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Crystal, Molecular and Electronic Structure of 1,1-Diaryl-2-halogenoethylenes.
I. 2-Bromo-1,1-di-*p*-tolylethylene

BY G. L. CASALONE, C. MARIANI, A. MUGNOLI AND M. SIMONETTA
Institute of Physical Chemistry, University of Milan, Milan, Italy

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The crystal structure of 2-bromo-1,1-di-*p*-tolylethylene, $C_{16}H_{15}Br$, at room temperature, has been determined by three-dimensional methods, including anisotropic refinement by full-matrix least-squares calculations (final R value, 9·7 %). There are four formula units in the orthorhombic cell, $a=16·89$, $b=13·07$, $c=6·26$ Å, with space group $P2_12_12_1$. In the molecule the atoms are distributed on three planes: the ethylene reference plane and the two tolyl rings which are rotated by 24·4° (*trans* to Br) and 67·9° (*cis* to Br). Bond lengths and angles are in the normal range; the C–Br distance is 1·87 Å. Bond angles and distances in the isolated molecule and in 'model' crystals were calculated by semi-theoretical methods and the correlation with experimental values is discussed.

Introduction

It is known that 1,1-diaryl-2-halogenoethylenes can react with sodium ethoxide following two different paths leading to nucleophilic substitution and to a Fritsch rearrangement (Beltrame & Favini, 1963; Beltrame, Carrà, Macchi & Simonetta, 1964). For the latter reaction, a geometrical and electronic model of the activated complex has been suggested (Simonetta & Carrà, 1963) in which the aryl group *trans* to the halogen lies in a plane perpendicular to the ethylenic bond. Since the geometry of the substrate might be a relevant factor in determining the relative amounts of the two possible reactions with the base, an investigation was undertaken of the crystal, molecular and electronic structure of some diarylethylenes, including 2-bromo-1,1-di-*p*-tolylethylene, 2-chloro-1,1-di-*p*-tolylethylene, 1,1-diphenylethylene and 2-bromo-1,1-diphenylprop-1-ene.

In this paper the results for 2-bromo-1,1-di-*p*-tolylethylene are given. The geometry of the molecule, as determined by X-ray diffraction, has been compared with the geometry of the isolated molecule calculated by semi-empirical methods and the interrelations between the two have been discussed.

Experimental

Crystal data

2-Bromo-1,1-di-*p*-tolylethylene, m.p. 52 °C, crystallizes from isopropyl alcohol in transparent plates. The unit-cell dimensions were determined from zero-layer Weissenberg films about the b and c axes, with Cu $K\alpha$ radiation. The crystal data given below have already been published in a preliminary communication (Mariani, Mugnoli & Casalone, 1965).

2-Bromo-1,1-di-*p*-tolylethylene
$C_{16}H_{15}Br$ F.W. 287·2
Orthorhombic, $a=16·89\pm0·01$, $b=13·07\pm0·01$, $c=6·26\pm0·01$ Å, with $\lambda(\text{Cu } K\alpha_1)=1·5405$, $\lambda(\text{Cu } K\alpha_2)=1·5443$, $\lambda(\text{Cu } K\alpha)=1·5418$ Å;
$V=1381·9$ Å^3; $D_m=1·37$ g.cm^{-3} (by flotation); $Z=4$; $D_c=1·38$ g.cm^{-3}; $F(000)=584$; Absorption coefficient for Cu $K\alpha$ radiation, 39·1 cm^{-1}. Space group $P2_12_12_1$ (no. 19), from systematic absences: $h00$ if $h=2n+1$, $0k0$ if $k=2n+1$, $00l$ if $l=2n+1$.

Intensity measurements

The X-ray intensities were estimated visually from sets of multiple-film equi-inclination Weissenberg photographs taken at room temperature about the *c* axis (6 layers) and the *b* axis (4 layers). Two crystals were used, with cross sections respectively of $0{\cdot}16\times 0{\cdot}34$ mm^2 and of $0{\cdot}15\times 0{\cdot}15$ mm^2. From a total number of 1835 possible reflexions, with Cu $K\alpha$ radiation, 1705 were collected, of which 505 were too low to be observed. The intensities were scaled together within the same layer by a method similar to the one described by Rae (1965) and then corrected for Lorentz, polarization and spot-size (Phillips, 1954) factors. An evaluation of the σ for each individual observation was obtained from a statistical analysis (Gramaccioli & Mariani, 1965). The data belonging to different layers were scaled together according to the method proposed by Rollett & Sparks (1960), modified in order to account for the dependence of the weights upon the final scale factors (Hamilton, Rollett & Sparks, 1965; Duchamp, 1964). 242 reflexions were measured about both axes. No absorption or extinction corrections were applied.

