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The Crystal and Molecular Structure of a Non-Conjugated 1,3-Diene, 2,3-Diisopropylidene-1,4-butanediol

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The crystal and molecular structure of 2,3-diisopropylidene-1,4-butanediol has been determined crystallographically using the 1502 unique and significant reflections for which $2\theta < 60°$, and refined to an R index of 0·082. Counter methods with graphite-monochromated Mo $K\alpha$ radiation were employed. All hydrogen atoms were located in a difference Fourier function and included in the least-squares refinement. Crystals form in the monoclinic space group $P2_1/c$ with cell dimensions $a = 7·893$ (3), $b = 9·194$ (6), $c = 14·373$ (9) Å and $\beta = 90·58$ (4)°. Estimated standard deviations in non-hydrogen bond lengths range from 0·004 to 0·006 Å, and in angles from 0·3 to 0·4°. The central (2–3) bond length in the butadiene moiety is found to be 1·509 (4) Å, with a dihedral angle (1–2–3–4) of 104·8 (4)°. After application of an empirical correction for the small amount of π-bond order in the central bond, this result is found to support the theoretically derived sp^2–sp^2 C–C single-bond length of 1·517 Å.

Introduction

Although it has been recognized that non-polar 1,3-dienes are inherently dissymmetric (Moscowitz, Charney, Weiss & Ziffer, 1961), no configurationally stable examples have been reported. The recent discovery in these laboratories of an unexpectedly large (21 kcal mol^{-1}) racemization barrier in a compound containing an exocyclic *vic*-diisopropylidene moiety (Kiefer, Levek, & Bopp, 1972) has prompted an exploration of the chemical and physical properties of simple compounds containing this structural unit. The readily prepared 2,3-diisopropylidene-1,4-butanediol represents the first of this series. To our considerable surprise, the nuclear magnetic resonance spectrum of this compound displayed magnetically nonequivalent methylene protons even well above room temperature ($T_{\text{coalescence}} \sim 138$ °C) indicating a high degree of configurational stability. The crystals demonstrated no optical activity, suggesting that they were racemic. The molecular structure was of interest primarily because the probability of a large dihedral angle between the π-bond planes presented an opportunity to measure accurately an sp^2–sp^2 carbon–carbon bond length in the absence of conjugation and severe strain effects. Precise molecular dimensions were also desired for theoretical calculations of the energy barrier to racemization.

Experimental

2,3-Diisopropylidene-1,4-butanediol was synthesized in 40% yield by reduction of ethyl hydrogen 2,3-diisopropylidenesuccinate (0·130 mol) with sodium bis-(2-methoxyethoxy)aluminum hydride ('Red-al', Aldrich Chemical Co., 0·520 mol) in 200 ml of refluxing toluene for 20 h. The diisopropylidene half-ester was prepared in *ca.* 90% yield by the Stobbe condensation (Stobbe, 1905) of acetone (0·200 mol) with diethyl isopropylidenesuccinate (0·170 mol) (Overberger & Roberts, 1949) using potassium tert-butoxide (0·280 mol) in refluxing tert-butyl alcohol (Johnson & Schneider, 1963). The neat, distilled diol (b.p. 112–116° C, 0·45–0·50 mm) was protected from light and air and allowed to remain undisturbed at 13°C for 3–4 days, during which time crystals formed. Subsequent attempts to grow crystals from a variety of solvents have so far been unsuccessful. The high-temperature n.m.r. spectrum was measured using 1-chloronaphthalene and quinoline as solvents.

A crystal of dimensions 0·75 × 0·3 × 0·3 mm was used for all crystallographic experiments. Oscillation and Weissenberg photographs indicated monoclinic symmetry with a β angle close to 90°. All reflections $h0l$ for l odd and $0k0$ for k odd were systematically absent, uniquely defining the space group $P2_1/c$.

A Syntex $P\bar{1}$ four-circle computer-controlled diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($K\alpha_1$, $\lambda = 0·70926$ Å; $K\alpha_2$, $\lambda = 0·71354$ Å) and pulse-height analyzer was used for preliminary experiments and for the measurement of diffraction intensities. The cell constants and their standard deviations were determined by a least-squares treatment of the angular coordinates of 15 independent reflections with 2θ values up to 21·8°. The program used was written by R. A. Sparks and is part of the diffractometer program library.

The θ–2θ scanning mode with scan speed variable from 2 to 24° min^{-1}, depending on the peak intensity of the reflection, was utilized during the data collection. Background counting time was equal to the scan time and the scan range varied from 2·0° at low 2θ to 2·4° at 60°. The temperature was maintained within 1° of 19°C. Three check reflections, which were re-

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measured after every 100 reflections during data collection, showed a linear decrease to 86% of the initial intensity. A decay correction was applied (Ottersen, 1973).

Standard deviations were assigned according to the formula

$$\sigma(I)=[\omega^2(CT+B_1+B_2)+(pI)^2]^{1/2},$$

where ω is the scan rate, CT is the total integrated count, B_1 and B_2 are the background counts, and the intensity is $I=\omega(CT-B_1-B_2)$. A value of 0·02 was assigned to the empirical parameter p to account for instrument instability. Of the 3054 unique reflections measured, all those for which $2\theta<60°$, 1502 had intensities larger than three times their standard deviations,

Table 1. *Observed and calculated structure factors*

The running index is l; values of h and k for each group immediately precede that group. The central column is $10|F_o|$; the right-hand column is $10\ F_c$. All of the X-ray diffraction intensities which were observed to be greater than three times their standard deviations were used in structure refinement and are listed in this table.

