Acta Cryst. (1966). **20**, 87

A Refinement of the Structure of Biphenylene

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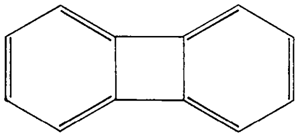
(*Received* 13 *May* 1965)

Crystals of biphenylene, $C_{12}H_8$, are monoclinic, $a=19{\cdot}72_8$, $b=10{\cdot}57_8$, $c=5{\cdot}86_1$ Å, $\beta=91°\ 10'$, $Z=6$, space group $P2_1/a$. The intensities of the reflexions were measured with a scintillation counter and Cu $K\alpha$ radiation, and the positional and thermal parameters of the carbon and hydrogen atoms were refined by least squares, the final R value being 0·062 for 2316 observed reflexions. The anisotropic thermal parameters of the carbon atoms were interpreted in terms of rigid-body vibrations, and the measured bond lengths were then corrected for rotational oscillation effects. The bonds joining the six-membered rings measure 1·514 ± 0·003 Å, and the bonds in the six-membered rings, starting with the bond in the four-membered ring, measure 1·426 ± 0·003, 1·372 ± 0·002, 1·423 ± 0·003, and 1·385 ± 0·004 Å. These dimensions reinforce the conclusion that the molecule must be considered as a cyclobutane derivative. The angles in the four-membered ring are all 90°, but those in the six-membered rings show significant deviations from 120°. The mean C–H distance is 1·06 ± 0·02 Å. The molecule which is situated at a centre of symmetry is completely planar; the other molecule is slightly non-planar as a result of crystal packing forces. All the intermolecular C · · · C, C · · · H, and H · · · H contacts correspond to van der Waals interactions.

Introduction

The chemical properties of biphenylene indicate that the molecule must be considered a derivative of cyclobutane (Baker, McOmie, Preston & Rogers, 1960), the preferred Kekulé structure being (I). The same conclusion is suggested by the molecular dimensions determined by X-ray analysis (Waser & Lu, 1944; Mak & Trotter, 1962), but the accuracy of bond length measurement was not very high, as facilities were not available for a three-dimensional refinement. The present paper describes an analysis based on new three-dimensional data.



(I)

Experimental

The unit cell parameters were remeasured, a^* and b^* being determined from least-squares treatment of 50 $hk0$ reflexions measured on a Weissenberg film, β from an $h0l$ precession film, and c from a number of rotation, oscillation, and precession films.

Crystal data (λ(Cu $K\alpha$) = 1·5418 Å, λ(Cu $K\alpha_1$) = 1·54051 Å, λ(Cu $K\alpha_2$) = 1·54433 Å, λ(Mo $K\alpha$) = 0·7107 Å).
Biphenylene, $C_{12}H_8$; $M=152{\cdot}2$; m.p. 110 °C.
Monoclinic, $a=19{\cdot}72_8 \pm 0{\cdot}010$, $b=10{\cdot}57_8 \pm 0{\cdot}006$, $c=5{\cdot}86_1 \pm 0{\cdot}011$ Å, $\beta=91°\ 10' \pm 3'$ (errors are 2σ).
$U=1222{\cdot}8$ Å^3.
$D_m=1{\cdot}24$, $Z=6$, $D_x=1{\cdot}242$ g.cm^{-3}.
$F(000)=480$.
Space group $P2_1/a$ (C_{2h}^5).

An initial set of intensity data was recorded on hkL Weissenberg films ($L=0 \rightarrow 4$), estimated visually, and the structure amplitudes were derived as usual, 818 reflexions being observed. Refinement of the structure with these data gave rather unsatisfactory results, and a more extensive and more accurate set of intensities was therefore measured with counter equipment. The intensities of all reflexions with 2θ(Cu $K\alpha$) $\leq 148°$ (corresponding to a minimum interplanar spacing $d=0{\cdot}80$ Å) were measured on a General Electric XRD-5 Spectrogoniometer with single-crystal orienter, scintillation counter, approximately monochromatic Cu $K\alpha$ radiation (nickel filter and pulse height analyser), and the moving-crystal moving-counter technique. All the intensities were corrected for background, Lorentz and polarization factors were applied and the structure amplitudes were derived. The crystal was mounted with c^* parallel to the φ axis of the goniostat, and had dimensions 0·18, 0·10, 0·80 mm parallel to **a**, **b**, **c** respectively; absorption was low and no corrections were applied. Of 2463 reflexions in the range $0 < 2\theta \leq 148°$, 2316 (94%) had measurable intensities.

Refinement of the structure

Starting with the parameters of Mak & Trotter (1962), the positional and thermal parameters and a scale factor were refined, using the visual data, by six cycles of (block-diagonal) least-squares, anisotropic temperature factors being used in the final three cycles. Contributions from the hydrogen atoms were included in the structure factor calculations, by assuming that they lay on the ring diagonals with C–H = 1·08 Å, but the hydrogen parameters were not refined. The scattering factors of *International Tables for X-ray Crystallography* (Vol. III) for carbon and hydrogen were used. The function minimized was $\Sigma w(F_o-F_c)^2$, with $\sqrt{w}=|F_o|/30$ when $|F_o|<30$, and $\sqrt{w}=30/|F_o|$ when $|F_o| \geq 30$,

Table 1. *Measured and calculated structure factors*

Each group of three columns contains *h*, 10 F_o, and 10 F_c; unobserved reflexions, for which 10 F_o is listed as 0, have threshold values in the range 6–9.

