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The Crystal Structure of 1,1-Di-*p*-tolylethylene

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The crystal structure of 1,1-di-*p*-tolylethylene has been determined by direct methods and refined by block-diagonal least-squares calculations with three-dimensional data collected at room temperature (final R index 0·069). The crystals are monoclinic, space group $P2_1/c$, with a = 6·362, b = 26·211, c = 7·718 Å, β = 103·42°, and 4 molecules in the unit cell. Intensity data were collected from Weissenberg photographs. In the molecule the atoms are distributed on three planes: the ethylene reference plane and the two phenyl rings which are rotated by 37 and 50°. Bond lengths and angles are in the normal range.

Introduction

The determination of the crystal structure of 1,1-di-*p*-tolylethylene has been undertaken as a continuation of previous studies (Casalone, Mariani, Mugnoli & Simonetta, 1966, 1967*a*, *b*). By virtue of the absence of heavy atoms, which were contained in other analogous compounds investigated up to the present time, more accurate experimental results can be obtained from 1,1-di-*p*-tolylethylene. This assures also a more reliable comparison with the results of a subsequent conformational analysis.

In this paper the geometry of the molecule, as determined by X-ray diffraction by the crystal, is given.

Experimental

Crystals of 1,1-di-*p*-tolylethylene (m.p. 61 °C) are white parallelepipeds elongated along **a**. The crystal data are collected in Table 1.

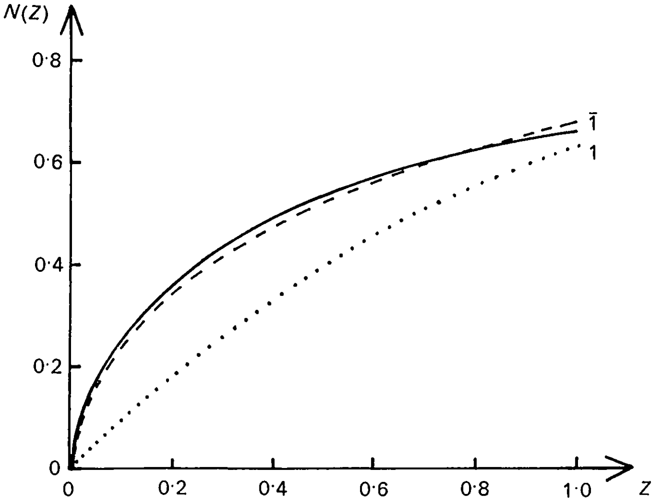

Fig. 1. $N(z)$ test for 1,1-di-*p*-tolylethylene. The solid curve represents the experimental values.

Table 1. *Crystal data*

1,1-Di-*p*-tolylethylene, $C_{16}H_{16}$, F.W. 208·3, monoclinic;
D_{meas} = 1·096 g.cm^{-3}, D_{calc} = 1·105 g.cm^{-3}, Z = 4, $F(000)$ = 448
λ Cu $K\alpha_1$ = 1·5405 Å, λ Cu $K\alpha_2$ = 1·5443 Å.

a = 6·362 ± 0·001 Å
b = 26·211 ± 0·002
c = 7·718 ± 0·001
β = 103·42 ± 0·02°.

Cell volume U = 1252 Å^3.
Systematic absences: $h0l$ for $l = 2n+1$, $0k0$ for $k = 2n+1$.
Space group $P2_1/c$.

The unit-cell parameters were obtained from a least-squares treatment of 71 measurements on zero-level Weissenberg photographs taken at room temperature around the crystallographic axes a and b, with Cu $K\alpha$ radiation.

For the determination of the structure, intensity data were collected from multiple-film equi-inclination Weissenberg photographs taken at room temperature with Cu $K\alpha$ radiation. Layers 0–5 around **a** were obtained from a crystal whose dimensions were 0·26 × 0·14 × 0·28 mm. The intensities were estimated visually, then scaled together within the same layer and corrected for Lorentz and polarization factors. No corrections either for absorption (μCu $K\alpha$ = 4·7 cm^{-1}) or for extinction were made. An evaluation of the standard deviation for each individual observation was obtained from a statistical analysis. Scaling factors between layers were obtained by comparison with 388 intensity measurements made on the same crystal with an equi-inclination diffractometer.

The whole processing of the observed data was carried on using a program for an IBM 1620 20K computer, written by Gramaccioli & Mariani (1967*a*). Of a total of 2867 reflexions within the effective sphere of Cu $K\alpha$ radiation, 2224 were collected, of which 518 were too low to be measured.

Structure determination and refinement

The crystal structure was solved with the aid of direct methods.

The intensities were brought to an approximately absolute scale by means of Wilson statistics and then the normalized structure factors were evaluated as

$$|E_{\mathbf{A}}| = |F_{\mathbf{A}}| \,.\, \varepsilon^{-1/2} \,.\, \exp\,[B(\sin^2\theta)/\lambda^2] \,.\, \left(\sum_{j=1}^{N} f_{j,\mathbf{A}}^2\right)^{-1/2},$$

where $\mathbf{A} = hkl$ and, for space group $P2_1/c$, $\varepsilon = 2$ for $h0l$ and $0k0$ reflexions and $\varepsilon = 1$ otherwise. The mean values of some functions of $|E|$ are given in Table 2, and the $N(z)$ test in Fig. 1.

