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The Crystal Structure of Triphenylene

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Crystals of triphenylene are orthorhombic with four molecules in a unit cell of dimensions $a = 13{\cdot}17$, $b = 16{\cdot}73$, $c = 5{\cdot}26$ Å, space group $P2_12_12_1$. The gross features of the structure, previously determined from two projections, have been confirmed using new three-dimensional data, the positional and isotropic thermal parameters of the carbon atoms have been refined by differential syntheses, and the hydrogen atoms have been located. There are small, but significant, deviations from a completely planar arrangement. These displacements are best described in terms of the plane of the central ring: atoms of two of the outer rings are displaced in one direction, and those of the third ring in the opposite direction from this plane. This slight molecular distortion is probably the result of intramolecular steric effects. The mean bond distances agree closely with the values predicted by valence-bond and molecular-orbital calculations. All the intermolecular separations correspond to normal van der Waals interactions.

Introduction

Pinnock, Taylor & Lipson (1956) have shown that the structure of triphenylene which was first derived by Klug (1950) had the molecules correctly oriented but incorrectly positioned in the unit cell. Their analysis of the [001] and [100] projections indicated that there are no unusually short intermolecular separations, but the available experimental data were not sufficiently accurate to allow precise determination of the molecular dimensions. The present paper describes a detailed analysis based on new three-dimensional intensity data.

Experimental

Crystal data

Triphenylene, $C_{18}H_{12}$; $M = 228{\cdot}28$; m.p. = 198·5 °C.
Orthorhombic, space group $P2_12_12_1$, remeasured cell dimensions
$a = 13{\cdot}17 \pm 0{\cdot}03$, $b = 16{\cdot}73 \pm 0{\cdot}03$, $c = 5{\cdot}26 \pm 0{\cdot}01$ Å.
Volume per unit cell = 1159 Å^3.
D_c (with $Z = 4$) = 1·308 g.cm^{-3},
D_m (Klug, 1950) $\simeq$ 1·3 g.cm^{-3}.
Absorption coefficient for X-rays,
$\lambda = 1{\cdot}542$ Å, $\mu = 6{\cdot}8$ cm^{-1}.

Total number of electrons per unit cell = $F(000) = 480$.

The intensities of the hkl reflections were measured visually on Weissenberg films of the $hk0, hk1, \ldots, hk4$ zones, and the structure amplitudes were derived from the usual formulae, no absorption corrections being considered necessary. The absolute scale was established separately for each level by comparison with the first set of calculated structure factors and re-examined following each stage of the refinement.

Structure analysis

Starting with the coordinates given by Pinnock, Taylor & Lipson (1956) for the carbon atoms, the structure factors were calculated using Freeman's (1959) scattering-factor curve. Refinement of the positional parameters proceeded by successive cycles of structure-factor calculation and differential syntheses using Ahmed's programs (1961) for the IBM 650 computer. In the second and succeeding cycles, differential syntheses were computed, also, with the calculated data in order to apply series-termination corrections. The isotropic thermal parameters were refined by comparison of the observed and calculated electron densities and their curvatures at the atomic positions, and by taking into account the overall correction derived from the plot of $\log_e (\Sigma|F_c|/\Sigma|F_o|)$ against $\sin^2\theta$. In the first S.F. calculation $B = 4{\cdot}5$ Å^2 was assumed for all the atoms, then in the second and third calculations three different temperature factors were applied to the three types of atoms in the molecule (depending on their distances from the centre of the molecule), and finally each atom was given the thermal parameter indicated by its own electron-density distribution. Progress of the refinement is

Table 1. *Progress of refinement*

Parameters from	R*
Pinnock, Taylor & Lipson (1956)	0·220
1st differential synthesis	0·186
2nd differential synthesis	0·133
2nd synthesis + ideal H positions	0·116
3rd differential synthesis	0·123
3rd synthesis + observed H positions	0·096
4th differential synthesis	—

* For the observed reflections only.