Atomic scattering factors were calculated by means of analytical expressions following Cromer & Waber (1965) for bromine and carbon, and Forsyth & Wells (1959) for hydrogen atoms.

All the calculations except the least-squares refinement were carried out on an IBM 1620-20K electronic computer. Structure factors and Fourier syntheses were calculated by the programs of Albano, Bellon & Pompa (1963) and Pompa, Albano, Bellon & Scatturin (1963). The intensity scaling program was written by Gramaccioli and Mariani, who also adapted and partially modified the least-squares ORFLS program of Busing, Martin & Levy (1962) for an IBM 7040 computer. All the programs for the theoretical calculations were written by one of us (C.M.).

Structure determination and refinement

A preliminary two-dimensional investigation by Patterson and Fourier methods on the ($hk0$) and the ($h0l$) projections (Mariani, Mugnoli & Casalone, 1965) gave a set of atomic coordinates and isotropic thermal factors, used as a starting point for the refinement. After two cycles of differential Fourier synthesis, and one three-dimensional difference synthesis calculation, final refinement was achieved by some cycles of full-matrix least-squares, using the program ORFLS written by Busing, Martin & Levy (1962). During these last cycles, anisotropic temperature factors were adopted for each atom in the structure, except for hydrogen atoms. These latter were omitted from the least-squares refinement, being introduced only in the structure factor calculations. Hydrogen atoms bonded to an sp^2 carbon atom were assumed to lie on the line bisecting the angle

Table 1. *Final coordinates with standard deviations* ($\times 10^4$)

	x/a	y/b	z/c
Br	1172 (1)	2463 (1)	3738 (2)
C(1)	464 (7)	2834 (8)	1574 (22)
C(2)	407 (6)	3790 (7)	799 (16)
C(3)	−177 (6)	4015 (7)	−941 (15)
C(4)	−445 (7)	3266 (7)	−2350 (19)
C(5)	−996 (7)	3518 (8)	−3939 (18)
C(6)	−1261 (6)	4521 (10)	−4162 (22)
C(7)	−987 (6)	5272 (9)	−2767 (20)
C(8)	−449 (5)	5019 (7)	−1151 (17)
C(9)	913 (6)	4674 (7)	1602 (19)
C(10)	808 (7)	5042 (9)	3672 (18)
C(11)	1274 (8)	5855 (8)	4393 (22)
C(12)	1840 (7)	6292 (7)	3049 (21)
C(13)	1942 (6)	5919 (7)	977 (20)
C(14)	1478 (6)	5104 (9)	254 (19)
C(15)	−1847 (8)	4779 (12)	−5898 (24)
C(16)	2341 (9)	7162 (9)	3853 (24)
H(1)	82	2251	915
H(2)	−228	2491	−2218
H(3)	−1216	2931	−4997
H(4)	−1190	6051	−2933
H(5)	−243	5602	−62
H(6)	370	4702	4710
H(7)	1196	6146	5994
H(8)	2378	6259	−65
H(9)	1557	4809	−1343

Table 2. *Thermal exponent coefficients* (*with e.s.d.'s*)

b_{ij} as given here are defined by $T=\exp\left[-10^{-4}(b_{11}h^2+b_{22}k^2+b_{33}l^2+2b_{12}hk+2b_{13}hl+2b_{23}kl)\right]$

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Br	76 (1)	75 (1)	651 (6)	−3 (1)	−5 (2)	71 (2)
C(1)	55 (4)	65 (6)	571 (40)	−10 (4)	4 (12)	25 (14)
C(2)	48 (4)	47 (4)	419 (29)	−3 (3)	11 (9)	0 (10)
C(3)	40 (3)	62 (5)	347 (28)	−3 (4)	9 (8)	−15 (10)
C(4)	59 (5)	57 (6)	486 (34)	−9 (5)	30 (12)	−10 (12)
C(5)	58 (5)	71 (6)	503 (37)	−21 (5)	11 (12)	−34 (14)
C(6)	41 (4)	90 (7)	426 (30)	−6 (5)	−21 (9)	−27 (14)
C(7)	36 (4)	75 (6)	484 (32)	6 (4)	−2 (9)	−49 (12)
C(8)	36 (3)	62 (5)	489 (33)	12 (3)	−6 (9)	−70 (12)
C(9)	39 (3)	51 (5)	419 (30)	−6 (3)	8 (8)	22 (10)
C(10)	44 (4)	84 (7)	418 (33)	−1 (4)	10 (9)	45 (14)
C(11)	72 (6)	51 (5)	456 (29)	10 (5)	−28 (12)	3 (11)
C(12)	57 (5)	48 (5)	565 (41)	8 (4)	−67 (12)	−11 (12)
C(13)	41 (4)	50 (5)	539 (37)	−7 (3)	−11 (10)	21 (12)
C(14)	40 (3)	68 (7)	525 (36)	6 (4)	25 (10)	−37 (13)
C(15)	69 (6)	125 (11)	459 (38)	−22 (7)	−13 (14)	−4 (18)
C(16)	77 (6)	65 (6)	646 (49)	−9 (5)	−49 (16)	−19 (16)