H=	0, K=	0
2	177	180
4	745	-711
6	24	13
8	27	23
10	292	281
12	81	91
14	31	-31
16	41	-41
H=	0, K=	1
1	17	-26
2	723	725
3	496	-466
4	145	-157
5	684	-648
6	69	57
7	125	124
8	123	-108
9	65	62
10	56	-52
11	37	-37
12	84	82
13	79	-79
16	36	-38
H=	0, K=	2
0	172	150
1	100	111
2	104	-104
3	446	431
4	189	173
5	113	-116
6	248	224
7	271	-279
8	113	104
10	75	-79
11	147	150
12	120	-118
13	77	75
15	57	-59
H=	0, K=	3
1	216	-203
2	470	463
3	366	344
4	86	94
5	113	-110
6	55	-45
7	37	33
8	163	-158
10	76	70
12	51	54
13	108	110
15	43	48
H=	0, K=	4
0	413	-409
1	428	-450
2	83	-86
3	115	113
4	158	160
5	85	88
6	26	-30
7	212	-206
8	158	-160
9	62	56
10	46	-48
11	22	-24
12	36	-46
13	71	-73
15	24	-22
17	50	45
18	41	-34
H=	0, K=	5
1	122	-123
2	63	-74
3	61	49
4	124	-119
5	302	318
6	134	133
7	27	31
8	101	96
9	60	-58
10	101	106
11	57	59
14	43	-43
17	52	42
H=	0, K=	6
1	22	-30
2	80	82
3	29	-32
4	23	30
5	97	-93
6	114	-116
8	92	-92
9	27	-29
10	60	61
11	54	-57
14	25	29
15	42	-29
H=	0, K=	7
1	22	17
2	125	125
5	76	-77
6	90	90
7	76	-81
9	23	33
11	34	34
14	32	20
15	53	-46
16	25	32
17	32	-26
H=	0, K=	8
0	107	-113
2	69	74
4	46	46
5	73	-71
6	67	65
9	20	24
11	40	-34
H=	0, K=	9
4	36	38
7	24	-23
10	20	31
11	44	-38
H=	0, K=	10
1	23	25
2	24	-14
3	24	27
4	35	-31
6	33	30
11	41	-36
H=	0, K=	11
1	27	20
2	26	-20
4	30	-25
5	40	45
6	35	29
7	33	27
8	37	24
H=	0, K=	12
3	45	-41
4	53	-43
H=	1, K=	0
-12	70	85
-10	163	153
-8	119	-102
-6	192	207
-4	423	456
-2	626	-650
0	444	437
2	411	334
4	194	-173
6	243	-220
8	325	-302
10	132	140
12	23	-24
14	40	-41
16	44	-41
20	24	30
H=	1, K=	1
-16	40	46
-15	30	-32
-12	144	-151
-11	43	-27
-10	104	-98
-9	203	-206
-8	22	7
-7	130	135
-6	165	118
-5	76	-97
-4	359	358
-3	264	-244
-2	456	-473
-1	44	-53
0	696	-639
1	94	-61
2	170	-85
3	625	612
4	104	34
5	85	-73
6	434	-18
7	120	-101
8	87	-81
9	103	88
10	219	-224
11	153	147
12	57	-44
13	31	25
15	52	-51
H=	1, K=	2
-15	30	32
-14	44	39
-13	49	37
-12	22	-24
-11	71	85
-10	27	31
-9	37	-17
-6	36	22
-5	277	244
-4	474	491
-3	313	-313
-2	340	-357
-1	244	252
0	213	-201
1	357	332
2	272	252
3	197	-172
4	238	-195
5	285	266
6	125	-134
7	64	60
9	142	-137
10	22	-5
11	40	44
12	41	-39
13	185	188
14	31	29
H=	1, K=	3
-16	44	-42
-15	26	25
-13	54	57
-12	20	19
-11	20	-5
-10	45	-46
-9	24	-33
-8	69	63
-7	65	-51
-6	219	-227
-5	195	-183
-4	74	-70
-3	203	205
-2	224	232
-1	93	-106
0	43	-54
1	180	-168
2	155	151
3	211	179
4	60	-67
5	62	-36
6	86	-69
7	226	232
8	122	-113
10	32	-34
11	123	-126
14	26	27
16	33	-29
17	27	29
18	67	-66
H=	1, K=	4
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-18	30	-27
-15	41	-40
-14	44	50
-11	41	27
-10	37	-44
-9	69	-81
-8	39	-39
-7	69	72
-6	40	20
-5	83	80
-4	64	53
-3	190	-179
-2	207	174
-1	175	140
0	52	57
1	497	-480
2	376	-344
3	163	-152
4	97	-86
5	181	171
6	137	130
7	21	15
9	65	60
11	69	-90
12	41	-40
16	40	36
19	43	42
H=	1, K=	5
-17	57	52
-16	24	-30
-13	54	-54
-12	82	87
-7	42	38
-6	94	-102
-5	25	-7
-4	164	177
-3	110	-112
-2	283	287
-1	137	144
0	105	99
1	48	36
2	167	151
3	144	-140
4	61	-53
5	107	102
6	84	84
7	25	22
8	39	35
9	24	-32
10	31	44
12	27	21
13	28	30
17	32	-30
H=	1, K=	6
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-14	41	-44
-12	33	-31
-11	56	60
-10	54	58
-9	55	-50
-8	137	142
-7	182	-196
-5	34	-31
-4	245	-266
-3	124	-134
-2	46	56
-1	40	-47
0	143	142
1	71	-68
2	55	-49
3	143	-147
4	86	74
5	111	-118
6	23	23
7	40	-84
8	129	-132
10	29	-21
12	42	45
15	34	-28
16	30	26
H=	1, K=	7
-15	27	-13
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-7	61	-64
-6	97	103
-5	88	-95
-4	175	192
-3	40	39
-2	48	-38
-1	53	52
0	26	-24
1	56	56
2	117	124
3	72	-64
4	56	51
5	56	-51
6	157	171
7	34	29
9	51	46
10	33	-33
12	30	27
14	27	-29
H=	1, K=	8
-15	44	42
