The Crystal Structure of the 2:1 Molecular Complex Between 1,3,7,9-Tetramethyluric Acid and 3,4-Benzpyrene

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Crystals of the 2:1 molecular complex between 1,3,7,9-tetramethyluric acid (TMU) and 3,4-benzpyrene (BP) are triclinic, space group P_1, with $a = 9.33 \pm 0.02$, $b = 10.59 \pm 0.02$, $c = 10.84 \pm 0.02$ Å, $\alpha = 119°37' \pm 12'$, $\beta = 113°20' \pm 12'$, $\gamma = 87°20' \pm 12'$, $Z = 1$. The crystal structure has been analysed by allowing systematic independent translations and rotations of the two TMU and the BP in their molecular planes and by calculating a large set of most significant structure factors which were compared with the experimental diffraction amplitudes. The structure is characterized by a plane to plane alternate stacking of two TMU and one BP molecule arranged in infinite columns parallel to the b axis. The molecular planes are almost exactly parallel with an average perpendicular separation of 3.48 Å. The strongest intermolecular forces are 'polarization bonding' and van der Waals interactions.

Introduction

As part of a research programme on the interactions between deoxyribonucleic acid and aromatic hydrocarbons (Liquori, Ascoli & Botrè, 1962; Liquori, De Lerma, Ascoli, Botrè & Trasciatti, 1962) the crystal structures of some molecular complexes between 1,3,7,9-tetramethyluric acid (TMU) and pyrene (PR), 3,4-benzpyrene (BP) and coronene (CR) have been undertaken. In previous papers the crystal structure of the 1:1 molecular complex between TMU and PR (Damiani, De Santis, Giglio, Liquori, Puliti & Ripamonti, 1965) and a preliminary account of the crystal structures of the 2:1 molecular complexes between TMU and BP and CR (Damiani, Giglio, Liquori, Puliti & Ripamonti, 1966, 1967) have been reported.

In this communication we wish to report the results of a three-dimensional crystal structure analysis carried out on the 2:1 molecular complex between TMU
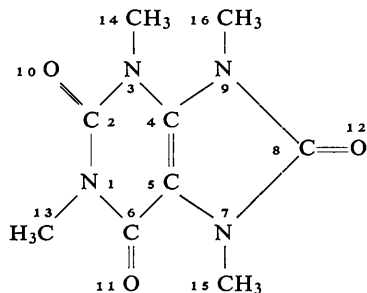
and BP
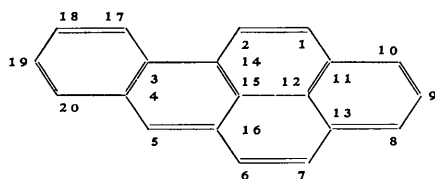
Experimental

Prismatic crystals of the 2:1 TMU–BP complex were prepared from benzene according to Weil–Malherbe (1946) and used to collect the X-ray data. 740 reflexions, about 20% of the total accessible reflexions, were recorded with a Wiebenga integrating Weissenberg camera. The intensities of the reflexions $h0l$, $h1l, \ldots, h5l$, $0kl$, $1kl, \ldots, 5kl$ and those collected by recording along the $0\bar{1}1$ diagonal were estimated photometrically, corrected for Lorentz and polarization factors and put on a common scale with the aid of the $h0l$ intensity data. No absorption corrections were applied.

Crystal data

$C_{20}H_{12} \cdot 2C_9N_4O_3H_{12}$, $M = 700.7$. Yellow crystals, triclinic.
$a = 9.33 \pm 0.02$, $b = 10.59 \pm 0.02$, $c = 10.84 \pm 0.02$ Å,
$\alpha = 119°37' \pm 12'$, $\beta = 113°20' \pm 12'$, $\gamma = 87°20' \pm 12'$,
$U = 840$ Å^3, $Z = 1$, $F(0,0,0) = 368$, λ Cu $K\alpha = 1.542$ Å.
Space group P_1. The theoretical density, 1.38 g.cm^{-3}, is in good agreement with the measured one, 1.39 g.cm^{-3}, if one BP and two TMU molecules are in the unit cell.

Determination of the structure

By inspection of the three-dimensional weighted reciprocal lattice it was deduced that the TMU and BP molecules lie in almost parallel planes. The coefficients of the equations of the mean molecular planes were derived by means of very strong reflexions belonging to the levels with $k = 3, 6, 9, 12$. These planes intersect the y axis at approximately 0, $\frac{1}{3}b$ and $\frac{2}{3}b$.

The structure was determined by performing systematic independent translations and rotations of the two TMU and the BP in their molecular planes and

Table 1. *Comparison between observed and calculated structure factors*

Values are multiplied by 10.