HKO		
K= 0		
2	96	94
4	62	55
6	-515	-508
8	0	-0
10	54	53
12	-298	-285
14	-28	-29
16	38	41
18	-341	-357
20	-87	-92
22	-55	-57
24	124	121
K= 1		
1	-25	-23
2	19	17
3	507	509
4	32	30
5	18	18
6	-504	-489
7	-24	-25
8	-31	-31
9	-64	-57
10	-13	-11
11	-8	-1
12	-9	-10
13	9	6
14	-18	-19
15	-18	-20
16	-37	-39
17	-25	-21
18	134	141
19	63	64
20	28	26
21	-219	-230
22	18	19
23	-18	-22
24	-27	-29
K= 2		
0	906	1009
1	11	10
2	-107	-96
3	1220	1396
4	35	32
5	61	56
6	29	34
7	-10	-2
8	-22	-19
9	332	327
10	44	46
11	48	48
12	-129	-119
13	25	25
14	-20	-20
15	-30	-29
16	18	15
17	25	23
18	-150	-157
19	41	42
20	-10	-7
21	-185	-189
22	17	14
23	-43	-46
24	-38	-38
K= 3		
1	7	1
2	-126	-117
3	963	1033
4	32	31
5	68	70
6	37	36
7	35	33
8	64	62
9	-360	-345
10	-33	-32
11	-20	-17
12	117	118
13	37	41
14	23	23
15	-201	-206
16	-20	-18
17	-55	-59
18	20	20
19	-9	-10
20	0	4
21	-61	-68
22	18	20
23	0	-7
K= 4		
0	105	100
1	-7	-12
2	14	15
3	-218	-198
4	-77	-68
5	-28	-27
6	-19	-13
7	-52	-48
8	-38	-31
9	300	290
10	12	10
11	8	3
12	149	147
13	27	29
14	21	24
15	-57	-62
16	17	11
17	-12	-15
18	-60	-69
19	-8	-15
20	0	-8
21	0	4
22	32	32
23	22	21
K= 5		
1	8	5
2	-31	-30
3	236	223
4	17	18
5	-70	-67
6	341	322
7	33	20
8	59	49
9	-134	-122
10	-18	-13
11	-9	-7
12	94	92
13	9	1
14	11	9
15	48	61
16	31	34
17	15	13
18	-84	-84
19	9	5
20	0	-3
21	-75	-76
22	0	-4
K= 6		
0	478	471
1	75	74
2	21	24
3	26	25
4	9	17
5	41	37
6	-326	-294
7	-74	-67
8	-30	-29
9	-14	-2
10	-22	-20
11	-29	-31
12	169	177
13	13	20
14	21	24
15	20	18
16	19	23
17	9	32
18	-122	-129
19	-8	-7
20	-28	-30
21	-10	-11
K= 7		
1	-25	-23
2	-20	-17
3	42	41
4	10	3
5	9	5
6	-11	-14
7	0	3
8	0	-1
9	-59	-60
10	-18	-15
11	10	12
12	-52	-76
13	-20	-22
14	-25	-25
15	70	70
16	-8	-4
17	0	-3
18	28	32
19	17	18
20	0	14
K= 8		
0	36	40
1	0	-1
2	-15	-14
3	81	73
4	24	22
5	12	13
6	-31	-36
7	0	3
8	29	31
9	-116	-208
10	-41	-47
11	-51	-56
12	71	85
13	0	3
14	-20	-21
15	92	96
16	10	11
17	16	18
18	-8	-9
19	6	3
K= 9		
1	8	14
2	-41	-41
3	49	53
4	-16	-12
5	-10	-16
6	-20	-11
7	8	11
8	11	9
9	-20	-8
10	17	10
11	12	14
12	-71	-75
13	0	-10
14	0	-3
15	-7	-9
16	0	-6
17	0	0
K=10		
0	154	164
1	30	33
2	50	50
3	-134	-136
4	-38	-37
5	-19	-17
6	18	16
7	8	3
8	37	37
9	-117	-124
10	-15	-17
11	9	11
12	-83	-87
13	-16	-18
14	-16	-20
15	-15	-9
K=11		
1	27	24
2	13	11
3	32	29
4	0	-2
5	0	1
6	-99	-102
7	-24	-28
8	-21	-24
9	0	10
10	12	13
11	7	11
12	-41	-43
13	0	-1
K=12		
0	228	233
1	74	76
2	14	8
3	21	22
4	13	14
5	12	17
6	-31	-34
7	-11	-11
8	-5	-8
9	-28	-28
10	-5	-0
K=13		
1	6	0
2	-16	-18
3	101	103
HK1		
K= 0		
-24	41	40
-22	-32	-35
-20	-57	-57
-18	-154	-144
-16	-147	-138
-14	38	36
-12	74	58
-10	43	30
-8	10	2
-6	316	305
-4	213	193
-2	-74	-64
0	-378	-350
2	584	560
4	216	201
6	-433	-420
8	29	29
10	58	49
12	59	54
14	-133	-123
16	-117	-114
18	290	277
20	-78	-81
22	-24	-29
24	-78	-81
K= 1		
-24	-11	-9
-23	45	42
-22	117	111
-21	39	39
-20	22	15
-19	-123	-121
-18	-62	-61
-17	-103	-100
-16	-33	-40
-15	73	67
-14	43	39
-13	-315	-292
-12	252	232
-11	-100	-100
-10	-109	-101
-9	-223	-200
-8	-189	-192
-7	214	196
-6	-260	-252
-5	103	97
-4	-533	-528
-3	-941	-958
-2	-255	-244
-1	860	854
0	-346	-311
1	487	462
2	645	626
3	702	685
4	393	382
5	356	340
6	-215	-205
7	49	41
8	35	31
9	232	217
10	6	0
11	-153	-162
12	267	255
13	-130	-119
14	51	57
15	66	75
16	33	36
17	-201	-203
18	-37	-34
19	-48	-51
20	-67	-65
21	-85	-84
22	-51	-52
23	15	7
24	-50	-49
K= 2		
-24	73	71
-23	13	10
-22	-47	-50
-21	20	12
-20	20	17
-19	29	30
-18	-77	-77
-17	-103	-103
-16	-199	-191
-15	-130	-124
-14	-135	-133
-13	-69	-55
-12	57	55
-11	71	64
-10	-107	-105
-9	-257	-255
-8	28	22
-7	116	113
-6	-446	-442
-5	-79	-72
-4	888	919
-3	791	821
-2	-30	-24
-1	-321	-303
0	63	53
1	94	86
2	144	135
3	411	390
4	583	574
5	334	326
6	286	284
7	-56	-53
8	121	105
9	-283	-283
10	-97	-98
11	-23	-34
12	73	70
13	90	84
14	-240	-244
15	-190	-193
16	-111	-109
17	47	48
18	70	73
19	-32	-29
20	14	12
21	96	93
22	-8	-11
23	-28	-34
K= 3		
-23	8	31
-22	40	38
-21	43	44
-20	23	20
-19	72	69
-18	-45	-48
-17	-79	-79
-16	52	52
-15	-163	-157
-14	-53	-52
-13	-155	-159
-12	76	62
-11	84	82
-10	-127	-108
-9	301	299
-8	-109	-107
-7	336	318
-6	237	234
-5	18	2
-4	-396	-402
-3	-624	-620
-2	71	72
-1	-328	-309
0	-257	-250
1	-167	-158
2	-146	-137
3	293	273
4	237	233
5	492	470
6	34	15
7	243	228
8	263	262
9	-252	-247
10	18	8
11	-124	-110
12	50	35
13	-103	-105
14	59	70
15	297	296
16	10	6
17	-41	-37
18	-8	-0
19	41	40