Table 2. *Some functions of* $|E|$

Function	Acentric case	Centric case	Experimental
$\langle \lvert E \rvert \rangle$	0·886	0·798	0·812
$\langle \lvert E \rvert^2 \rangle$	1·000	1·000	1·087
$\langle \lvert E^2 - 1 \rvert \rangle$	0·736	0·968	1·083

The sign determination was undertaken by applying the Sayre relation (Sayre, 1952) and the Σ_2 relation for centrosymmetric crystals (Hauptman & Karle, 1953) to 197 reflexions with $|E| \geq 1{\cdot}50$.

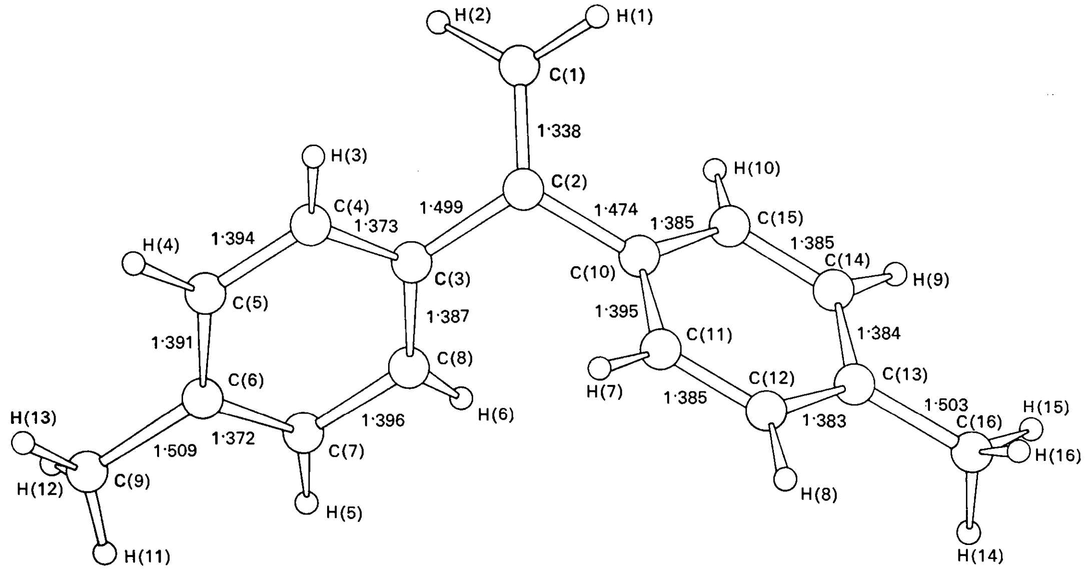

Fig. 2. Bond distances and numbering of atoms.

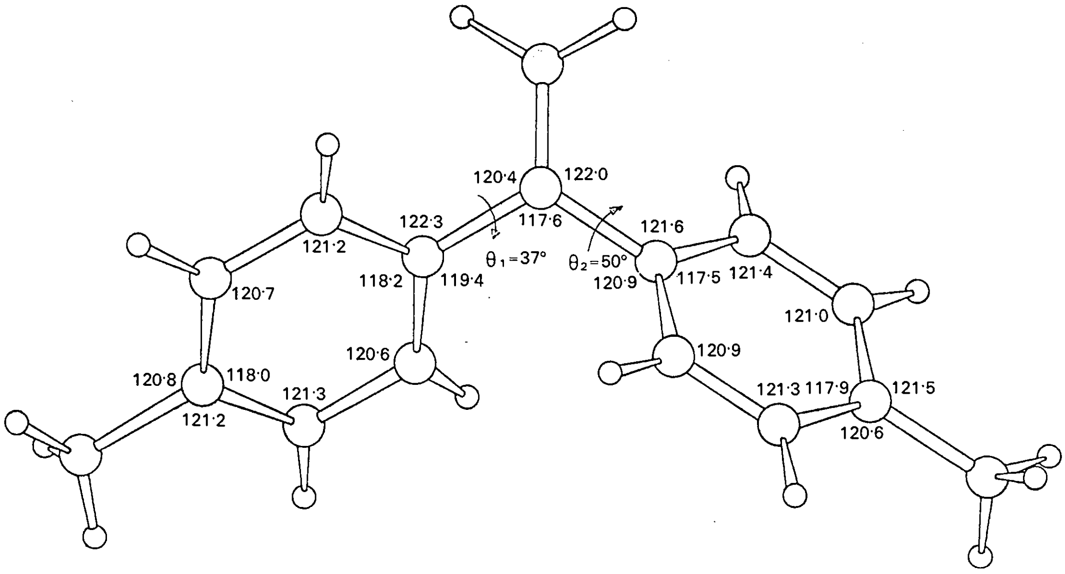

Fig. 3. Bond angles and angles of rotation θ_1 and θ_2 of the phenyl rings with respect to the ethylene plane C(1), C(2), C(3), C(10), here coincident with the plane of the paper.

