	52
0	68	61
1	66	58
H,K=	9	4
-8	48	44
-7	-*	17
-6	57	61
-5	40	-51
-4	-*	-13
-3	35	42
-2	34	-35
-1	130	130
0	91	91
H,K=	9	5
-8	35	42
-7	46	48
-6	204	206
-5	41	43
-4	30	40
-3	52	-58
-2	-*	-1
-1	-*	-22
0	58	-58
H,K=	10	0
-8	25	-59
-6	59	64
-4	101	-108
-2	99	-93
0	54	-37
H,K=	10	1
-6	55	-62
-5	-*	33
-4	74	-64
-3	-*	-10
-2	-*	-1
-1	-*	16
0	33	26
1	199	-175
H,K=	10	2
-7	117	-94
-6	147	136
-5	172	-166
-4	-*	-26
-3	-*	-37
-2	-*	-30
-1	133	119
H,K=	10	3
-6	38	-53
-5	-*	-10
-4	-*	-29
-3	36	-31
-2	34	40
-1	133	116
0	36	32
H,K=	10	4
-7	25	31
-6	93	88
-5	105	-101
-4	-*	-16
-3	119	-113
-2	29	32
-1	-*	-1
0	66	86
H,K=	10	5
-6	43	46
-5	-*	8
-4	35	43
-3	41	-41
-2	-*	27
-1	28	23
H,K=	11	0
-8	88	-92
-6	88	78
-4	-*	6
-2	101	-87
H,K=	11	1
-2	86	68
-1	116	109
H,K=	11	2
-6	106	80
H,K=	11	3
-7	98	116
-6	40	-50
-5	40	44
-4	49	44
-3	71	-67
-2	54	59
H,K=	11	4
-6	49	67
-5	64	74
-4	43	-45
-3	22	29

group $P2_1/c$, it was most plausible that each of the acid and base moieties should be centrosymmetric and occupy the center of symmetry of the cell. Thus, the center of gravity of the acid moiety was chosen to be (0, 0, 0) and that of the base moiety (1/2, 0, 0), a half of their molecular unit being taken as the asymmetric unit. Orientation of the acid moiety was sought using two-dimensional Patterson projections onto (1 0 0), (0 1 0), and (0 0 1), the (0 1 0) projection being especially suggestive. Approximate positional parameters of all non-hydrogen atoms were then determined by interpretation of the three-dimensional Patterson map. Position of the nitrogen atom was identified by short interatomic distances of about 2.6 Å from the two carboxyl oxygen atoms in the trial structure. The structure was refined by the block-diagonal least-squares method[2] with isotropic temperature factors to an R value of 0.165 and with anisotropic temperature factors to that of 0.125. A difference Fourier synthesis at this stage revealed all eight hydrogen atoms as shown in Fig. 1(b). Further refinement was made with anisotropic temperature factors for the non-hydrogen atoms and with fixed isotropic temperature factors (B=1.7 Å^2) for the hydrogen atoms using the following weighting scheme:

$$\sqrt{w} = 0.0, \quad \text{if } F_o < F_{\min} \ (=1.0),$$

$$\sqrt{w} = 1.0, \quad \text{if } F_{\min} \leq F_o \leq F_{\max} \ (=17.0)$$

and

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

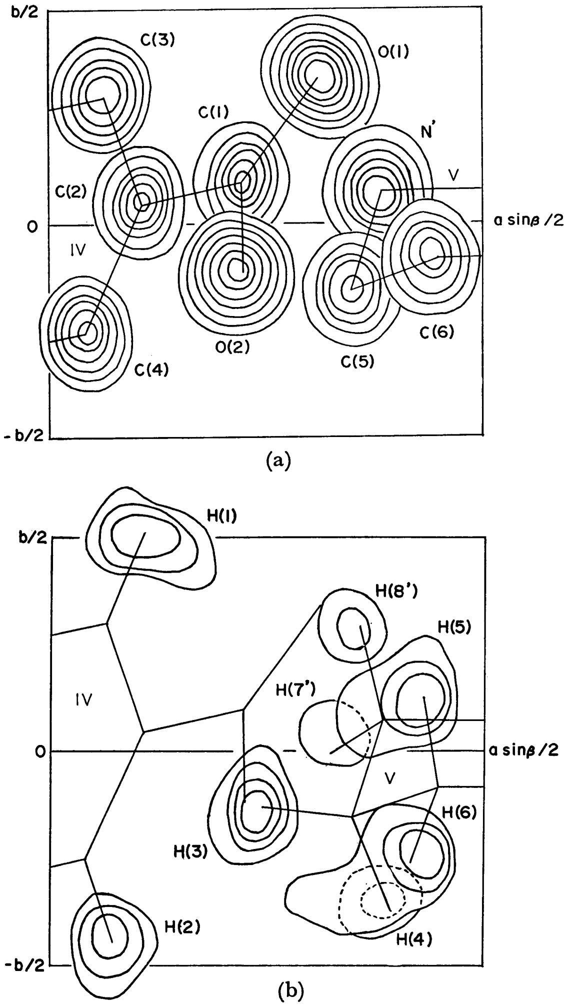

Fig. 1. (a) Composite drawing of final electron-density map. (b) The difference electron-density map at the stage of R=0.125. The contours are at equally spaced intervals on an arbitrary scale. IV and V will be illustrated in Fig. 2.

The final R value was 0.108 for 941 non-zero reflections. The final atomic parameters and their estimated standard deviations for non-hydrogen atoms are given in Table 1, and the final positional parameters for hydrogen atoms in Table 2. A composite drawing of the final electron-density map is shown in Fig. 1 along with the difference synthesis map. The observed and calculated structure factors are listed in Table 3.

The atomic scattering factors used were those of Hanson, Herman, Lea, and Skillman.[3] The numerical calculations were performed with the aid of a HITAC 5020E computer of the Computer Center, the University of Tokyo.

Results and Discussion

The projections of the crystal structure along the b and a axes are shown in Fig. 2. Two hydrogen bonds of nearly equal length link the nitrogen atom of piperazine with the carboxyl oxygen atoms to form a three-dimensional hydrogen bond network, in which each oxygen atom accepts one hydrogen bond; hydrogen bonds of length 2.737 Å link the acid and base moieties along [1 1 1] and other ones of length 2.616 Å link them along [1 0 2] infinitely. This hydrogen bond scheme explains the high melting point of this compound.

As shown in Fig. 3, the nitrogen atom is nearly tetrahedrally coordinated with the atoms C(6) and C(5′) covalently and with the atoms O(1) and O(2′) through hydrogen bonds. A difference map (Fig. 1(b)) shows that two hydrogen atoms belong to each nitrogen atom, the N–H bond lengths being determined to be 1.03 and 0.97 Å by the least-squares refinements. It can therefore be concluded that the present compound is composed of piperazinium cation and terephthalate anion, the hydrogen bonds between them being of the type N^+–H···O^-.

Bond angle C(1′)–O(2′)–N (111.9°) is approximately tetrahedral, but the angle C(1)–O(1)–N (147.0°) deviates considerably from regular tetrahedral angle. Corresponding to the difference, the hydrogen bond length between O(2′) and N (2.612 Å) is significantly shorter than that between O(1) and N (2.737 Å). Similar geometries of the hydrogen bond system have been found in the 1 : 1 addition compounds of piperidine with p-bromo- and p-chlorobenzoic acids.[1]

Bond lengths and angles of each ion are shown in Fig. 4. The two C–O bond lengths are almost equal to each other (1.251 and 1.255 Å) and shorter than

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[2] Y. Okaya and T. Ashida, "HBLS IV, The Universal Crystallographic Computing System (I)," The Crystallographic Society of Japan, Tokyo (1967), p. 65.

[3] H. H. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Crystallogr.*, **17**, 1040 (1964).