-11	33	-31
-8	56	-55
-3	27	-21
-2	122	137
-1	78	-85
0	35	-39
1	96	-114
2	34	-27
3	79	77
4	40	-53
6	24	-17
7	83	-82
8	65	63
9	26	20
15	37	38
H=	1, K=	9
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-9	20	29
-7	25	-25
-4	54	-56
2	40	37
5	40	48
6	61	-63
8	44	-47
11	35	-31
H=	1, K=	10
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-8	64	-57
-7	45	50
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0	25	-16
3	43	44
8	36	31
9	72	68
H=	1, K=	11
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-5	57	51
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0	37	34
3	34	-38
4	49	-53
7	27	-24
H=	1, K=	12
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1	37	34
2	70	66
3	30	-23
4	27	25
5	26	-16
H=	2, K=	0
-18	27	30
-16	32	29
-14	51	-51
-12	139	-143
-10	42	-43
-8	77	69
-6	131	-144
-4	70	-92
-2	356	-382
0	698	-666
2	672	-696
4	106	87
6	115	117
8	247	-244
10	51	48
12	140	-135
14	40	-41
16	51	53
H=	2, K=	1
-16	35	29
-15	27	-28
-13	25	-11
-12	44	-48
-11	124	133
-10	69	-70
-8	52	-35
-7	102	104
-6	166	167
-5	40	42
-4	151	150
-3	74	48
-2	352	-393
-1	740	802
0	100	-93
1	274	180
2	171	151
3	270	291
4	85	-79
5	90	83
6	171	147
7	30	-21
8	62	-64
10	35	-21
11	40	35
12	36	37
13	82	85
14	24	-26
16	30	38
H=	2, K=	2
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-14	24	24
-13	26	-29
-11	49	54
-10	122	123
-9	28	19
-7	90	-99
-6	476	-504
-5	264	297
-4	90	57
-3	240	-284
-2	36	19
-1	369	-382
0	91	-106
1	445	453
2	156	148
3	142	117
4	261	-265
5	82	34
6	170	-77
7	35	37
8	56	-55
10	65	65
11	77	-73
12	62	64
16	27	-13
18	33	-27
H=	2, K=	3
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-12	26	26
-11	43	-37
-10	77	-78
-9	34	-41
-8	107	115
-7	55	-43
-6	33	13
-5	44	31
-4	121	-119
-3	182	189
-2	125	120
-1	186	-175
0	175	-167
1	306	-287
2	167	150
3	93	82
4	97	-97
5	65	-61
6	135	-138
7	151	141
8	30	23
10	44	35
11	155	-162
13	31	-34
14	35	-38
15	33	-42
16	28	30
19	31	27
H=	2, K=	4
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-14	50	52
-13	69	-75
-12	62	56
-11	36	-41
-9	62	37
-8	37	-34
-7	33	-25
-6	104	98
-5	26	11
-4	156	155
-3	73	-84
-1	31	24
0	45	36
1	47	38
3	100	104
4	56	38
5	89	-77
6	204	203
7	66	-66
8	33	34
9	205	206
11	47	-46
12	35	35
13	31	26
15	30	32
16	41	40
17	43	-46
H=	2, K=	5
-14	27	-30
-10	72	75
-9	94	-101
-8	155	167
-7	46	-2
-6	53	-44
-5	36	-39
-4	121	-125
-3	105	-103
-2	122	125
-1	42	45
0	42	-41
2	95	88
3	26	-11
4	108	-94
5	21	-25
6	52	-47
7	184	-186
8	54	-36
9	35	-19
10	69	-70
15	26	26
17	40	-41
H=	2, K=	6
-13	41	-31
-11	32	31
-10	52	-56
-7	160	-165
-6	211	227
-5	31	-26
-4	61	-54
-3	65	-57
-2	144	-155
-1	143	145
0	44	46
1	55	42
2	40	-25
3	175	-185
4	35	31
5	102	102
6	100	89
7	99	91
9	52	56
10	39	-36
17	20	13
H=	2, K=	7
-16	32	28
-12	29	26
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-5	31	31
-4	120	124
-3	22	23
-2	106	118
-1	70	-70
1	106	111
2	108	-110
3	36	31
4	166	-173
5	31	-35
6	86	93
7	33	31
8	59	58
9	43	42
10	68	-70
14	36	-34
H=	2, K=	8
-8	51	-50
-5	49	-47
-4	103	-109
-3	31	-35
-2	29	-24
-1	46	50
0	81	81
1	54	-59
2	62	62
4	129	-138
5	125	128
6	117	-117
8	43	43
H=	2, K=	9
-9	51	54
-8	37	35
-5	20	-23
-1	25	24
0	53	-47
1	80	88
2	27	35
3	26	-34
5	27	-24
6	47	-47
9	59	53
11	39	40
H=	2, K=	10
-11	34	-33
-9	26	-25
-7	33	33
-6	25	15
-2	36	41
3	26	23
4	30	29
7	45	-43
11	61	58
H=	2, K=	11
-9	30	-27
-7	37	-28
-6	29	34
-2	71	-69
2	50	47
3	36	-36
6	41	-36
7	31	-34
8	41	-41
9	42	-40
H=	2, K=	12
-4	47	49
-2	36	30
-1	35	-32
0	37	-36
3	37	31
4	75	74
5	26	12
H=	3, K=	0
-14	40	-51
-10	175	-182
-8	76	79
-6	66	-48
-4	186	-191
-2	266	267
0	137	139
2	426	-373
4	82	87
6	275	274
8	65	-72
10	121	107
14	30	-34
16	62	63
H=	3, K=	1
-12	91	88
-11	93	90
-10	103	105
-9	59	61