Table 3. *Observed and calculated structure factors*

Each group of four columns contains in order h, $10|F_o|$, $10|F_c|$, and the phase angle. A minus sign before the $10|F_o|$ value designates unobserved reflexion. Reflexions indicated by an asterisk were given zero weight in the least-squares refinement and excluded from the R calculation.

H 0 0			
2	623	782	0
* 4	1215	1444	180
6	389	366	180
8	564	484	0
10	251	241	0
12	392	363	180
14	205	253	180
16	46	46	0
18	-35	4	180
20	27	20	0
H 1 0			
1	270	324	270
2	750	785	180
3	108	136	90
4	647	577	180
5	151	135	90
6	912	821	0
7	-24	13	270
8	140	146	0
9	146	138	90
10	359	342	180
11	160	164	90
12	114	99	180
13	-35	31	90
14	167	150	0
15	64	75	270
16	103	98	0
17	-38	37	270
18	-35	3	0
19	38	39	90
20	-27	25	180
21	-21	11	90
H 2 0			
0	205	206	180
1	626	513	270
2	24	5	0
3	783	789	270
4	257	307	0
5	130	144	90
6	332	270	0
7	-24	9	270
8	632	595	180
9	54	54	90
10	91	72	180
11	89	83	90
12	294	277	0
13	-35	14	90
14	143	124	0
15	76	69	90
16	91	102	180
17	-38	17	90
18	103	92	180
19	-30	15	270
20	46	31	0
21	-21	7	90
H 3 0			
1	238	159	90
* 2	1396	1581	0
3	543	435	270
4	173	128	180
5	154	130	90
6	824	772	180
7	345	285	90
8	94	83	180
9	54	40	90
10	465	398	0
11	91	75	90
12	259	222	0
13	-38	29	270
14	257	228	180
15	148	142	270
16	-38	29	180
17	-35	22	270
18	108	92	0
19	-30	0	270
20	24	37	0
21	-19	9	270
H 4 0			
* 0	1266	1337	0
1	200	164	90
2	135	163	0
3	67	77	90
4	1026	1048	180
5	24	38	270
6	532	467	180
7	130	119	270
8	537	481	0
9	116	127	270
10	105	84	0
11	-35	21	270
12	165	149	180
13	73	47	270
14	46	50	180
15	-38	14	270
16	-38	17	0
17	-35	29	270
18	33	37	0
19	33	30	90
20	-24	6	0
21	-16	23	90
H 5 0			
1	235	224	90
2	1021	1022	180
3	87	82	90
4	492	431	180
5	160	127	270
6	602	555	0
7	191	156	90
8	359	319	0
9	57	49	270
10	200	198	180
11	124	143	90
12	224	223	180
13	76	58	270
14	64	51	0
15	146	152	270
16	111	90	0
17	-35	26	270
18	-33	16	0
19	-27	23	270
20	-21	9	180
H 6 0			
0	764	596	180
1	38	42	90
2	121	86	0
3	221	171	90
4	505	523	0
5	130	100	270
6	46	13	180
7	63	58	90
8	586	544	180
9	140	139	90
10	245	210	180
11	57	57	270
12	227	224	0
13	38	33	90
14	64	70	0
15	-38	47	270
16	116	114	180
17	-33	17	270
18	-30	34	180
19	-24	23	90
20	49	41	0
H 7 0			
1	-27	28	90
2	694	599	0
3	91	79	270
4	184	187	0
5	265	215	90
6	483	429	180
7	-33	22	90
8	-35	11	180
9	30	27	270
10	292	256	0
11	-38	25	90
12	-38	14	180
13	-38	11	270
14	154	153	180
15	60	59	270
16	81	79	180
17	46	50	270
18	-27	21	0
19	-21	20	270
H 8 0			
0	924	851	0
1	143	131	270
2	130	107	0
3	365	308	90
4	602	492	180
5	154	126	90
6	103	87	180
7	35	33	90
8	205	186	0
9	81	103	270
10	114	93	0
11	-38	3	270
12	105	113	180
13	-38	40	90
14	81	82	180
15	-35	33	270
16	33	25	0
17	-27	24	270
18	-24	19	0