Table 2. *Observed and calculated structure amplitudes*

h	k	l	$10F_o$	$10F_c$
00	00	0	—	4800
00	02	0	410	427
00	04	0	428	431
00	06	0	171	133
00	08	0	78	96
00	10	0	136	115
00	12	0	68	78
00	14	0	165	183
00	16	0	72	62
00	18	0	105	129
00	20	0	41	41
01	01	0	289	271
01	02	0	632	646
01	03	0	384	389
01	04	0	395	370
01	05	0	271	254
01	06	0	199	159
01	07	0	90	92
01	08	0	20	29
01	09	0	22	20
01	10	0	11	14
01	11	0	15	19
01	12	0	31	36
01	13	0	49	59
01	14	0	62	62
01	15	0	34	47
01	16	0	335	268
01	17	0	65	74
01	18	0	64	66
01	19	0	9	7
01	20	0	8	14
02	00	0	784	785
02	01	0	135	135
02	02	0	564	559
02	03	0	218	197
02	04	0	84	66
02	05	0	16	21
02	06	0	61	58
02	07	0	86	74
02	08	0	73	83
02	09	0	<10	5
02	10	0	80	80
02	11	0	44	46
02	12	0	<12	16
02	13	0	24	31
02	14	0	32	47
02	15	0	<13	13
02	16	0	<12	17
02	17	0	20	19
02	18	0	13	14
02	19	0	9	12
02	20	0	10	7
03	01	0	476	455
03	02	0	219	203
03	03	0	385	347
03	04	0	315	287
03	05	0	116	105
03	06	0	288	259
03	07	0	357	341
03	08	0	235	210
03	09	0	91	84
03	10	0	93	85
03	11	0	106	91
03	12	0	34	36
03	13	0	<12	3
03	14	0	<12	5
03	15	0	<12	20
03	16	0	39	32
03	17	0	16	31
03	18	0	15	13
03	19	0	15	16
03	20	0	14	23
04	00	0	52	73
04	01	0	5	19
04	02	0	281	247
04	03	0	17	25
04	04	0	245	225
04	05	0	398	366
04	06	0	176	167
04	07	0	69	72
04	08	0	<10	1
04	09	0	283	254
04	10	0	226	194
04	11	0	16	19
04	12	0	22	27
04	13	0	<12	0
04	14	0	<12	7
04	15	0	<13	0
04	16	0	<12	15
04	17	0	13	17
05	01	0	165	158
05	02	0	24	39
05	03	0	31	59
05	04	0	158	136
05	05	0	111	115
05	06	0	329	313
05	07	0	159	154
05	08	0	20	20
05	09	0	31	35
05	10	0	40	26
05	11	0	161	142
05	12	0	89	77
05	13	0	17	15
05	14	0	29	37
05	15	0	<13	14
05	16	0	22	29
05	17	0	<12	15
05	18	0	11	15
05	19	0	<9	9
06	00	0	90	109
06	01	0	30	29
06	02	0	101	106
06	03	0	73	70
06	04	0	61	72
06	05	0	86	73
06	06	0	11	30
06	07	0	78	91
06	08	0	54	57
06	09	0	12	18
06	10	0	48	58
06	11	0	36	39
06	12	0	25	35
06	13	0	<13	7
06	14	0	29	24
06	15	0	<12	6
06	16	0	<12	11
06	17	0	15	21
06	18	0	<9	10
07	01	0	40	58
07	02	0	195	183
07	03	0	38	44
07	04	0	<10	4
07	05	0	18	18
07	06	0	34	33
07	07	0	<11	10
07	08	0	81	86
07	09	0	22	15
07	10	0	20	24
07	11	0	37	57
07	12	0	84	98
07	13	0	34	56
07	14	0	21	26
07	15	0	<12	0
07	16	0	<11	16
07	17	0	<10	0
07	18	0	14	19
08	00	0	66	78
08	01	0	60	56
08	02	0	9	13
08	03	0	189	175
08	04	0	271	249
08	05	0	197	158
08	06	0	61	69
08	07	0	21	29
08	08	0	32	42
08	09	0	17	23
08	10	0	14	25
08	11	0	<12	8
08	12	0	25	34
08	13	0	46	60
08	14	0	28	43
09	01	0	32	44
09	02	0	12	36
09	03	0	93	92
09	04	0	75	77
09	05	0	<12	6
09	06	0	56	56
09	07	0	<12	4
09	08	0	<12	3
09	09	0	<12	7
09	10	0	52	60
09	11	0	<13	26
09	12	0	46	57
09	13	0	<12	24
10	00	0	<12	20
10	01	0	<12	20
10	02	0	24	32
10	03	0	<12	14
10	04	0	68	74
10	05	0	25	20
10	06	0	38	61
10	07	0	<12	3
10	08	0	18	3
10	09	0	10	14
10	10	0	<13	12
10	11	0	17	20
10	12	0	<12	15
10	13	0	18	24
10	14	0	31	24
10	15	0	28	23
11	01	0	32	53
11	02	0	145	159
11	03	0	178	181
11	04	0	155	157
11	05	0	<12	18
11	06	0	46	51
11	07	0	<13	4
11	08	0	14	15
11	09	0	<13	5
11	10	0	10	16
11	11	0	28	13
11	12	0	27	12
11	13	0	<10	7
11	14	0	42	37
11	15	0	40	37
12	00	0	196	166
12	01	0	129	143
12	02	0	29	36
12	03	0	21	22
12	04	0	56	58
12	05	0	29	37
12	06	0	<13	3
12	07	0	23	32
12	08	0	<12	5
12	09	0	<11	12
12	10	0	12	21
12	11	0	20	33
12	12	0	35	36
12	13	0	76	73
12	14	0	72	70
13	01	0	81	103
13	02	0	114	139
13	03	0	59	84
13	04	0	<12	5
13	05	0	22	38
13	06	0	<12	2
13	07	0	<12	5
13	08	0	<11	13
13	09	0	<10	1
13	10	0	<9	12
13	11	0	14	12
13	12	0	15	12
14	00	0	<11	9
14	01	0	<11	14
14	02	0	<11	8
14	03	0	18	31
14	04	0	<11	8
14	05	0	<11	2
14	06	0	<10	14
14	07	0	14	16
14	08	0	<9	5
14	09	0	21	22
15	01	0	<10	5
15	02	0	16	19
15	03	0	17	22
15	04	0	<9	13
15	05	0	8	7
15	06	0	12	16
15	07	0	32	37
15	08	0	24	23
16	00	0	<9	7
16	01	0	14	25
00	01	1	<9	10
00	02	1	318	300
00	03	1	21	3
00	04	1	269	256
00	05	1	60	69
00	06	1	80	85
00	07	1	<16	8
00	08	1	80	78
00	09	1	90	87
00	10	1	<18	3
00	11	1	67	81
00	12	1	<19	7
00	13	1	62	56
00	14	1	34	42
00	15	1	96	81
00	16	1	50	48
00	17	1	<20	19
00	18	1	42	24
00	19	1	23	24
00	20	1	<16	12
01	00	1	80	163
01	01	1	302	388
01	02	1	558	647
01	03	1	572	592
01	04	1	106	115
01	05	1	85	91
01	06	1	204	206
01	07	1	280	246
01	08	1	79	79
01	09	1	172	156
01	10	1	129	119
01	11	1	35	49
01	12	1	35	38
01	13	1	91	96
01	14	1	132	128
01	15	1	79	87
01	16	1	57	56
01	17	1	<20	15
01	18	1	62	47
01	19	1	18	13
01	20	1	16	12
02	00	1	383	385
02	01	1	330	351
02	02	1	834	868
02	03	1	812	817
02	04	1	440	398
02	05	1	87	94
02	06	1	163	150
02	07	1	271	254
02	08	1	133	129
02	09	1	294	260