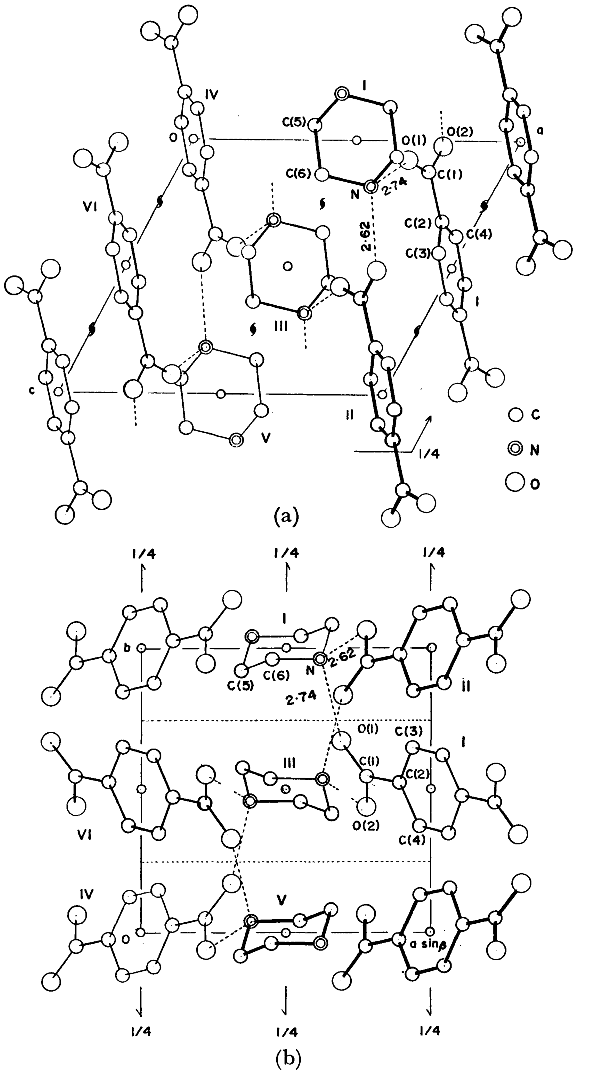

Fig. 2. (a) The projection of the crystal structure along the *b* axis. (b) The projection of the crystal structure along the *a* axis. Hydrogen bonds are shown by broken lines. Key for molecules I: x/a, y/b, z/c (given in Table 1) II: $-x/a+1$, $y/b+1/2$, $-z/c+3/2$ III: (0 −1 −1)II IV: (−1 −1 −1)II V: (0 −1 1)I VI: (−1 0 0)I

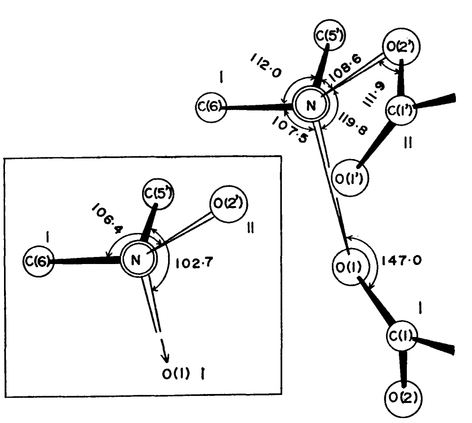

Fig. 3. Molecular geometries around nitrogen atom. Key for molecules is given in Fig. 2. Atoms translated by a center of symmetry in the molecule are shown with prime.

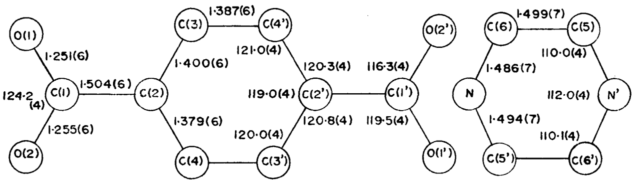

Fig. 4. Bond lengths (Å) and angles (°). The estimated standard deviations are shown in parentheses.