H	K	L	FO	FC
0	1	0	133	128
0	2	0	186	167
0	3	0	170	145
0	5	0	81	57
1	0	0	702	741
1	1	0	647	622
-1	1	0	26	111
1	2	0	180	162
-1	2	0	254	241
1	3	0	53	57
-1	3	0	363	330
1	4	0	179	165
-1	5	0	152	189
-1	5	0	74	68
-1	6	0	99	89
2	6	0	86	62
2	0	0	104	84
2	1	0	315	268
2	2	0	125	99
-2	2	0	116	116
2	3	0	198	162
-2	4	0	44	84
3	0	0	152	150
3	1	0	50	56
-3	1	0	272	271
3	2	0	150	148
-3	2	0	171	153
-3	3	0	141	144
3	4	0	216	150
-3	4	0	170	161
-3	5	0	214	280
-3	6	0	128	124
4	0	0	148	157
4	1	0	154	196
4	1	0	306	283
-4	2	0	132	100
-4	3	0	260	301
-4	3	0	65	144
-4	4	0	127	119
-4	4	0	182	154
-4	5	0	145	114
-4	5	0	89	44
4	6	0	74	76
-5	1	0	64	50
-5	1	0	74	31
-5	1	0	167	168
-5	3	0	158	138
-5	4	0	107	40
-6	0	0	59	48
6	1	0	46	39
-6	1	0	53	60
-6	2	0	96	112
-6	5	0	45	34
-7	0	0	68	74
-7	1	0	64	85
-7	1	0	62	57
-7	2	0	163	207
-7	3	0	83	127
0	0	1	742	783
0	-1	1	59	53
0	1	1	179	180
0	-2	1	68	59
0	2	1	184	151
0	-3	1	1381	1336
0	3	1	77	75
0	-4	1	135	128
0	5	1	172	182
0	6	1	167	201
0	-6	1	76	72
0	-7	1	85	88
0	-8	1	86	77
1	0	1	75	62
-1	0	1	737	765
1	-1	1	237	147
1	-1	1	131	125
1	1	1	324	300
1	1	1	81	90
1	2	1	97	89
1	2	-1	115	118
1	-2	1	172	156
1	2	1	163	155
1	-3	1	378	320
1	3	-1	983	912
1	4	1	342	290
1	5	1	106	106
1	5	1	116	120
1	6	1	156	131
-1	6	1	103	87
1	6	-1	83	61
1	6	-1	38	41
1	7	-1	73	65
2	-8	1	40	116
2	0	1	14	47
2	0	1	487	452
2	1	1	115	129
2	-1	1	106	119
2	2	1	172	174
2	2	-1	27	63
2	2	1	242	205
2	-2	1	177	145
2	3	1	105	105
2	3	1	117	135
2	3	1	129	136
2	3	1	46	34
2	4	-1	63	119
2	4	1	104	90
2	5	1	94	42
2	5	1	160	134
2	5	-1	106	121
2	5	1	160	189
2	6	1	152	173
-2	6	1	78	75
2	7	1	96	140
2	7	1	62	42
-2	8	-1	83	84
3	0	1	301	363
3	1	1	136	118
3	1	1	232	184
3	2	1	31	45
-3	1	1	194	205
-2	2	1	82	61
3	3	1	358	400
3	3	1	81	34

H	K	L	FO	FC
3	-3	1	261	260
-3	3	1	130	257
3	4	1	180	168
-3	4	1	99	40
3	5	-1	109	132
3	5	1	61	75
-3	6	1	89	78
3	6	1	74	64
4	6	-1	106	131
4	0	1	80	87
4	0	1	70	67
-4	0	1	131	178
-4	0	1	251	254
4	1	1	71	127
4	-1	1	78	56
4	-1	1	186	202
-4	1	1	162	107
4	2	1	130	38
4	2	1	171	160
4	3	1	87	58
4	3	1	124	139
4	3	1	132	115
4	4	1	140	98
4	-5	1	117	75
4	5	1	59	110
4	6	1	81	99
4	-6	1	107	101
4	7	1	90	77
5	0	1	107	107
5	0	-1	89	98
5	1	-1	80	80
5	-1	1	97	105
5	-1	1	51	91
5	2	1	174	188
5	-2	1	138	174
-5	2	1	130	106
-5	3	1	125	98
5	3	-1	53	55
5	3	0	49	75
6	0	1	33	45
6	0	1	101	132
6	-2	1	135	93
6	3	-1	66	96
6	-4	1	47	61
6	5	-1	144	136
-7	0	1	27	102
7	-1	-1	151	151
7	-1	1	88	62
7	1	1	133	93
-7	-2	1	87	55
-8	0	2	36	44
0	0	2	118	71
0	-1	2	126	157
0	1	2	163	173
0	-2	2	622	584
0	3	2	256	227
0	-3	2	885	821
0	4	2	108	166
0	-4	2	133	138
0	5	2	96	93
0	-5	2	176	159
0	6	2	67	91
1	0	2	202	167
1	0	2	218	421
1	1	2	134	150
1	-1	2	112	111
1	2	-2	269	213
1	2	2	75	109
1	2	2	171	176
1	-2	2	219	187
2	0	2	243	199
2	1	2	281	226
2	-1	2	155	218
2	-2	2	63	29
2	2	-2	2035	2184
2	2	2	120	134
2	-2	2	49	61
2	-2	2	126	103
2	3	2	112	111
2	-3	2	84	55
2	4	-2	194	139
2	4	2	194	122
2	-5	2	169	208
2	5	2	325	322
2	5	2	323	276
2	-6	2	122	113
3	0	2	32	47
3	1	-2	56	86
3	-1	2	115	133
3	-2	2	107	102
3	2	-2	326	371
3	-2	2	122	124
3	3	-2	216	183
3	-3	2	188	150
3	4	-2	371	301
3	4	2	138	158
3	-4	2	106	102
3	5	2	99	70
3	5	-2	130	94
3	-6	2	46	70
3	-6	2	55	4
3	-8	2	126	177
-3	0	2	275	328
-3	0	2	209	202
-3	1	2	255	244
-3	-1	2	79	103
3	2	-2	87	57
3	-2	2	237	231
3	-2	2	56	59
3	-3	2	213	241
3	3	2	66	58
3	3	-2	78	71
3	-4	2	192	188
3	-4	2	243	247
3	-5	2	74	17
3	-5	2	126	83
3	-7	2	77	119
4	0	2	136	164