02	10	1	57	58
02	11	1	104	118
02	12	1	57	74
02	13	1	138	137
02	14	1	132	123
02	15	1	40	39
02	16	1	37	39
02	17	1	<20	13
02	18	1	83	71
02	19	1	51	47
02	20	1	24	25
03	00	1	30	43
03	01	1	246	248
03	02	1	504	489
03	03	1	440	441
03	04	1	374	356
03	05	1	171	178
03	06	1	95	95
03	07	1	260	241
03	08	1	156	157
03	09	1	127	125
03	10	1	<18	12
03	11	1	22	21
03	12	1	71	78
03	13	1	146	145
03	14	1	57	56
03	15	1	<21	16
03	16	1	<20	12
03	17	1	44	25
03	18	1	49	36
03	19	1	55	53
03	20	1	37	34
04	00	1	173	191
04	01	1	129	153
04	02	1	97	92
04	03	1	265	269
04	04	1	49	52
04	05	1	198	190
04	06	1	39	41
04	07	1	33	32
04	08	1	32	42
04	09	1	78	79
04	10	1	29	38
04	11	1	72	75
04	12	1	35	37
04	13	1	34	26
04	14	1	<21	18
04	15	1	<21	4
04	16	1	23	11
04	17	1	<19	8
04	18	1	19	12
04	19	1	17	15
05	00	1	305	322
05	01	1	101	109
05	02	1	251	239
05	03	1	67	71
05	04	1	126	128
05	05	1	120	117
05	06	1	173	167
05	07	1	66	61
05	08	1	<19	9
05	09	1	21	9
05	10	1	30	34
05	11	1	52	33
05	12	1	74	78
05	13	1	65	53
05	14	1	37	43
05	15	1	39	47
05	16	1	46	44
05	17	1	<19	11
05	18	1	18	18
05	19	1	37	26
06	00	1	245	245
06	01	1	80	86
06	02	1	117	116
06	03	1	302	284
06	04	1	196	202
06	05	1	79	85
06	06	1	67	70
06	07	1	34	40
06	08	1	29	34
06	09	1	34	28
06	10	1	35	30
06	11	1	35	31
06	12	1	71	51
06	13	1	44	26
06	14	1	66	65
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07	01	1	160	155
07	02	1	243	243
07	03	1	32	39
07	04	1	157	153
07	05	1	51	67
07	06	1	19	21
07	07	1	43	52
07	08	1	40	39
07	09	1	44	45
07	10	1	23	24
07	11	1	24	19
07	12	1	24	20
07	13	1	57	47
07	14	1	39	29
07	15	1	<20	4
07	16	1	26	24
07	17	1	18	11
08	00	1	30	38
08	01	1	52	46
08	02	1	19	23
08	03	1	24	23
08	04	1	37	47
08	05	1	55	65
08	06	1	71	72
08	07	1	57	59
08	08	1	<20	24
08	09	1	<20	25
08	10	1	<21	24
08	11	1	33	20
08	12	1	62	47
08	13	1	<20	16
08	14	1	28	29
09	00	1	50	54
09	01	1	21	18
09	02	1	35	33
09	03	1	<19	15
09	04	1	76	91
09	05	1	99	117
09	06	1	175	174
09	07	1	23	32
09	08	1	<20	13
09	09	1	89	89
09	10	1	37	44
09	11	1	65	55
09	12	1	93	79
09	13	1	35	24
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10	02	1	35	41
10	03	1	106	107
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10	05	1	127	127
10	06	1	37	49
10	07	1	121	115
10	08	1	60	56
10	09	1	<21	20
10	10	1	100	95
10	11	1	102	87
10	12	1	66	57
10	13	1	40	34
11	00	1	46	52
11	01	1	<20	11
11	02	1	29	25
11	03	1	78	89
11	04	1	67	74
11	05	1	67	72
11	06	1	62	63
11	07	1	57	48
11	08	1	<20	17
11	09	1	56	48
11	10	1	23	15
11	11	1	52	40
11	12	1	56	53
11	13	1	37	33
12	00	1	44	38
12	01	1	55	59
12	02	1	48	46
12	03	1	24	21
12	04	1	29	36
12	05	1	<21	19
12	06	1	29	29
12	07	1	28	21
12	08	1	<20	15
12	09	1	<19	18
12	10	1	<19	11
12	11	1	<18	6
12	12	1	28	26
13	00	1	51	63
13	01	1	56	51
13	02	1	48	50
13	03	1	23	22
13	04	1	35	38
13	05	1	35	32
13	06	1	35	34
13	07	1	<19	6
13	08	1	<19	5
13	09	1	19	16
13	10	1	<17	14
13	11	1	<16	20
13	12	1	22	18
14	00	1	109	108
14	01	1	67	64
14	02	1	69	60
14	03	1	<19	12
14	04	1	<19	9
14	05	1	32	31
14	06	1	19	18
14	07	1	27	22
14	08	1	<12	13
14	09	1	<15	15
14	10	1	22	25
15	00	1	63	67
15	01	1	33	36
15	02	1	44	45
15	03	1	18	13
15	04	1	17	12
15	05	1	21	21
15	06	1	<15	11
15	07	1	18	17
16	00	1	<13	1
16	01	1	<13	13
16	02	1	<12	8
00	00	2	35	35
00	01	2	85	112
00	02	2	122	126
00	03	2	197	210
00	04	2	311	306
00	05	2	118	121
00	06	2	260	248
00	07	2	195	170
00	08	2	32	34
00	09	2	81	78
00	10	2	<11	22
00	11	2	149	132
00	12	2	149	142
00	13	2	18	21
00	14	2	<12	3
00	15	2	<12	1
00	16	2	18	28
00	17	2	<11	5
00	18	2	<11	4
00	19	2	10	7
00	20	2	14	15
01	00	2	45	60
01	01	2	133	143
01	02	2	129	131
01	03	2	165	168
01	04	2	225	240
01	05	2	249	252
01	06	2	36	30
01	07	2	76	75
01	08	2	21	12
01	09	2	89	82
01	10	2	118	111
01	11	2	39	40
01	12	2	89	79
01	13	2	73	68
01	14	2	18	15
01	15	2	<12	4
01	16	2	18	16
01	17	2	12	9
01	18	2	11	8
01	19	2	12	13
01	20	2	21	15
02	00	2	16	29
02	01	2	28	43
02	02	2	148	157
02	03	2	38	38
02	04	2	114	108
02	05	2	109	119
02	06	2	102	98
02	07	2	141	132
02	08	2	39	42
02	09	2	27	23
02	10	2	43	36
02	11	2	46	47
02	12	2	53	47
02	13	2	67	63
02	14	2	<13	5
02	15	2	27	20
02	16	2	<12	0
02	17	2	21	20
02	18	2	<10	2
02	19	2	21	16
03	00	2	107	104
03	01	2	177	182
03	02	2	179	181
03	03	2	193	185
03	04	2	158	156
03	05	2	252	250
03	06	2	185	181
03	07	2	14	4
03	08	2	41	40
03	09	2	36	34
03	10	2	66	71
03	11	2	144	150
03	12	2	123	110
03	13	2	65	70
03	14	2	27	33
03	15	2	27	28
03	16	2	43	37
03	17	2	23	22
03	18	2	31	29
03	19	2	12	11
03	20	2	19	18
04	00	2	259	229
04	01	2	257	256
04	02	2	185	179
04	03	2	144	147
04	04	2	249	234
04	05	2	416	370
04	06	2	337	289
04	07	2	116	111