-8	72	-74
-7	51	35
-6	52	-60
-5	26	24
-4	102	-101
-3	113	-109
-2	80	84
-1	300	335
0	505	483
1	194	-169
2	107	104
3	66	-65
4	136	-134
5	76	-76
6	42	29
7	80	-82
8	91	-88
9	46	44
10	76	79
11	114	-112
12	146	150
H=	3, K=	2
-13	70	-72
-12	30	-22
-11	62	-68
-9	40	46
-8	70	66
-7	86	-75
-6	205	-213
-5	36	26
-4	90	-67
-3	86	-82
-2	51	-23
-1	70	-70
0	161	153
1	140	-110
2	237	217
3	159	-136
4	235	-229
5	126	129
6	142	142
7	116	-115
8	30	34
11	31	-22
12	63	57
13	104	-107
14	36	-39
15	29	-32
H=	3, K=	3
-16	34	35
-15	24	15
-13	45	-46
-10	47	-51
-9	30	31
-8	63	63
-6	117	114
-5	77	77
-4	34	-46
-3	31	-18
-2	78	87
-1	53	-61
0	178	-194
1	29	36
2	72	56
3	80	-79
4	92	79
5	153	-150
6	50	32
7	20	11
8	70	70
9	40	40
10	31	-21
12	57	59
13	33	34
18	43	41
H=	3, K=	4
-15	33	31
-11	55	-52
-9	91	93
-7	57	-24
-5	68	-73
-3	114	118
-2	112	-123
-1	28	17
1	74	72
2	163	171
3	231	232
5	40	-46
6	40	29
7	236	-239
9	70	79
10	30	-36
11	33	28
15	24	28
17	55	-47
H=	3, K=	5
-17	20	-26
-13	41	48
-11	24	23
-10	62	-67
-9	65	-70
-7	52	48
-6	42	35
-5	23	-13
-4	127	-132
-3	26	-26
-2	74	-94
-1	70	72
0	226	-219
1	126	-118
2	30	14
4	44	-31
5	93	90
6	94	-92
7	115	-116
9	27	25
10	49	-44
13	52	-49
15	30	37
H=	3, K=	6
-8	116	-121
-7	27	29
-5	169	203
-4	124	130
-3	29	26
-1	61	49
0	56	-56
1	156	151
2	43	-37
3	40	-36
4	36	1
5	143	137
7	53	55
8	81	76
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14	31	-25
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1	63	-92
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3	85	-75
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14	40	-47
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6	31	30
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7	31	28
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2	37	-34
H=	5, K=	0
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15	35	33
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8	126	125
9	70	68
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5	90	-94
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1	35	-39
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13	31	-24
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9	47	-42
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7	34	32
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12	34	30
13	34	-38
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3	40	37
5	45	-42
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9	47	-46
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13	42	42
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H=	7, K=	9
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H=	8, K=	0
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6	36	-38
8	47	42
12	24	27
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1	35	-35
2	33	33
5	29	-28
6	37	-36
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5	27	22
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11	52	54
H=	8, K=	4
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11	30	-25
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1	30	-32
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5	29	-11
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2	33	31
4	41	-33
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H=	9, K=	5
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5	30	-23
H=	9, K=	6
5	33	-57
H=	10, K=	0
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-2	52	-54
2	32	24
4	32	-28
6	45	-36
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0	48	-46
1	62	56
4	30	26
H=	10, K=	2
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3	66	70
H=	10, K=	3
1	47	-46
5	34	33
H=	10, K=	4
-4	35	34
6	34	32
H=	10, K=	5
-3	32	23