H	K	L	FO	FC
4	1	-2	62	123
4	1	2	180	181
4	2	-2	145	174
4	2	2	173	260
4	3	-2	187	203
4	-3	2	79	65
4	3	2	223	201
4	-4	2	114	72
4	4	2	72	94
4	-5	2	130	129
4	5	-2	81	93
4	-6	2	86	108
4	7	-2	121	65
5	0	2	22	25
5	0	2	207	164
5	1	2	122	87
5	2	2	117	87
5	-2	2	121	125
5	2	2	126	117
5	-3	2	110	125
5	-3	2	85	86
5	3	2	95	76
5	4	-2	57	87
5	5	-2	83	104
-6	0	2	65	96
-6	1	2	108	91
6	1	-2	86	92
6	2	2	136	122
6	-1	2	106	79
6	2	2	50	56
6	-3	2	90	105
6	3	2	59	81
6	-5	2	168	188
7	1	-2	129	124
7	1	2	50	45
7	2	-2	93	45
-7	3	2	78	124
-8	0	2	95	124
8	1	2	47	104
0	0	3	132	208
0	-1	3	57	110
0	-2	3	66	88
0	2	3	202	158
0	3	3	79	129
0	-3	3	153	127
0	-4	3	111	52
0	4	3	81	64
0	-5	3	75	45
0	5	3	242	220
0	-6	3	79	78
0	6	3	28	44
-1	0	3	76	124
1	0	3	48	47
-1	1	3	67	51
1	1	3	108	116
-1	1	3	212	165
1	2	3	297	286
-1	2	3	122	118
1	-2	3	106	89
-1	3	3	171	217
1	3	3	201	160
1	-3	3	148	87
1	-4	-3	34	32
1	4	-3	116	107
1	-6	3	983	948
1	-8	3	47	70
2	0	3	43	29
2	0	3	37	59
2	1	3	163	113
-2	0	3	212	171
2	1	-3	257	259
2	1	-3	117	166
2	2	3	210	171
2	2	3	135	115
2	-2	3	237	242
2	-2	3	84	27
2	-3	3	266	253
2	3	3	196	144
2	-4	-3	296	308
2	4	3	96	124
2	-5	3	140	135
2	5	3	110	112
2	-5	3	137	123
2	6	3	36	43
2	-6	3	129	126
2	6	-3	93	93
3	0	3	570	483
3	0	-3	268	216
3	-1	3	74	94
3	0	3	93	65
3	-1	3	108	164
3	1	-3	212	100
3	1	3	275	243
3	-2	3	171	190
3	2	-3	125	148
3	2	3	162	149
3	-3	3	177	153
3	3	3	225	281
3	-3	3	139	123
3	4	3	40	100
3	-3	3	111	114
3	-5	3	114	101
3	5	3	107	112
3	-7	3	70	76
3	-8	3	61	62
4	0	3	84	46
4	0	3	37	67
4	0	-3	106	256
4	-1	3	323	382
4	-1	3	77	90
4	-1	3	74	117
4	-3	3	177	200
4	-3	3	129	113
4	4	3	108	130
4	-4	-3	81	98
4	-4	3	48	51
4	-5	3	69	55
4	-5	3	64	96
5	0	3	38	43
-5	0	3	175	147

H	K	L	FO	FC
5	1	3	54	44
5	2	-3	46	75
5	2	3	180	175
-5	3	-3	81	112
5	3	3	86	113
5	-4	3	54	57
5	-5	3	61	25
5	8	-3	126	144
6	0	3	86	111
6	0	3	71	64
6	1	3	66	83
6	-4	3	84	53
6	8	-3	51	69
7	1	3	40	58
-7	3	3	79	74
-7	3	3	91	31
-8	1	3	43	26
-8	1	3	99	137
0	0	4	110	172
0	-1	4	279	274
0	-2	4	123	130
0	3	4	119	73
0	-3	4	99	94
0	-3	4	69	20
0	4	4	86	89
0	-4	4	200	162
0	-9	4	94	37
-1	0	4	86	119
1	0	4	380	401
1	1	-4	147	168
1	1	4	139	174
1	-1	4	199	166
1	2	4	169	233
1	-2	4	125	121
1	-3	4	296	263
1	3	-4	61	40
1	-4	4	183	242
1	4	4	37	40
1	6	4	88	56
1	-6	4	280	264
1	-9	4	457	400
2	0	4	95	50
2	0	4	131	71
2	1	4	50	130
-2	0	4	43	69
2	1	-4	76	77
-2	1	4	310	257
2	-1	4	272	270
2	-2	4	72	116
-2	2	4	324	310
2	2	-4	144	138
2	3	-4	283	273
2	-3	4	143	146
2	4	4	71	50
2	4	-4	89	80
2	-5	4	266	237
2	5	4	169	156
2	6	4	127	130
2	6	-4	72	56
2	-7	4	751	697
2	-8	4	81	104
2	8	4	92	86
3	0	4	221	158
-3	0	4	172	197
3	1	-4	280	331
3	1	4	129	112
3	-1	4	131	117
3	1	4	101	82
3	-3	4	64	17
3	5	-4	60	53
-3	6	4	130	72
-4	0	4	105	77
-4	-1	4	72	113
-4	3	4	176	127
-4	3	4	85	92
-4	3	-4	145	174
4	4	4	55	66
-4	4	4	62	76
4	5	4	96	107
-4	6	4	34	83
-5	0	4	82	19
-5	0	4	218	225
-5	1	4	63	136
-5	1	4	82	108
5	-2	4	54	94
-5	3	4	95	111
-5	3	4	103	119
5	4	4	108	119
5	-4	4	82	81
5	-6	4	93	123
5	-8	4	93	107
6	1	-4	87	89
-6	1	4	64	60
6	-4	4	124	112
6	-4	4	91	69
6	8	4	78	101
-7	1	4	94	94
-7	1	4	77	77
-7	1	4	45	49
8	1	4	101	102
8	1	4	92	82
8	-2	4	54	94
-9	0	4	47	49
0	-1	5	101	72
0	-2	5	45	85
-2	3	5	86	85
-4	5	5	200	194
-4	5	5	122	99
-6	5	5	72	72
-6	5	5	137	99
-1	0	5	133	140

