References

BARRICELLI, L. B. (1958). *Acta Cryst.* **11**, 75–79.

BITHER, T. A., DONOHUE, P. C. & YOUNG, H. S. (1971). *J. Solid State Chem.* **3**, 300–307.

BROSTIGEN, G. & KJEKSHUS, A. (1970). *Acta Chem. Scand.* **24**, 2993–3012.

BUSMANN, E. (1961). *Z. anorg. allgem. Chem.* **313**, 90–106.

DONOHUE, P. C., SIEMONS, W. J. & GILLSON, J. L. (1968). *J. Phys. Chem. Solids*, **29**, 807–813.

HULLIGER, F. (1968). *Structure and Bonding*, **4**, 83–229.

HULLIGER, F. & MOOSER, E. (1963). *J. Phys. Chem. Solids*, **24**, 283–295.

KJEKSHUS, A. (1964). *Acta Chem. Scand.* **18**, 2379–3284.

MACHATSCHKI, F. (1947). *Mh. Chem.* **77**, 334–342.

MCWHAN, D. B., COMPTON, V. B., SILVERMAN, M. S. & SOULEN, J. R. (1967). *J. Less-Common Metals*, **12**, 75–76.

PARTHÉ, E. (1961). *Z. Kristallogr.* **115**, 52–79.

PARTHÉ, E. (1963). *Z. Kristallogr.* **119**, 204–225.

PARTHÉ, E. (1972). *Cristallochimie des Structures Tétraédriques*. Paris & New York: Gordon & Breach.

PAULING, L. (1960). *The Nature of the Chemical Bond*, third ed. Ithaca: Cornell Univ. Press.

PEARSON, W. B. (1964). *Acta Cryst.* **17**, 1–15.

STISHOV, S. M. & BELOV, N. V. (1962). *Dokl. Akad. Nauk SSSR*, **143**, 951–954.

Acta Cryst. (1973). B**29**, 2815

The Crystal Structure of Methyltriphenylphosphonium Bis-7,7,8,8-tetracyanoquinodimethanide at 53°C

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The crystal structure of the high-temperature modification of $(CH_3PPh_3)^+(TCNQ)_2^-$ has been determined at 53°C. The crystals are triclinic with the space group $P\bar{1}$ and lattice constants: $a=15\cdot780$ (5), $b=14\cdot545$ (4), $c=8\cdot910$ (3) Å, $\alpha=117\cdot22$ (4), $\beta=98\cdot05$ (7), $\gamma=97\cdot02$ (6)° and $Z=2$. The structure was refined by the block-diagonal least-squares method with 2514 reflexions measured on a four-circle manual diffractometer to give an R value of 0·051. The structure is closely related to that of the low-temperature modification, consisting of tetrads of TCNQ molecules and methyltriphenylphosphonium ions. The tetrads are arranged to form a columnar structure along the b axis. The average interplanar distances in the tetrads increased to 3·32 and 3·26 Å, which are longer by 0·08 and 0·04 Å, respectively, than the corresponding distances in the low-temperature modification, whereas the interplanar distance between the two adjacent tetrads of 3·55 Å was shortened by about 0·02 Å. The overlapping mode of the TCNQ moieties within a tetrad is unaltered. The nearest neighbour overlap between the two adjacent tetrads changed from a modified ring–ring overlap to an overlap involving a diagonal shift of the molecular centres. The conformation of $(CH_3PPh_3)^+$ ion is different from that of the low-temperature form; two of the phenyl groups are rotated by about 56° and 45° from the positions observed in the low-temperature form. Moreover, the conformation of the phosphonium ion is disordered, two of the phenyl rings taking different orientations with a probability of about 0·1. These changes of the structure are in accord with the change in physical properties of the high-temperature phase.

Introduction

Crystals of $(CH_3PPH_3)^+(TCNQ)_2^-$ undergo a first-order phase transition at 315·7°K (Kepler, 1963). The temperature dependence of physical properties such as electrical conductivity, magnetic susceptibility *etc.*, has been extensively studied by a number of workers (for example, Jones & Chesnut, 1963; Iida, Kinoshita, Sano & Akamatu, 1964; Iida, Kinoshita, Kawamori & Suzuki, 1964; Nordio, Soos & McConnell, 1966; Kosaki, Iida, Sorai, Suga & Seki, 1970; Shirotani, Kawamura & Iida, 1972). Models for this transition were also proposed (Chesnut, 1964; Merkl, Hughes, Berliner & McConnell, 1965). The crystal structure of this compound at room temperature has been determined by the photographic method (McPhail, Semeniuk & Chesnut, 1971). Quite independently we have determined the crystal structure by the counter method (Tsuchiya, Marumo & Saito, 1973). Positions of hydrogen atoms were also determined. The final R value was 0·060 for 3574 observed reflexions. Both results agree well, although the cell dimensions are somewhat different. The crystal structure of the high-temperature modification was determined in order to gain a better understanding of the phase transition. The result will be discussed with particular reference to the structure of the low-temperature phase.

Experimental

The crystals of $(CH_3PPh_3)^+(TCNQ)_2^-$ were kindly supplied by Dr Iida of Hokkaido University. A single-crystal specimen was found to transform into the high-temperature form without breaking, if the temperature was raised slowly at a rate of 0·4° per min. A part of the reciprocal-lattice network containing those reflexions of which the intensities change sensitively with the phase transition was recorded on Weissenberg photo-