04	08	2	65	71
04	09	2	46	52
04	10	2	137	158
04	11	2	147	148
04	12	2	83	86
04	13	2	60	69
04	14	2	43	55
04	15	2	52	52
04	16	2	30	33
04	17	2	15	14
04	18	2	25	29
04	19	2	15	18
05	00	2	161	147
05	01	2	129	133
05	02	2	140	137
05	03	2	30	25
05	04	2	168	152
05	05	2	267	227
05	06	2	248	204
05	07	2	120	121
05	08	2	64	63
05	09	2	67	74
05	10	2	139	141
05	11	2	60	67
05	12	2	38	31
05	13	2	<12	3
05	14	2	30	27
05	15	2	36	40
05	16	2	<11	12
05	17	2	30	31
05	18	2	<10	11
05	19	2	14	9
06	00	2	64	67
06	01	2	60	66
06	02	2	10	6
06	03	2	21	26
06	04	2	21	19
06	05	2	62	63
06	06	2	96	88
06	07	2	21	37
06	08	2	85	86
06	09	2	123	111
06	10	2	54	56
06	11	2	41	36
06	12	2	14	19
06	13	2	18	17
06	14	2	12	6
06	15	2	21	22
06	16	2	21	17
06	17	2	<10	13
06	18	2	11	11
07	00	2	129	124
07	01	2	144	145
07	02	2	74	72
07	03	2	24	28
07	04	2	62	56
07	05	2	64	68
07	06	2	21	31
07	07	2	160	164
07	08	2	<12	6
07	09	2	237	224
07	10	2	45	42
07	11	2	21	34
07	12	2	24	32
07	13	2	21	16
07	14	2	20	16
07	15	2	11	17
07	16	2	18	14
07	17	2	<10	7
07	18	2	15	17
08	00	2	118	105
08	01	2	84	72
08	02	2	100	93
08	03	2	27	33
08	04	2	47	49
08	05	2	64	63
08	06	2	92	109
08	07	2	224	218
08	08	2	80	78
08	09	2	143	148
08	10	2	74	67
08	11	2	24	26
08	12	2	<12	9
08	13	2	28	31
08	14	2	11	12
08	15	2	21	29
08	16	2	43	45
08	17	2	18	22
09	00	2	160	162
09	01	2	25	37
09	02	2	53	51
09	03	2	21	33
09	04	2	42	42
09	05	2	30	32
09	06	2	96	111
09	07	2	74	86
09	08	2	45	50
09	09	2	91	94
09	10	2	53	57
09	11	2	25	26
09	12	2	23	25
09	13	2	<11	4
09	14	2	21	18
09	15	2	<10	9
09	16	2	27	24
10	00	2	49	48
10	01	2	<12	13
10	02	2	30	38
10	03	2	18	19
10	04	2	27	37
10	05	2	24	22
10	06	2	14	12
10	07	2	18	24
10	08	2	27	25
10	09	2	32	36
10	10	2	21	33
10	11	2	16	21
10	12	2	11	19
10	13	2	15	12
10	14	2	10	12
10	15	2	14	9
11	00	2	24	31
11	01	2	27	39
11	02	2	14	17
11	03	2	32	38
11	04	2	18	18
11	05	2	27	35
11	06	2	<12	14
11	07	2	32	36
11	08	2	60	64
11	09	2	<11	8
11	10	2	20	24
11	11	2	15	12
11	12	2	18	19
11	13	2	21	25
11	14	2	21	26
12	00	2	12	9
12	01	2	18	27
12	02	2	30	41
12	03	2	38	46
12	04	2	21	29
12	05	2	12	19
12	06	2	28	25
12	07	2	24	32
12	08	2	32	40
12	09	2	27	32
12	10	2	15	12
12	11	2	34	25
12	12	2	21	19
12	13	2	12	18
13	00	2	12	9
13	01	2	18	18
13	02	2	16	16
13	03	2	30	37
13	04	2	16	26
13	05	2	24	23
13	06	2	11	14
13	07	2	11	13
13	08	2	14	15
13	09	2	35	30
13	10	2	19	18
13	11	2	11	11
14	00	2	19	22
14	01	2	11	12
14	02	2	19	20
14	03	2	11	7
14	04	2	20	21
14	05	2	<10	7
14	06	2	14	12
15	00	2	<10	3
15	01	2	21	19
15	02	2	32	31
15	03	2	32	37
15	04	2	<9	5
15	05	2	27	25
16	00	2	23	25
16	01	2	16	11
16	02	2	20	25
00	01	3	<34	0
00	02	3	35	20
00	03	3	73	86
00	04	3	<35	13
00	05	3	156	149
00	06	3	53	31
00	07	3	59	61
01	00	3	48	63
01	01	3	103	110
01	02	3	64	76
01	03	3	70	81
01	04	3	88	101
01	05	3	119	130
01	06	3	53	46
01	07	3	<38	41
01	08	3	51	44
02	00	3	<34	7
02	01	3	112	111
02	02	3	158	164
02	03	3	210	243
02	04	3	84	93
02	05	3	99	99
02	06	3	64	60
03	00	3	106	129
03	01	3	84	89
03	02	3	90	109
03	03	3	91	89
03	04	3	118	118
03	05	3	44	36
03	06	3	48	46
03	07	3	51	49
04	00	3	90	60
04	01	3	57	45
04	02	3	41	40
04	03	3	<37	25
04	04	3	91	96
04	05	3	59	53
04	06	3	71	70
04	07	3	84	84
04	08	3	<40	43
04	09	3	59	43
05	00	3	44	33
05	01	3	55	33
05	02	3	72	65
05	03	3	<38	24
05	04	3	120	128
05	05	3	80	82
05	06	3	<39	51
05	07	3	68	56
05	08	3	165	145
05	09	3	180	175
05	10	3	149	143
05	11	3	87	97
06	00	3	<39	39
06	01	3	<38	20
06	02	3	<39	41
06	03	3	52	52
06	04	3	75	67
06	05	3	86	99
06	06	3	203	210
06	07	3	275	273
06	08	3	198	198
06	09	3	61	45
06	10	3	<41	44
06	11	3	96	104
07	00	3	<39	4
07	01	3	<39	31
07	02	3	<39	17
07	03	3	<40	50
07	04	3	<40	37
07	05	3	109	100
07	06	3	<40	61
07	07	3	86	91
07	08	3	167	163
07	09	3	156	141
07	10	3	75	84
08	00	3	59	64
08	01	3	<40	16
08	02	3	<40	36
08	03	3	<40	21
08	04	3	<41	7
08	05	3	<41	29
08	06	3	<41	9
08	07	3	<41	57
08	08	3	<41	49
08	09	3	<41	54
08	10	3	<40	58
08	11	3	<40	23
09	00	3	61	79
09	01	3	74	74
10	00	3	<41	55
10	01	3	62	54
10	02	3	87	89
10	03	3	<41	41
00	00	4	73	73
00	01	4	<20	4
00	02	4	21	17
00	03	4	37	30
00	04	4	43	26
00	05	4	96	69
00	06	4	87	89
00	07	4	56	55
00	08	4	72	71
00	09	4	43	70
00	10	4	84	96
01	00	4	44	67
01	01	4	35	36
01	02	4	<20	10
01	03	4	43	40
01	04	4	59	60
01	05	4	34	34
01	06	4	74	76
01	07	4	93	77
01	08	4	42	37
01	09	4	54	62
01	10	4	45	41
02	00	4	<20	14
02	01	4	35	40
02	02	4	39	44
02	03	4	29	28
02	04	4	40	38
02	05	4	<21	11
02	06	4	<23	15
02	07	4	50	47
03	00	4	<21	10
03	01	4	125	126
03	02	4	83	86
03	03	4	98	104
03	04	4	117	121
03	05	4	70	67
03	06	4	49	43
04	00	4	<22	0
04	01	4	133	118
04	02	4	65	70