H	K	L	FO	FC
-1	-1	5	143	105
-1	1	5	36	42
-1	2	5	88	82
1	1	-5	74	118
1	3	5	153	116
1	-3	5	85	98
1	4	-5	57	99
1	-5	5	260	226
1	-5	5	72	87
1	5	5	85	91
1	-7	5	62	54
1	8	-5	183	171
1	9	-5	131	86
2	0	5	47	61
2	0	5	206	163
2	1	5	108	108
2	-1	5	236	205
2	2	5	40	42
2	-2	5	94	53
2	3	5	69	127
2	3	-5	61	41
2	3	-5	101	123
2	-4	5	126	97
2	4	-5	157	124
2	4	5	76	75
2	-5	5	142	133
2	5	5	148	211
2	6	5	99	100
2	-8	5	59	26
2	8	5	125	109
2	9	5	36	77
3	0	5	231	195
3	0	-5	114	141
3	2	-5	144	115
3	3	5	92	95
3	4	-5	121	164
3	5	5	80	82
3	6	-5	117	115
3	-7	5	64	66
3	8	-5	119	108
3	9	5	227	181
4	10	-5	125	109
4	1	5	70	68
4	-1	5	103	105
4	-1	5	71	24
4	-1	5	77	91
4	2	-5	132	148
4	2	5	140	148
4	5	-5	46	50
4	5	-5	53	84
-5	5	5	69	95
-5	5	-5	42	73
5	1	-5	64	75
5	3	-5	135	160
5	4	5	88	80
5	-5	5	151	194
5	5	5	73	129
-6	0	5	81	90
-6	5	5	58	42
6	1	5	36	56
6	3	-5	132	103
6	4	5	72	55
6	-4	5	60	95
6	-5	5	100	100
6	-7	5	70	81
7	-8	5	64	83
0	1	5	46	40
0	-8	5	37	50
0	-8	5	85	108
0	8	5	27	31
0	-1	6	120	83
0	-3	6	81	89
0	4	6	119	9
0	5	6	99	118
0	6	6	105	85
0	-6	6	82	66
0	-7	6	97	95
0	-8	6	145	120
1	-1	6	70	100
1	-2	6	41	36
1	3	6	81	57
1	-4	6	133	161
1	5	6	70	66
1	-5	6	213	217
1	7	6	65	43
1	-7	6	108	103
1	-9	6	90	119
1	0	6	71	88
1	1	6	75	95
1	1	6	109	139
1	-6	6	99	99
2	1	6	190	196
2	-2	6	62	92
2	2	6	79	79
2	3	-6	281	299
2	3	-6	209	207
2	-6	6	64	60
2	-6	6	70	62
2	8	-6	176	131
2	9	-6	109	134
3	-1	6	72	75
3	-2	6	61	43
3	6	6	134	121
3	6	6	148	103
3	-6	6	119	103
3	-6	6	127	132
3	9	-6	221	173
3	12	-6	127	115
4	-1	6	29	99
-4	-1	6	63	65