20	-66	-63
21	-12	-12
22	-7	-11
23	-27	-29
K= 4		
-23	-6	-3
-22	-45	-43
-21	19	20
-20	32	31
-19	88	82
-18	19	10
-17	24	16
-16	-35	-24
-15	-67	-71
-14	-126	-121
-13	-102	-110
-12	24	19
-11	-55	-55
-10	-114	-98
-9	0	3
-8	47	36
-7	-432	-432
-6	-691	-698
-5	-134	-134
-4	291	278
-3	60	52
-2	-99	-37
-1	287	268
0	107	98
1	-117	-105
2	-135	-117
3	96	94
4	172	162
5	198	188
6	439	432
7	269	263
8	205	199
9	-13	-4
10	-68	-56
11	110	109
12	77	81
13	66	74
14	-154	-151
15	-28	-41
16	15	14
17	-99	-101
18	-46	-49
19	-59	-60
20	0	0
21	0	-5
22	-12	-15
23	11	13
K= 5		
-22	-22	-23
-21	18	18
-20	0	7
-19	-58	-62
-18	-17	-19
-17	-15	-15
-16	100	105
-15	-88	-95
-14	-70	-72
-13	-32	-24
-12	-152	-148
-11	-34	-34
-10	-101	-93
-9	-77	-77
-8	-36	-36
-7	228	205
-6	308	302
-5	-171	-171
-4	50	50
-3	-142	-143
-2	59	61
-1	162	171
0	82	92
1	117	120
2	-207	-201
3	232	234
4	28	30
5	-201	-214
6	22	5
7	121	110
8	232	210
9	24	25
10	65	64
11	-9	-7
12	-193	-196
13	-45	-39
14	-12	-9
15	99	107
16	-38	-39
17	17	22
18	25	19
19	-20	-24
20	0	0
21	-32	-42
22	5	4
K= 6		
-21	-19	-17
-20	0	3
-19	-8	-9
-18	15	17
-17	-9	-12
-16	76	77
-15	0	-12
-14	-20	-24
-13	43	52
-12	-29	-8
-11	-33	-31
-10	99	90
-9	109	99
-8	-9	-8
-7	-47	-29
-6	-266	-251
-5	-16	-3
-4	-199	-183
-3	-54	-49
-2	-33	-29
-1	-83	-79
0	-92	-38
1	58	52
2	-16	-15
3	-12	-4
4	-43	-40
5	-82	-84
6	242	232
7	23	13
8	86	82
9	-8	-4
10	36	33
11	93	95
12	48	47
13	-8	-11
14	35	43
15	-8	-4
16	55	59
17	-8	-3
18	45	46
19	17	20
20	-35	-38
21	-7	-10
K= 7		
-20	-14	-13
-19	-20	-15
-18	-7	-6
-17	-7	-2
-16	-30	-29
-15	-64	-66
-14	0	-6
-13	61	68
-12	-19	-22
-11	-10	-8
-10	-42	-38
-9	-144	-129
-8	20	17
-7	62	63
-6	-8	-13
-5	-109	-107
-4	-61	-54
-3	-144	-133
-2	-107	-100
-1	-47	-46
0	94	90
1	-19	-23
2	196	188
3	244	234
4	83	74
5	-107	-99
6	20	20
7	64	68
8	-65	-70
9	11	42
10	12	3
11	46	47
12	-17	-13
13	38	42
14	-42	-43
15	38	42
16	31	32
17	0	2
18	-9	-5
19	0	-1
20	-7	-3
K= 8		
-19	-5	-0
-18	-30	-30
-17	-7	-4
-16	-40	-38
-15	0	12
-14	-52	-52
-13	39	39
-12	-33	-36
-11	10	12
-10	36	35
-9	55	55
-8	-36	-28
-7	158	153
-6	-136	-133
-5	-50	-54
-4	134	132
-3	44	43
-2	-59	-55
-1	-106	-106
0	0	6
1	77	81
2	-76	-72
3	-108	-105
4	92	92
5	-74	-77
6	168	167
7	-25	-27
8	-39	-39
9	49	56
10	0	6
11	-37	-39
12	11	14
13	-26	-25
14	-27	-25
15	-21	-21
16	-14	-11
17	38	42
18	10	8
19	8	7
K= 9		
-17	-27	-27
-16	-6	-4
-15	-39	-39
-14	-7	-6
-13	0	-7
-12	-41	-44
-11	-37	-38
-10	85	85
-9	-8	-1
-8	53	55
-7	83	83
-6	10	3
-5	-22	-24
-4	121	129
-3	-186	-189
-2	12	8
-1	-158	-157
0	10	12
1	-20	-12
2	-88	-78
3	175	175
4	-49	-54
5	84	85
6	52	49
7	68	70
8	-79	-81
9	0	2
10	-45	-45
11	0	3
12	-42	-46
13	-28	-32
14	-17	-19
15	54	53
16	22	24
17	6	1
K=10		
-15	0	4
-14	-13	-17
-13	6	10
-12	-15	-12
-11	0	-2
-10	0	-8
-9	14	11
-8	16	21
-7	28	28
-6	-57	-52
-5	10	4
-4	115	117
-3	-24	-25
-2	-87	-92
-1	73	76
0	67	67
1	-21	-16
2	-37	-38
3	-29	-28
4	65	68
5	-61	-59
6	-8	-14
7	-11	-15
8	9	13
9	62	65
10	28	26
11	-34	-34
12	36	37
13	0	-4
14	-54	-55
15	0	1
K=11		
-13	-40	-44
-12	-22	-22
-11	-45	-45
-10	33	34
-9	-49	-47
-8	0	-6
-7	37	38
-6	55	55
-5	-12	-7
-4	138	135
-3	-84	-83
-2	-27	-29
-1	106	109
0	-75	-73
1	74	72
2	-114	-115
3	86	88
4	-11	-4
5	-12	-9
6	64	67
7	30	31
8	-49	-49
9	50	47
10	0	6
11	-30	-32
12	-9	-7
K=12		
-9	-19	-17
-8	-31	-28
-7	45	44
-6	-14	-14
-5	40	40
-4	28	26
-3	6	9
-2	14	11
-1	40	39
0	-14	-11
1	-27	-26
2	42	38
3	66	67
4	56	62
5	-60	-62
6	7	2
7	-41	-41
8	0	-2
9	-22	-24
K=13		
-1	84	82
0	-25	-24
1	-7	-1
HK2		
K= 0		
-22	-68	-69
-20	31	30
-18	-35	-32
-16	172	166
-14	-90	-87
-12	0	-2
-10	-563	-535
-8	-67	-68
-6	116	107
-4	559	552
-2	119	198
0	10	4
2	-493	-465
4	150	136
6	77	66
8	528	510
10	55	63
12	45	46
14	-35	-34
16	-117	-111
18	-59	-60
20	-35	-31
22	16	19
K= 1		
-23	15	14
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7	143	138
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6	326	323
7	202	213
8	91	96
9	94	96
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8	19	19
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-10	-86	-84
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-8	-163	-154
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8	52	54
9	17	9
10	22	17
11	47	48
12	59	57
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14	23	23
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3	146	139
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Table 1 (*cont.*)