and all of the remaining reflections were excluded from Fourier calculations and least-squares refinements. The intensities were corrected for Lorentz and polarization effects (Ottersen, 1973); the contribution of the monochromator crystal was calculated assuming that it was half perfect and half mosaic in character.

The atomic scattering factors used were those of Doyle & Turner (1968) for C^0 and O^0 and those of Stewart, Davidson & Simpson (1965) for hydrogen.

Crystal data

2,3-Diisopropylidene-1,4-butanediol, $C_{10}H_{18}O_2$, monoclinic, $P2_1/c$; $a=7{\cdot}893$ (3), $b=9{\cdot}194$ (6), $c=14{\cdot}373$ (9) Å, $\beta=90{\cdot}58$ (4)°. Figures in parentheses are estimated standard deviations in units of the least significant digit given for the corresponding parameter. $V=1042{\cdot}9$ Å^3; M.W. 170·2; D_{obs} (flotation) $=1{\cdot}05$ g cm^{-3}; $D_{\text{calc}}=1{\cdot}084$ g cm^{-3}; $Z=4$; $F(000)=376$; melting point 46–47°C.

Structure determination

The phase problem was solved by a computer procedure (Long, 1965), utilizing a reiterative application of Sayre's equation (Karle, 1964). The 336 values of E, the normalized structure factor, larger than 1·5 were used. Positions for all 12 non-hydrogen atoms were indicated in the E-map. The fast-Fourier program *ALFF* (Hubbard, Quicksall & Jacobson, 1971) was used for all calculations of Fourier functions.

The structure model was refined to $R_1=0{\cdot}17$ [$R_1=(\sum|F_o-|F_c||)/\sum F_o$ and $R_2=\{\sum w(F_o-|F_c|)^2/\sum wF_o^2)^{1/2}\}$. The introduction of anisotropic thermal parameters followed by least-squares refinement reduced R_1 to 0·12. The weights, w, used in the least-squares were the reciprocal squares of $\sigma(F_o)$. The program used (*UCLALS*4) was that of Gantzel, Sparks & Trueblood (1960) which minimizes $\sum w(\Delta F)^2$.

Positions for the 18 hydrogen atoms were indicated in a difference Fourier function. These were included in the least-squares refinement with individual isotropic thermal parameters.

Full-matrix least-squares refinement of all positional parameters, anisotropic thermal parameters for non-hydrogen atoms, and isotropic thermal parameters for hydrogen atoms converged to give the final error indices, $R_1=0{\cdot}082$ and $R_2=0{\cdot}096$. The 'goodness-of-fit', $\{[\sum w(F_o-|F_c|)^2]/(m-s)\}^{1/2}$, is 2·44, and the overdetermination ratio, m/s, is 8·3. The number of observations is m, and s, the number of parameters, is 181. In the final cycle of least-squares, all shifts involving non-hydrogen atoms were less than 1 % of their standard deviations. Shifts in parameters for hydrogen atoms were less than 60 % of their e.s.d.'s. The largest peak on the final difference Fourier function had a density of less than 0·3 e Å^{-3}; the standard deviation of the electron density is calculated to be 0·1 e Å^{-3}.

Table 1 is a tabulation of the observed and calculated structure factors (× 10), and the final parameters of the non-hydrogen atoms are listed in Table 2. Final parameters for hydrogen atoms are given in Table 3.

Table 3. *Fractional atomic coordinates* (× 10^3) *and isotropic thermal parameters* (Å^2) *for hydrogen atoms.*

See Fig. 1 for the identities of the atoms. The e.s.d. is in the units of the least significant digit given for the corresponding parameter.

	x	y	z	B
H(13)	55 (9)	130 (8)	302 (5)	9·6 (17) Å
H(14)	−56 (9)	362 (8)	273 (5)	8·9 (16)
H(15)	269 (10)	−112 (10)	489 (6)	9·4 (20)
H(16)	190 (9)	−72 (8)	574 (5)	7·8 (15)
H(17)	340 (14)	−61 (11)	556 (7)	12·0 (27)
H(18)	220 (7)	315 (7)	575 (4)	7·1 (13)
H(19)	120 (9)	192 (8)	633 (5)	8·4 (15)
H(20)	336 (9)	176 (8)	615 (5)	7·9 (15)
H(21)	352 (9)	134 (8)	285 (5)	8·8 (16)
H(22)	335 (7)	−8 (5)	350 (3)	5·4 (11)
H(23)	−13 (6)	476 (5)	403 (3)	4·3 (9)
H(24)	−41 (5)	328 (5)	457 (3)	4·3 (9)
H(25)	184 (10)	606 (7)	357 (4)	5·7 (16)
H(26)	315 (11)	586 (10)	284 (7)	11·9 (22)
H(27)	312 (11)	657 (10)	420 (6)	10·8 (21)
H(28)	541 (9)	353 (8)	319 (6)	8·1 (18)
H(29)	523 (9)	280 (9)	391 (5)	9·2 (17)
H(30)	583 (10)	429 (9)	414 (5)	8·1 (17)

Table 2. *Fractional atomic coordinates and thermal parameters with estimated standard deviations* (*all* × 10^4)

See Fig. 1. for the identities of the atoms. The e.s.d. is in the units of the least significant digit given for the corresponding parameter. The temperature factor is $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)]$.