H	K	L	FO	FC
4	2	-6	88	100
4	3	-6	147	144
4	4	-6	144	154
4	5	-6	114	105
-5	0	6	82	100
5	1	-6	88	142
5	1	-6	41	53
5	2	-6	144	137
5	3	6	81	92
5	5	-6	55	108
5	6	-6	73	98
5	7	-6	50	62
-6	0	6	86	94
6	3	-6	117	142
-7	0	6	24	39
7	1	6	76	76
7	2	-6	46	47
-7	6	6	67	53
8	1	6	72	68
8	1	6	51	96
8	2	-6	76	77
9	1	6	63	100
9	2	-6	104	141
0	1	-6	41	53
0	2	-6	81	92
0	3	-7	117	104
-6	0	7	153	100
-7	0	7	162	58
-8	0	7	161	143
-8	1	7	114	133
0	1	7	117	122
0	3	-7	43	49
0	3	-7	118	117
0	5	-7	104	92
0	6	-7	95	141
0	7	-7	87	93
0	8	-7	104	108
0	0	7	27	21
0	0	7	58	50
0	0	7	90	112
2	2	-7	84	83
2	3	-7	52	125
2	4	-7	76	75
2	6	-7	70	104
2	6	-7	72	92
2	6	-7	90	77
2	12	-7	90	77
3	1	-7	84	97
3	3	-7	96	140
3	4	-7	81	49
3	7	-7	75	56
3	12	-7	215	240
4	9	-7	158	128
5	1	-7	59	47
5	4	-7	72	74
6	9	-7	65	68
5	0	7	46	169
-5	0	7	77	158
-6	0	7	62	60
6	1	-7	67	63
6	2	-7	65	46
-7	0	7	73	91
-7	3	-7	76	41
0	0	8	66	56
0	-3	8	156	130
0	-8	8	95	90
0	-8	8	27	18
1	0	8	51	16
1	1	-8	127	94
1	1	-8	100	91
2	2	-8	78	78
2	4	-8	96	106
2	4	-8	77	62
3	5	-8	126	118
3	2	-8	131	112
3	5	-8	98	134
3	7	-8	103	111
4	5	-8	89	103
-5	6	-8	109	107
6	0	-8	37	17
6	2	-8	72	71
-7	5	-8	79	78
0	1	-8	99	143
0	1	-8	81	76
0	3	-8	36	33
3	4	-8	102	112
1	5	-8	103	57
3	6	-8	98	103
3	7	-8	75	103
7	1	-8	106	107
-3	9	-9	106	103
-5	9	-9	94	92
1	5	-9	51	106
2	9	-9	85	106
-6	0	9	67	60
-8	0	9	48	66
-6	10	-10	45	101
5	5	-10	92	104
5	5	-10	99	85
6	6	-10	80	111
6	6	-11	49	69
6	6	-11	49	53
7	7	-11	36	53
8	-12	-11	52	51

by computing the minimum residual of a set of most significant structure factors. During this trial process the calculated diffraction amplitudes were compared with the observed ones (Albano, Bellon, Pompa & Scatturin, 1963; Bhuiya & Stanley, 1963, 1964).

The analysis was started assuming for the BP a rigid model with bond lengths of 1·40 Å and bond angles of 120°, which are values not far away from the data found by Iball & Young (1956), whereas for the TMU Sutor's (1963) bond distances and angles were used. This procedure was repeated three times, using first 30, then 60 and finally 122 structure factors, corresponding to all the reflexions in the spheres of radius $2 \sin \theta/\lambda =$ 0·26, 0·33 and 0·44 respectively. 15 minima were located for the reliability index R in the range 0·26–0·36 for all 740 reflexions. Such a large number of minima is partly due, at low Bragg angles, to a pseudo twofold axis in the Fourier transform passing approximately, in real space, through C(9) and C(19) of BP and partly to a pseudo mirror plane in the TMU molecule passing through C(8) and the middle point of the bond C(2)–N(1). Moreover two different TMU couplings, the first one resembling the centrosymmetrical arrangements found in crystals of pure TMU (Sutor, 1963; De Santis, Giglio & Liquori, 1960), the second one an iso-oriented arrangement, turned out to have scarcely any effect on the values of R.

At this point all the minima, except four belonging to the second coupling, were discarded because of some short intermolecular distances. No criteria were found for preferring one rather than another of these four minima, which differ from each other mainly in the BP arrangement (Damiani, Giglio, Liquori & Ripamonti, 1967). The aromatic hydrocarbon takes in fact four orientations corresponding to a rotation through 180° in the molecular plane and to the above mentioned pseudo-twofold operation. Moreover it was clear that for these four arrangements even the refinement could not decide about the true structure.

Nevertheless the structure corresponding to the deepest minimum was refined somewhat by means of a Fourier differential synthesis computed to refine individual parameters of C, N and O atoms (Damiani, De Santis, Giglio & Ripamonti, 1963) as a test of the goodness of the analysis. The refinement was carried out with approximate anisotropic temperature factors, one for each chemical species (see Table 3). The disagreement index dropped from 0·26 to 0·18, and Table 1 compares the observed and calculated structure factors, computed with the use of the atomic scattering factors of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for C, N and O and that of McWeeny (1951) for H. The atomic parameters used in the structure factor calculations are reported in Table 2. In spite of the rather high final value of R and the low resolution, mainly caused by the small percentage of the total accessible reflexions recorded, we feel that our results are an adequate representation of the complexity of the structure. For this purpose

Figs. 1, 2 and 3 show the good agreement between the three-dimensional Fourier syntheses observed and calculated, evaluated in the molecular planes of the two TMU and of the BP (Damiani, Giglio & Ripamonti, 1967).