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4	152	140
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11	195	202
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7	57	58
8	43	43
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-1	46	48
0	0	-0
1	-102	-103
2	90	90
3	133	134
4	-164	-162
5	76	76
6	-58	-58
7	132	146
8	-215	-218
9	-71	-70
10	62	69
11	58	66
12	-69	-69
13	29	28
14	-20	-16
15	-35	-32
16	42	45
17	-99	-101
18	42	46
19	-24	-24
K= 3		
-20	0	3
-19	0	-9
-18	-54	-55
-17	62	65
-16	-80	-75
-15	-102	-102
-14	67	66
-13	14	8
-12	-18	-11
-11	-89	-81
-10	-67	-64
-9	210	215
-8	-15	-9
-7	52	52
-6	59	59
-5	-116	-123
-4	136	143
-3	-74	-73
-2	-114	-125
-1	-29	-28
0	30	24
1	-65	-60
2	93	96
3	53	52
4	-52	-50
5	114	116
6	40	37
7	83	87
8	-70	-70
9	-146	-147
10	86	100
11	-200	-209
12	11	1
13	11	1
14	-65	-64
15	61	62
16	26	26
17	57	64
18	-14	-15
19	8	12
K= 4		
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-18	0	-1
-17	-38	-39
-16	-53	-54
-15	-69	-68
-14	105	103
-13	-85	-86
-12	61	62
-11	-18	-19
-10	183	184
-9	20	21
-8	-96	-82
-7	91	88
-6	-52	-56
-5	-28	-28
-4	-101	-96
-3	29	33
-2	-108	-119
-1	8	1
0	-44	-46
1	82	88
2	80	73
3	88	94
4	-136	-125
5	134	128
6	60	61
7	-24	-29
8	-120	-123
9	-10	-7
10	106	110
11	-70	-72
12	-28	-30
13	-12	-8
14	63	63
15	-37	-38
16	28	30
17	-40	-40
18	17	16
K= 5		
-18	-6	-1
-17	32	36
-16	0	-6
-15	-14	-18
-14	31	30
-13	34	36
-12	-107	-105
-11	42	41
-10	-33	-37
-9	17	17
-8	-48	-42
-7	-58	-51
-6	72	62
-5	45	63
-4	87	84
-3	-8	-0
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-1	12	15
0	12	20
1	-238	-248
2	-46	-36
3	-8	-3
4	0	12
5	76	73
6	92	90
7	-60	-52
8	62	62
9	-42	-41
10	92	91
11	-78	-72
12	-68	-66
13	62	62
14	-78	-78
15	16	14
16	22	19
17	-10	-8
18	-12	-2
K= 6		
-17	20	19
-16	0	1
-15	-21	-20
-14	0	-5
-13	-46	-42
-12	10	9
-11	41	40
-10	0	5
-9	26	27
-8	-17	-16
-7	35	31
-6	-37	-36
-5	-82	-82
-4	-46	-48
-3	19	22
-2	-161	-170
-1	-21	-3
0	-33	-32
1	-32	-40
2	-8	-6
3	0	-15
4	0	10
5	24	14
6	37	39
7	25	30
8	45	46
9	0	5
10	52	44
11	0	-38
12	-7	-0
13	63	61
14	15	13
15	13	15
16	15	15
K= 7		
-16	15	11
-15	8	7
-14	-45	-48
-13	0	-0
-12	23	24
-11	24	24
-10	24	24
-9	0	-0
-8	-35	-38
-7	-64	-64
-6	-56	-61
-5	0	-6
-4	-36	-37
-3	-54	-66
-2	101	109
-1	48	45
0	54	68
1	-144	-155
2	-12	-4
3	0	3
4	-20	-19
5	60	61
6	11	4
7	-16	-11
8	14	9
9	22	22
10	-21	-27
11	-36	-32
12	-8	-5
13	30	29
14	0	6
15	20	25
K= 8		
-14	43	48
-13	20	23
-12	17	15
-11	-40	-34
-10	45	46
-9	0	34
-8	0	70
-7	16	19
-6	-39	-42
-5	19	13
-4	-74	-75
-3	-47	-43
-2	-93	-93
-1	-12	-8
0	15	18
1	-44	-68
2	63	68
3	-13	-5
4	-123	-132
5	-106	-111
6	-9	-11
7	39	43
8	-20	-25
9	0	1
10	24	23
11	23	23
12	-28	-25
13	21	17
K= 9		
-12	9	12
-11	-13	-14
-10	11	11
-9	63	61
-8	-13	-14
-7	14	13
-6	7	8
-5	-54	-58
-4	-81	-77
-3	-109	-110
-2	0	-2
-1	-43	-48
0	-30	-31
1	-39	-41
2	-64	-65
3	40	39
4	7	9
5	60	62
6	-11	-13
7	15	16
8	52	50
9	-16	-14
10	26	22
11	-29	-28
K=10		
-8	-16	-14
-7	34	33
-6	33	30
-5	31	50
-4	-11	-10
-3	-59	-60
-2	-70	-24
-1	-80	-79
0	-27	-32
1	38	42
2	101	104
3	15	18
4	-67	-69
5	-10	-11
6	-17	-14
7	-31	-35
8	-71	-71
K=11		
0	-68	-61
HK5		
K= 0		
-18	72	74
-16	-25	-22
-14	131	134
-12	0	4
-10	8	14
-8	155	160
-6	70	73
-4	173	177
-2	265	262
0	-315	-313
2	-82	-79
4	-384	-389
6	118	115
8	-47	-51
10	-81	-83
12	29	31
14	-45	-47
16	-51	-53
K= 1		
-18	81	82
-17	29	28
-16	-9	-0
-15	-87	-89
-14	0	-0
-13	28	26
-12	-15	-13
-11	72	70
-10	28	30
-9	-61	-60
-8	-29	-26
-7	64	61
-6	-94	-102
-5	203	211
-4	35	33
-3	-25	-2
-2	18	14
-1	-104	-100
0	-27	-20
1	-38	-42
2	-93	-96
3	77	82
4	18	8
5	63	65
6	83	100
7	-165	-164
8	16	15
9	-21	-24
10	19	13
11	10	2
12	18	12
13	-63	-65
14	36	37
15	-51	-54
16	0	-1
17	-16	-19
K= 2		
-17	-87	-93
-16	-11	-2
-15	0	0
-14	50	50
-13	-23	-23
-12	-46	-45
-11	-19	-20
-10	31	31
-9	24	28
-8	140	149
-7	-71	-70
-6	-19	-23
-5	0	8
-4	12	5
-3	154	156
-2	121	119
-1	109	112
0	-51	-13
1	216	214
2	-18	-6
3	-151	-151
4	-179	-180
5	26	26
6	61	56
7	-71	-67
8	18	13
9	-24	-25
10	-90	-91
11	-28	-29
12	-25	-26
13	-41	-39
14	-22	-24
15	20	23
16	-23	-20
17	-42	-44
K= 3		
-17	33	33
-16	-25	-24
-15	32	31
-14	-44	-45
-13	-18	-14
-12	20	18
-11	80	79
-10	13	17
-9	42	45
-8	-17	-15
-7	64	70
-6	-37	-46
-5	152	163
-4	52	51
-3	-100	-101
-2	61	67
-1	27	32
0	-32	-26
1	-54	-60
2	-35	-31
3	-62	-63
4	65	69
5	-46	-50
6	58	58
7	-153	-156
8	-9	-2
9	54	54
10	-8	-6
11	-30	-34
12	0	-3
13	-38	-38
14	17	17
15	23	22
16	-35	-38
K= 4		
-16	21	18
-15	-6	-6
-14	17	17
-13	-13	-10
-12	-54	-58
-11	-79	-77
-10	19	15
-9	29	32
-8	35	36
-7	19	21
-6	-32	-31
-5	57	70
-4	-27	-22
-3	-74	-87
-2	38	45
-1	-12	-17
0	41	50
1	58	51
2	-16	-17
3	31	39
4	-47	-52
5	10	13
6	22	21
7	27	34
8	53	55
9	8	5
10	-20	-22
11	0	-2
12	-43	-47
13	-68	-72
14	-18	-20
15	12	9
K= 5		
-15	-46	-47
-14	-43	-48
-13	-39	-41
-12	25	25
-11	-8	-6
-10	-14	-14
-9	39	38
-8	-13	-9
-7	30	33
-6	31	31
-5	70	69
-4	0	6
-3	-32	-36
-2	73	81
-1	-15	-13
0	-12	-7
1	-47	-56
2	34	37
3	-11	-13
4	43	44
5	13	20
6	-21	-24
7	-39	-32
8	-19	-18
9	37	35
10	-29	-26
11	-16	-20
12	-11	-10
13	10	7
14	-8	-5
K= 6		
-14	56	58
-13	14	13
-12	-56	-57
-11	-22	-20
-10	-11	-13
-9	16	10
-8	-49	-52
-7	-12	-11
-6	77	78
-5	8	3
-4	27	29
-3	-32	-31
-2	90	94
-1	28	30
0	-90	-95
1	20	21
2	-45	-48
3	0	4
4	-99	-103
5	-36	-35
6	61	58
7	8	7
8	40	41
9	11	16
10	59	64
11	27	27
12	-32	-32
13	-6	-7
K= 7		
-12	-34	-34
-11	-23	-25
-10	-24	-26
-9	34	33
-8	-18	-4
-7	28	28
-6	14	13
-5	13	14
-4	12	17
-3	-23	-24
-2	-7	-6
-1	-28	-25
0	-11	-10
1	-12	-11
2	-20	-21
3	0	0
4	-34	-36
5	14	9
6	0	-1
7	-7	-4
8	7	7
9	19	19
10	6	0
11	-21	-18
K= 8		
-10	14	15
-9	-41	-43
-8	-20	-24
-7	-14	-12
-6	31	27
-5	-65	-64
-4	-27	-30
-3	28	25
-2	12	10
-1	0	2
0	0	-3
1	9	11
2	0	1
3	-22	-20
4	-26	-24
5	-41	-42
6	16	5
7	-51	-49
8	0	1
9	34	32
K= 9		
-6	41	38
-5	45	51
-4	8	9
-3	-5	-0
-2	-52	-50
-1	-10	-12
0	-10	-9
1	-12	-7
2	0	6
3	8	5
4	-34	-31
5	0	-2
HK6		
K= 0		
-14	6	0
-12	76	78
-10	-7	-0
-8	-48	-55
-6	20	16
-4	66	67
-2	20	21
0	-20	-3
2	-38	-37
4	55	55
6	-22	-18
8	-28	-28
10	28	20
12	-49	-49
K= 1		
-14	7	4
-13	8	2
-12	-68	-71
-11	-17	-19
-10	-13	-4
-9	139	148
-8	-17	-21
-7	-17	-13
-6	8	5
-5	-8	-0
-4	17	16
-3	130	133
-2	64	72
-1	49	50
0	120	130
1	87	84
2	-23	-22
3	-153	-155
4	-38	-41
5	-20	-19
6	0	-0
7	-11	-8
8	22	24
9	-107	-108
10	19	19
11	-28	-32
12	-53	-53
13	-9	-0
K= 2		
-13	-7	-1
-12	45	49
-11	13	15
-10	-8	-1
-9	45	49
-8	-39	-41
-7	-8	-3
-6	120	127
-5	40	38
-4	0	5
-3	-49	-53
-2	75	80
-1	59	62
0	-56	-53
1	-59	-59
2	32	32
3	12	7
4	-13	-13
5	-29	-32
6	-70	-76
7	0	-20
8	-38	-40
9	30	32
10	14	12
11	-13	-10
12	-53	-52
13	-8	-1
K= 3		
-13	33	32
-12	-86	-89
-11	-9	-5
-10	14	13
-9	20	21
-8	24	24
-7	-25	-27
-6	0	2
-5	-70	-88
-4	-7	-3
-3	-12	-13
-2	-31	-32
-1	79	80
0	108	115
1	167	173
2	34	34
3	-14	-3
4	-10	-7
5	-55	-58
6	36	36
7	-46	-48
8	-8	-4
9	-8	-10
10	10	6
11	10	9
12	-56	-60
K= 4		
-12	7	2
-11	27	27
-10	-17	-14
-9	-36	-38
-8	-58	-58
-7	38	33
-6	109	114
-5	27	29
-4	15	14
-3	74	80
-2	110	120
-1	-7	-2
0	-60	-62
1	24	24
2	57	59
3	35	42
4	24	22
5	13	13
6	-48	-52
7	-62	-63
8	-35	-36
9	-7	-3
10	-14	-12
11	-19	-17
K= 5		
-10	34	33
-9	-5	-3
-8	59	61
-7	-7	-1
-6	-7	-5
-5	38	39
-4	-13	-7
-3	-34	-34
-2	-74	-75
-1	24	20
0	9	7
1	56	52
2	41	41
3	-35	-29
4	13	14
5	10	10
6	32	35
7	-27	-25
8	-36	-36
9	37	35
K= 6		
-8	-40	-43
-7	-10	-7
-6	-26	-28
-5	-20	-17
-4	51	47
-3	35	39
-2	67	68
-1	15	14
0	-12	-10
1	-7	-7
2	21	20
3	12	17
4	70	71
5	17	16
6	8	4
7	-6	-2
K= 7		
-5	41	39
-4	22	23
-3	-33	-31
-2	31	34
-1	44	43
0	-12	-9
1	60	61
2	-14	-13
3	-24	-22
4	-23	-27
HK7		
K= 0		
-6	62	70
-4	-43	-40
-2	-16	-14
0	0	-5
2	26	25
4	22	21
6	58	67
K= 1		
-7	15	17
-6	23	27
-5	-12	-12
-4	-11	-11
-3	18	13
-2	9	8
-1	-6	-3
0	-7	-3
1	21	22
2	14	15
3	-20	-19
4	-5	-4
5	8	3
6	-43	-49
K= 2		
-6	10	0
-5	22	25
-4	-23	-20
-3	29	29
-2	-28	-29
-1	5	11
0	46	54
1	17	19
2	43	48
3	-38	-39
4	19	18
5	27	24
K= 3		
-4	28	31
-3	56	62
-2	19	24
-1	-28	-29
0	0	-5
1	28	33
2	29	36
3	31	38