The whole process was performed using a FORTRAN IV computer program (Long, 1965). The first step is the evaluation, for each reflexion, of the number of terms in the Σ_2 sums. Then the origin specifying reflexions according to the space group requirements and four other reference reflexions are chosen among the largest values of $|E_{\mathbf{A}}|.\sum_{\mathbf{A}-B+C}|E_B|\,.\,|E_C|$. The next

Table 3. *Observed and calculated structure factors*

The columns are *k*, *l*, $10\lvert F_o\rvert$, $10F_c$. Negative F_o values denote unobserved reflexions.

k	l	$10\lvert F_o\rvert$	$10F_c$
H = 0			
0	2	278	-287
0	4	142	-145
0	6	203	-210
0	8	78	71
1	1	402	430
1	2	449	-487
1	3	285	-290
1	4	35	-29
1	5	30	-30
1	6	-14	-07
1	7	-14	08
1	8	42	36
1	9	-11	19
2	1	50	48
2	2	575	-606
2	3	219	-220
2	4	94	97
2	5	-12	-11
2	6	67	73
2	7	119	-120
2	8	46	-47
2	9	-11	-10
3	1	111	-105
3	2	663	-724
3	3	-9	-03
3	4	92	97
3	5	104	105
3	6	18	-15
3	7	53	-61
3	8	67	67
3	9	-11	-08
4	0	554	-561
4	1	844	-875
4	2	432	-441
4	3	11	-11
4	4	165	163
4	5	46	46
4	6	76	80
4	7	168	166
4	8	-14	-25
4	9	16	18
5	1	60	55
5	2	209	-209
5	3	27	-27
5	4	149	146
5	5	46	40
5	6	32	-35
5	7	18	-21
5	8	-14	-09
5	9	39	32
6	0	893	923
6	1	136	-118
6	2	76	76
6	3	110	117
6	4	51	56
6	5	41	-41
6	6	27	-26
6	7	-14	-07
6	8	42	37
6	9	-11	07
7	1	532	-515
7	2	177	165
7	3	145	140
7	4	179	189
7	5	92	99
7	6	111	-112
7	7	76	83
7	8	25	-20
7	9	53	-44
8	0	384	-380
8	1	324	301
8	2	55	-51
8	3	318	296
8	4	-12	-17
8	5	104	-103
8	6	30	29
8	7	119	-121
8	8	44	-39
8	9	39	-31
9	1	265	254
9	2	329	-310
9	3	104	-101
9	4	129	132
9	5	104	-99
9	6	65	-68
9	7	-14	-18
9	8	64	55
9	9	-9	-06
10	0	51	-39
10	1	145	-120
10	2	32	-30
10	3	122	-107
10	4	110	-113
10	5	126	131
10	6	21	-13
10	7	65	72
10	8	28	23
10	9	-9	08
11	1	198	181
11	2	202	-205
11	3	80	-74
11	4	110	105
11	5	42	-41
11	6	-14	19
11	7	28	-24
11	8	27	-21
11	9	-7	31
12	0	149	-132
12	1	71	-73
12	2	333	317
12	3	39	-27
12	4	-12	-14
12	5	35	32
12	6	42	45
12	7	-14	-10
12	8	21	21
12	9	-7	01
13	1	138	-129
13	2	32	38
13	3	108	96
13	4	81	86
13	5	76	74
13	6	14	-16
13	7	18	22
13	8	48	-43
14	0	133	-131
14	1	110	-107
14	2	21	-18
14	3	99	92
14	4	41	38
14	5	103	-109
14	6	85	-88
14	7	16	-18
14	8	-11	-05
15	1	34	37
15	2	97	-101
15	3	12	-17
15	4	-14	-02
15	5	37	-38
15	6	-14	-08
15	7	44	-43
15	8	35	26
16	0	87	-91
16	1	46	52
16	2	41	-36
16	3	16	-16
16	4	25	28
16	5	69	73
16	6	57	-61
16	7	32	35
16	8	-9	10
17	1	28	26
17	2	-12	01
17	3	-14	-09
17	4	18	15
17	5	14	12
17	6	23	-22
17	7	30	-31
17	8	21	21
18	0	35	-27
18	1	81	-86
18	2	212	209
18	3	39	42
18	4	55	-59
18	5	50	-53
18	6	44	46
18	7	16	14
18	8	-7	05
19	1	65	67
19	2	74	-72
19	3	42	-44
19	4	28	-26
19	5	-14	09
19	6	-14	02
19	7	-11	05
20	0	131	-136
20	1	202	-217
20	2	32	-26
20	3	-14	05
20	4	-14	13
20	5	90	-95
20	6	-12	-12
20	7	-11	16
21	1	111	-125
21	2	-14	11
21	3	41	40
21	4	-14	03
21	5	18	21
21	6	-12	05
21	7	19	19
22	0	246	-242
22	1	-14	07
22	2	-14	03
22	3	58	58
22	4	42	48
22	5	55	62
22	6	-12	13
22	7	-9	03
23	1	62	-70
23	2	64	69
23	3	74	81
23	4	27	28
23	5	12	04
23	6	-11	-13
23	7	-7	17
24	0	34	30
24	1	30	29
24	2	138	141
24	3	62	66
24	4	46	-53
24	5	-12	-15
24	6	-11	-02
25	1	69	69
25	2	42	43
25	3	-14	-02
25	4	44	-42
25	5	50	-53
25	6	-9	-01
26	0	46	-49
26	1	50	51
26	2	18	14
26	3	14	17
26	4	25	-23
26	5	46	-48
26	6	-7	-11
27	1	-14	06
27	2	78	90
27	3	-12	00
27	4	39	-35
27	5	46	-42
28	0	-14	-04
28	1	-14	-20
28	2	-12	-02
28	3	55	-51
28	4	28	-27
28	5	19	19
29	1	-12	-02
29	2	51	-45
29	3	-11	06
29	4	44	-41
30	0	111	99
30	1	-12	-02
30	2	-11	-01
30	3	41	-42
30	4	-7	-07
31	1	-11	-13
31	2	-11	-00
31	3	-9	06
32	0	64	-62
32	1	73	72
32	2	23	-23
H = 1			
0	-2	267	-267
0	2	991	1023
0	-4	407	-410
0	4	163	-169
0	-6	219	-223
0	6	-18	-15
0	8	-16	00
1	-1	511	-554
1	1	716	749
1	-2	27	26
1	2	92	94
1	-3	42	-46
1	3	106	98
1	-4	39	32
1	4	156	-164
1	-5	42	-35
1	5	42	-40
1	-6	44	55
1	6	41	-43
1	7	-18	-01
1	8	-16	04
1	9	18	-18
2	0	472	-559
2	-1	226	226
2	1	1178	1229
2	-2	308	302
2	2	92	99
2	-3	124	-110
2	3	80	89
2	-4	90	94
2	4	106	-113
2	-5	81	-85
2	5	108	-106
2	-6	103	100
2	6	18	18