Table 2 (*cont.*)

h	k	l	$10F_o$	$10F_c$	h	k	l	$10F_o$	$10F_c$	h	k	l	$10F_o$	$10F_c$	h	k	l	$10F_o$	$10F_c$	h	k	l	$10F_o$	$10F_c$	h	k	l	$10F_o$	$10F_c$
04	03	4	133	130	05	06	4	43	38	07	01	4	< 23	22	07	10	4	42	45	08	07	4	44	42	09	04	4	44	44
04	04	4	151	148	06	00	4	< 23	4	07	02	4	< 23	16	07	11	4	40	36	08	08	4	43	42	09	05	4	54	58
04	05	4	79	79	06	01	4	< 22	9	07	03	4	63	74	08	00	4	45	27	08	09	4	42	39	09	06	4	43	49
05	00	4	92	83	06	02	4	< 23	10	07	04	4	< 23	6	08	01	4	45	45	08	10	4	49	53	09	07	4	< 22	30
05	01	4	89	62	06	03	4	42	46	07	05	4	< 24	21	08	02	4	45	47	08	11	4	36	39	09	08	4	40	13
05	02	4	104	90	06	04	4	43	46	07	06	4	56	57	08	03	4	< 23	26	09	00	4	< 23	1	09	09	4	38	33
05	03	4	63	71	06	05	4	< 23	27	07	07	4	71	72	08	04	4	71	72	09	01	4	< 23	12	09	10	4	< 19	27
05	04	4	76	78	06	06	4	44	43	07	08	4	55	41	08	05	4	84	89	09	02	4	< 23	41	09	11	4	32	38
05	05	4	72	73	07	00	4	< 23	1	07	09	4	< 22	12	08	06	4	70	68	09	03	4	< 23	17					

shown in Table 1. The hydrogen atoms were first assumed to be situated on the diagonals of the outer rings with C–H = 1·08 Å, but their positions were determined later from a three-dimensional difference map, of which a section in the mean molecular plane is shown in Fig. 1. In this synthesis the calculated structure factors were those from the second cycle excluding hydrogen-atom contributions, but the F_o phases were derived from F_c with hydrogens included (that is the theoretically estimated hydrogen positions were employed for correction of the F_o phases slightly). The hydrogen atoms appear as well-defined electron-density concentrations with maxima between 0·3 and 0·6 e.Å^{-3}; there is also some residual electron density as high as 0·5 e.Å^{-3} at the centre of the bond between atoms 12 and 13, but otherwise the rest of the difference map is quite flat and featureless.

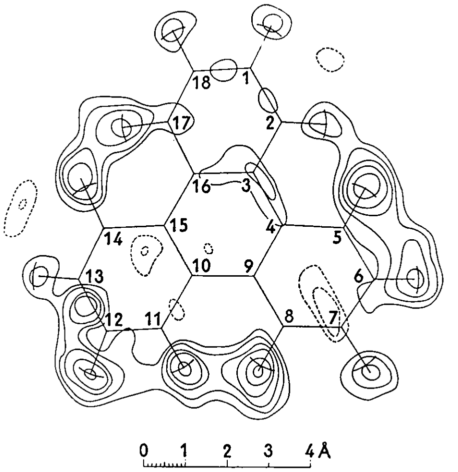


Fig. 1. Difference synthesis in the mean molecular plane. First contour lines are ±0·2 e.Å^{-3}, and the others are at intervals of 0·1 e.Å^{-3}. Dotted lines indicate negative electron densities. Arcs show C–H distances of 1·09 Å.