and during the refinement process R, for the 818 observed reflexions, was reduced from 0·262 to 0·156. The differences between chemically equivalent bond lengths and valency angles at the end of this refinement, while much smaller than in the previous analysis (Mak & Trotter, 1962), were still large enough (maximum differences 0·06 Å and 9°) to suggest that the results were of limited accuracy. A more accurate set of data was therefore collected by counter methods, and the whole refinement was repeated. Since the intensity measurements were reliable for all but the very weak reflexions, the weighting scheme used was $\sqrt{w}=|F_o|/3$ when $|F_o|<3$, and $\sqrt{w}=1$ when $|F_o|\geq 3$. The initial parameters were the final positional parameters of the refinement with visual data, with an overall isotropic thermal parameter $B=4\cdot5$ Å^2; the parameters refined were carbon and hydrogen positional parameters, carbon anisotropic and hydrogen isotropic thermal parameters,

Table 2. *Final positional parameters (fractional,* × 10^4) *and standard deviations* (Å), *carbon anisotropic thermal parameters* (Å^2 × 10^2, *mean standard deviation is* 0·0030 Å^2), *hydrogen isotropic thermal parameters* (Å^2, mean $\sigma = 1{\cdot}9$ Å^2), *and deviations* (Δ) *from the mean molecular planes*