2	7	51	-55
2	8	25	-28
2	9	-11	02
3	0	529	527
3	-1	115	-123
3	1	131	144
3	-2	67	-67
3	2	180	-189
3	-3	113	100
3	3	375	-395
3	-4	184	164
3	4	136	-155
3	-5	-14	-02
3	5	-16	11
3	-6	113	-110
3	6	18	-14
3	-7	78	-84
3	7	28	34
3	8	44	41
3	9	-11	-13
4	0	387	-385
4	-1	62	66
4	1	449	-474
4	-2	133	119
4	2	41	-36
4	-3	92	83
4	3	499	-522
4	-4	34	36
4	4	117	-122
4	-5	-14	-01
4	5	80	78
4	-6	159	160
4	6	57	56
4	-7	131	-133
4	7	25	24
4	8	14	-12
4	9	25	23
5	0	80	72
5	-1	202	-190
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5	-2	35	29
5	2	67	78
5	-3	35	28
5	3	304	-324
5	-4	73	-59
5	4	96	-89
5	-5	62	-58
5	5	60	62
5	-6	126	-126
5	6	78	85
5	-7	64	66
5	7	18	-11
5	8	44	-39
5	9	19	23
6	0	458	468
6	-1	333	310
6	1	193	-180
6	-2	-9	04
6	2	163	-157
6	-3	76	-68
6	3	191	-189
6	-4	124	-103
6	4	110	-99
6	-5	44	45
6	5	126	131
6	-6	159	-156
6	6	103	106
6	-7	-18	-04
6	7	-18	-18
6	8	62	59
6	9	-9	03
7	0	458	-450
7	-1	80	70
7	1	492	-501
7	-2	103	-92
7	2	27	31
7	-3	51	58
7	3	18	-23
7	-4	92	89
7	4	80	72
7	-5	207	204
7	5	74	71
7	-6	88	88
7	6	80	83
7	-7	28	-31
7	7	78	83
7	8	60	-59
7	9	18	-20
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8	4	120	121
8	-5	71	63
8	5	143	145
8	-6	-18	08
8	6	21	-27
8	-7	90	92
8	7	60	-63
8	8	48	-46
9	0	379	354
9	-1	356	-340
9	1	14	-15
9	-2	140	-120
9	2	324	-339
9	-3	97	-91
9	3	96	110
9	-4	170	152
9	4	83	86
9	-5	25	29
9	5	21	22
9	-6	73	-72
9	6	30	-31
9	-7	28	-27
9	7	55	-65
9	8	44	42
10	0	108	-102
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10	1	216	-195
10	-2	338	-303
10	2	186	170
10	-3	271	-235
10	3	152	-134
10	-4	80	66
10	4	73	69
10	-5	48	-43
10	5	46	49
10	-6	81	81
10	6	73	-76
10	-7	21	-26
10	7	19	-27
10	8	50	-48
11	0	186	175
11	-1	76	67
11	1	320	300
11	-2	188	-148
11	2	168	162
11	-3	23	32
11	3	71	-45
11	-4	195	-176
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11	5	18	-09
11	-6	-18	-13
11	6	21	-22
11	-7	-18	09
11	7	65	-66
11	-8	44	-09
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12	2	200	-183
12	-3	246	-232
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14	-7	-16	08
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14	-8	34	43
14	8	42	-37
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15	-1	-14	-02
15	1	108	-92
15	-2	30	38
15	2	241	-240
15	-3	-16	-17
15	3	64	73
15	-4	58	52
15	4	-18	26
15	-5	103	-98
15	5	48	-46
15	-6	51	-46
15	6	-18	-06
15	-7	80	65
15	7	-14	-11
15	-8	51	10
15	8	30	32
16	0	-14	-19
16	-1	182	-159
16	1	216	-198
16	-2	50	-42
16	2	50	43
16	-3	60	57
16	3	97	-91
16	-4	16	-14
16	4	-18	03
16	-5	78	-77
16	5	88	99
16	-6	-18	06
16	6	39	-41
16	-7	-16	09
16	7	-14	01
16	-8	-12	43
16	8	32	-30
17	0	-14	09
17	-1	74	73
17	1	108	-102
17	-2	58	55
17	2	115	-118
17	-3	32	40
17	3	129	124
17	-4	18	18
17	4	28	25
17	-5	57	-61
17	5	18	-17
17	-6	67	-56
17	6	16	17
17	-7	-14	05
17	7	-12	-10
17	-8	46	-18
18	0	122	-114
18	-1	-16	-14
18	1	50	43
18	-2	126	105
18	2	-16	-03
18	-3	83	73
18	3	73	-72
18	-4	35	-35
18	4	67	66
18	-5	-18	-15
18	5	21	26
18	-6	27	-25
18	6	58	53
18	-7	14	-16
18	7	-12	-11
18	-8	18	-31
19	0	149	146
19	-1	19	-17
19	1	73	-71
19	-2	53	-46
19	2	-16	00
19	-3	18	13
19	3	110	115
19	-4	51	55
19	4	28	-27
19	-5	-18	-13
19	5	-18	-09
19	-6	51	-51
19	6	23	-25
19	-7	-14	09
19	7	14	-16
20	0	51	-53
20	-1	122	115
20	1	255	255
20	-2	50	-43
20	2	-18	-02
20	-3	-18	13
20	3	37	-41
20	-4	65	72
20	4	34	38
20	-5	-18	-19
20	5	80	-84
20	-6	-16	14
20	6	42	-43
20	-7	27	-27
20	7	14	-15
21	0	21	24
21	-1	34	35
21	1	193	-195
21	-2	92	-87
21	2	94	95
21	-3	81	78
21	3	21	-19
21	-4	-18	-00
21	4	30	-35
21	-5	16	20
21	5	-16	04
21	-6	14	15
21	6	-14	04
21	-7	-12	-12
21	7	-9	08
22	0	27	30
22	-1	257	-260
22	1	51	-51
22	-2	32	29
22	2	142	-145
22	-3	37	37
22	3	-18	10
22	-4	60	63
22	4	-16	11
22	-5	16	17
22	5	50	43
22	-6	-14	-07
22	6	-12	-13
22	-7	-11	05
22	7	-7	14
23	0	44	-45
23	-1	117	120
23	1	108	-106
23	-2	57	-64
23	2	42	-44
23	-3	35	-35
23	3	18	25
23	-4	46	46
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25	-1	-14	02
25	1	-11	-03
25	-2	-14	04
25	-3	-14	04
25	-4	-11	06
26	0	-11	-05
26	-1	25	21
26	-2	37	-32
26	-3	-11	06