Table 1. *Observed and calculated structure factors*

H	FO	FC
H 0 0		
1	237	260
2	396	625
4	154	169
5	284	313
6	313	345
7	112	122
9	153	172
12	94	111
13	134	145
14	109	115
H 1 0		
-14	264	262
-11	60	59
-10	52	92
-9	47	51
-8	29	24
-7	34	31
-6	62	56
-5	274	276
-4	182	199
-3	164	180
-2	82	84
-1	149	147
0	26	30
1	245	246
2	296	318
3	296	318
4	493	479
5	887	885
6	55	62
7	39	58
8	254	263
9	168	175
10	77	75
13	69	78
14	98	109
H 2 0		
-14	136	165
-13	97	107
-12	105	115
-11	67	60
-10	242	265
-9	287	273
-8	73	70
-7	117	117
-6	114	135
-5	59	61
-4	347	361
-3	453	477
-2	365	368
-1	447	468
0	395	406
1	99	75
2	432	470
3	404	381
4	139	112
5	308	301
6	140	130
7	275	273
8	131	136
9	168	164
11	62	61
12	177	179
13	41	53
14	49	66
H 3 0		
-14	136	129
-13	102	94
-12	31	25
-11	92	94
-9	302	305
-8	190	191
-7	88	80
-6	642	632
-5	1127	1122
-4	520	521
-3	935	947
-2	386	393
-1	185	178
0	268	276
1	706	703
2	67	35
3	127	152
4	59	46
5	36	56
6	91	105
7	92	104
9	198	196
10	111	121
11	191	190
12	71	62
13	182	164
H 4 0		
-14	34	20
-11	25	17
-10	150	145
-9	48	44
-8	51	53
-7	273	228
-6	205	198
-5	82	69
-4	122	131
-3	56	75
-2	528	536
-1	2014	2033
0	2114	2124
1	496	500
2	314	334
3	97	82
4	270	205
5	176	162
6	30	42
7	52	56
8	132	132
10	55	57
11	68	73
H 5 0		
-13	97	100
-12	140	151
-11	76	83
-10	161	158
-9	119	119
-8	156	168
-7	219	215
-6	367	366
-4	66	45
-3	32	10
-2	163	164
-1	58	46
0	37	23
1	126	133
2	46	55
3	482	464
[illegible]	274	265
[illegible]	279	239
[illegible]	298	235
8	36	176
9	120	114
10	46	67
11	84	67
12	158	138
H 6 0		
-12	95	96
-11	46	40
-10	339	341
-9	35	36
-8	78	65
-7	103	92
-6	126	118
-5	53	41
-4	169	167
-3	117	105
-2	53	46
-1	47	37
0	155	148
1	93	87
2	90	83
3	111	129
5	97	98
7	106	118
11	116	108
H 7 0		
-13	48	54
-12	162	171
-11	124	135
-10	255	270
-9	221	217
-8	42	74
-7	393	396
-6	473	443
-5	491	488
-4	239	240
-3	34	34
-2	87	89
-1	106	97
0	49	56
1	214	206
2	34	52
3	103	99
5	61	62
6	116	114
8	79	103
10	81	83
H 8 0		
-10	186	176
-9	157	147
-8	90	88
-7	130	126
-6	78	69
-5	39	29
-4	32	10
-3	191	185
-2	234	235
-1	695	669
0	355	344
1	225	215
2	223	221
3	78	85
5	90	89
6	40	69
8	74	84
9	69	62
H 9 0		
-12	87	84
-9	94	93
-8	67	72
-7	77	88
-6	35	41
-5	97	97
-4	137	129
-3	134	115
-2	212	205
-1	42	31
0	46	37
1	30	46
4	125	127
5	58	61
H 10 0		
-11	61	50
-8	114	113
-7	90	75
-6	61	59
-5	143	145
-4	82	80
-3	90	90
-2	101	103
-1	83	82
2	115	115
3	53	52
4	145	142
5	48	61
H 11 0		
-9	82	95
-8	90	109
-7	205	217
-6	177	194
-5	74	78
-1	72	71
1	74	80
2	102	98
4	45	59
H 12 0		
-7	61	67
-6	120	112
-5	123	122
-4	77	89
-2	108	120
-1	91	97
0	200	193
H-12 1		
-3	135	119
-2	214	209
-1	269	267
0	427	424
1	154	153
3	111	109
4	169	165
6	60	58
7	60	72
H-11 1		
-2	134	124
0	76	70
1	62	55
2	52	52
3	48	52
4	236	234
5	81	74
6	98	107
7	77	89
9	73	86
H-10 1		
-7	48	61
-6	87	90
-5	106	101
-4	86	53
-3	83	81
-2	79	64
-1	223	217
1	109	90
2	35	28
3	35	21
6	57	64
9	121	112
10	95	91
H -9 1		
-6	243	261
-5	57	67
-4	109	117
-3	125	128
-2	159	163
-1	249	271
0	44	15
1	182	176
2	59	57
3	157	154
4	59	53
5	29	35
6	51	45
7	116	123
8	164	168
9	92	86
10	74	56
H -8 1		
-7	70	70
-6	62	66
-5	36	40
-3	108	107
-2	297	297
-1	1026	1076
0	847	835
1	87	87
2	69	65
3	276	264
4	68	58
5	64	68
6	22	15
7	126	133
8	22	13
9	79	68
10	110	110
12	76	78
H -7 1		
-9	77	71
-7	102	97
-6	52	57
-5	60	48
-4	54	36
-3	267	271
-2	34	13
-1	168	165
0	117	103
1	136	157
2	196	188
3	422	414
4	25	29
5	161	151
6	313	303
7	78	87
8	327	318
9	215	209
10	161	172
11	89	79
13	162	162
H -6 1		
-10	194	177
-7	167	161
-6	47	50
-5	166	169
-4	50	47
-3	306	304
-2	40	44
-1	381	402
0	182	199
1	241	268
2	29	37
3	59	49
4	61	73
5	55	68
6	117	113
7	243	234
9	22	4
10	203	194
12	64	65
13	307	314
H -5 1		
-12	99	93
-11	49	52
-10	91	106
-8	177	170
-7	322	323
-6	498	502
-5	342	351
-4	305	304
-3	405	400
-2	170	184
-1	511	537
0	43	30
1	119	126
2	583	585
3	406	390
4	302	285
5	300	289
6	171	175
7	152	168
8	129	125
9	100	94
10	21	4
12	92	100
13	421	414
14	163	178
H -4 1		
-13	55	48
-12	85	76
-11	87	74
-10	139	136
-9	132	144
-8	108	117
-7	201	187
-6	325	317
-5	409	415
-4	171	183
-3	532	543
-2	823	814
-1	2508	2541
0	137	134
1	61	44
2	428	425
3	100	90
4	40	40
5	179	172
6	260	255
8	64	53
9	153	148
10	55	26
11	71	64
12	72	68
13	154	153
14	90	88
H -3 1		
-13	124	129
-12	66	67
-11	94	97
-10	87	87
-9	57	57
-8	77	82
-7	125	124
-6	173	167
-5	203	193
-4	32	46
-3	401	392
-2	252	261
-1	303	325
0	165	159
1	539	542
2	1096	1114
3	621	618
4	317	330
5	390	384
6	263	273
7	300	290
8	116	110
9	139	136
10	132	34
12	112	117
13	222	226
14	145	151
H -2 1		
-12	94	102
-11	260	267
-9	78	88
-8	357	367
-7	50	26
-6	154	153
-5	67	54
-4	288	285
-3	85	64
-2	463	467
-1	230	251
0	352	378
1	212	234
2	294	313
3	254	258
4	157	157
5	228	232
6	211	220
7	148	136
8	419	422
9	110	121
10	54	53
11	135	134
12	386	386
13	116	121
14	238	236
H -1 1		
-12	74	68
-10	37	35
-9	410	424
-8	127	111
-7	838	851
-6	578	586
-5	90	108
-4	660	688
-3	73	81
-2	570	608
-1	155	168
0	224	232
1	143	141
2	389	407
3	263	277
4	132	134
5	119	118
6	161	169
7	24	30
9	65	67
10	23	27
11	83	76
12	275	273
13	517	517
14	146	160
H 0 1		
-14	58	53
-13	64	61
-12	36	37
-11	115	109
-10	134	131
-9	85	78
-8	291	286
-7	156	162
-6	173	179
-5	133	144
-4	322	306
-3	113	95
-2	2038	1961
-1	184	173
0	620	643
1	281	286
2	496	482
3	408	369
4	177	193
5	122	132
6	73	73
8	135	143
9	93	97
11	77	83
12	120	123
H 1 1		
-14	129	111
-13	151	144
-12	74	76
-11	107	100
-10	138	134
-9	30	24
-8	154	144
-7	142	138
-6	92	94
-5	191	203
-4	21	23
-3	54	29
-2	502	513
-1	403	419
0	225	239
1	40	38
2	509	520
3	1487	1475
4	385	345
5	91	91
8	314	311
9	59	71
10	71	75
11	134	134
12	341	336
13	95	109
H 2 1		
-13	84	89
-12	148	147
-11	235	226
-10	155	149
-9	309	296
-8	56	48
-7	258	238
-6	293	279
-5	465	475
-4	229	225
-3	29	12
-2	339	337
-1	182	165
0	131	117
1	453	451
2	142	145
3	73	70
5	57	52
6	85	82
7	167	169
8	399	382
9	50	54
10	84	88
12	341	333
13	138	128
H 3 1		
-14	114	94
-13	141	130
-11	36	37
-10	197	194
-9	228	217
-8	372	368
-7	405	382
-6	389	373
-5	444	448
-4	226	234
-3	30	25
-2	253	259
-1	391	397
0	178	186
1	167	175
2	91	101
3	38	40
4	204	203
5	188	202
6	92	111
7	88	105
8	211	217
9	117	115
10	189	181
11	103	101
12	288	286
H 4 1		
-13	77	78
-12	96	101
-11	108	112
-10	204	191
-9	47	44
-8	88	83
-7	103	78
-6	151	137
-5	276	276
-4	356	351
-3	270	280
-2	64	40
-1	405	395
0	195	182
1	242	233
2	86	95
4	174	175
5	216	219
6	95	106
8	256	244
9	216	201
10	134	124
H 5 1		
-13	55	53
-9	170	158
-8	180	168
-7	224	210
-6	67	34
-5	48	48
-4	116	111
-3	31	22
-2	34	13
-1	32	23
0	43	58
1	164	152
2	317	301
3	443	449
4	210	203
5	299	293
7	156	150
8	49	54
10	109	106
11	238	208
H 6 1		
-13	236	238
-11	106	117
-10	139	140
-9	353	352
-8	207	212
-7	273	272
-6	226	221
-5	211	210
-4	134	136
-3	119	124
-1	59	65
0	60	59
1	107	110
2	172	170
3	104	134
4	238	229
5	68	82
6	343	325
8	210	209
9	41	58
H 7 1		
-11	63	62
-9	103	87
-8	334	306
-6	146	156
-5	129	112
-4	73	66
-3	98	86
1	152	142
2	119	122
9	111	120
H 8 1		
-12	81	71
-11	188	175
-10	190	186
-9	248	243
-8	99	89
-7	134	135
-6	203	196
-5	103	109
-4	225	221
-2	155	162
-1	281	276
0	68	77
2	98	98
3	118	119
4	56	66
7	131	135
H 9 1		
-7	51	50
-6	55	35
-4	67	62
-1	45	58
0	84	87
1	140	150
2	165	177
3	48	56
5	108	128
H 10 1		
-7	81	75
-6	91	85
-5	84	83
-4	60	61
-3	60	56
3	54	55
H 11 1		
-7	98	98
-5	87	89
-4	76	74
-3	91	92
-2	79	77
-1	89	82
0	99	111
1	45	69
H-12 2		
-4	49	57
-3	114	104
-2	294	285
-1	207	209
0	47	35
2	75	74
4	42	51
6	55	37
7	94	101
H-11 2		
-5	56	57
-4	97	96
-3	111	114
-2	121	126
-1	161	159
0	162	156
1	49	59
2	58	74
3	254	257
4	63	57
5	102	113
6	62	65
7	48	25
8	168	176
9	89	75
10	88	90
H-10 2		
-8	86	68
-7	94	99
-5	46	38
-4	70	63
-2	38	42
-1	27	32
0	114	110
1	191	177
2	40	26
3	70	56
4	50	49
7	112	116
8	65	57
10	57	63
11	264	265
H -9 2		
-9	79	86
-8	184	176
-7	129	119
-6	91	86
-5	145	140
-3	189	195
-2	73	57
-1	35	39
0	76	71
1	188	183
2	297	298
3	73	55
4	52	48
5	54	44
6	177	168
7	137	125
8	80	71
11	105	112
12	342	340
H -8 2		
-8	61	63
-7	80	90
-6	112	113
-4	90	91
-3	47	25
-2	485	495
-1	85	79
0	261	262
1	368	363
2	330	314
3	132	129
4	85	82
5	46	56
6	193	191
7	56	57
8	135	131
9	64	68
10	65	58
11	117	108
12	101	108
H -7 2		
-8	76	85
-7	102	108
-6	124	[illegible]
-4	113	120
-2	39	23
-1	55	45
0	20	4
1	394	397
2	855	837
3	198	183
4	28	31
5	110	104
6	213	208
7	281	275
8	24	15
9	39	16
10	77	87
11	75	64
12	354	367
H -6 2		
-12	79	81
-10	113	104
-9	206	198
-8	67	65
-7	135	125
-6	120	124
-5	141	140
-4	231	229
-3	122	118
-2	222	228
-1	325	320
0	296	289
1	132	144
2	311	302
3	309	296
4	393	389
5	254	236
6	221	216
7	306	308
8	137	136
9	301	289
10	78	80
11	562	560
12	164	164
13	141	154
H -5 2		
-11	73	69
-10	236	223
-9	37	31
-8	228	221
-7	174	166
-6	86	82
-5	204	191
-4	417	418
-3	379	368
-2	285	292
-1	129	131
0	404	405
1	427	434
2	142	139
3	157	148
4	86	74
5	91	83
6	75	82
7	84	83
8	63	63
9	31	66
10	137	134
11	161	161
12	435	442
13	146	158
14	72	52
H -4 2		
-13	147	127
-12	165	170
-11	146	154
-9	80	79
-8	89	91
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5	92	101
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H 7 4		
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H -12 5		
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-4	156	164
-2	167	162
-1	109	113
0	95	96
1	39	37
2	70	60
3	72	72
4	149	143
5	133	130
6	107	108
7	137	126
8	182	171
9	121	126
10	163	170
H -8 5		
-11	83	79
-10	94	101
-8	70	65
-7	45	44
-6	129	134
-4	226	223
-3	245	230
-2	201	198
0	51	57
1	97	98
2	47	47
3	127	124
4	146	145
7	123	123
8	194	192
9	139	143
H -7 5		
-9	126	119
-8	156	154
-7	61	58
-6	75	65
-5	79	76
-4	106	105
-2	241	245
0	189	178
1	145	152
2	263	262
3	97	90
4	47	37
5	140	136
6	66	67
7	46	47
9	95	108
H -6 5		
-12	68	75
-11	70	74
-9	78	76
-8	231	241
-7	116	119
-6	125	129
-5	80	79
-4	37	38
-3	124	116
-2	27	10
0	167	171
1	284	283
2	141	142
3	159	151
4	336	338
5	219	228
6	152	149
7	182	180
8	60	51
9	151	144
H -5 5		
-11	122	106
-10	329	338
-9	216	217
-8	241	245
-7	67	59
-5	76	76
-4	112	113
-3	95	97
-2	122	121
-1	46	42
1	78	32
2	110	115
3	154	148
4	42	38
5	68	70
6	102	98
9	203	187
10	63	67
H -4 5		
-13	109	121
-12	191	198
-11	216	219
-10	98	92
-8	173	176
-7	60	55
-6	106	110
-5	204	193
-4	190	184
-3	377	387
-2	114	122
-1	126	144
0	59	63
1	33	-7
2	173	178
3	228	226
5	119	121
6	160	159
7	106	112
8	62	75
H -3 5		
-11	114	114
-10	90	94
-9	119	118
-8	202	209
-7	59	48
-4	73	82
-3	46	47
-2	513	527
-1	240	231
0	135	147
1	64	69
2	54	59
3	143	147
4	57	57
5	79	75
6	55	56
8	86	58
9	62	74
H -2 5		
-13	98	109
-12	89	90
-11	60	51
-10	55	42
-9	124	119
-8	98	102
-7	53	63
-6	35	34
-5	87	84
-4	169	153
-3	237	236
-2	66	69
-1	40	47
1	26	28
2	99	89
3	167	162
4	259	254
5	53	39
6	77	77
8	117	125
H -1 5		
-11	211	220
-10	438	443
-9	391	395
-8	192	200
-7	130	134
-6	86	90
-5	160	165
-4	128	128
-3	331	318
-2	40	37
-1	79	76
0	72	78
1	45	24
3	100	97
4	77	80
5	75	68
6	51	51
9	176	183
H 0 5		
-13	49	46
-11	92	89
-10	92	92
-9	151	148
-8	216	224
-7	156	155
-6	50	44
-5	334	318
-4	131	133
-3	314	314
-1	97	94
0	99	94
1	72	65
2	90	86
3	172	167
4	33	37
5	23	9
6	40	26
7	58	39
8	64	45
H 1 5		
-9	113	116
-7	135	138
-6	119	109
-5	148	124
-3	289	291
-2	70	57
-1	71	66
0	454	447
1	157	148
2	33	31
3	65	52
4	111	113
5	106	98
6	89	83
7	72	57
8	82	63
H 2 5		
-10	60	45
-9	125	118
-7	130	129
-6	113	113
-5	122	127
-4	117	114
-3	196	213
-2	128	136
-1	127	130
0	58	59
1	49	46
2	121	131
3	261	262
4	95	85
5	115	115
6	33	21
7	80	65
H 3 5		
-11	277	298
-10	469	460
-9	283	280
-8	130	135
-4	103	106
-2	110	106
-1	147	145
0	151	142
1	195	196
2	175	176
3	98	104
4	57	59
5	92	93
H 4 5		
-10	62	54
-9	242	248
-8	97	83
-7	76	63
-6	153	149
-4	253	252
-3	136	130
-2	120	120
-1	57	60
0	44	39
1	52	47
2	91	84
3	45	76
4	116	112
H 5 5		
-5	57	86
-1	201	177
0	32	35
1	50	38
2	42	40
H 6 5		
-6	69	60
-4	78	71
H -12 6		
-5	144	134
-4	129	146
-3	92	98
-1	101	104
0	77	88
3	117	123
H -11 6		
-5	56	73
-4	95	103
-3	212	222
-2	88	97
-1	148	147
0	43	46
3	54	48
4	89	96
5	58	67
H -10 6		
-6	71	64
-4	77	77
-3	62	68
-2	135	153
-1	149	159
0	215	208
1	151	149
2	114	111
3	258	261
5	47	50
8	122	131
H -9 6		
-9	176	175
-8	121	130
-7	90	109
-6	123	127
-5	68	80
-4	64	67
-1	79	90
6	54	59
7	81	90
8	154	165
H -8 6		
-10	60	54
-9	75	70
-7	98	95
-6	288	281
-5	74	70
-4	209	198
-2	49	58
-1	68	68
0	45	46
1	179	178
2	200	199
3	49	42
4	55	47
5	68	65
6	168	179
7	179	186
8	96	97
H -7 6		
-10	81	57
-4	46	26
-3	171	172
-2	195	196
-1	233	241
0	22	17
1	82	85
2	104	100
3	103	105
5	85	86
6	85	86
7	65	95
8	98	114
9	44	39
H -6 6		
-10	93	90
-8	70	63
-7	54	44
-3	45	46
-1	71	82
0	106	111
1	180	184
2	273	270
3	168	162
4	200	204
6	87	84
H -5 6		
-11	418	411
-10	426	439
-9	79	81
-8	126	113
-7	86	89
-6	115	118
-5	115	115
-4	83	84
-3	34	35
-2	84	85
-1	65	73
1	27	22
2	114	106
3	169	165
4	219	220
5	191	177
6	53	49
8	165	178
9	51	83
H -4 6		
-11	93	96
-9	190	189
-7	56	57
-6	284	282
-4	60	67
-3	70	87
-2	38	9
-1	32	5
0	170	118
1	56	43
2	55	62
3	107	108
4	107	103
5	44	44
H -3 6		
-12	78	68
-11	125	130
-10	119	129
-9	105	120
-8	77	62
-7	82	84
-6	107	107
-5	109	117
-4	127	129
-3	170	170
-2	62	69
-1	342	358
0	316	314
1	36	39
3	137	135
5	53	52
6	130	130
7	84	87
H -2 6		
-10	73	75
-9	53	64
-8	88	77
-7	86	78
-6	56	41
-5	80	86
-4	81	104
-3	135	144
-2	94	93
-1	101	102
0	53	44
1	184	181
2	263	263
3	363	356
4	253	263
5	171	173
6	80	69
8	43	52
H -1 6		
-12	298	293
-11	470	470
-10	181	192
-9	76	75
-8	55	63
-7	67	70
-6	54	68
-4	117	104
-3	96	89
-2	215	215
-1	173	157
0	113	120
1	62	64
3	56	55
4	124	106
6	83	93
7	97	101
H 0 6		
-11	70	64
-10	96	103
-9	61	55
-7	164	172
-6	98	105
-5	53	53
-4	267	286
-3	196	201
-2	213	215
-1	155	160
0	136	130
1	32	20
2	85	91
3	150	155
4	81	89
5	50	40
6	47	24
H 1 6		
-10	52	40
-5	115	119
-4	90	83
-2	119	128
-1	133	137
0	137	126
2	102	113
3	71	58
4	52	46
5	79	75
H 2 6		
-10	71	56
-9	80	88
-8	98	100
-7	102	93
-6	129	124
-5	124	111
-4	159	158
-3	126	134
-2	157	159
-1	81	70
0	170	143
1	145	155
2	162	165
3	494	507
4	169	168
H 3 6		
-1	67	57
0	36	3
1	40	2
2	45	16
H 4 6		
-7	96	87
-5	137	141
H -12 7		
1	101	106
2	94	97
H -11 7		
-3	96	103
0	160	167
1	187	192
2	125	128
3	95	95
H -10 7		
-6	66	58
-5	71	57
-4	71	65
-3	107	112
-2	88	94
-1	152	152
0	161	158
1	111	118
2	274	281
3	279	270
4	164	162
5	87	92
H -9 7		
-6	94	102
-5	61	50
-4	65	77
-3	68	69
-	122	121
0	99	94
1	149	143
2	66	52
3	95	101
H -8 7		
-8	59	67
-7	107	103
-6	76	63
-5	132	132
-2	51	47
-1	86	76
1	113	120
2	269	276
3	185	192
4	131	137
5	72	73
6	71	73
H -7 7		
-9	56	45
-8	56	45
-7	121	110
-6	90	94
-4	97	93
-3	144	137
-1	292	286
0	69	72
1	162	169
2	266	268
3	54	46
4	134	134
5	178	183
6	167	168
H -6 7		
-7	77	80
-6	55	60
-5	61	56
-3	49	49
0	80	79
1	183	192
2	590	594
3	365	370
4	79	78
5	130	133
6	140	141
H -5 7		
-4	70	71
-2	168	179
-1	122	116
0	150	143
1	127	128
2	244	239
3	186	189
4	121	118
5	62	64
6	81	77
H -4 7		
-10	200	207
-9	74	81
-7	283	279
-6	52	52
-5	166	166
-4	225	224
-3	79	83
-2	95	102
1	229	231
2	360	367
3	76	74
4	78	71
H -3 7		
-6	52	63
-4	173	171
-3	125	131
-2	293	291
-1	86	91
1	310	321
2	184	184
3	73	65
4	95	84
5	64	69
H -2 7		
-10	104	97
-9	116	105
-8	130	129
-7	72	88
-6	93	102
-5	117	117
-4	182	197
-3	170	170
-2	175	175
-1	138	131
0	130	129
1	340	338
2	327	325
3	210	222
H -1 7		
-5	65	60
-3	129	132
-1	65	56
0	77	65
H 0 7		
-8	245	248
-6	91	91
-5	180	179
-3	104	107
0	106	110
1	205	213
2	133	126
H 1 7		
-5	69	65
-4	244	233
-3	122	125
-2	83	90
-1	138	138
0	36	21
1	266	251
H -10 8		
-1	94	79
0	206	213
1	253	264
H -9 8		
-5	179	177
-3	162	162
-2	170	177
-1	144	141
0	150	141
1	114	115
2	90	101
H -8 8		
-6	90	85
-5	195	189
-3	129	130
-2	66	49
-1	64	63
0	200	192
1	175	176
H -7 8		
-5	226	219
-4	52	70
-3	87	101
-2	219	218
-1	72	60
0	296	304
1	68	74
2	79	89
3	65	79
H -6 8		
-7	65	62
-6	77	56
-5	108	104
-4	106	110
-3	75	76
-2	47	56
0	211	215
1	240	270
H -5 8		
-7	70	56
-6	75	74
-5	90	94
-4	65	71
-3	72	62
-2	66	55
-1	96	102
0	117	126
1	71	71
H -4 8		
-7	86	100
-6	201	203
-4	77	67
-1	38	64
0	188	183
1	62	54
2	84	96
H -3 8		
-6	63	66
-5	147	159
-3	103	101
-2	79	77
0	193	195
1	83	89