Atom	x	y	z	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	Δ (Å)
C(1)	0285	0040	−1469	0·0053	0·0060	0·0054	−0·004
C(2)	0730	−0083	−3224	0·0057	0·0066	0·0057	+0·006
C(3)	1207	−1073	−2965	0·0061	0·0066	0·0060	−0·003
C(4)	1233	−1853	−1074	0·0061	0·0065	0·0063	−0·003
C(5)	0771	−1706	0754	0·0061	0·0065	0·0060	+0·002
C(6)	0308	−0749	0491	0·0055	0·0059	0·0055	+0·005
C(7)	3649	0000	5747	0·0055	0·0060	0·0053	+0·016
C(8)	4090	−0140	7565	0·0061	0·0067	0·0059	−0·019
C(9)	4603	−1065	7266	0·0061	0·0069	0·0062	−0·023
C(10)	4651	−1781	5307	0·0061	0·0067	0·0064	−0·005
C(11)	4187	−1638	3441	0·0061	0·0065	0·0059	+0·018
C(12)	3693	−0742	3727	0·0055	0·0058	0·0053	+0·025
C(13)	3068	−0099	2761	0·0053	0·0060	0·0053	+0·003
C(14)	2611	−0006	0973	0·0059	0·0068	0·0057	−0·020
C(15)	2096	0910	1259	0·0063	0·0072	0·0063	−0·025
C(16)	2059	1663	3189	0·0063	0·0069	0·0064	+0·006
C(17)	2533	1540	5039	0·0065	0·0066	0·0063	+0·012
C(18)	3026	0656	4766	0·0055	0·0059	0·0053	+0·011
H(2)	0733	0632	−4514	0·070	0·076	0·069	+0·15
H(3)	1610	−1191	−4141	0·079	0·082	0·076	+0·11
H(4)	1572	−2557	−0984	0·069	0·074	0·067	−0·03
H(5)	0784	−2383	2162	0·066	0·072	0·065	−0·07
H(8)	4065	0495	9007	0·079	0·082	0·076	+0·06
H(9)	4993	−1245	8552	0·078	0·082	0·075	−0·02
H(10)	5013	−2466	5204	0·079	0·079	0·077	−0·06
H(11)	4203	−2301	2166	0·072	0·078	0·071	−0·13
H(14)	2627	−0693	−0474	0·074	0·077	0·072	−0·15
H(15)	1722	0999	−0008	0·079	0·084	0·077	−0·08
H(16)	1675	2395	3358	0·074	0·081	0·072	+0·05
H(17)	2523	2222	6381	0·075	0·080	0·073	+0·17

$$\overline{u^2} = \sum_{i=1}^{3} \sum_{j=1}^{3} U_{ij} l_i l_j$$

	U_{11}	U_{12}	U_{13}	U_{22}	U_{23}	U_{33}	B
C(1)	3·63	0	−0·23	3·93	−0·23	3·98	
C(2)	4·20	−0·17	0·15	4·92	−0·23	4·23	
C(3)	4·27	−0·08	0·24	5·16	−1·05	4·74	
C(4)	4·30	0·54	−0·16	4·45	−0·63	5·59	
C(5)	4·54	0·21	−0·16	4·32	−0·09	4·80	
C(6)	3·73	−0·14	−0·08	3·84	−0·18	3·97	
C(7)	3·89	0·03	0·47	4·00	0·07	3·72	
C(8)	4·69	−0·34	−0·16	5·09	0·21	4·26	
C(9)	4·34	−0·23	−0·41	5·70	1·19	5·08	
C(10)	4·40	0·55	0·63	4·95	0·94	5·65	
C(11)	4·67	0·43	0·80	4·61	0·09	4·50	
C(12)	3·89	−0·06	0·41	3·89	0·19	3·56	
C(13)	3·75	−0·01	0·49	4·00	−0·05	3·72	
C(14)	4·34	−0·11	−0·06	5·26	−0·22	4·30	
C(15)	4·24	0·25	−0·36	6·18	0·36	5·04	
C(16)	4·56	0·77	0·62	5·28	0·47	5·50	
C(17)	4·93	0·52	0·85	4·75	−0·08	4·40	
C(18)	4·01	−0·08	0·41	4·00	0·21	3·43	
H(2)							4·64
H(3)							5·68
H(4)							3·90
H(5)							3·72
H(8)							5·79
H(9)							5·80
H(10)							4·74
H(11)							4·69
H(14)							4·94
H(15)							6·07
H(16)							4·92
H(17)							5·23

and an overall scale factor. R, for the 2316 observed reflexions, was reduced from 0·250 to 0·062 in four cycles, the maximum parameter shift in the final cycle being one-half of a standard deviation. Measured and calculated structure factors are listed in Table 1.

Atomic parameters and molecular dimensions

The final positional and thermal parameters, those from the last least-squares cycle with the counter data, are listed in Table 2, together with their standard deviations computed from the least-squares residuals. x, y, z are fractional coordinates with respect to the monoclinic crystal axes, and U_{ij} are the components of the mean-square vibration tensors with respect to orthogonal axes a, b, and c^*. The equations of the mean molecular planes are:

Molecule I [C(1)–C(6) and C(1′)–C(6′)]:

$$0{\cdot}6245X' + 0{\cdot}6340\,Y + 0{\cdot}4560\,Z' = 0\,,$$

Molecule II [C(7)–C(18)]:

$$0{\cdot}5936\,X' + 0{\cdot}6922\,Y - 0{\cdot}4105\,Z' = 2{\cdot}8332\,,$$

where X', Y, Z' are coordinates in Å referred to orthogonal axes a, b, and c^*. The deviations of the atoms from these planes are included in Table 2.