step is to perform a reiterative calculation for each of the sixteen starting sets of signs in order to obtain the remaining signs, using the Σ_2 relation. (The program was run so that newly determined signs were utilized in a subsequent cycle.) For each solution the consistency index, c, is evaluated as

$$c = \frac{\langle |E_{\mathbf{A}} \, . \sum_{\mathbf{A}=B+C} E_B \, . \, E_C| \rangle}{\langle |E_{\mathbf{A}}| \, . \sum_{\mathbf{A}=B+C} |E_B| \, . \, |E_C| \rangle}$$

The E map corresponding to the solution of highest consistency index ($c=0{\cdot}799$) revealed all the atomic positions. The structure factor calculation performed on all the three-dimensional observed data gave an index $R=0{\cdot}26$.

Refinement was first performed on the carbon-atom parameters by several cycles of isotropic block-diagonal least-squares calculations including only data for which $F_o \geq 7$. The quantity minimized was $\Sigma w(|kF_o|-|F_c|)^2$. Initially weights $w=1/\bar{f}^2$ were assigned, where $\bar{f}$ is the average scattering factor. Later a weighting function $w=(A+B|kF_o|+C|kF_o|^2)^{-1}$ was used, where the parameters $A=7$, $B=1$ and $C=0{\cdot}02$ were chosen in order to give nearly constant mean values of $w(|kF_o|-|F_c|)^2$ as a function of F_o and $\sin^2 \theta/\lambda^2$. At this stage the R index was $0{\cdot}21$.

Further refinement on the carbon atoms was accomplished by anisotropic block-diagonal least-squares process, using the same weighting function and including all the observed data. Unobserved reflexions were included only when $|F_c|$ exceeded a threshold value of $|kF_o|$. This led to an index $R=0{\cdot}11$ for all the observed reflexions.

In order to locate the hydrogen atoms a three-dimensional difference Fourier synthesis was computed in the ethylene, phenyl and methyl hydrogen atom planes. The corresponding two-dimensional maps revealed well-defined peaks near the expected positions; accordingly, the coordinates of the hydrogen atoms were allowed to vary in subsequent least-squares calculations. In the final stages of refinement the isotropic temperature factors of the hydrogen atoms were also allowed to vary; however, their shifts were not credible. These temperature factors were therefore held fixed at assumed values of $B=4\cdot9$ for H(1)–H(10) and $B=5\cdot5$ for the methyl hydrogen atoms H(11)–H(16).

At the end the shifts for all parameters were lower than the corresponding standard deviation. Of the 518 reflexions too weak to be measured, only 55 had $|F_c|$ greater than the threshold value of $|kF_o|$. The final reliability index based on all the observed reflexions is $R=0\cdot069$. The observed and calculated structure factors are listed in Table 3, the final carbon atom parameters and their standard deviations in Table 4, and the hydrogen atom parameters in Table 5. The numbering of the atoms is shown in Fig. 2.