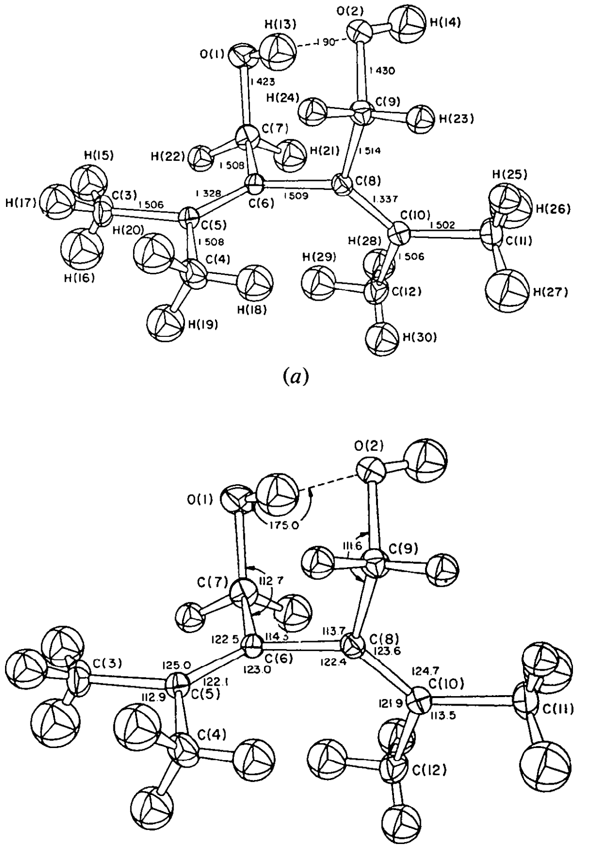
	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O(1)	1013 (4)	479 (4)	2927 (2)	310 (8)	148 (4)	67 (2)	21 (9)	−97 (6)	−76 (5)
O(2)	−667 (3)	3062 (3)	3188 (2)	180 (5)	121 (3)	65 (2)	−7 (7)	−70 (4)	18 (4)
C(3)	2621 (6)	−370 (5)	5276 (4)	236 (9)	106 (5)	80 (3)	22 (11)	11 (8)	72 (6)
C(4)	2232 (6)	2156 (5)	5905 (3)	282 (10)	147 (6)	36 (2)	23 (12)	22 (6)	2 (5)
C(5)	2429 (4)	1221 (4)	5050 (2)	133 (5)	82 (3)	44 (2)	0 (7)	−14 (4)	10 (4)
C(6)	2416 (4)	1779 (3)	4198 (2)	120 (5)	78 (4)	39 (2)	6 (7)	−7 (4)	−2 (4)
C(7)	2600 (6)	853 (4)	3339 (3)	234 (8)	109 (4)	45 (2)	27 (10)	−1 (6)	−37 (5)
C(8)	2033 (4)	3358 (3)	4001 (2)	157 (6)	83 (4)	34 (1)	18 (8)	−18 (4)	−1 (4)
C(9)	159 (4)	3708 (4)	3977 (2)	145 (6)	102 (4)	51 (2)	42 (8)	−13 (5)	−7 (4)
C(10)	3241 (5)	4315 (4)	3783 (3)	164 (7)	104 (4)	51 (2)	13 (9)	−20 (5)	12 (5)
C(11)	2924 (6)	5877 (5)	3527 (4)	248 (10)	115 (5)	85 (3)	25 (11)	−13 (8)	66 (6)
C(12)	5089 (6)	3908 (5)	3790 (4)	157 (7)	142 (6)	96 (3)	−41 (11)	−8 (7)	42 (7)

Standard deviations were calculated from the correlation matrix ignoring standard deviations in cell parameters. The estimated standard deviations in the C–C and C–O bond lengths [Fig. 1(*a*)] range from 0·004 to 0·006 Å, and the e.s.d.'s of the angles [Fig. 1(*b*)] involving these non-hydrogen atoms are 0·3 to 0·4°. Geometrical features involving hydrogen are summarized in Table 4, and the two 'ethylene' planes are described in Table 5.

Table 4. *Average bond distances* (Å) *and bond angles involving hydrogen*

Estimated standard deviations are in the units of the least significant digit given for the corresponding parameter.

	Average value	Number averaged	Range
O—H	0·85 Å	2	0·84 (7) -0·85 (7) Å
C—H	0·98	16	0·77 (10)-1·17 (10)
O···H	1·94	2	1·90 (7) -1·98 (7)
C–C–H	111·6°	16	89 (4)-128 (6)°
C–O–H	102·4	2	96 (5)-109 (5)
O–C–H	111·3	4	107 (2)-115 (4)
H–C–H	104·2	14	77 (6)-143 (7)



(*a*)

(*b*)

Fig. 1. The 2,3-diisopropylidene-1,4-butanediol molecule. Ellipsoids of 15% probability are used (Johnson, 1965). Bond lengths and bond angles are given.

Table 5. *Deviations from least-squares planes* ($\text{Å} \times 10^3$)

Bold-face deviations indicate the atoms used to define the least-squares plane. A negative deviation indicates that the atom with the coordinates given in Table 2 (Table 3 for hydrogens) lies between that plane and the origin. The direction cosines ($\times 10^4$), q, are with respect to orthogonal axes. The r.m.s. deviation ($\text{Å} \times 10^3$) of the boldface atoms from the plane is δ. D is the distance (in Å) from the plane to the origin.