Fig. 4 shows composite projections along the b axis of the electron density distributions calculated through sections containing the atoms of the first TMU, the

Table 2. *Fractional atomic coordinates*

	x/a	y/b	z/c
First TMU			
C(2)	0·1731	0·2980	0·0069
C(4)	0·0273	0·4206	0·1600
C(5)	−0·1101	0·3792	0·0285
C(6)	−0·1034	0·2943	−0·1203
C(8)	−0·1574	0·4916	0·2184
C(13)	0·0380	0·1707	−0·2675
C(14)	0·3371	0·4214	0·2866
C(15)	−0·3918	0·4124	−0·0010
C(16)	0·1385	0·5690	0·4602
N(1)	0·0395	0·2599	−0·1170
N(3)	0·1782	0·3811	0·1516
N(7)	−0·2165	0·4347	0·0903
N(9)	0·0065	0·4935	0·2859
O(10)	0·3012	0·2572	−0·0109
O(11)	−0·2299	0·2677	−0·2388
O(12)	−0·1932	0·5666	0·3406
Second TMU			
C(2)	0·0150	−0·4476	−0·1916
C(4)	−0·1649	−0·3536	−0·0981
C(5)	−0·0712	−0·2890	−0·0604
C(6)	0·0690	−0·3018	0·0971
C(8)	−0·2991	−0·2374	0·0490
C(13)	0·2856	−0·3952	0·0114
C(14)	−0·2338	−0·5084	−0·3972
C(15)	−0·1007	−0·1245	0·3268
C(16)	−0·4654	−0·3665	−0·2444
N(1)	0·1214	−0·3782	−0·0231
N(3)	−0·1308	−0·4306	−0·2249
N(7)	−0·1622	−0·2181	0·1477
N(9)	−0·3086	−0·3205	−0·1005
O(10)	0·0780	−0·5061	−0·2783
O(11)	0·1767	−0·2485	0·2605
O(12)	−0·4130	−0·1955	0·0701
BP			
C(1)	0·2114	−0·0700	−0·0245
C(2)	0·0587	−0·0887	−0·1285
C(3)	−0·2267	−0·0723	−0·2255
C(4)	−0·3348	−0·0034	−0·1547
C(5)	−0·3173	0·0734	−0·0109
C(6)	−0·1065	0·1835	0·2709
C(7)	0·0265	0·1993	0·3590
C(8)	0·3168	0·1745	0·4457
C(9)	0·4290	0·1179	0·3969
C(10)	0·4044	0·0383	0·2468
C(11)	0·2448	0·0179	0·1382
C(12)	0·1274	0·0714	0·1823
C(13)	0·1500	0·1482	0·3252
C(14)	−0·0538	−0·0422	−0·0982
C(15)	−0·0382	0·0380	0·0497
C(16)	−0·1490	0·1078	0·1225
C(17)	−0·2590	−0·1431	−0·3661
C(18)	−0·4030	−0·1678	−0·4687
C(19)	−0·5189	−0·1108	−0·4260
C(20)	−0·4995	−0·0315	−0·2776

second TMU and the BP molecule. Fig.5 shows a composite projection of the complex along the a axis. The difference between observed and calculated electron density is always lower than ± 0.5 e.Å^{-3}.

At this stage eight atoms, six in BP and two in TMU molecules, are not resolved, as can be seen in the Fourier synthesis computed with observed data. It appeared clear that no further refinement would be profitable, mainly because of the low number of observed reflexions and the rather anomalous thermal motion of the atoms. The molecular packing of this crystalline structure is shown in Figs.6, 7 and 8.

The similarity between the computed structure factors of the possible four structures selected as above described indicates that for all the models the same degree of uncertainty could be foreseen. A few refinement cycles on a second model confirmed it, and therefore no further refinement work has been carried out on the other models. It seemed therefore that the selection of a single model is not possible on the basis of the available experimental data.

The full description of the method used in the analysis and the rigid body coordinates corresponding to all the minima found in the R function is given in a separate paper (Damiani, Giglio, Liquori & Ripamonti, 1967).

All the calculations were performed on an IBM 1620 basic computer.

Fig.2. Three-dimensional Fourier syntheses observed (a) and calculated (b), computed in the molecular plane, of the second TMU. Contours are at intervals of 1 e.Å^{-3} starting with 2 e.Å^{-3}.
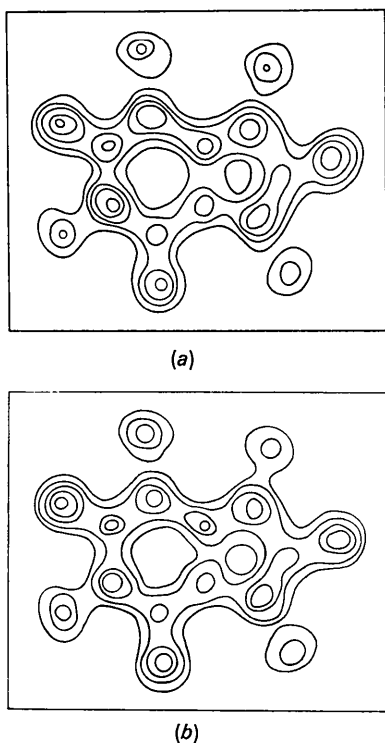
Fig.1. Three-dimensional Fourier syntheses observed (a) and calculated (b), computed in the molecular plane, of the first TMU. Contours are at intervals of 1 e.Å^{-3} starting with 2 e.Å^{-3}.
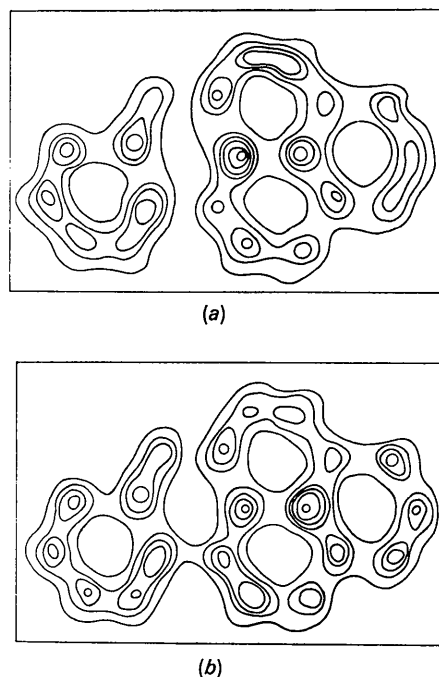
Fig.3. Three-dimensional Fourier syntheses observed (a) and calculated (b), computed in the molecular plane, of the BP. Contours lines 2, 3, 3·5, 4, 4·5, 5 e.Å^{-3}.