The observed structure amplitudes, and those calculated with the carbon penultimate set of positional parameters, the hydrogen coordinates derived from the difference map, and the final isotropic temperature factors are listed in Table 2. The corresponding overall R-factor for the observed data is $0{\cdot}09_6$, and a summary of the agreement of the individual reflections (cf. Hanson & Ahmed, 1958) is given in Table 3. The categories have been chosen on the basis of $|F_o|_{\text{min.}} = 1{\cdot}0$, $|F_o|_{\text{max.}} = 83{\cdot}4$, and $R \simeq 0{\cdot}1$. Categories (3) and (4) which correspond to high discrepancies, include only 11 observed reflections and 6 unobserved, all of which are quite weak.

Table 3. *Agreement summary*

Each category includes all reflections which meet the specified conditions and which have not been included in the preceding categories

F_{th} = threshold value

Observed reflections:

Category	Number
1. $\|\Delta F\| \leq 1{\cdot}0$ or $\|\Delta F\| \leq 0{\cdot}2F_o$	694
2. $\|\Delta F\| \leq 2{\cdot}0$ or $\|\Delta F\| \leq 0{\cdot}4F_o$	80
3. $\|\Delta F\| \leq 3{\cdot}0$ or $\|\Delta F\| \leq 0{\cdot}6F_o$	10
4. $\|\Delta F\| > 3{\cdot}0$ and $\|\Delta F\| > 0{\cdot}6F_o$	1
	Σ 785

Unobserved reflections:

Category	Number
1. $F_c \leq 1{\cdot}0F_{th}$	132
2. $F_c \leq 1{\cdot}5F_{th}$	45
3. $F_c \leq 2{\cdot}0F_{th}$	5
4. $F_c \leq 2{\cdot}5F_{th}$	1
	Σ 183

Table 4. *Electron densities* (e.Å^{-3}) *and curvatures* (e.Å^{-5}) *from final cycle*

	ϱ		$-\varrho_{xx}$		$-\varrho_{yy}$		$-\varrho_{zz}$	
Atom	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
C1	5·52	5·42	38·7	40·0	39·3	37·8	27·1	26·7
2	5·94	5·81	42·2	43·3	44·9	43·0	29·5	29·1
3	6·48	6·40	50·6	50·8	50·1	47·6	35·3	34·9
4	6·64	6·53	52·5	52·0	51·3	49·7	36·0	35·8
5	5·71	5·71	41·5	42·7	39·6	39·0	29·1	28·9
6	5·69	5·69	42·8	43·2	39·1	39·8	29·0	28·2
7	5·30	5·40	38·3	37·6	35·1	37·1	26·5	27·2
8	5·70	5·72	43·3	43·1	37·7	39·3	29·6	29·5
9	6·23	6·19	48·1	47·6	48·0	46·9	32·7	32·4
10	6·20	6·16	47·0	47·2	47·2	44·7	31·9	31·6
11	5·64	5·65	38·5	40·6	44·1	41·8	26·9	27·2
12	5·26	5·27	33·0	35·4	39·2	36·0	24·5	24·8
13	5·35	5·33	34·4	36·5	39·3	37·6	24·3	24·8
14	5·61	5·63	37·7	38·4	41·5	39·8	28·3	28·5
15	6·42	6·31	48·3	48·3	51·7	47·9	33·9	33·6
16	6·41	6·36	50·2	49·8	50·6	48·4	34·3	34·1
17	6·06	5·95	46·8	47·0	43·6	43·0	30·5	30·0
18	5·57	5·57	39·2	39·5	40·3	39·8	27·8	27·7

The fourth and final set of *obs* and *calc* differential syntheses suggested some very small changes in carbon atom positional parameters (mean corrected shifts of $0{\cdot}001_5$, $0{\cdot}002_5$, and $0{\cdot}004_4$ Å along x, y, and z respectively). These corrections were applied, but structure factors were not recalculated, as the shifts were too small to produce any appreciable changes.

The final observed and calculated electron densities and curvatures at the carbon positions are listed in Table 4; the agreement between them indicates no significant thermal anisotropy for any of the atoms.

Results and discussion

The final positional and temperature parameters are given in Table 5, *x*, *y*, *z* being coordinates referred to the usual origin and expressed as fractions of the unit-cell edges. The carbon coordinates are those given by the fourth differential syntheses after correction for the series termination errors by Booth's back-shift method (1946), and the hydrogen coordinates are those measured directly from the difference map (Fig. 1). The standard deviations of the atomic positions, which are included in Table 5, are those calculated from Cruickshank's formulae (1949) with the observed data only, taking $\sigma(F)=|\Delta F|$ for the centrosymmetric zones, $\sigma(F)=2|\Delta F|$ for the general reflections, and allowing for the multiplicity of the reflections. Nearly the same standard deviations are also obtained if Cruickshank's expressions are multiplied by a factor of 1·60 and $\sigma(F)$ is taken as $|\Delta F|$ for all reflections (Shoemaker, Donohue, Schomaker & Corey, 1950).

The bond lengths, and their standard deviations estimated according to the equation of Ahmed & Cruickshank (1953), are presented in Fig. 2(*a*). The valency angles are given in Fig. 2(*b*); their standard deviations as estimated from the expression in the *International Tables for X-ray Crystallography* (1959) are between 0·6° and 0·8°.

The mean plane through the 18 carbon atoms of the molecule whose coordinates are listed in Table 5 is represented by the equation

$$0{\cdot}5412X-0{\cdot}5451Y+0{\cdot}6405Z+1{\cdot}3103=0\ ,$$

where *X*, *Y*, *Z* are the coordinates in Å, referred to the unit-cell axes. The deviations (Δ_1) of the atoms from this plane are given in Table 5. They vary in an irregular pattern between $\pm 0{\cdot}05$ Å, and although they are small, yet they are highly significant; since $\chi^2=240$, and for $\nu=15$, $P \ll 0{\cdot}001$ (for $\nu=15$ and $P=0{\cdot}001$, $\chi^2=37{\cdot}7$ only). Thus the triphenylene molecule as a whole appears to be significantly non-planar.