Results and discussion

The standard deviations in the coordinates, derived from the residual and the reciprocals of the diagonal elements of the matrix of the final least-squares cycle,

Table 4. *The carbon atom parameters and their standard deviations*

All the values in this Table have been multiplied by 10^4. The temperature factor is in the form $\exp[-(b_{11}h^2+b_{12}hk+b_{13}hl+b_{22}k^2+b_{23}kl+b_{33}l^2)]$.

	x	y	z	$\underline{b}_{11}$	$\underline{b}_{12}$	$\underline{b}_{13}$	$\underline{b}_{22}$	$\underline{b}_{23}$	$\underline{b}_{33}$
C(1)	-2324(6)	2096(1)	1026(4)	451(10)	15(3)	209(13)	14(0)	-13(3)	264(6)
C(2)	-1833(4)	1667(1)	267(4)	278(8)	2(3)	77(10)	14(0)	0(2)	180(5)
C(3)	-2406(4)	1157(1)	907(3)	287(8)	9(3)	103(9)	13(0)	-6(2)	148(4)
C(4)	-4267(5)	1078(1)	1482(4)	331(9)	21(3)	171(10)	16(0)	9(2)	205(5)
C(5)	-4707(5)	607(1)	2160(4)	342(9)	4(3)	212(11)	18(0)	22(3)	223(5)
C(6)	-3265(5)	203(1)	2272(4)	385(9)	-2(3)	195(11)	14(0)	5(2)	203(5)
C(7)	-1406(5)	283(1)	1698(4)	405(10)	37(3)	245(12)	14(0)	10(2)	251(6)
C(8)	-976(5)	753(1)	1002(4)	292(8)	15(3)	184(10)	15(0)	2(2)	226(5)
C(9)	-3752(7)	-309(1)	2984(5)	652(14)	-5(4)	403(16)	16(0)	31(3)	334(8)
C(10)	-669(4)	1674(1)	-1176(3)	293(8)	6(3)	52(9)	12(0)	5(2)	162(4)
C(11)	-1405(5)	1389(1)	-2725(4)	326(9)	-25(3)	74(11)	16(0)	-3(2)	185(5)
C(12)	-304(5)	1393(1)	-4076(4)	380(10)	-9(3)	85(11)	16(0)	-12(2)	172(5)
C(13)	1575(5)	1672(1)	-3926(4)	334(9)	24(3)	115(10)	13(0)	17(2)	193(5)
C(14)	2311(5)	1954(1)	-2389(4)	311(9)	-7(3)	98(11)	15(0)	16(2)	206(5)
C(15)	1200(5)	1957(1)	-1044(4)	337(8)	-13(3)	62(10)	13(0)	-2(2)	174(5)
C(16)	2776(6)	1663(1)	-5389(4)	423(10)	41(4)	263(12)	21(1)	21(3)	242(6)

Table 5. *The hydrogen atom parameters*

Estimated standard deviations in the coordinates (in brackets) are multiplied by 10^4.

	x	y	z	B
H(1)	−0·1935 (57)	0·2444 (14)	0·0569 (49)	4·9
H(2)	−0·3050 (57)	0·2082 (15)	0·2073 (48)	4·9
H(3)	−0·5401 (57)	0·1349 (15)	0·1299 (50)	4·9
H(4)	−0·6072 (58)	0·0564 (15)	0·2562 (51)	4·9
H(5)	−0·0393 (59)	0·0032 (15)	0·1713 (50)	4·9
H(6)	0·0449 (59)	0·0799 (14)	0·0598 (48)	4·9
H(7)	−0·2678 (57)	0·1198 (14)	−0·2824 (50)	4·9
H(8)	−0·0764 (57)	0·1183 (14)	−0·5177 (49)	4·9
H(9)	0·3724 (58)	0·2138 (15)	−0·2208 (49)	4·9
H(10)	0·1843 (58)	0·2130 (14)	0·0019 (47)	4·9
H(11)	−0·3285 (62)	−0·0569 (16)	0·2355 (55)	5·5
H(12)	−0·2712 (61)	−0·0372 (15)	0·4182 (54)	5·5
H(13)	−0·5034 (61)	−0·0335 (15)	0·3280 (53)	5·5
H(14)	0·3537 (61)	0·1363 (15)	−0·5459 (51)	5·5
H(15)	0·4063 (60)	0·1866 (15)	−0·5188 (49)	5·5
H(16)	0·1962 (61)	0·1783 (16)	−0·6516 (49)	5·5

correspond to positional uncertainties of 0·003 Å for carbon atoms and of 0·04 Å for hydrogen atoms. The corresponding standard deviations in bond lengths and angles do not exceed 0·005 Å and 0·3° for C–C bonds and CCC angles respectively, whereas they range from 0·03 to 0·04 Å for C–H bonds and from 2 to 4° for HCC and HCH angles. Bond distances and angles are reported in Figs. 2 and 3. All these values are uncorrected for librational effects. The two C_{ethylene}–H bond distances are 1·02 and 1·03 Å respectively. The C_{phenyl}–H bond distances range from 0·92 to 1·03 Å and the C_{methyl}–H bond distances range from 0·90 to 1·02 Å. Benzenic and ethylenic bond angles involving hydrogen atoms range from 116 to 123°. In the methyl groups, HCC angles range from 109 to 116° and HCH from 92 to 120°.