19	-16	16	90
H 9 0			
1	170	145	270
2	562	532	180
3	-35	21	270
4	208	204	180
5	87	87	270
6	351	307	0
7	84	80	270
8	148	143	0
9	-38	13	90
10	230	229	180
11	60	73	90
12	114	116	180
13	-35	14	90
14	35	48	0
15	-33	3	270
16	43	26	0
17	-24	2	270
18	-19	0	180
H 10 0			
0	241	222	180
1	43	28	90
2	-35	2	180
3	81	82	270
4	467	438	0
5	-38	22	270
6	160	157	0
7	-38	41	90
8	238	239	180
9	-38	41	90
10	157	144	180
11	-38	0	270
12	63	62	0
13	-35	14	90
14	46	54	0
15	-30	17	270
16	43	28	180
17	-19	6	90
H 11 0			
1	84	84	270
2	262	235	0
3	76	63	270
4	103	113	180
5	227	225	90
6	281	230	180
7	148	169	90
8	46	39	180
9	-38	14	90
10	121	91	0
11	-35	28	270
12	-33	24	0
13	38	28	90
14	49	40	180
15	-24	10	270
16	-19	3	180
H 12 0			
0	281	258	0
1	38	43	270
2	60	54	0
3	-38	21	270
4	251	234	180
5	-38	25	270
6	46	36	180
7	-38	19	270
8	165	125	0
9	-35	31	270
10	33	41	0
11	-33	13	90
12	87	81	180
13	-27	6	90
14	-21	3	0
15	-16	5	270
H 13 0			
1	-38	22	90
2	167	166	180
3	73	71	90
4	-38	8	180
5	-35	24	90
6	238	206	0
7	-35	3	90
8	154	127	0
9	-33	5	90
10	73	62	180
11	-27	19	90
12	54	49	180
13	24	17	90
14	-8	8	0
H 14 0			
0	135	136	180
1	73	67	90
2	43	47	180
3	70	64	270
4	146	134	0
5	63	48	270
6	-33	17	0
7	33	43	90
8	121	85	180
9	-27	41	90
10	63	59	180
11	43	47	270
12	-13	18	0
H 15 0			
1	46	40	270
2	167	147	0
3	51	38	270
4	-30	2	0
5	-27	13	90
6	94	86	180
7	-24	2	90
8	43	44	180
9	27	27	270
10	-11	53	0
H 16 0			
0	51	54	0
1	-24	24	90
2	-24	21	0
3	-21	15	90
4	78	64	180
5	30	27	90
6	-16	3	0
7	-11	6	270
H 0 1			
* 1	389	594	90
2	286	327	270
* 3	753	877	270
4	378	350	270
5	224	283	270
6	435	421	90
7	-19	2	270
8	130	141	90
9	162	215	90
10	289	315	270
11	-33	28	90
12	60	74	270
13	89	118	270
14	-38	36	90
15	38	45	90
16	-38	49	90
17	-38	49	90
18	43	67	270
19	24	30	270
20	-27	38	270
21	-16	9	270
H 1 1			
0	426	510	270
1	372	450	252
* 2	807	908	8
* 3	1045	1234	250
* 4	967	1078	64
5	324	345	175
6	216	215	61
7	286	325	93
8	342	368	256
9	278	285	301
10	227	246	272
11	262	278	288
12	173	161	57
13	46	44	93
14	64	68	68
15	97	101	74
16	67	63	265
17	63	64	34
18	27	44	216
19	24	34	220
20	33	31	170
21	-16	27	186
H 2 1			
* 0	448	517	180
* 1	562	703	296
* 2	826	983	82
3	453	508	38
4	416	390	271
5	478	496	96
6	613	689	259
7	335	313	242
8	221	208	268
9	362	368	280
10	248	256	102
11	194	184	89
12	97	102	72
13	205	205	96
14	89	81	280
15	51	56	159
16	57	53	208
17	100	89	247
18	40	31	69
19	-24	27	260
20	-19	14	45
21	-16	24	166
H 3 1			
* 0	510	704	90
* 1	499	641	89
2	413	432	74
* 3	489	575	77
* 4	634	714	288
5	421	403	285
6	381	361	201
7	254	245	258
8	456	461	114
9	-24	11	106
10	140	124	92
11	230	218	83
12	121	122	267
13	73	67	216
14	81	88	303
15	130	133	284
16	35	29	33
17	-27	20	344
18	40	34	123
19	-24	30	158
20	-19	19	259