Discussion

Because of the low resolution obtained in the crystal structure determination it is impossible to achieve detailed information about the molecular geometry. However the structure can be considered as established as far as the geometrical aspects common to all four models are concerned. In fact the other three possible models may be derived from this one through pseudo-symmetry operations as previously described.

The least-squares planes of the BP and TMU molecules, calculated according to Schomaker, Waser, Marsh & Bergman (1959) with unitary weights for all the atoms, are:

$$2 \cdot 632x + 10 \cdot 283y - 5 \cdot 906z = \quad 0 \cdot 002 \text{ (Å)} \quad \text{for BP};$$

$$2 \cdot 313x + 10 \cdot 364y - 5 \cdot 782z = \quad 3 \cdot 482 \text{ (Å)} \quad \text{for the first TMU};$$

$$2 \cdot 476x + 10 \cdot 320y - 5 \cdot 749z = -3 \cdot 488 \text{ (Å)} \quad \text{for the second TMU}.$$

The equations are referred to crystal axes and x, y, z are fractional coordinates. The molecular planes are nearly parallel with an average perpendicular interplanar spacing of 3·48 Å, and the structure is characterized by a plane to plane alternate stacking of two TMU and one BP molecule arranged sandwich-like in infinite columns parallel to the b axis. These geometrical features are very similar to those found in the TMU–PR complex and do not seem to indicate the existence of charge transfer forces, even if the projection of three molecules, TMU–BP–TMU, of the same stack on the BP plane (Fig.6), shows a little more marked degree of overlap than in the pyrene complex.

Fig. 4. Composite drawing of the final electron density series, viewed along the b axis. Contours are at intervals of 1 e.Å⁻³ starting with 1 e.Å⁻³. (a) First TMU. (b) Second TMU. (c) BP.
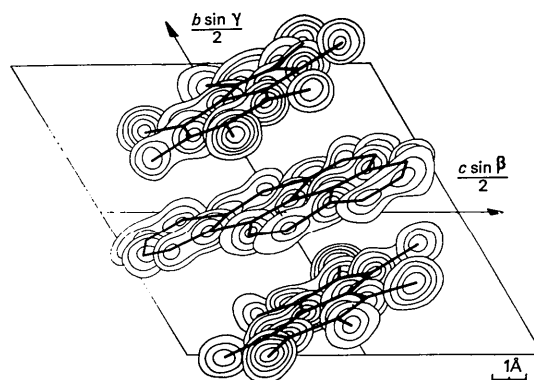
Fig. 5. Composite drawing of the final electron density series, viewed along the a axis. Contours are at intervals of 1 e.Å⁻³ starting with 1 e.Å⁻³.

Table 3. *Temperature factors for the different atomic species in the form*:

$$\exp[-(b_{11}h^2 + b_{12}hk + b_{13}hl + b_{22}k^2 + b_{23}kl + b_{33}l^2)]$$

	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
C	0·0195	0·0045	0·0180	0·0120	0·0175	0·0190
N	0·0190	0·0045	0·0170	0·0115	0·0170	0·0185
O	0·0195	0·0045	0·0180	0·0120	0·0175	0·0190
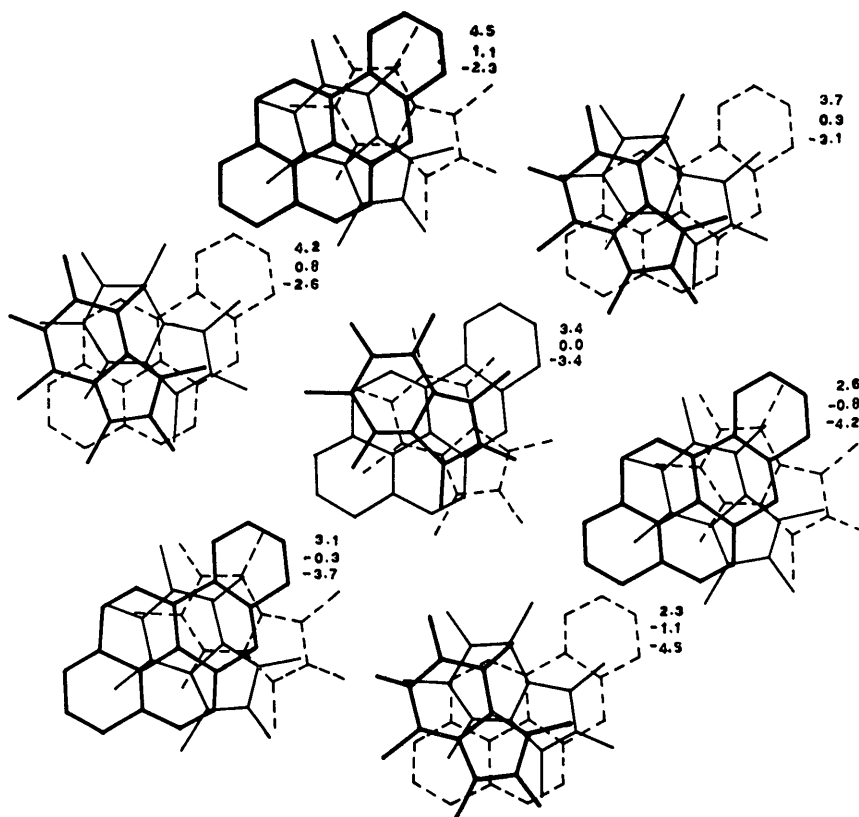
Fig. 6. Projection on to the BP least-squares plane showing the degree of overlap of an asymmetric unit and the packing with neighbouring molecules. The mean coordinate (Å) of each molecule along the perpendicular to the plane of plotting is quoted. In a triplet the highest molecule is shown by heavy lines, the middle one by full light lines, and the lowest one by dashed lines.
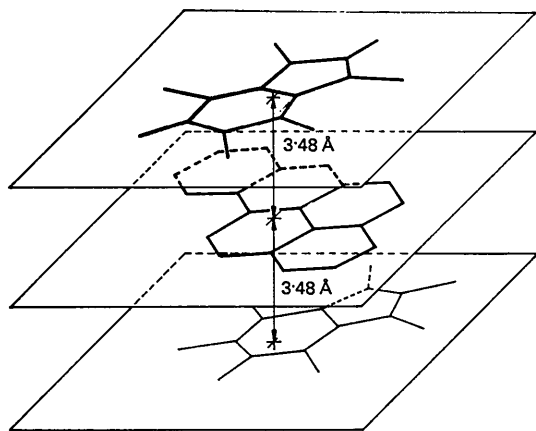
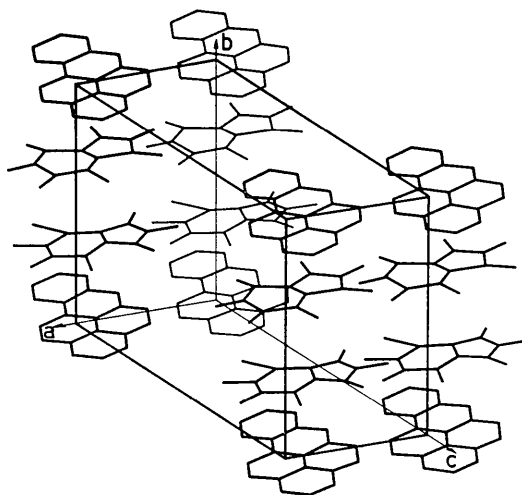Fig. 7. Schematic drawing of the perpendicular separation of the molecules in the asymmetric unit.

Fig. 8. Clinographic view of the structure.

Spectroscopic properties of the complexes in solution and in the solid state (Van Duuren, 1964) support the view that the intermolecular attractions are due to 'polarization bonding' (Wallwork, 1961) and to van der Waals interactions. Moreover, it is interesting to note that the coupling of two adjacent TMU molecules, related by a pseudo glide plane, is compatible with an antiparallel direction of the TMU's π dipole moments which lie almost perpendicular to the long axis of the molecule.

Inspection of the three-dimensional Fourier syntheses suggests that the molecules are undergoing

strong librations in their own planes as indicated by the elongation of the peripheral atoms. This is also supported by the temperature factors used in the molecular planes which are higher than those in the perpendicular direction. However, the presence in the X-ray photographs of some streaks, and the nearly identical orientations which either TMU or BP may adopt, indicate the possibility of disorder phenomena, not checked in this work, like those found in the indole-*s*-trinitrobenzene complex (Hanson, 1964). In fact the molecular arrangements corresponding to the four minima fill the available space equally well and are practically equivalent with respect to the Fourier transform.

Like the least-squares refinement with rigid groups (Scheringer, 1963), the method of analysis used in this work can be considered as a very convenient one, particularly when the ratio between the experimental data and the parameters is not too high. Moreover, it must be emphasized that, in the minimum residual search, convergence can be reached even if few reflexions are used.

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Minimum Residual Analysis of Crystal Structures

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When the approximate geometrical features of the molecule or molecules present in a unit cell of a crystal are known it is possible to utilize a few X-ray experimental intensities of low Bragg angle to scan systematically both the orientation and the positions in the cell with the help of the 'minimum residual' function R. The regions in which a reasonable agreement has been observed can subsequently be explored more carefully, increasing the number of reflexions and decreasing the rotational and translational increments. Then computation of intermolecular distances and potential energy as well as rigid-body least-squares techniques can be powerfully coupled together in the search for the true minimum. In this way it is possible to locate the individual molecules in the unit cell with such an accuracy as to allow the subsequent use of standard refinement techniques. The result of such an analysis in the case of a trimolecular complex (2:1 complex of 1,3,7,9-tetramethyluric acid and 3,4-benzpyrene) is discussed in detail.

Introduction

If the geometry of a molecule is known its Fourier transform can be evaluated as originally done by Knott (1940) or reproduced through the 'optical diffractom-eter' derived by Taylor, Hinde & Lipson (1951) from the X-ray microscope of Bragg (1939). Since the first application by Lipson & Taylor (1951) its usefulness has been widely recognized and exploited, stimulating many investigations to enlarge the field of its applica-