graphs at different temperatures. It was confirmed that the phase change was completed in a very short time by this heating rate and no indication was observed of the low-temperature phase migrating into the high-temperature phase. The crystal specimen was heated by a stream of electrically heated air. Thermocouple measurements indicated that the temperature was constant at 53 ± 1 °C throughout the experiment. Intensity data were collected on a manual four-circle diffractometer. The crystals disintegrated during exposure to X-rays and measurements had to be made with half a dozen specimens, whose maximum dimensions ranged from 0·3 to 0·4 mm and which were cut from larger crystals. Mo $K\alpha$ radiation was used with the ω–2θ scan technique. Data were recorded for 3250 independent reflexions up to $2\theta = 40°$, of which 2514 with $|F| \geq 3\sigma$, were regarded as 'observed'. A standard reflexion was measured every two hours. The intensities were corrected for Lorentz and polarization effects, but corrections for absorption and extinction were not applied. The crystal data are: $(C_{19}H_{18}P)(C_{12}H_4N_4)_2$, M.W. 685·7. Triclinic, $a = 15{\cdot}780$ (5), $b = 14{\cdot}545$ (4), $c = 8{\cdot}910$ (3) Å, $\alpha = 117{\cdot}22$ (4), $\beta = 98{\cdot}05$ (7), $\gamma = 97{\cdot}02$ (6)°; $U = 1759{\cdot}9$ Å^3, $Z = 2$, $D_x = 1{\cdot}299$ g cm^{-3}, at 53 °C, Mo $K\alpha$ ($\lambda = 0{\cdot}7107$ Å), $\mu = 1{\cdot}28$ cm^{-1}. Space group $P\bar{1}$.