The orientation angles of the molecules in the crystal [L, M, and N being the molecular axes (Fig. 1) previously defined (Mak & Trotter, 1962)] are:

$\chi_L = 38{\cdot}7,\ 36{\cdot}8$ $\chi_M = 90{\cdot}9,\ 94{\cdot}4$ $\chi_N = 51{\cdot}4,\ 126{\cdot}4$
$\psi_L = 119{\cdot}8,\ 117{\cdot}4$ $\psi_M = 54{\cdot}0,\ 56{\cdot}2$ $\psi_N = 50{\cdot}7,\ 133{\cdot}8$
$\omega_L = 112{\cdot}3,\ 67{\cdot}5$ $\omega_M = 144{\cdot}0,\ 34{\cdot}1$ $\omega_N = 62{\cdot}9,\ 65{\cdot}8$

slightly different from the previous values (Mak & Trotter, 1962).

The measured bond distances and valency angles, before correction for rotational oscillation errors, are shown in Fig. 1, together with the standard deviations computed from the least-squares residuals.

The anisotropic thermal parameters of the carbon atoms were transformed to U_{ij} referred to the orthogonal molecular axes L, M, and N, and the thermal motion was then analysed in terms of the rigid-body vibrations of the molecules (Cruickshank, 1956*a*). The **T** and **ω** tensors are:

Molecule I:

$$\mathbf{T} = \begin{pmatrix} 0{\cdot}039 & -0{\cdot}022 & 0{\cdot}001 \\ & 0{\cdot}041 & 0 \\ & & 0{\cdot}033 \end{pmatrix} \text{Å}^2$$

$$\boldsymbol{\omega} = \begin{pmatrix} 12{\cdot}87 & 0{\cdot}97 & 1{\cdot}47 \\ & 2{\cdot}89 & -0{\cdot}32 \\ & & 5{\cdot}48 \end{pmatrix} \text{deg}^2$$

Molecule II:

$$\mathbf{T} = \begin{pmatrix} 0{\cdot}042 & -0{\cdot}006 & 0{\cdot}001 \\ & 0{\cdot}036 & -0{\cdot}003 \\ & & 0{\cdot}033 \end{pmatrix} \text{Å}^2$$

$$\boldsymbol{\omega} = \begin{pmatrix} 14{\cdot}23 & -0{\cdot}28 & 1{\cdot}88 \\ & 4{\cdot}53 & 0{\cdot}92 \\ & & 7{\cdot}82 \end{pmatrix} \text{deg}^2$$

The r.m.s. amplitudes of translational oscillation in the directions of the molecular axes, L, M, and N, are,

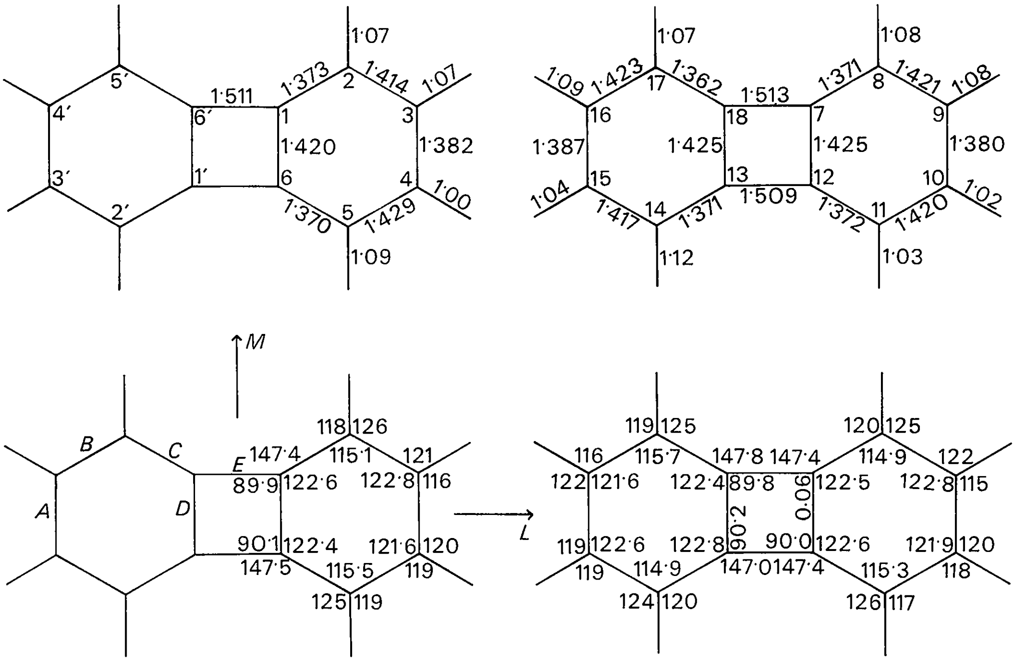

Fig. 1. Bond lengths (Å, $\sigma = 0{\cdot}008 - 0{\cdot}009$ Å for C–C, 0·08 Å for C–H) and valency angles (degrees, $\sigma = 0{\cdot}7° - 0{\cdot}8°$ for C–C–C, 4° for C–C–H).

for molecule I, 0·20, 0·20 and 0·18 Å respectively, and, for molecule II, 0·20, 0·19, and 0·18 Å. The translation motion is thus very nearly isotropic, being slightly smaller normal to the molecular planes than in the planes. The corresponding amplitudes of angular oscillation are 3·6°, 1·7°, and 2·3° for molecule I, and 3·8°, 2·1°, and 2·8° for molecule II. The largest oscillation is about the long molecular axis *L* as found also in anthracene (Cruickshank, 1956*c*), and the smallest is about axis *M*.

Slight corrections were applied to the bond distances to allow for the angular oscillations, which cause the atoms to appear too close to the centre of the molecule (Cruickshank, 1956*b*, 1961). These varied from 0·002 to 0·003 Å; the corresponding corrections to the bond angles were negligible.

Table 3. *Shortest intermolecular contacts* (Å)

All C · · · C, C · · · H, and H · · · H contacts ≤4·0 Å between standard molecules (1) and neighbouring molecules were calculated; only the shortest separations are listed.