The most interesting result of this structure analysis concerns the conformation of the molecule in the crystal. Both phenyl rings are rotated with respect to the ethylenic plane C(1), C(2), C(3), C(10), the rotation angles being $\theta_1 = 37°$ and $\theta_2 = 50°$ (see Fig. 3). A twist value near to θ_1 was found for gaseous biphenyl, both experimentally (Almenningen & Bastiansen, 1958) and on semi-theoretical grounds (Casalone, Mariani, Mugnoli & Simonetta, 1968). Also in crystals of *p,p'*-bitolyl the twist angle lies between 36 and 40° (Casalone, Mariani, Mugnoli & Simonetta, 1969). The considerable difference between the two angles θ_1 and θ_2 could be explained by packing interactions. Conformational analysis should give a better insight into this problem. Calculations are in progress to establish the minimum-energy conformation for the isolated molecule of 1,1-di-*p*-tolylethylene and for the same molecule packed in the crystal.

The average planes in the molecule were determined by the method of Schomaker, Waser, Marsh & Bergman (1959) using a program written by Mariani & Gramaccioli (1967) for the IBM 1620 computer. The results are reported in Table 6. A considerable out-of-plane bending takes place along both phenyl ring axes, as indicated by the deviations in Table 6 for atoms marked by an asterisk. A similar behaviour has been found in *p,p'*-bitolyl for example (Casalone, Mariani, Mugnoli & Simonetta, 1969). All the intermolecular distances are longer than the corresponding van der Waals distances, as computed with $r_C = 1{\cdot}6$ and $r_H = 1{\cdot}2$ Å. A view of the packing of the molecules in the crystal is shown in Fig. 4. The lengths and direction cosines of the principal axes of thermal vibration are given in Table 7, as computed by a program of Gra-

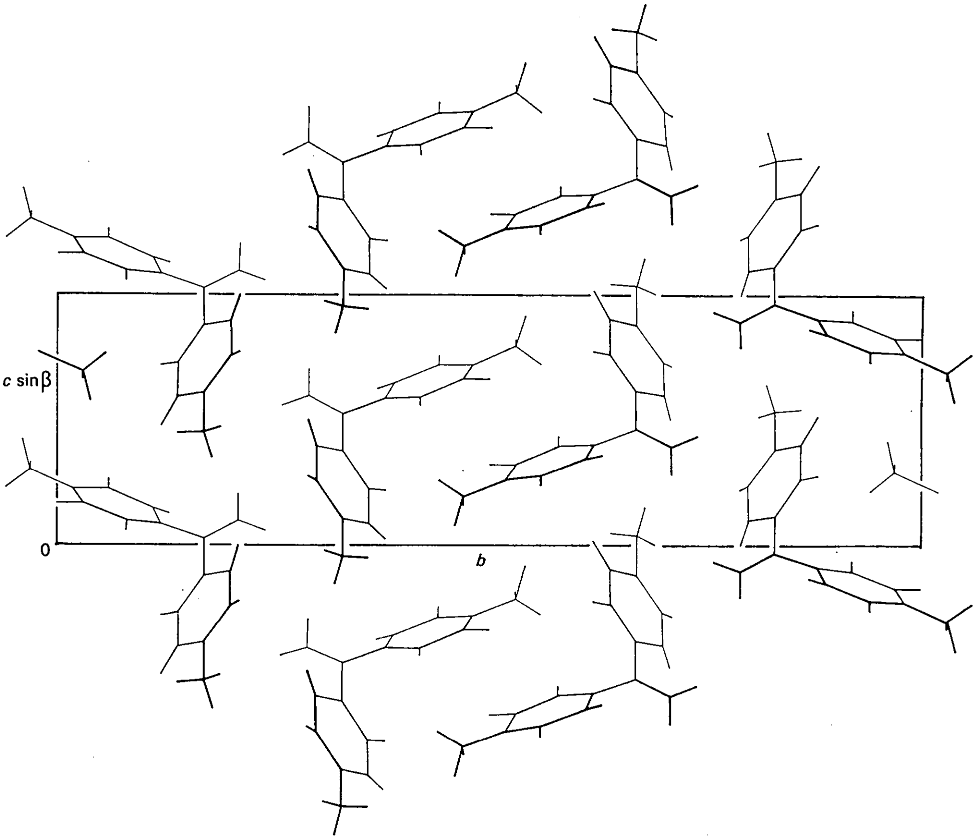

Fig. 4. Arrangement of the molecules in the crystal as viewed along the *a* axis.

maccioli & Mariani (1967*b*). The anisotropy is particularly evident for the C(1) and the methyl carbon atoms.

Table 6. *Some least-squares planes*

The coefficients q_i are the direction cosines relative to the crystallographic axes a,b,c. Atoms were omitted from the calculation of the least-squares plane where indicated by an asterisk; the remaining atoms were given equal weights.

Ethylene	Atom	Deviation
$q_1 = 0{\cdot}7406$	C(1)	0·003 Å
$q_2 = -0{\cdot}0334$	C(2)	−0·009
$q_3 = 0{\cdot}4809$	C(3)	0·003
$D = -0{\cdot}901$ Å	C(10)	0·003
	*C(6)	0·188
	*C(9)	0·268
	*C(13)	0·040
	*C(16)	0·064
1st tolyl group		
$q_1 = 0{\cdot}2627$	C(3)	0·000
$q_2 = 0{\cdot}2914$	C(4)	−0·001
$q_3 = 0{\cdot}8337$	C(5)	0·002
$D = 1{\cdot}065$ Å	C(6)	0·006
	C(7)	0·009
	C(8)	−0·008
	C(9)	−0·008
	*C(2)	0·074
	Angle with the ethylene plane: 37°	
2nd tolyl group		
$q_1 = 0{\cdot}4529$	C(10)	0·006
$q_2 = -0{\cdot}7819$	C(11)	0·005
$q_3 = 0{\cdot}3115$	C(12)	−0·010
$D = -3{\cdot}912$ Å	C(13)	−0·005
	C(14)	−0·001
	C(15)	−0·004
	C(16)	0·008
	*C(2)	0·032
	Angle with the ethylene plane: 50°	