	Plane 1	Plane 2
O(1)	−1297	−2139
O(2)	−2219	−1285
C(3)	**−60**	1019
C(4)	**31**	2432
C(5)	**10**	1046
C(6)	**42**	**−18**
C(7)	**12**	−1408
C(8)	**−36**	**38**
C(9)	−1447	**−6**
C(10)	1032	**2**
C(11)	999	**−26**
C(12)	2413	**9**
H(13)	−1537	
H(14)		−1798
$q_{\mathbf{b}\times(\mathbf{a}\times\mathbf{b})}$	9866	595
$q_{\mathbf{b}}$	1574	2396
$q_{\mathbf{a}\times\mathbf{b}}$	419	9690
D	2·289	6·366
δ	36	21

Discussion

Intramolecular crowding in 2,3-diisopropylidene-1,4-butanediol, particularly between the *cis,cis*-methyl groups, C(4) and C(12), but also between the methylene groups, C(7) and C(9), forces the diene system to adopt a severely skewed conformation: the C(5)–C(6)–C(8)–C(10) dihedral angle is 104·8 (4)°. (Dihedral angles are given in Table 6.) This configuration is stabilized by the intramolecular van der Waals potential minimum occupied by the C(4) group between the C(9) and C(12) groups, by that found by the C(12) group between the C(4) and C(7) groups, and by the formation of an intramolecular hydrogen bond [2·75 (1) Å] between O(1) and O(2). The O(1)–H(13)···O(2) angle is 175 (4)°. This compound may, in fact, owe its unexpected ease of crystallization to the conformational rigidity imparted by these steric and hydrogen-bonding constraints. The observation that replacement of 1-chloronaphthalene with quinoline (a good hydrogen-bond acceptor) as solvent has no significant effect on the n.m.r. coalescence temperature implies that hydro-

Table 6. *Dihedral angles* (°)

Estimated standard deviations, in parentheses, are in the units of the least significant digit given for the corresponding parameter.

C(5)—C(6)–C(8)–C(10)	104·8 (4)
C(7)—C(6)–C(8)–C(9)	92·7 (4)
C(5)—C(6)–C(7)–O(1)	96·1 (4)
C(8)—C(6)–C(7)–O(1)	77·8 (4)
C(6)—C(8)–C(9)–O(2)	68·8 (4)
C(10)–C(8)–C(9)–O(2)	105·1 (4)

gen bonding does not contribute significantly to hindered rotation about the C(6)–C(8) bond. The intramolecular hydrogen bond also does not appear to induce any significant angular distortion: all of the observed C–C–C and C–C=C bond angles [Fig. 1(*b*)] are within 2° of the corresponding angles determined by electron diffraction for isobutylene (Bartell & Bonham, 1960) and tetramethylethylene (Pauling, 1960).

Although a case for some shortening of the carbon–carbon double bonds might be made, all of the bond lengths except that of the central C(6)–C(8) single bond appear to fall within the normally observed ranges (Lide, 1962). The latter bond length, 1·509 Å, is well above the accepted value of 1·48 ± 0·01 Å for 'normal' sp^2–sp^2 C–C single bonds (Lide, 1962; Stoicheff, 1962; Bastiansen & Trætteberg, 1962), which, however, actually have bond orders greater than one, owing to conjugation effects. It seems very unlikely that this apparent bond stretching is due to conformational strain, since such strain should be reflected in distortions of other bond lengths and especially of bond angles, which relieve strain by deformation much more efficiently than do bond lengths (Westheimer, 1956). The only statistically significant bond-angle deformation observed, in C(3)–C(5)–C(6) and C(8)–C(10)–C(11) (average 124·9°), is in the wrong direction to correlate with stretching of the C(6)–C(8) bond; if anything, the forces responsible for widening that angle should tend to compress the C(6)–C(8) bond. The data of Table 5 indicate very little deviation from planarity in the two ethylene planes.

Based on the above considerations, we suggest that the conformation adopted by 2,3-diisopropylidene-1,4-butanediol in the crystalline state is substantially strain-free, and that the C(6)–C(8) bond length, 1·509 (4) Å, must be very close to the equilibrium value for an sp^2–sp^2 C–C single bond *in the absence of conjugation effects*. As such, the present work represents probably the most precise determination of this theoretically important number to date.

A number of authors have discussed the influence of electron delocalization on the length of the single bond between two π bonds as a function of the dihedral angle (ψ) between π bond planes. The most widely cited value for a pure non-conjugated sp^2–sp^2 bond ($\psi = 90 \pm 10°$) is 1·515 (15) Å, determined for the interannular distance in hexaphenylbenzene by electron diffraction (Almenningen, Bastiansen & Skancke, 1958). Though the uncertainty in the measurement is high, it is close to the theoretical value of 1·517 Å derived and impressively supported with empirical correlations by Bak & Hansen-Nygaard (1960). The effects of conjugation for values of ψ between 0 and 90° have also been calculated for biphenyl and other systems (Adrian, 1958; Fischer-Hjalmars, 1962), and offer further support for the assumption that partial conjugation leads to systematic bond shortening. Using the bond-order–bond-length relationship given by Bak & Hansen-Nygaard (bond shortening = 0·168 Å × π-bond order) and a C(6)–C(8) π-bond order calculated (relative to planar butadiene = 0·20) for $\psi = 104·8°$ by the simple Hückel method (Roberts, 1961), the predicted sp^2–sp^2 single-bond length in 2,3-diisopropylidene-1,4-butanediol is 1·507 Å, which is within experimental error limits of the measured value. If the correction (0·010 Å) were applied instead to the observed distance, the pure sp^2–sp^2 bond length would be 1·519 (4) Å, ignoring the e.s.d. of the correction.