Crystal data of the low-temperature modification are: Triclinic, $a = 15{\cdot}762$ (3), $b = 14{\cdot}725$ (5), $c = 9{\cdot}022$ (4) Å, $\alpha = 120{\cdot}01$ (3), $\beta = 97{\cdot}32$ (6), $\gamma = 96{\cdot}21$ (7)°, $U = 1762{\cdot}1$ Å^3. (Tsuchiya, Marumo & Saito, 1973). Space group $P\bar{1}$. Triclinic, $a = 15{\cdot}74$, $b = 14{\cdot}67$, $c = 9{\cdot}01$ Å, $\alpha = 119{\cdot}98$, $\beta = 97{\cdot}04$, $\gamma = 96{\cdot}55°$, $U = 1751$ Å^3 (McPhail *et al.*, 1971).

McPhail's data ($\mathbf{a}', \mathbf{b}', \mathbf{c}'$) were transformed according to the relations: $\mathbf{a} = \mathbf{b}' + \mathbf{c}'$, $\mathbf{b} = -\mathbf{a}' - \mathbf{b}'$, $\mathbf{c} = \mathbf{a}'$.

Structure determination

Initial positional parameters for the non-hydrogen atoms were taken from the final parameters of the low-temperature modification (Tsuchiya *et al.*, 1973), since the general features of the intensity distribution indicated that the structure is closely related to that of the low-temperature modification. The conventional R value was 0·35 at this stage. The atomic positions and thermal parameters were refined in the usual way by the least-squares method with a block-diagonal program *HBLS*-4 written by Dr Ashida. With the introduction of anisotropic temperature factors further cycles of least-squares refinement reduced the R index to 0·13. A difference Fourier synthesis showed all the hydrogen atoms in plausible positions. Further refinement cycles were carried out with anisotropic temperature factors for non-hydrogen atoms and with isotropic temperature factors for hydrogen atoms. The R value converged to 0·070. In a difference Fourier synthesis at this stage, however, there were several well defined peaks with heights of 0·4 e Å^{-3}. The maps can be explained if two of the phenyl rings are considered to assume different orientations with a population of about one tenth. This disorder was taken into account and the populations of the carbon atoms were also refined. Isotropic temperature factors were assumed for these carbon atoms. Positions of hydrogen atoms attached to the carbon atoms in this less populated position could not be determined. After several refinement cycles the structure converged with $R=0{\cdot}051$ and $R_2=0{\cdot}048$. At the final stage of the refinement all the parameter shifts were less than one eighth of the corresponding standard deviations. Unit weight was given to all the reflexions. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). Table 1 gives the observed and calculated structure factors. The atomic parameters and their standard deviations are listed in Table 2.

Thermal motion

The motion of two TCNQ molecules has been analysed in terms of the rigid-body tensors of translation (**T**) and libration (**ω**) (Cruickshank, 1965). Rigid-body parameters for the two quinodimethane moieties are listed in Table 3. There are two crystallographically independent TCNQ moieties, hereafter designated as TCNQ I and II, respectively. In both molecules, the translation is quite isotropic, whereas the libration is quite anisotropic and the axis of the largest r.m.s. amplitude corresponds to the long axis of the molecule

Table 2. *Atomic parameters of non-hydrogen atoms* (× 10^4)

The values of β_{ij} refer to the expression: $\exp\left[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)\right]$.

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

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Population
P	4992 (1)	2989 (1)	1541 (2)	34 (1)	58 (1)	120 (2)	13 (1)	13 (1)	39 (1)	
C(1)	4303 (4)	3495 (4)	3048 (7)	53 (3)	89 (5)	163 (11)	20 (3)	35 (5)	24 (6)	
C(2)	4376 (3)	2434 (4)	−607 (6)	30 (2)	57 (4)	174 (10)	8 (2)	−7 (4)	54 (5)	
C(3)	4800 (4)	2092 (5)	−1973 (6)	66 (4)	122 (6)	115 (11)	13 (4)	29 (5)	62 (7)	
C(4)	4289 (5)	1622 (6)	−3645 (7)	126 (6)	137 (7)	127 (12)	21 (5)	37 (7)	65 (8)	
C(5)	3395 (4)	1534 (5)	−3904 (8)	87 (4)	118 (6)	265 (15)	−7 (4)	−82 (7)	101 (8)	
C(6)	2992 (4)	1829 (5)	−2585 (8)	65 (4)	92 (6)	320 (16)	11 (4)	−12 (6)	98 (8)	
C(7)	3475 (3)	2288 (4)	−937 (7)	50 (3)	77 (5)	182 (11)	13 (3)	−14 (5)	50 (6)	
C(8)	5445 (3)	2010 (4)	1828 (6)	28 (3)	56 (4)	103 (10)	5 (3)	13 (4)	39 (5)	0·9
C(9)	4927 (4)	1339 (5)	2189 (8)	65 (4)	84 (6)	265 (15)	34 (4)	70 (6)	93 (8)	0·9
C(10)	5275 (5)	559 (5)	2409 (9)	95 (5)	88 (6)	272 (16)	28 (4)	58 (7)	108 (9)	0·9
C(11)	6136 (4)	485 (5)	2315 (8)	61 (4)	97 (6)	257 (15)	29 (4)	27 (6)	101 (8)	0·9
C(12)	6614 (4)	1110 (5)	1869 (10)	42 (3)	110 (6)	390 (20)	28 (4)	46 (7)	139 (10)	0·9
C(13)	6275 (4)	1884 (5)	1649 (9)	48 (4)	89 (6)	327 (17)	23 (4)	54 (6)	121 (9)	0·9
C(14)	5855 (3)	4063 (4)	1986 (7)	33 (3)	56 (4)	161 (11)	10 (3)	1 (5)	50 (6)	0·9
C(15)	6487 (4)	4510 (5)	3450 (8)	44 (3)	101 (6)	204 (14)	−4 (4)	−17 (5)	102 (8)	0·9
C(16)	7146 (4)	5346 (5)	3841 (8)	53 (4)	109 (7)	236 (15)	−9 (4)	−26 (6)	87 (9)	0·9
C(17)	7201 (4)	5759 (5)	2785 (9)	50 (4)	80 (6)	306 (17)	−12 (4)	−14 (6)	70 (9)	0·9
C(18)	6597 (5)	5288 (5)	1207 (9)	82 (5)	72 (6)	302 (17)	1 (4)	17 (7)	99 (9)	0·9
C(19)	5915 (4)	4457 (5)	801 (8)	56 (4)	74 (5)	204 (14)	2 (4)	−6 (6)	62 (7)	0·9
C(20)	−955 (3)	1131 (4)	−1640 (5)	32 (2)	49 (4)	101 (9)	11 (2)	11 (4)	33 (5)	
C(21)	−1100 (3)	1331 (4)	31 (6)	33 (2)	55 (4)	123 (9)	12 (2)	22 (4)	40 (5)	
C(22)	−98 (3)	1020 (4)	−1939 (5)	38 (3)	64 (4)	93 (9)	13 (3)	19 (4)	37 (5)	
C(23)	−1631 (3)	1055 (4)	−2905 (6)	37 (3)	60 (4)	117 (9)	10 (3)	22 (4)	40 (5)	
C(24)	−2483 (3)	1168 (4)	−2632 (6)	40 (3)	81 (5)	144 (10)	7 (3)	7 (4)	48 (6)	
C(25)	−1505 (3)	860 (4)	−4572 (6)	37 (3)	69 (4)	147 (10)	9 (3)	4 (4)	45 (6)	
N(26)	−3168 (3)	1256 (4)	−2437 (6)	43 (3)	153 (6)	280 (12)	26 (3)	28 (5)	106 (7)	
N(27)	−1433 (3)	690 (4)	−5927 (6)	66 (3)	129 (5)	168 (10)	24 (3)	24 (4)	79 (6)	
C(28)	410 (3)	1312 (3)	975 (6)	34 (2)	44 (4)	111 (9)	10 (2)	10 (4)	33 (5)	
C(29)	555 (3)	1106 (4)	−708 (6)	34 (3)	56 (4)	114 (9)	10 (3)	26 (4)	36 (5)	
C(30)	−448 (3)	1402 (4)	1248 (6)	40 (3)	62 (4)	102 (9)	12 (3)	18 (4)	43 (5)	
C(31)	1086 (3)	1408 (4)	2255 (6)	32 (2)	61 (4)	120 (9)	8 (3)	16 (4)	44 (5)	
C(32)	1940 (3)	1327 (4)	1981 (6)	41 (3)	70 (4)	154 (10)	7 (3)	1 (4)	59 (6)	
C(33)	976 (3)	1610 (4)	3933 (6)	32 (3)	68 (4)	155 (10)	9 (3)	−4 (4)	51 (6)	
N(34)	2642 (3)	1277 (4)	1796 (6)	37 (2)	133 (5)	299 (12)	17 (3)	16 (4)	117 (7)	
N(35)	913 (3)	1782 (4)	5291 (5)	61 (3)	123 (5)	159 (9)	20 (3)	14 (4)	79 (6)	
C(36)	−1386 (3)	3564 (4)	−2050 (6)	37 (3)	58 (4)	128 (10)	16 (3)	21 (4)	46 (5)	
C(37)	−1547 (3)	3739 (4)	−391 (6)	31 (3)	67 (4)	142 (10)	17 (3)	28 (4)	42 (5)	
C(38)	−520 (3)	3487 (4)	−2304 (6)	42 (3)	74 (4)	143 (10)	17 (3)	28 (4)	67 (6)	
C(39)	−2036 (3)	3504 (4)	−3325 (6)	40 (3)	77 (4)	162 (11)	16 (3)	23 (4)	69 (6)	
C(40)	−2914 (4)	3591 (5)	−3169 (6)	55 (3)	110 (5)	151 (11)	28 (3)	28 (5)	85 (7)	
C(41)	−1865 (3)	3364 (4)	−4936 (6)	40 (3)	99 (5)	166 (11)	14 (3)	7 (4)	81 (6)	
N(42)	−3618 (3)	3682 (5)	−3087 (7)	60 (3)	202 (7)	313 (13)	49 (4)	55 (5)	156 (8)	
N(43)	−1734 (3)	3262 (4)	−6219 (6)	54 (3)	172 (6)	195 (10)	15 (3)	20 (4)	118 (7)	
C(44)	−49 (3)	3728 (4)	580 (6)	40 (3)	49 (4)	115 (9)	14 (2)	22 (4)	42 (5)	
C(45)	113 (3)	3567 (4)	−1068 (6)	32 (3)	65 (4)	166 (10)	12 (3)	19 (4)	61 (6)	
C(46)	−915 (3)	3808 (4)	844 (6)	40 (3)	66 (4)	137 (10)	17 (3)	26 (4)	57 (5)	
C(47)	621 (3)	3799 (4)	1832 (6)	33 (3)	47 (4)	146 (10)	12 (2)	18 (4)	35 (5)	
C(48)	1492 (3)	3762 (4)	1583 (6)	41 (3)	71 (4)	164 (11)	13 (3)	8 (4)	49 (6)	
C(49)	505 (3)	3918 (4)	3475 (6)	35 (3)	56 (4)	136 (10)	12 (3)	3 (4)	33 (5)	
N(50)	2190 (3)	3741 (4)	1423 (7)	43 (3)	131 (5)	311 (13)	27 (3)	34 (5)	97 (7)	
N(51)	459 (3)	4005 (4)	4795 (5)	61 (3)	94 (4)	151 (9)	19 (3)	21 (4)	55 (5)	