Table 7. *Magnitudes and direction cosines, relative to the crystallographic axes, of the principal axes of the thermal ellipsoids*

	B_i	q_i^a	q_i^b	q_i^c		B_i	q_i^a	q_i^b	q_i^c
C(1)	7.03	0.898	0.109	0.206	C(9)	10.56	0.816	0.053	0.370
	5.90	0.367	0.347	-0.925		6.80	0.532	-0.458	-0.816
	3.67	0.242	-0.931	-0.320		3.69	0.225	0.888	-0.443
C(2)	4.50	0.885	0.076	-0.653	C(10)	4.84	0.955	0.059	-0.504
	3.93	0.456	0.062	0.758		3.66	0.227	0.484	0.770
	3.72	0.096	-0.995	-0.003		3.11	0.190	-0.873	0.392
C(3)	4.52	0.937	0.342	-0.143	C(11)	5.67	0.862	-0.493	-0.318
	3.66	0.211	-0.724	0.591		4.28	0.151	0.477	-0.877
	3.06	0.280	-0.600	-0.794		3.68	0.484	0.728	0.360
C(4)	5.66	0.705	0.474	0.350	C(12)	6.01	0.994	-0.103	-0.259
	4.22	0.444	0.286	-0.929		4.69	0.076	0.866	-0.498
	3.93	0.554	-0.833	-0.120		3.60	0.076	0.489	0.828
C(5)	6.16	0.427	0.534	0.611	C(13)	5.47	0.857	0.424	0.086
	5.03	0.723	-0.686	-0.091		4.56	0.441	-0.308	-0.922
	3.74	0.543	0.495	-0.786		3.13	0.267	-0.852	0.377
C(6)	6.02	0.881	0.002	0.256	C(14)	5.33	0.616	-0.505	-0.731
	4.27	0.417	-0.477	-0.849		4.62	0.763	0.193	0.422
	3.76	0.224	0.879	-0.462		3.69	0.194	0.842	-0.535
C(7)	7.07	0.731	0.321	0.416	C(15)	5.56	0.961	-0.202	-0.409
	4.85	0.540	0.267	-0.902		3.92	0.094	-0.412	0.860
	3.26	0.417	-0.909	-0.118		3.48	0.261	0.888	0.306
C(8)	5.40	0.466	0.199	0.730	C(16)	7.89	0.655	0.552	0.349
	4.34	0.545	0.703	-0.571		4.80	0.296	-0.815	0.415
	3.55	0.697	-0.683	-0.375		4.47	0.695	-0.174	-0.840

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A Refinement of the Crystal Structure of Copper(II) Oxide with a Discussion of Some Exceptional E.s.d.'s

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The crystal structure of copper(II) oxide has been refined from single-crystal diffractometer data. It is found that the coordination of oxygen around copper is more properly described as a plane four coordination rather than a 4+2 distorted octahedral one. The copper atom shows anisotropy of thermal vibration, the largest component of vibration being approximately perpendicular to the plane formed by the coordinated oxygen atoms. An anomaly in the magnitudes of the $\sigma(U_{ij})$'s of the copper is explained. This anomaly is found to be connected with the fact that there are weak contributions from the copper atom to reflexions which according to the space group should contain only oxygen contributions. In connexion with the extinction correction a modification is pointed out which should be made in Zachariasen's formula when the crystal is of 'arbitrary shape'.

Introduction

In connexion with studies of oxidation products of copper based β-brass (Norrby, Kierkegaard & Magnéli, 1963; Norrby, Johansson, Kierkegaard & Magnéli, 1964; Norrby, Nygren, Lindberg, Kierkegaard & Magnéli, 1966) it became desirable to undertake a redetermination of the previously investigated crystal structure of CuO (Tunell, Posniak & Ksanda, 1935). Furthermore, a need for accurate Cu(II)–O distances of various compounds became acute when studying spinels containing copper and other transition metals (Åsbrink, 1965). In the course of this investigation, which included the use of an automatic single crystal X-ray diffractometer, some interesting problems of methodological character arose. The physical interpretation of the least-squares refined parameters and the significance of their estimated standard deviations also presented problems. Thus the emphasis of this study was laid not only on the structural features of CuO, but also on more general aspects of the methods used.

Experimental

Single crystals of CuO were obtained by a flux method. Powdered commercial analytical grade copper(II) oxide was mixed in equimolar proportions with sodium carbonate and melted in a platinum crucible, heated in a conventional resistance furnace. The melt was kept at 900 °C for 20 hours and then cooled to 500 °C at a rate of 1·5 °C.min^{-1}. The solidified material was then air quenched and the sodium carbonate dissolved in hot water. The residue consisted of small, needle-shaped, dark, highly reflecting crystals of CuO. Out of this material a prismatic single crystal with a parallelogram-shaped base was selected. The dimensions of the crystal were 0·057 × 0·013 × 0·010 mm, the long edge being parallel to the *c* axis.