A stereo view of the packing is given in Fig. 2. The intermolecular forces in the crystal are relatively weak, consistent with its low melting point. Each molecule participates in only two intermolecular hydrogen bonds for which O(2)···O(1) is 2·75 (1) Å. [O(1) has coordinates related to those given in Table 2 by the symmetry operation: $-x, 0·5+y, 0·5-z$].

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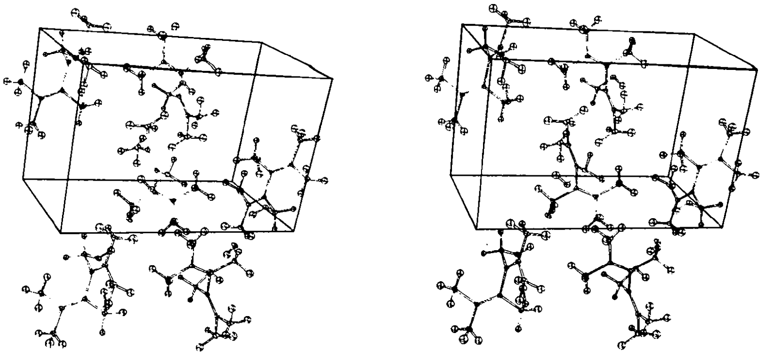

Fig. 2. A stereo view (Johnson, 1965) illustrating the packing of the molecules in the crystal. The view is approximately along the *b* axis, with *c* horizontal and *a* vertical in the plane of the page. Ellipsoids of 5% probability are used.

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Structural Chemistry of Copper and Zinc Minerals. II. Stereochemistry of Copper(II) and Iodine(V) in Bellingerite, $3Cu(IO_3)_2.2H_2O$

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Bellingerite, $3Cu(IO_3)_2.2H_2O$, is triclinic, space group $P\bar{1}$, with a_0 = 7·256 (2), b_0 = 7·950 (2), c_0 = 7·856 (2) Å, α = 105·10 (2), β = 92·95 (2), and γ = 96·95 (2)°, Z = 1. The heavy-atom positions were determined from a three-dimensional Patterson map. The crystal structure was determined by the heavy-atom method and refined by the method of least-squares, with anisotropic temperature factors, to an R of 0·038 for 3156 reflections measured on an automatic single-crystal diffractometer. The standard error in Cu–O and I–O bond lengths is ±0·005 Å and in O–Cu–O and O–I–O angles ±0·02°. The crystal structure of bellingerite is a three-dimensional framework consisting of a corner-sharing tetragonally distorted $Cu(1)O_6$ octahedron, a $[Cu(2)_2O_8(H_2O)_2]$ octahedral dimer and three independent pyramidal iodate groups. Cu(1) at a symmetry center is bonded to four oxygens at 1·936 Å (×2) and 1·967 Å (×2) approximately in a square plane, while two oxygens at 2·528 Å (×2) complete the octahedron. Cu(2) has three oxygen atoms at 1·942, 1·946 and 1·973 Å and a water molecule at 1·950 Å approximately in a square plane, while one oxygen at 2·456 Å and a water molecule at 2·483 Å form the apices of the distorted octahedron. Two Cu(2) octahedra form a dimer by sharing an octahedral edge. The pyramidal $I(1)O_3$ group, with point-group symmetry $3m$, has three oxygens at 1·815, 1·823 and 1·824 Å from the iodine atom, with O–I–O angles 96·0, 95·7 and 97·3°. I(1) is weakly bonded to three further oxygens at 2·755, 2·676 and 2·796 Å. The $I(1)O_6$ coordination polyhedron is a distorted octahedron. I(2) is bonded to three oxygens at 1·817, 1·815 and 1·825 Å, the O–I–O angles being 99·1, 99·4, and 95·1°. Four further oxygens form weak bonds at 2·737, 2·957, 3·050 and 3·172 Å. The $I(2)O_7$ polyhedron can be described as a square pyramid with two domes below the equatorial plane. I(3) is bonded to three oxygens at 1·801, 1·823 and 1·795 Å, with O–I–O angles 96·7, 101·0 and 101·1°. I(3) is weakly bonded to two further oxygens at 2·771 and 2·873 Å. The $I(3)O_5$ polyhedron is a distorted trigonal bipyramid. Both $I(2)O_3$ and $I(3)O_3$ groups approximate very closely to the point-group symmetry m. Both H atoms belonging to the water molecule are involved in strong hydrogen bonds (both O–H$\cdots$O = 2·663 Å).

Introduction

In part I of this series, we described the structure of veszelyite, $(Cu,Zn)_2ZnPO_4(OH)_3.2H_2O$ (Ghose, Leo & Wan, 1974), which has a novel type of octahedral sheet structure. In this paper we describe the structure determination of a copper iodate mineral, bellingerite, $3Cu(IO_3)_2.2H_2O$ from Chuquicamata, Chile. The