21	-13	21	169
H 4 1			
0	289	290	0
1	589	596	93
2	513	537	275
3	292	289	300
4	386	383	255
5	540	607	254
6	257	294	133
7	146	149	124
8	257	255	86
9	329	329	86
10	218	210	284
11	-27	29	275
12	103	104	290
13	54	45	240
14	105	118	115
15	-30	20	170
16	97	99	113
17	27	32	81
18	-24	8	36
19	-21	12	335
20	-19	15	355
21	-11	33	233
H 5 1			
0	634	627	270
1	338	357	269
2	-19	15	348
3	368	392	288
4	580	605	52
5	413	416	55
6	127	139	320
7	327	346	117
8	270	264	259
9	87	96	311
10	64	70	221
11	205	209	304
12	189	200	113
13	-30	34	89
14	73	82	53
15	60	71	86
16	81	74	248
17	27	31	260
18	60	53	199
19	43	43	231
20	-16	26	129
H 6 1			
0	135	130	0
1	499	534	286
2	680	624	85
3	281	266	98
4	27	10	145
5	368	360	88
6	486	538	271
7	94	106	234
8	178	187	207
9	191	192	272
10	267	265	66
11	114	121	76
12	97	107	45
13	167	182	89
14	51	41	194
15	-30	21	91
16	-27	34	197
17	63	62	306
18	-21	29	112
19	19	32	293
20	-13	31	50
H 7 1			
0	227	242	90
1	191	205	94
2	241	221	348
3	329	313	88
4	362	390	286
5	167	160	277
6	218	234	249
7	275	277	251
8	170	164	107
9	100	112	80
10	151	154	100
11	200	202	49
12	51	70	301
13	-30	20	141
14	51	47	269
15	49	43	280
16	27	34	120
17	-24	15	252
18	-21	23	128
19	33	29	107
H 8 1			
0	197	220	0
1	318	353	89
2	383	366	259
3	262	255	272
4	143	150	222
5	214	213	271
6	232	245	98
7	100	76	56
8	184	165	49
9	140	163	135
10	138	152	316
11	35	53	347
12	67	78	287
13	89	101	308
14	57	57	111
15	-27	22	43
16	24	30	106
17	46	38	44
18	30	30	240
19	-11	18	259
H 9 1			
0	389	400	270
1	254	269	231
2	63	60	216
3	254	247	262
4	302	327	91
5	121	142	91
6	162	175	11
7	251	274	104
8	245	282	281
9	57	54	309
10	38	60	215
11	105	112	305
12	89	88	100
13	49	60	33
14	-27	40	63
15	30	36	91
16	33	22	268
17	-19	7	310
18	-13	19	259
H 10 1			
0	-30	42	0
1	160	175	299
2	243	232	52
3	94	84	77
4	91	89	314
5	178	158	62
6	154	157	253
7	97	106	300
8	73	86	201
9	118	115	263
10	60	64	107
11	30	36	40
12	-27	30	100
13	49	63	82
14	64	61	253
15	-21	22	154
16	46	41	197
17	-13	24	264
H 11 1			
0	265	300	90
1	160	190	97
2	97	112	48
3	138	146	81
4	124	150	286
5	124	130	231
6	116	106	254
7	121	134	266
8	103	112	71
9	-30	11	106
10	63	71	49
11	64	67	95
12	49	47	268
13	-24	18	39
14	51	45	242
15	38	44	273
16	-13	10	33
H 12 1			
0	103	116	0
1	57	72	141
2	181	236	267
3	124	147	261
4	160	185	232
5	140	154	276
6	114	140	115
7	70	78	86
8	46	60	10
9	132	125	99
10	116	113	295
11	-24	22	161
12	-21	38	255
13	-19	12	270
14	40	41	121
15	-11	29	82
H 13 1			
0	118	163	270
1	63	87	280
2	60	73	150
3	60	77	294
4	91	89	91
5	-27	35	128
6	73	60	11
7	70	68	112
8	-24	29	292
9	24	29	318
10	27	27	205
11	43	40	311
12	49	49	130
13	-13	11	323
H 14 1			
0	60	65	180
1	43	49	257
2	87	86	105
3	63	65	77
4	-27	30	21
5	84	90	99
6	89	90	276
7	57	58	209