The best plane through the six atoms of the central ring is

$$0{\cdot}5325X-0{\cdot}5328Y+0{\cdot}6578Z+1{\cdot}2299=0\ .$$

Deviations (Δ_2) of the atoms from this plane are listed in Table 5 and are illustrated in Fig. 2(*c*). The central ring itself is quite planar ($\chi^2=0{\cdot}8$ and for $\nu=3$, $P>0{\cdot}50$), but the Δ_2 deviations for the other atoms are of course highly significant, and suggest a regular distortion of the molecule from a planar configuration, with the atoms of rings *B* and *C* (Fig. 2(*c*)) being displaced in the same direction, and those of ring *A* in the opposite direction. This

Table 5. *Final positional parameters (fractional), with standard deviations* (Å), *isotropic thermal parameters* (Å^2), *and deviations* (Δ_1) *from the mean molecular plane and* (Δ_2) *from plane of central ring* (Å)

Atom	x	y	z	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	B	Δ_1	Δ_2
C1	0·4405	0·6996	0·5767	0·008	0·008	0·010	5·3	0·013	0·078
2	0·5199	0·7012	0·4031	0·007	0·007	0·009	4·9	−0·021	0·020
3	0·5327	0·6414	0·2175	0·006	0·007	0·008	4·4	−0·009	0·001
4	0·6181	0·6420	0·0451	0·006	0·006	0·008	4·5	0·013	−0·002
5	0·6917	0·7052	0·0477	0·007	0·008	0·009	5·1	−0·030	−0·040
6	0·7703	0·7075	−0·1188	0·007	0·008	0·009	5·3	−0·052	−0·086
7	0·7817	0·6476	−0·2986	0·008	0·009	0·010	5·5	−0·030	−0·094
8	0·7132	0·5839	−0·3065	0·007	0·008	0·009	5·3	0·036	−0·034
9	0·6309	0·5811	−0·1377	0·007	0·007	0·008	4·5	0·044	−0·002
10	0·5558	0·5166	−0·1501	0·007	0·007	0·009	4·4	0·055	0·004
11	0·5642	0·4559	−0·3394	0·008	0·007	0·010	5·1	0·031	−0·052
12	0·4918	0·3968	−0·3616	0·009	0·008	0·011	5·5	−0·021	−0·109
13	0·4088	0·3966	−0·1937	0·008	0·008	0·011	5·5	−0·045	−0·109
14	0·3997	0·4539	−0·0086	0·008	0·008	0·009	5·1	−0·009	−0·043
15	0·4718	0·5163	0·0171	0·006	0·006	0·008	4·5	0·022	−0·004
16	0·4605	0·5785	0·2017	0·006	0·006	0·008	4·5	−0·004	0·001
17	0·3793	0·5793	0·3748	0·007	0·007	0·009	4·9	−0·006	0·023
18	0·3692	0·6369	0·5594	0·008	0·008	0·010	5·3	0·018	0·078
H1	0·425	0·750	0·740	—	—	—	5·3	—	—
2	0·578	0·750	0·402	—	—	—		—	—
5	0·692	0·751	0·197	—	—	—		—	—
6	0·826	0·753	−0·117	—	—	—		—	—
7	0·840	0·655	−0·453	—	—	—		—	—
8	0·720	0·535	−0·460	—	—	—		—	—
11	0·630	0·458	−0·467	—	—	—		—	—
12	0·497	0·362	−0·533	—	—	—		—	—
13	0·360	0·348	−0·200	—	—	—		—	—
14	0·335	0·455	0·130	—	—	—		—	—
17	0·328	0·526	0·345	—	—	—		—	—
18	0·319	0·635	0·713	—	—	—		—	—

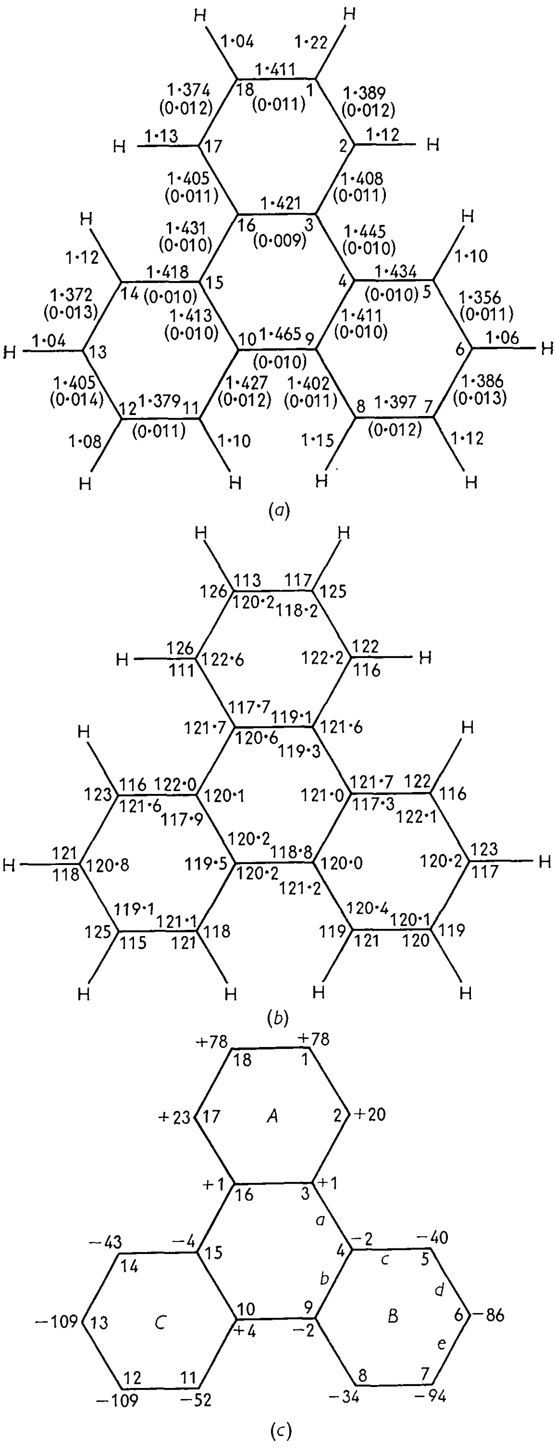


Fig. 2. (*a*) Measured bond lengths (Å), and standard deviations (Å) in parentheses. (*b*) Measured valency angles (°) ($\sigma = 0{\cdot}6°$ to $0{\cdot}8°$ for C–C–C angles). (*c*) Deviations from mean plane of central ring (10^{-3} Å).