Table 2 (*cont.*)

				B^* (Å^2)	Population
C'(8)	5534 (31)	1957 (37)	1786 (60)	4·4 (1·1)	0·1
C'(9)	5566 (22)	1895 (27)	3317 (43)	1·2 (0·7)	0·1
C'(10)	6008 (26)	1226 (32)	3464 (51)	2·4 (0·8)	0·1
C'(11)	6294 (33)	491 (40)	2040 (65)	5·3 (1·1)	0·1
C'(12)	6247 (32)	563 (39)	325 (63)	4·6 (1·1)	0·1
C'(13)	5782 (24)	1329 (30)	359 (48)	2·1 (0·8)	0·1
C'(14)	5775 (33)	4076 (40)	2003 (64)	5·0 (1·1)	0·1
C'(15)	6635 (38)	3982 (46)	2245 (75)	6·7 (1·4)	0·1
C'(16)	7179 (36)	4912 (44)	2670 (71)	6·4 (1·3)	0·1
C'(17)	6912 (37)	5752 (44)	2794 (73)	6·1 (1·3)	0·1
C'(18)	6063 (28)	5861 (35)	2679 (56)	3·7 (0·9)	0·1
C'(19)	5490 (20)	4912 (25)	2174 (39)	0·9 (0·6)	0·1

* Isotropic temperature factor

Positional parameters for the hydrogen atoms ($\times 10^3$)

	x	y	z	Population
H(C3)	548 (3)	218 (4)	−176 (6)	
H(C4)	453 (4)	141 (5)	−457 (8)	
H(C5)	301 (3)	123 (4)	−498 (7)	
H(C6)	234 (3)	173 (4)	−274 (6)	
H(C7)	322 (3)	255 (3)	26 (5)	
H(C9)	431 (4)	148 (5)	239 (8)	0·9
H(C10)	488 (5)	−2 (6)	265 (9)	0·9
H(C11)	637 (4)	−18 (5)	238 (7)	0·9
H(C12)	725 (4)	103 (5)	179 (8)	0·9
H(C13)	665 (4)	237 (5)	136 (8)	0·9
H(C15)	645 (3)	433 (4)	435 (6)	0·9
H(C16)	752 (4)	557 (4)	490 (7)	0·9
H(C17)	766 (4)	636 (5)	311 (8)	0·9
H(C18)	662 (4)	556 (4)	25 (8)	0·9
H(C19)	548 (4)	409 (4)	−39 (7)	0·9
Ha(Cl)	457 (4)	384 (5)	428 (8)	
Hb(Cl)	382 (4)	285 (4)	277 (7)	
Hc(Cl)	398 (5)	406 (6)	277 (9)	
H(C21)	−173 (3)	141 (4)	21 (6)	
H(C22)	−4 (3)	91 (4)	−307 (6)	
H(C29)	117 (4)	98 (4)	−93 (7)	
H(C30)	−53 (4)	147 (5)	241 (7)	
H(C37)	−214 (4)	380 (5)	−33 (8)	
H(C38)	−45 (4)	327 (5)	−361 (7)	
H(C45)	71 (4)	345 (4)	−118 (7)	
H(C46)	−104 (4)	385 (5)	194 (8)	

Mean isotropic temperature factor of hydrogen atom is 3·5 (1·4) Å^2

for which the moment of inertia is the smallest. A similar analysis was carried out for the entire molecules; however, the r.m.s. deviation ΔU_{ij} between observed and calculated thermal parameters increased by a factor of two. This poor agreement is probably due to the wagging of the cyano groups. *ORTEP* plots of the thermal-motion ellipsoids for the $(CH_3PPh_3)^+$ ion of the low and high-temperature phases are illustrated in Fig. 1 (Johnson, 1965). A rigid-body analysis for an entire $(CH_3PPh_3)^+$ ion gave a r.m.s. deviation ΔU_{ij} of 0·0128 Å^2; thus the validity of using the rigid-body approximation is questionable. As discerned from Fig. 1, each phenyl ring exhibits the largest librational motion around the P–C bond. The amplitudes of the thermal motions increase in the high-temperature phase whereas those of the phenyl ring II in the low-temperature phase were larger compared with those of phenyl ring I and III and these large amplitudes did not alter appreciably in the high-temperature phase.

Description of the structure and discussion

The structure viewed along the *b* axis is illustrated in Fig. 2. It consists of columns of TCNQ's packed almost parallel to each other. Within the columns, which run parallel to the *b* axis, a tetrad of molecules may be recognized. The columns are packed side by side to form layers parallel to (100). The $(CH_3PPh_3)^+$ ions are arranged between the layers of TCNQ columns. The average interplanar spacings between TCNQ I···II and between I···I' in a tetrad are 3·26 and 3·32 Å respectively, where the prime indicates the molecule related to the first by a centre of symmetry. Between the tetrads the interplanar spacing II···II' is 3·55 Å. Fig. 3 shows the dimensions of TCNQ I and II. Deviations of the atoms from the least-squares plane through the quinodimethane moiety are also indicated. The standard deviations of atomic coordinates are not small enough to determine from these dimensions whether the TCNQ's occur as TCNQ^0 and TCNQ$^-$ or whether they are really indistinguishable as TCNQ$^{1/2-}$. A

Table 3. *Rigid-body thermal parameters of* TCNQ (*quinodimethane moiety*)

(*a*) Principal axes of the molecules in the form: $La+Mb+Nc$

Moment of inertia (A.W. × Å^2)	TCNQ I L	TCNQ I M	TCNQ I N	Moment of inertia (A.W. × Å^2)	TCNQ II L	TCNQ II M	TCNQ II N
71·9	0·0484	0·0063	0·0918	72·2	0·0474	0·0054	0·0926
259·2	−0·0409	0·0124	0·0803	256·7	−0·0422	0·0100	0·0774
331·1	0·0167	0·0779	0·0433	328·9	0·0161	0·0783	0·0469

(*b*) Molecular vibrational tensors

	TCNQ I				TCNQ II		
	382	41	8		415	−10	49
T × 10^4		329	24 Å^2	T × 10^4		354	0 Å^2
			345				412
	298	−66	−10		284	−32	20
ω × 10		62	14 (°)^2	ω × 10		37	6 (°)^2
			15				32

Table 3 (*cont.*)

(*c*) Principal axes of the **T** and **ω** tensors relative to the molecular axes.

R.m.s. amplitude	TCNQ I Direction cosines			R.m.s. amplitude	TCNQ II Direction cosines		
0·172 Å	0·409	0·799	0·442	0·187 Å	0·350	0·895	−0·276
0·189	0·285	0·348	−0·893	0·192	0·599	−0·440	−0·669
0·201	0·867	−0·491	0·085	0·215	0·721	−0·069	0·690
0·88°	0·116	0·373	0·920	1·51°	−0·134	−0·627	0·767
2·26	−0·223	−0·893	0·390	2·02	−0·048	−0·769	−0·637
5·62	0·968	−0·251	−0·020	5·38	0·990	−0·123	0·073