8	21	34	194
9	57	51	263
10	43	50	86
11	-13	10	230
H 15 1			
0	63	75	90
1	63	72	78
2	-21	33	7
3	57	57	104
4	78	82	258
5	-21	20	273
6	43	47	236
7	43	45	265
8	63	70	81
9	-13	35	51
H 16 1			
0	21	42	0
1	33	39	96
2	63	79	288
3	30	32	266
4	27	24	212
5	-13	39	285
6	-11	33	95
H 0 2			
0	118	147	0
* 1	489	695	0
2	162	129	180
* 3	505	610	0
4	43	58	180
5	626	667	180
6	187	197	0
* 7	794	1028	180
8	127	157	0
9	57	78	0
10	54	62	180
11	202	196	0
12	54	50	180
13	-38	29	180
14	60	52	0
15	73	85	180
16	-35	19	0
17	33	27	0
18	-30	10	180
19	-30	72	0
20	-21	12	180
21	-13	8	180
H 1 2			
0	89	54	90
1	381	425	344
2	124	113	35
3	445	476	200
4	262	262	99
5	462	467	175
6	194	213	141
7	292	314	11
8	121	126	230
9	389	387	347
10	87	83	297
11	-33	11	72
12	33	38	94
13	157	163	171
14	-35	14	27
15	43	43	341
16	-35	20	48
17	78	57	34
18	30	8	29
19	27	27	90
20	-21	22	291
21	-13	27	201
H 2 2			
0	275	274	0
* 1	661	757	185
2	127	126	83
3	359	413	173
4	167	141	80
5	259	267	357
6	248	250	35
7	345	370	356
8	162	155	90
9	111	104	205
10	175	151	158
11	254	271	193
12	89	85	175
13	-35	38	132
14	43	42	61
15	124	109	6
16	35	35	337
17	-33	26	343
18	-30	10	146
19	-27	12	146
20	-21	3	217
21	-11	13	169
H 3 2			
0	278	261	90
1	523	609	181
2	275	300	49
3	467	541	7
4	30	26	317
* 5	745	841	10
6	197	160	206
7	272	286	174
8	173	165	251
9	341	350	175
10	70	47	325
11	124	97	16
12	84	72	299
13	184	175	349
14	46	38	291
15	-35	40	273
16	-35	15	12
17	78	58	180
18	-30	5	84
19	-24	12	95
20	-19	10	66
H 4 2			
0	57	45	180
1	426	444	351
2	197	179	180
3	475	483	338
4	121	108	99
5	202	205	203
6	165	157	339
7	419	454	172
8	103	73	222
9	170	157	24
10	97	99	231
11	262	253	6
12	60	48	102
13	-35	22	142
14	91	89	70
15	73	54	153
16	33	29	37
17	30	43	352
18	-27	12	249
19	49	42	354
20	-16	5	115
H 5 2			
0	76	74	90
1	467	478	351
2	278	291	339
3	399	408	190
4	162	168	77
5	342	364	169
6	111	90	291
7	167	153	14
8	184	171	272
9	254	244	352
10	33	19	282
11	-35	27	318
12	-35	31	319
13	167	162	188
14	35	33	224
15	-35	24	222
16	-33	17	145
17	78	51	10
18	-27	17	213
19	-21	17	352
20	-13	17	135
H 6 2			
0	157	153	180
1	378	392	178
2	187	184	120
3	411	416	166
4	91	51	101
5	335	333	29
6	84	74	316
7	311	335	352
8	160	160	273
9	211	211	206
10	49	56	206
11	167	160	181
12	35	32	34
13	87	74	15
14	43	35	27
15	124	114	355
16	30	18	256
17	35	39	331
18	-24	17	260
19	19	20	188
H 7 2			
0	160	141	90
1	440	442	167
2	118	116	25
3	248	261	2
4	89	63	264
5	386	391	350
6	64	58	159
7	148	148	206
8	124	120	245
9	284	312	191
10	-35	31	179
11	51	60	99
12	57	61	293
13	91	98	2
14	-33	26	324
15	-33	32	230
16	-30	35	107
17	43	24	133
18	-21	16	194
19	-13	17	33
H 8 2			
0	38	53	0
1	305	274	10
2	140	131	309
3	316	284	5
4	103	95	289
5	214	225	191
6	70	67	79
7	272	309	171
8	94	68	273