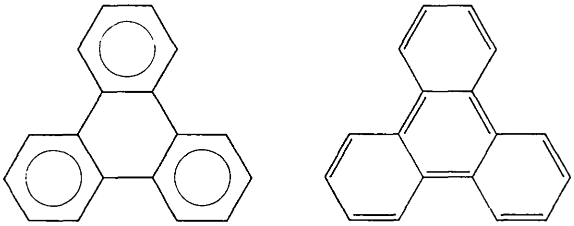
distortion might be due to intra- or intermolecular steric effects (or both). Intramolecular overcrowding occurs due to close approaches of atoms 2 and 5, 8 and 11, 14 and 17, and especially between the hydrogen atoms attached to them. Steric repulsions between atoms 2 and 5, and between 14 and 17 (and the associated hydrogens) would be relieved somewhat by the observed deviations from planarity, but since rings *B* and *C* are displaced in the same direction, interactions between atoms 8 and 11 would not be reduced. However, the distance between atoms 8 and 11 seems to be increased, in comparison with a planar configuration, by a slightly greater displacement of ring *C*; in addition bond 9–10 is slightly, though only just significantly, longer than corresponding chemically equivalent bonds in the other positions. The distances between atoms 2 and 5, 8 and 11, 14 and 17 are $2{\cdot}93_6$, $2{\cdot}91_0$, and $2{\cdot}92_2$ Å respectively, so that the observed distortions from a planar molecule relieve intramolecular overcrowding about equally in all three regions. Such distortions, however, are not observed in biphenyl (Trotter, 1961) where similar steric interferences are present (except that the central bond is rather longer than bonds such as 9–10 in triphenylene), and where the molecule might be expected to distort more easily. Also, a slight twisting of each of the outside rings in triphenylene might be the expected distortion, since this would give a more symmetrical relief of the steric strain.

Table 6. *Shortest intermolecular contacts* (Å) *between carbon atoms*

I molecule at	x,	y,	z
II molecule at	x,	y,	$1+z$
III molecule at	$1\frac{1}{2}-x$,	$1-y$,	$-\frac{1}{2}+z$
IV molecule at	$-\frac{1}{2}+x$,	$1\frac{1}{2}-y$,	$-z$

$I_{18}\cdots II_{15}$	3·42	$I_{2}\cdots II_{8}$	3·56
$I_{16}\cdots II_{11}$	3·45	$I_{17}\cdots II_{10}$	3·57
$I_{2}\cdots II_{9}$	3·47	$I_{3}\cdots II_{8}$	3·58
$I_{1}\cdots II_{4}$	3·53	$I_{11}\cdots III_{7}$	3·60
$I_{1}\cdots II_{9}$	3·53	$I_{1}\cdots IV_{7}$	3·61
$I_{18}\cdots II_{10}$	3·53	$I_{1}\cdots IV_{6}$	3·64
$I_{17}\cdots II_{11}$	3·53	$I_{17}\cdots II_{12}$	3·67

All the intermolecular C–C and C–H distances correspond to normal van der Waals interactions; the C–C approaches which are less than 3·7 Å are listed in Table 6. The perpendicular distance between molecules I and II which are related by translation *c* (see Table 6) is 3·37 Å, and the shortest intermolecular C–C separation in the structure is 3·42 Å between atoms 18 and 15 of molecules I and II, respectively. All but one (I_{11} to III_7) of the fourteen shortest contacts listed in Table 6 are between atoms 1, 2, 3, 16, 17, and 18 of ring *A* in molecule I, and atoms 4, 6, 7, 8, 9, 10, 11, 12, and 15 of rings *B* and *C* in the neighbouring molecules II and IV. In fact, the van der Waals interactions between atoms of ring *A* and of rings *B* and *C* of the neighbouring molecules are relieved somewhat by the observed displacement of atoms 1, 2, 17, and 18 of ring *A* in the opposite direction to the displacement of atoms 5, 6, 7, 8, 11, 12, 13, and 14 of rings *B* and *C* of the same molecule. However, the non-planarity could scarcely be due to these approaches alone, for any strain introduced by these contacts could more readily be relieved by a slight reorientation of the whole molecule.



8 1

Fig. 3. Kekulé structures for triphenylene.

The measured C–C bond distances (Fig. 2(*a*)) fall into three distinct ranges: bonds of type *a* (Fig. 2(*c*)) have lengths in the range 1·431–1·465 Å, types *b*, *c*, and *e* (except bond 6–7) are in the range 1·402–1·434 Å, and type *d* is in the range 1·356–1·397 Å. Some of the differences between chemically equivalent bonds and angles are in the possibly significant region, and may be real, and a consequence of the slight molecular distortion described earlier. However, for comparison with theoretical values, the measured bond lengths which are chemically equivalent have been averaged according to their e.s.d.'s assuming D_{3h} symmetry, and their weighted means are listed in Table 7. Their standard deviations σ_m as calculated from internal estimate of the experimental errors (Cruickshank, 1949), and σ'_m as derived directly from the deviations between the measured values and the means, are also given in Table 7. Both σ_m and σ'_m are nearly equal for bond types *b*, *c*, *d*, and *e*, but σ'_m is slightly higher than σ_m for type *a* due to the possibly significant elongation of bond 9–10. For comparison with these measured mean distances, the theoretical bond lengths have been calculated from the nine non-excited valence bond structures illustrated in Fig. 3, and from the LCAO bond orders (*Dictionary of Values of Molecular Constants*, 1955) and the usual correlation curves, and are given in Table 7. The general variation of the measured distances is well reproduced in both sets of calculated values, and the individual agreements are also extremely good, particularly for the molecular orbital method.

Table 7. *Measured and calculated mean bond lengths* (Å)

Bond (Fig. 2(*c*))	Measured			Calculated	
	l_m	σ_m	σ_m'	Kekulé	M.O.
a	1·447	0·006	0·010	1·466	1·440
b	1·415	0·006	0·003	1·401	1·416
c	1·416	0·004	0·005	1·401	1·409
d	1·377	0·005	0·006	1·386	1·393
e	1·402	0·007	0·007	1·401	1·403

The hydrogen atom positions have been determined rather imprecisely, so that the variations in the C–H bond distances are not significant. The mean value for the C–H length is 1·11 Å.

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