Atom (Molecule 1)	to atom	in molecule	*d*
C(3)	C(15)	1	3·66
C(4)	C(14)	1	3·54
C(4)	C(15)	1	3·64
C(8)	C(13)	2	3·69
C(8)	C(14)	2	3·57
C(1′)	C(2)	2	3·67
C(8)	C(10)	4	3·65
C(9)	C(10)	4	3·69
C(2)	C(11)	6	3·65
C(11)	C(16)	9	3·66
C(12)	C(16)	9	3·62
C(10)	H(2)	7	2·88
C(7)	H(16)	9	2·88
C(10)	H(16)	9	2·88
C(11)	H(16)	9	2·76
C(12)	H(16)	9	2·72
H(8)	H(9)	5	2·45
H(2)	H(10)	6	2·52
H(2)	H(11)	6	2·59
H(5)	H(8)	9	2·37
H(10)	H(5)	10	2·37

Molecule 1	at *x*	*y*	*z*
2	*x*	*y*	1+*z*
4	1−*x*	−*y*	1−*z*
5	1−*x*	−*y*	2−*z*
6	½−*x*	½+*y*	−*z*
7	½−*x*	−½+*y*	−*z*
9	½−*x*	−½+*y*	1−*z*
10	½+*x*	−½−*y*	*z*

All the C · · · C, C · · · H, and H · · · H intermolecular separations less than 4 Å were calculated; all these contacts correspond to normal van der Waals interactions, and the more significant distances are given in Table 3, the shortest C · · · C, C · · · H, and H · · · H contacts being 3·54, 2·72, and 2·37 Å respectively.

Discussion

The deviations of the carbon atoms from the mean molecular planes (Table 2) are quite small. Molecule I is completely planar within experimental error, but some of the displacements in molecule II are about three standard deviations, and are therefore significant. Closer examination of the displacements indicates that they follow a regular pattern, which involves a slight bending of molecule II. This distortion is probably a result of crystal packing forces, as in other similar polynuclear hydrocarbons (Trotter, 1964).

The differences between chemically equivalent bond lengths and valency angles are very small and in no case are the differences significant. For comparison with theoretical values the measured bond lengths which are chemically equivalent were averaged, and the mean values are given in Table 4, together with their standard deviations, σ_m being calculated from the least-squares standard deviations of the individual bond distances (Fig. 1) and σ_m' being derived directly from the deviations between the individual measured values and the means. The significantly smaller values of σ_m' suggest that the least-squares standard deviations

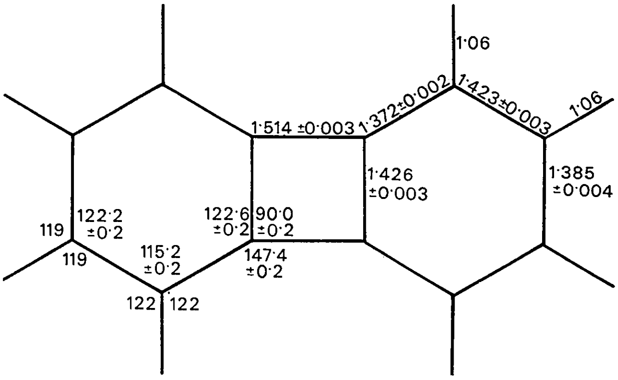

Fig. 2. Final mean bond lengths (Å) and valency angles (°), and standard deviations [σ(C–H) = 0·02 Å, σ(C–C–H) = 1°].

Table 4. *Mean measured and calculated bond lengths* (Å) *in biphenylene*

	Measured				Calculated			
	l_m		σ_m	σ_m'	V.B.			M.O.
Bond (Fig. 1)	Uncorrected	Corrected for rotational oscillation			5 Kekulé structures	I only	Model *d*	
A	1·383	1·385	0·0052	0·0021	1·411	1·337	1·375	1·383
B	1·421	1·423	0·0037	0·0021	1·384	1·477	1·421	1·401
C	1·370	1·372	0·0033	0·0016	1·411	1·337	1·375	1·385
D	1·423	1·426	0·0046	0·0017	1·411	1·477	1·421	1·416
E	1·511	1·514	0·0046	0·0012	1·442	1·477	1·477	1·497

are an overestimate of the errors. Using the mean of σ_m and σ'_m as a measure of the accuracy, the final bond distances may be given as 1·514 ± 0·003 Å for the bonds joining the six-membered rings, and for the bonds in the six-membered rings, starting with the bond in the four-membered ring, 1·426 ± 0·003 Å, 1·372 ± 0·002 Å, 1·423 ± 0·003 Å, and 1·385 ± 0·004 Å. The mean valency angle in the four-membered ring is 90·0° ± 0·2° (mean σ as for bond lengths), but the angles in the six-membered rings differ significantly from 120°. The angle adjacent to the four-membered ring is 122·6° ± 0·2° (with the external angle being 147·4° ± 0·2°), and the other angles are 115·2° ± 0·2° and 122·2° ± 0·2°. The differences between the various C–H bonds are not significant, and the mean C–H bond length is 1·06 ± 0·02 Å (no thermal oscillation correction). The final mean molecular dimensions are summarized in Fig. 2. The dimensions are very similar to (but much more accurate than) the values of the previous two-dimensional study; the largest difference is for bond *D*, which has increased from 1·38 Å to 1·426 Å.

The theoretical bond distances, derived with the use of standard correlations (Trotter, 1964) from the molecular-orbital bond-orders and from various valence-bond models (Mak & Trotter, 1962), are compared with the measured lengths in Table 4. As before, the molecular-orbital method gives a much closer estimation of the bond distances in the molecule than does simple valence-bond theory (with all Kekulé structures given equal weight); the best valence-bond model is *d* (Mak & Trotter, 1962), which considers the molecule as predominantly a cyclobutane derivative, with a smaller amount of cyclobutene, but negligible cyclobutadiene, character. The individual agreement between measured and calculated bond lengths is quite good.

Grateful acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research under Grant PRF 1704-A5. All the computations were performed on the IBM 7040 computer with our own programs, and we thank the staff of the University of British Columbia Computing Centre for assistance.

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The Crystal Structure of the Blue Potassium Molybdenum Bronze, $K_{0·28}MoO_3$

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(*Received* 11 *May* 1965)

$K_{0·28}MoO_3$ crystallizes in the monoclinic system, space group $C2/m$, with unit-cell dimensions $a = 18·249$, $b = 7·560$, $c = 9·855$, $\beta = 117°\ 32'$. Its structure was determined from two-dimensional Patterson projections and refined by three-dimensional Fourier methods and full-matrix least-squares. The layer structure is built up from subunits consisting of ten distorted octahedra sharing edges; the subunits are linked by corners. The octahedrally coordinated layers are joined solely by interlayer potassium ions which in this structure occupy two kinds of site, one seven- and the other ten-coordinated, the potassium sites being fractionally occupied. The bronze structure is discussed from the viewpoints of both close-packing and coordination polyhedra, and compared with that of the related bronze $K_{0·26}MoO_3$.

Introduction

Wold, Arnott, Kunnmann & Ferretti (1964) recently succeeded in making two potassium molybdenum oxide 'bronzes' by electrolysing fused salt mixtures of K_2MoO_4 and MoO_3. Unless the composition of the melt and the temperature were strictly confined to a minute portion of the liquidus in the equilibrium phase diagram, the product was MoO_2, and it is presumably for this reason that molybdenum bronzes, although sought on many previous occasions, have never before been found. The formulae of the bronzes were established by chemical analysis to be simply K_xMoO_3, a red phase corresponding to $x = 0·26$, and a blue to