9	-35	26	166
10	143	163	245
11	132	129	352
12	49	35	132
13	-33	31	30
14	-33	4	74
15	30	34	187
16	27	27	149
17	21	10	343
18	-16	13	261
H 9 2			
0	46	51	90
1	214	188	335
2	-33	23	356
3	232	226	196
4	76	75	39
5	278	286	157
6	64	65	233
7	181	176	36
8	43	25	193
9	160	160	347
10	-35	37	126
11	84	78	204
12	57	55	96
13	78	64	169
14	33	35	18
15	-27	10	356
16	27	13	242
17	54	49	1
H 10 2			
0	60	53	0
1	272	299	211
2	154	153	94
3	254	280	169
4	-35	27	63
5	121	114	22
6	35	50	46
7	87	96	358
8	35	39	261
9	94	86	204
10	-35	14	240
11	173	163	176
12	-33	17	95
13	64	76	82
14	-27	14	322
15	73	66	6
16	-19	13	251
H 11 2			
0	170	186	90
1	202	212	186
2	162	173	66
3	105	103	15
4	105	101	292
5	160	162	3
6	57	65	259
7	60	63	234
8	54	63	97
9	100	88	176
10	-33	11	293
11	67	52	17
12	35	45	266
13	87	62	11
14	-21	22	302
15	-16	15	20
H 12 2			
0	64	52	0
1	121	114	27
2	49	39	207
3	218	232	343
4	60	67	139
5	70	81	217
6	-33	18	33
7	165	153	171
8	-33	12	333
9	-30	28	50
10	30	32	330
11	78	58	351
12	35	16	73
13	-21	8	273
14	-16	32	89
H 13 2			
0	-33	9	90
1	160	183	340
2	51	49	51
3	94	108	202
4	51	46	131
5	91	84	131
6	-30	31	269
7	51	58	49
8	43	27	266
9	89	75	353
10	-24	24	227
11	21	26	242
12	-16	13	348
H 14 2			
0	-30	11	0
1	64	50	183
2	35	40	77
3	87	90	184
4	-30	21	111
5	84	67	36
6	60	69	256
7	51	46	349
8	-21	13	261
9	-21	55	219
10	38	35	92
11	19	32	186
H 15 2			
0	87	69	90
1	89	90	153
2	60	62	355
3	57	56	37
4	54	50	288
5	84	93	354
6	24	32	281
7	-19	23	204
8	13	17	306
H 16 2			
0	-16	11	0
1	54	60	23
2	35	33	309
3	49	59	331
H 0 3			
1	419	450	90
2	294	378	90
3	335	344	270
4	-27	41	270
5	205	225	270
6	230	221	270
7	30	27	270
8	21	23	90
9	108	103	90
10	121	150	90
11	-38	27	270
12	24	10	90
13	67	82	270
14	51	53	270
15	24	21	270
16	-19	14	270
17	-16	9	90
18	30	32	90
19	-13	8	90
20	-8	8	90
H 1 3			
0	191	234	90
1	227	232	276
2	197	223	3
3	354	440	285
4	368	448	288
5	143	155	94
6	87	78	268
7	216	234	95
8	214	250	71
9	63	68	295
10	157	155	46
11	181	169	261
12	94	92	259
13	54	59	204
14	33	24	229
15	49	44	108
16	35	39	55
17	-16	7	26
18	-16	17	67
19	-13	18	291
20	-8	11	240
H 2 3			
0	143	147	180
1	294	311	249
2	324	361	278
3	40	37	164
4	121	106	357
5	181	193	85
6	318	334	90
7	151	145	277
8	227	223	127
9	175	162	278
10	178	172	236
11	162	160	83
12	121	118	258
13	103	108	97
14	46	36	129
15	-19	13	343
16	30	36	106
17	51	56	276
18	19	21	293
19	-13	3	329
20	-8	10	307
H 3 3			
0	369	373	270
1	243	237	111
2	33	33	244
3	162	175	77
4	372	382	81
5	270	275	283
6	89	73	63
7	224	198	252
8	197	204	295
9	-19	27	258
10	118	119	268
11	91	86	58
12	73	83	153
13	38	41	254
14	38	53	135
15	63	64	249
16	-19	16	321
17	-16	11	29
18	-13	12	269
19	-11	6	79
H 4 3			
0	245	229	180
1	308	316	73
2	365	377	105
3	270	275	282
4	124	110	38