(*d*) R.m.s. deviation between obs. and calc. U_{ij}

	TCNQ I	TCNQ II
	26×10^{-4} Å^2	38×10^{-4} Å^2

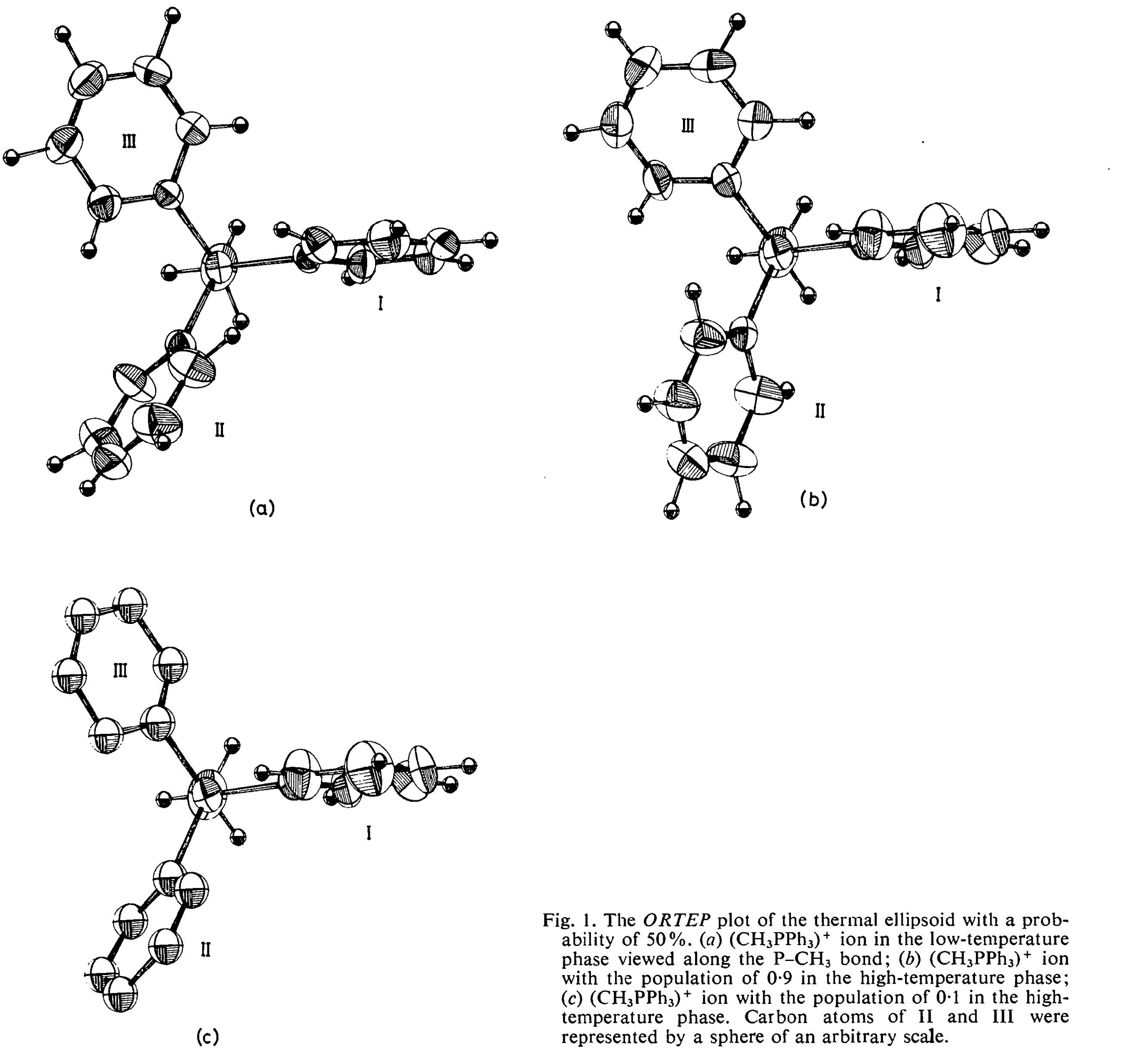

Fig. 1. The *ORTEP* plot of the thermal ellipsoid with a probability of 50%. (*a*) $(CH_3PPh_3)^+$ ion in the low-temperature phase viewed along the P–CH_3 bond; (*b*) $(CH_3PPh_3)^+$ ion with the population of 0·9 in the high-temperature phase; (*c*) $(CH_3PPh_3)^+$ ion with the population of 0·1 in the high-temperature phase. Carbon atoms of II and III were represented by a sphere of an arbitrary scale.

multivariate significance test (Cruickshank & Robertson, 1953) of the differences in dimensions between the two TCNQ moieties gave a value of $T^2 = 7$ which is not significant for four degrees of freedom. Within a tetrad there is one type of overlap between adjacent TCNQ units: ring–external bond type. This overlapping mode is the same as that observed in the low-temperature modification. However, the nearest neighbour overlap between adjacent tetrads changed slightly as shown in Fig. 4. Above the transition temperature it is an overlap involving diagonal shift of molecular centres similar to that observed in *N*-(n-propyl)quinolinium $TCNQ_2$ (Sundaresan & Wallwork, 1972). The least-squares planes through the TCNQ's indicate that they are not quite planar but bowed slightly; in molecule I in particular the terminal cyano groups are twisted slightly around the C=C bond. These features are the same as those observed in the low-temperature modification (McPhail *et al.*, 1971).

Bond distances and angles for the cation are listed in Table 4 with their estimated standard deviations.

As discerned from Fig. 1, the configuration of the $(CH_3PPh_3)^+$ ion is quite different from a symmetrical propeller shape in both modifications. In the low-temperature phase, one phenyl ring (I) is nearly parallel to the P–CH_3 bond and the other two rings, II and III, are inclined by about −19 and −67°, respectively with respect to the P–CH_3 bond. In the high-temperature phase, the cation takes two different configurations with different probability. In one configuration with larger population (0·9), phenyl ring I is almost parallel to the P–CH_3 bond as in the case of the low-temperature phase; however, rings II and III are inclined at

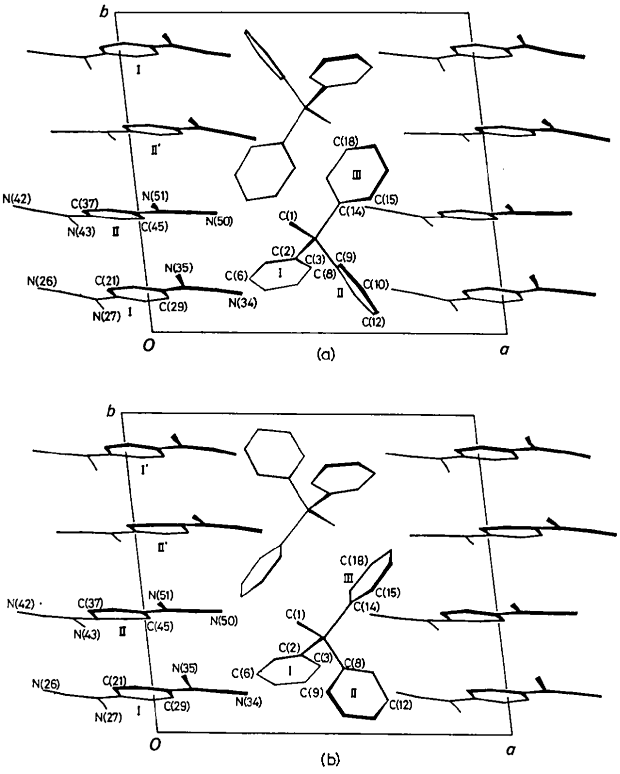

Fig. 2. The structure viewed along the *b* axis. (*a*) Low-temperature phase. (*b*) High-temperature phase.

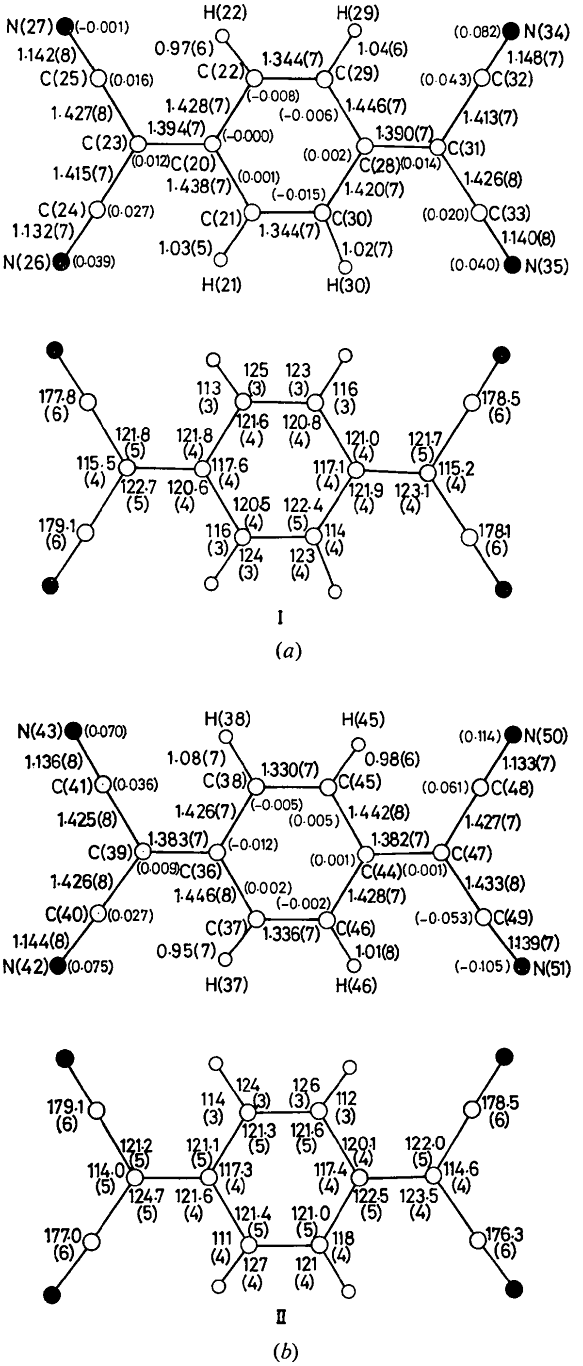

Fig. 3. Bond distances (Å) and bond angles (°) in TCNQ I and II with their standard deviations. The numbers in parentheses are the atomic displacements from the mean plane through the quinodimethane moiety.