those found in terephthalic acid (1.262 and 1.272 Å),⁴⁾ supporting the fact that the acid is ionized. The angles C(2)–C(1)–O(1) and C(2)–C(1)–O(2) differ significantly; the former is 119.5° and the latter 116.3°. The mean C–C bond length in the benzene ring is 1.388 Å in agreement with that found in terephthalic acid (1.392 Å).⁴⁾ However, a quinonoid character in the benzene ring, which has been found in the terephthalic acid⁴⁾ and in terephthalate ion of calcium terephthalate trihydrate,⁵⁾ is not appreciable in this compound. The bond length between carboxyl carbon C(1) and aromatic carbon C(2) (1.504 Å) is significantly longer than the corresponding ones in the terephthalic acid (1.483 Å)⁴⁾ and in the terephthalate ion of calcium terephthalate trihydrate (1.487 and 1.495 Å).⁵⁾ In these two compounds the twisting angle of carboxyl group with respect to the plane of benzene ring are only 5.7—2.2°. In the present compound the angle amounts to 17.3°; distances of atoms C(1), O(1), and O(2) from the benzene ring plane are −0.009, −0.332, and 0.327 Å, respectively. A plausible explanation for the lengthening of the bond between aromatic C and carboxyl C is the diminution of the π-bond character resulting from a large twisting angle. A qualitatively similar relation between the bond length and twisting angle has been found in pyromellitic acid dihydrate.⁶⁾

The molecular geometry of piperazinium ion is

TABLE 4. INTERMOLECULAR DISTANCES WITH THEIR ESTIMATED STANDARD DEVIATIONS GIVEN IN PARENTHESES[a)]

From molecule I	To atom	Of molecule	Trans- lation			Distance (Å)
i) Hydrogen bonds						
O (1)	N	I	0	0	0	2.737 (7)
N	O (2′)	II	0	0	0	2.616 (7)
ii) Other distances less than 3.5 Å						
O (1)	C (6)	I	0	0	0	3.485 (7)
O (1)	C (5′)	I	0	0	0	3.394 (8)
O (1)	C (6′)	I	0	0	0	3.482 (7)
C (3)	O (1′)	II	0	0	0	3.348 (8)
C (6)	O (1′)	II	0	0	0	3.495 (9)
N	O (1′)	II	0	0	0	3.268 (9)
O (2)	C (5′)	I	0	−1	0	3.343 (7)
C (6)	O (2′)	II	0	0	0	3.354 (7)
C (5′)	O (2′)	II	0	0	0	3.401 (11)
N	C (1′)	II	0	0	0	3.297 (10)
C (2)	C (6)	II	0	−1	−1	3.466 (9)

a) Key for molecules is given in Fig. 2. Atoms translated by a center of symmetry in the molecule are shown with a prime.

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4) M. Bailey and C. J. Brown, *Acta Crystallogr.* **22**, 387 (1967).

5) T. Matsuzaki and Y. Iitaka, *ibid.*, **B28**, 1977 (1972).

6) F. Takusagawa, K. Hirotsu, and A. Shimada, This Bulletin, **44**, 1274 (1971).

identical within the limit of experimental errors with that found by Rérat[7] in piperazine dihydrochloride monohydrate. In the ion one nitrogen atom deviates upward from the plane through four carbon atoms by 0.65 Å and the other must deviate downward by the same distance. Thus the piperazine ring takes a normal chair form. The C–C bond length in the ring (1.499 Å) is in agreement with that found in piperazine hexahydrate (1.491 Å)[8] but significantly shorter than that found in piperazine by gas electron diffraction (1.540 Å).[9] The average C–N bond length is 1.490 Å, which is slightly longer than that observed in the hexahydrate (1.458 Å)[8] and in piperazine (1.467 Å).[9] The C–C–N angles are 110.1 and 111.0°, which are in agreement with those found in the hexahydrate (109.5 and 110.2°), but the C–N–C angle (112.0°) is slightly larger than that found in the hydrate (109.3°).

Intermolecular distances less than 3.5 Å are listed in Table 4. The structure is maintained by closely packed moieties to give a comparatively high density (1.44 g cm^{-3}).

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[7] C. Rérat, *Acta Crystallogr.*, **13**, 459 (1960).

[8] D. Schwarzenbach, *J. Chem. Phys.*, **48**, 4134 (1968).

[9] A. Yokozeki and K. Kuchitsu, This Bulletin, **44**, 2352 (1971).