Table 4. *Bond distances and angles for* $(CH_3PPh_3)^+$

P·······C(1)	1·797 (6) Å	C(18)···C(19)	1·387 (9) Å
P·······C(2)	1·770 (5)	C(19)···C(14)	1·421 (11)
P·······C(8)	1·769 (6)	C(1)····H(1a)	0·97 (6)
P·······C(14)	1·793 (6)	C(1)····H(1b)	1·04 (6)
C(2)····C(3)	1·390 (8)	C(1)····H(1c)	1·11 (9)
C(3)····C(4)	1·391 (8)	C(3)····H(3)	1·04 (5)
C(4)····C(5)	1·377 (10)	C(4)····H(4)	0·89 (7)
C(5)····C(6)	1·336 (10)	C(5)····H(5)	0·93 (5)
C(6)····C(7)	1·359 (8)	C(6)····H(6)	1·00 (5)
C(7)····C(2)	1·380 (7)	C(7)····H(7)	1·11 (5)
C(8)····C(9)	1·375 (10)	C(9)····H(9)	1·04 (6)
C(9)····C(10)	1·397 (12)	C(10)···H(10)	1·11 (9)
C(10)···C(11)	1·386 (10)	C(11)···H(11)	1·10 (7)
C(11)···C(12)	1·342 (12)	C(12)···H(12)	1·04 (7)
C(12)···C(13)	1·383 (12)	C(13)···H(13)	1·01 (7)
C(13)···C(8)	1·366 (8)	C(15)···H(15)	0·96 (6)
C(14)···C(15)	1·350 (7)	C(16)···H(16)	0·92 (6)
C(15)···C(16)	1·373 (9)	C(17)···H(17)	0·96 (7)
C(16)···C(17)	1·334 (13)	C(18)···H(18)	1·10 (8)
C(17)···C(18)	1·392 (9)	C(19)···H(19)	1·04 (5)
P·······C′(8)	1·90 (6)	P·······C′(14)	1·73 (5)
C′(8)····C′(9)	1·40 (7)	C′(14)···C′(15)	1·38 (8)
C′(9)····C′(10)	1·31 (6)	C′(15)···C′(16)	1·37 (9)
C′(10)···C′(11)	1·41 (6)	C′(16)···C′(17)	1·30 (10)
C′(11)···C′(12)	1·57 (9)	C′(17)···C′(18)	1·36 (8)
C′(12)···C′(13)	1·40 (8)	C′(18)···C′(19)	1·39 (6)
C′(13)···C′(8)	1·33 (6)	C′(19)···C′(14)	1·30 (7)
C(1)PC(2)	110·2 (3)°	H(1a)C(1)H(1b)	108 (4)°
C(1)PC(8)	109·2 (2)	H(1a)C(1)H(1c)	109 (5)
C(1)PC(14)	108·1 (2)	H(1b)C(1)H(1c)	108 (4)
C(2)PC(8)	109·8 (2)	C(2)C(3)H(3)	121 (3)
C(2)PC(14)	110·1 (2)	C(4)C(3)H(3)	121 (3)
C(8)PC(14)	109·6 (2)	C(3)C(4)H(4)	121 (4)
PC(2)C(3)	119·6 (4)	C(5)C(4)H(4)	118 (4)
PC(2)C(7)	120·4 (4)	C(4)C(5)H(5)	125 (3)
C(7)C(2)C(3)	119·9 (5)	C(6)C(5)H(5)	114 (3)
C(2)C(3)C(4)	117·8 (5)	C(5)C(6)H(6)	123 (3)
C(3)C(4)C(5)	120·1 (6)	C(7)C(6)H(6)	117 (3)
C(4)C(5)C(6)	121·4 (7)	C(6)C(7)H(7)	126 (2)
C(5)C(6)C(7)	119·7 (6)	C(2)C(7)H(7)	113 (2)
C(6)C(7)C(8)	120·9 (5)	C(8)C(9)H(9)	118 (3)
PC(8)C(9)	118·3 (4)	C(10)C(9)H(9)	123 (3)
PC(8)C(13)	122·2 (4)	C(9)C(10)H(10)	122 (3)
C(13)C(8)C(9)	119·5 (4)	C(11)C(10)H(10)	117 (3)
C(8)C(9)C(10)	118·9 (6)	C(10)C(11)H(11)	118 (2)
C(9)C(10)C(11)	120·5 (6)	C(12)C(11)H(11)	121 (2)
C(10)C(11)C(12)	119·6 (6)	C(11)C(12)H(12)	118 (4)
C(11)C(12)C(13)	120·2 (6)	C(13)C(12)H(12)	122 (4)
C(12)C(13)C(14)	121·1 (5)	C(12)C(13)H(13)	120 (3)
PC(14)C(15)	120·7 (4)	C(8)C(13)H(13)	119 (3)
PC(14)C(19)	121·7 (4)	C(14)C(15)H(15)	122 (3)
C(19)C(14)C(15)	117·5 (4)	C(16)C(15)H(15)	116 (3)
C(14)C(15)C(16)	122·0 (5)	C(15)C(16)H(16)	112 (4)
C(15)C(16)C(17)	121·8 (6)	C(17)C(16)H(16)	127 (4)
C(16)C(17)C(18)	118·6 (5)	C(16)C(17)H(17)	120 (3)
C(17)C(18)C(19)	120·6 (6)	C(18)C(17)H(17)	122 (3)
C(18)C(19)C(14)	119·4 (5)	C(17)C(18)H(18)	123 (4)
PC(1)H(1a)	118 (4)	C(19)C(18)H(18)	117 (4)
PC(1)H(1b)	106 (2)	C(18)C(19)H(19)	121 (3)
PC(1)H(1c)	108 (3)	C(14)C(19)H(19)	120 (3)
C(2)PC′(8)	109 (1)	C′(12)C′(13)C′(8)	121 (4)
C(2)PC′(14)	110 (1)	PC′(14)C′(15)	117 (3)
C′(8)PC′(14)	110 (2)	PC′(14)C′(19)	116 (3)
PC′(8)C′(9)	119 (3)	C′(19)C′(14)C′(15)	127 (4)
PC′(8)C′(13)	112 (3)	C′(14)C′(15)C′(16)	110 (3)
C′(13)C′(8)C′(9)	129 (3)	C′(15)C′(16)C′(17)	124 (5)
C′(8)C′(9)C′(10)	116 (4)	C′(16)C′(17)C′(18)	125 (4)
C′(9)C′(10)C′(11)	121 (4)	C′(17)C′(18)C′(19)	112 (3)
C′(10)C′(11)C′(12)	122 (4)	C′(18)C′(19)C′(14)	121 (3)
C′(11)C′(12)C′(13)	110 (4)		

37 and 68° respectively; in other words the 'handedness' of the propeller is inverted. In the other configuration (population 0·1), the handedness is the same as that at low temperature, phenyl rings II and III making angles of −20 and −49° respectively. As shown in Table 4, the shape and size of the cation are similar to those of the low-temperature phase. Relevant intermolecular contacts are listed in Table 5. The closest approach between tetrads packed side by side in the (100) layer occurs between hydrogen and nitrogen atoms. The N···H distances range from 2·48 to 2·80 Å. The closest N···N distance is 3·288 Å between N(51) and that related to this by a centre of symmetry at $0,\frac{1}{2},\frac{1}{2}$. The neighbours of $(CH_3PPh_3)^+$ will be discussed in the next section.

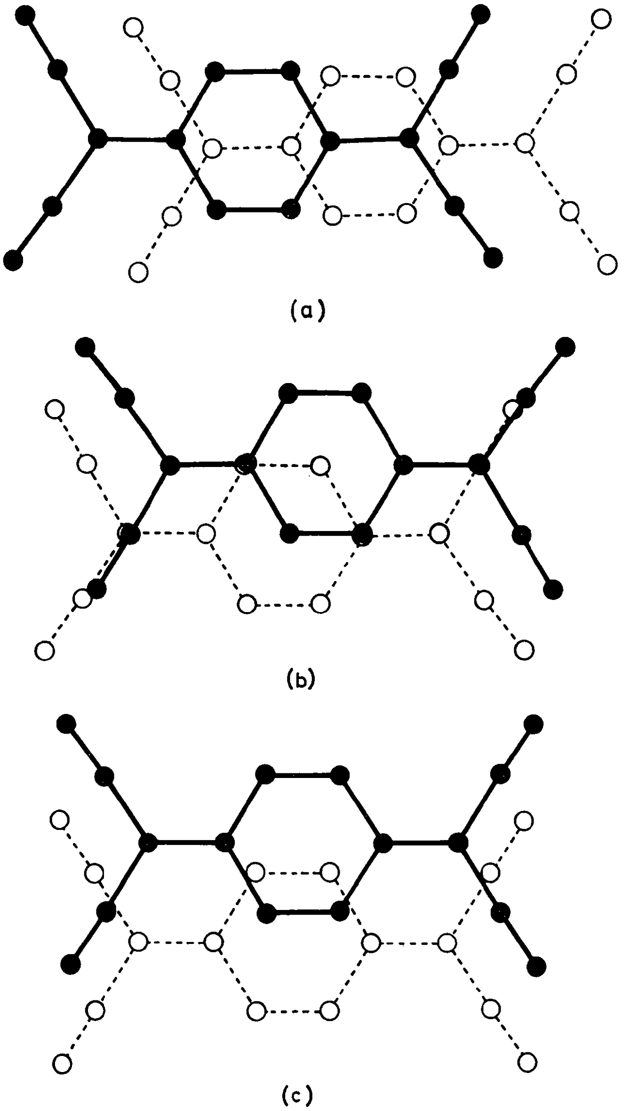

Fig. 4. Nearest neighbour overlap. (*a*) molecules I and I′, II and I; (*b*) molecules II′ and II in the high-temperature modification; (*c*) molecules II′ and II in the low-temperature modification.

Table 5. *Relevant intermolecular distances*

The C···C and C···N distances shorter than 3·5 Å and those involving the hydrogen atom shorter than 3·0 Å are listed. Key to symmetry operations

i	$-x$,	$-y$,	$-z$	vi	$1+x$,	y,	$1+z$
ii	$-x$,	$1-y$,	$-z$	vii	$1-x$,	$1-y$,	$1-z$
iii	$1+x$,	y,	z	viii	x,	y,	$1+z$
iv	$1-x$,	$-y$,	$-z$	ix	x,	y,	$1-z$
v	$1-x$,	$1-y$,	$-z$				

Between TCNQ I and TCNQ II within a TCNQ tetrad			
C(20)···C(44)	3·358 (6) Å	C(20)···C(46)	3·475 (6) Å
C(21)···C(44)	3·455 (7)	C(21)···C(46)	3·298 (8)
C(22)···C(45)	3·380 (8)	C(23)···C(36)	3·328 (8)
C(23)···C(37)	3·474 (7)	C(24)···C(36)	3·468 (8)
C(24)···C(37)	3·338 (7)	C(25)···C(36)	3·488 (7)
C(25)···C(38)	3·422 (7)	C(28)···C(47)	3·299 (7)
C(28)···C(49)	3·376 (6)	C(29)···C(47)	3·493 (6)
C(29)···C(48)	3·439 (6)	C(30)···C(49)	3·281 (6)
Between TCNQ I and TCNQ I′ within a TCNQ tetrad			
C(20)···C(31^{i})	3·452 (8)	C(21)···C(32^{i})	3·415 (7)
C(22)···C(33^{i})	3·393 (7)	C(28)···C(28^{i})	3·370 (9)
C(29)···C(30^{i})	3·433 (8)		
Between TCNQ II and TCNQ II′ of the two adjacent tetrads			
C(39)···C(48^{ii})	3·479 (7)	C(40)···N(50^{ii})	3·418 (8)
Between adjacent TCNQ columns			
C(46)···N(43^{viii})	3·428 (9)	H(46)···N(43^{viii})	2·48 (8)
H(30)···N(27^{viii})	2·69 (8)	H(22)···N(35^{ix})	2·80 (6)
C(38)···N(51^{ix})	3·500 (8)	H(38)···N(51^{ix})	2·61 (7)
N(51)···N(43^{viii})	3·358 (6)	N(51)···N(51^{iv})	3·288 (11)
C(49)···N(51^{iv})	3·366 (7)		
Between cation and TCNQ columns			
Phenyl I			
C(7)····N(50)	3·342 (7)	H(7)····N(50)	2·49 (5)
H(7)····N(34)	2·90 (6)	H(3)····N(26^{iii})	2·66 (5)
H(5)····N(34^{ix})	2·88 (7)	H(6)····N(35^{ix})	2·68 (6)
Phenyl II			
H(9)····N(34)	2·57 (6)	H(12)···H(21^{iii})	2·45 (10)
H(12)···N(27^{vi})	2·94 (8)	C(12)···C(41^{vi})	3·499 (7)
C(12)···N(43^{vi})	3·374 (8)	H(12)···N(43^{vi})	2·99 (6)
C(13)···N(43^{vi})	3·286 (7)	H(13)···N(43^{vi})	2·81 (5)
Phenyl III			
C(18)···N(42^{iii})	3·387 (8)	*H(18)···N(42^{iii})	2·91 (5)
C(19)···N(42^{iii})	3·341 (9)	H(19)···N(42^{iii})	2·83 (7)
*H(18)···N(50^{v})	2·91 (8)	H(15)···C(40^{vi})	2·98 (6)
H(15)···N(42^{vi})	2·85 (6)	H(16)···C(48^{vii})	2·95 (6)
H(16)···N(50^{vii})	2·90 (6)	*H(17)···N(35^{vii})	2·92 (6)
Methyl			
H(1b)····N(34)	2·48 (6)	H(1c)···N(50)	2·81 (7)
Between cations			
H(4)····C(10^{ix})	2·89 (7)	C(3)····H(10^{iv})	2·91 (9)
C(2)····H(11^{iv})	2·91 (6)	C(3)····H(11^{iv})	2·99 (7)
C(4)····H(11^{iv})	2·95 (8)	C(5)····H(11^{iv})	2·89 (8)
C(6)····H(11^{iv})	2·79 (7)	C(7)····H(11^{iv})	2·79 (6)

* The distance with an asterisk is shorter than the corresponding distance at low temperature.

Structural change with the transition

The volume of the unit cell contracts by about 2 Å^3 above the transition temperature. This contraction is consistent with the observed phase diagram (Merkl *et al.*, 1965). Because of this very small change in cell dimensions, a single-crystal specimen transforms into the high-temperature phase without breaking. Thus the reported volume of the unit cell, 1751 Å^3 seems to be somewhat incorrect (McPhail *et al.*, 1971). Changes in interplanar spacings between TCNQ moieties are shown in Table 6. The interplanar spacings within a tetrad increase by 0·08 and 0·04 Å, respectively, whereas that between two adjacent tetrads decreases by 0·02 Å. The overlapping mode in a tetrad is unaltered, but the nearest neighbour overlap between the tetrads changes as shown in Fig. 4.

Short intermolecular contacts between hydrogen atoms of the phenyl groups and nitrogen atoms of TCNQ moieties in the low-temperature modification are tabulated in Table 7. There are some short contacts less than the sum of van der Waals radii (2·70 Å) at room temperature. Such short contacts are similar to those observed in the crystals of methyltriphenylphosphonium bis-(1,2-dicyanoethylene-1,2-dithiolato)nickelate(III) (Fritchie, 1966), tetraphenylarsonium 3-fluoro-1,1,4,5,5-pentacyano-2-azapentadienide (Palenik, 1966) and tetraphenylphosphonium $(TCNQ)_2^-$ (Goldstein, Seff & Trueblood, 1968). As shown in Table 5, with one exception [H(9)···N(34), 2·57 Å], no N···H contact less than 2·70 Å is observed above the transition temperature. However, the rotation of the phenyl ring III increases the number of contacts less than 3·0 Å between hydrogen atoms of the cation with the nitrogen atoms of TCNQ II and II′. In Table 5 those distances with an asterisk are shorter than those in the low-temperature phase. In contrast to this, the rotation of the phenyl ring II simply gives rise to an increase in H···N separations: they range from 2·41 to 2·80 Å in the low-temperature phase, whereas they are in the range 2·81 ~ 2·99 Å above the transition temperature apart from H(9)···N(34) of 2·57 Å. These changes may be responsible for the elongation of the *a* axis by about 0·02 Å.

On the other hand the *b* and *c* axes contract by 0·18 and 0·11 Å respectively and the axial angle α decreases by about 3°. The plane of TCNQ moiety is inclined at an average angle of 64° with the *b* axis at room temperature; however, this angle of tilt increases to 67° above the transition temperature. Owing to this change in angle of tilt and the change in overlapping mode between adjacent tetrads, the increase in interplanar spacing within the tetrad may be alleviated, resulting in overall contraction of the volume.

Table 6. *Interplanar spacings in both modifications*

		Low-temperature phase	High-temperature phase	Difference
I···I′	within a tetrad	3·24 Å	3·32 Å	0·08 Å
I···II		3·22	3·26	0·04
II···II′	between tetrads	3·57	3·55	−0·02

Table 7. *Short intermolecular contacts between cation and TCNQ moieties in the low temperature phase*(*Tsuchiya, Marumo & Saito*, 1973)

Phenyl II			
$C(13)\cdots N(26^{iii})$*	3·33 (1) Å	$H(13)\cdots N(26^{iii})$	2·65 (8) Å
$H(12)\cdots N(34^{iv})$	2·41 (10)	$C(9)\cdots N(42^{vi})$	3·38 (1)
$H(9)\cdots N(42^{vi})$	2·80 (8)	$C(10)\cdots C(40^{vi})$	3·48 (1)
$H(10)\cdots C(40^{vi})$	2·96 (7)	$C(10)\cdots N(26^{vi})$	3·62 (1)
$H(10)\cdots N(26^{vi})$	2·51 (9)		
Phenyl III			
$H(19)\cdots N(42^{ii})$	2·82 (7)	$C(16)\cdots H(37^{iii})$	2·86 (7)
$C(15)\cdots N(43^{vi})$	3·30 (1)	$H(15)\cdots N(43^{vi})$	2·51 (7)
$H(16)\cdots N(43^{vi})$	2·86 (10)	$H(16)\cdots C(49^{vii})$	2·83 (7)
$H(16)\cdots N(51^{vii})$	2·64 (7)		

* Key to symmetry operation is given in Table 5.

The disorder in the conformation of $(CH_3PPh_3)^+$ ion contributes to the increase in the entropy of transition by 2·9 J°K^{-1}. This is still 41% of the observed ΔS of transition (Kosaki *et al.*, 1970).

Values of anisotropic temperature factor indicate that the thermal vibration of the atoms is more vigorous above the transition temperature. Thus some other effect such as excitation of a new mode of thermal vibration might be responsible for the rest of ΔS. The increase in interplanar spacings in the tetrad may well account for the increase in magnetic susceptibility in the high-temperature phase. The decrease in interplanar spacing between the two tetrads is certainly related to the abrupt decrease in the line width of the exchange-narrowed line in the e.p.r. spectrum (Jones & Chesnut, 1963). The widening of interplanar spacing in the tetrads does not appear to favour the electrical conductivity. On the other hand, the decrease in interplanar spacing between the two adjacent tetrads, the approach of phenyl ring III to the nearest TCNQ II and II′ and the decrease in the $N(51)\cdots N(51^{viii})$ distance of 0·12 Å, might all be favourable to the electrical conductivity.

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References

CHESNUT, D. B. (1964). *J. Chem. Phys.* **40**, 405–411.

CRUICKSHANK, D. W. J. (1956). *Acta Cryst.* **9**, 754–756.

CRUICKSHANK, D. W. J. & ROBERTSON, A. P. (1953). *Acta Cryst.* **6**, 698–705.

FRITCHIE, C. J. (1966). *Acta Cryst.* **20**, 107–118.

GOLDSTEIN, P., SEFF, K. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* B**24**, 778–791.

IIDA, Y., KINOSHITA, M., KAWAMORI, A. & SUZUKI, K. (1964). *Bull. Chem. Soc. Japan*, **37**, 764.

IIDA, Y., KINOSHITA, M., SANO, M. & AKAMATU, H. (1964). *Bull. Chem. Soc. Japan*, **37**, 428–429.

International Tables for X-ray Crystallography (1962). Vol. III, pp. 202–203. Birmingham: Kynoch Press.

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

JONES, M. T. & CHESNUT, D. B. (1963). *J. Chem. Phys.* **38**, 1311–1317.

KEPLER, R. G. (1963). *J. Chem. Phys.* **39**, 3528–3532.

KOSAKI, A., IIDA, Y., SORAI, M., SUGA, H. & SEKI, S. (1970). *Bull. Chem. Soc. Japan*, **43**, 2280.

McPHAIL, A. T., SEMENIUK, G. M. & CHESNUT, D. B. (1971). *J. Chem. Soc.* (*A*), pp. 2174–2180.

MERKL, A. W., HUGHES, R. C., BERLINER, L. J. & McCONNELL, H. M. (1965). *J. Chem. Phys.* **43**, 953–957.

NORDIO, P. L., SOOS, Z. G. & McCONNELL, H. M. (1966). *Ann. Rev. Phys. Chem.* **17**, 237–260.

PALENIK, G. J. (1966). *Acta Cryst.* B**20**, 471–482.

SHIROTANI, I., KAWAMURA, H. & IIDA, Y. (1972). *Chemistry Lett.* pp. 1053–1056.

SUNDARESAN, T. & WALLWORK, S. C. (1972). *Acta Cryst.* B**28**, 1163–1169.

TSUCHIYA, H., MARUMO, F. & SAITO, Y. (1973). Unpublished data.