5	254	247	269
6	281	289	264
7	94	93	127
8	91	81	238
9	259	246	84
10	157	149	95
11	118	110	65
12	57	67	358
13	24	16	258
14	57	55	275
15	27	37	206
16	-19	21	197
17	-16	13	75
18	-13	12	62
19	-11	10	355
H 5 3			
0	216	216	90
1	189	174	305
2	76	68	208
3	278	297	274
4	227	222	273
5	116	126	104
6	78	66	153
7	205	221	90
8	132	146	109
9	91	92	272
10	38	48	138
11	105	99	252
12	124	126	232
13	64	73	157
14	38	38	287
15	46	49	114
16	57	52	102
17	-16	20	10
18	-13	17	115
19	-8	21	294
H 6 3			
0	63	49	180
1	221	214	240
2	189	185	275
3	265	253	121
4	27	29	247
5	187	200	96
6	211	214	77
7	76	75	319
8	97	104	89
9	140	148	247
10	114	105	290
11	51	50	110
12	70	76	290
13	87	99	80
14	-19	12	102
15	-16	12	276
16	21	25	92
17	30	28	279
18	-11	15	271
H 7 3			
0	375	311	270
1	257	228	141
2	89	77	217
3	243	229	59
4	275	290	68
5	89	93	359
6	87	93	76
7	49	45	213
8	146	153	289
9	91	94	111
10	78	84	241
11	91	83	94
12	64	59	126
13	-19	29	27
14	30	37	46
15	30	35	258
16	-13	12	186
17	-11	9	249
18	-8	26	186
H 8 3			
0	57	49	0
1	194	169	78
2	289	293	100
3	138	148	283
4	114	126	19
5	175	183	269
6	135	164	304
7	84	94	126
8	38	45	224
9	116	112	65
10	64	62	98
11	24	31	328
12	-19	28	114
13	43	39	235
14	24	28	293
15	33	35	177
16	19	23	324
17	-8	13	116
H 9 3			
0	114	108	90
1	245	239	291
2	81	87	34
3	184	204	265
4	111	104	313
5	103	103	129
6	78	96	344
7	132	150	81
8	130	118	57
9	38	41	333
10	33	32	2
11	91	103	253
12	70	68	262
13	38	54	155
14	27	26	274
15	63	54	86
16	-11	19	130
H 10 3			
0	51	46	0
1	173	172	218
2	81	94	263
3	100	107	188
4	-21	26	124
5	84	88	74
6	91	93	65
7	54	57	295
8	-19	20	118
9	63	60	241
10	64	61	283
11	21	30	140
12	43	41	226
13	27	31	93
14	49	43	105
15	-11	23	33
H 11 3			
0	170	188	270
1	121	116	123
2	-19	13	264
3	78	73	56
4	127	146	107
5	127	134	319
6	70	60	54
7	121	112	259
8	78	73	290
9	-16	39	181
10	30	38	237
11	21	29	74
12	19	12	47
13	-11	4	138
14	-8	16	80
H 12 3			
0	-19	39	180
1	111	107	55
2	105	118	95
3	124	143	289
4	89	77	80
5	97	95	253
6	64	56	264
7	49	67	132
8	-16	22	262
9	67	71	78
10	40	41	115
11	38	40	356
12	13	12	140
13	-6	35	262
H 13 3			
0	103	93	90
1	46	51	329
2	43	52	356
3	51	61	240
4	40	44	272
5	27	36	136
6	-16	19	216
7	97	88	71
8	24	29	134
9	30	32	299
10	-11	11	87
11	-8	32	229
H 14 3			
0	46	49	180
1	94	86	245
2	-13	29	257
3	67	66	151
4	-13	13	216
5	81	61	80
6	30	35	105
7	33	39	359
8	11	21	338

Table 3 (*cont.*)

9	-8	25	227
H	15	3	
0	49	44	270
1	73	88	127
2	-11	3	245
3	63	61	43
4	38	41	47
5	27	47	317
6	-6	13	64
H	0	4	
0	575	575	180
1	38	47	180
2	70	84	180
3	57	72	0
4	241	248	0
5	24	7	180
6	97	106	0
7	111	144	180
8	114	128	180
9	-21	29	0
10	64	78	180
11	-21	5	0
12	63	63	0
13	-21	31	180
14	-35	54	0
15	-21	3	180
16	24	26	180
17	-16	10	180
18	-13	2	180
19	-6	6	0
H	1	4	
0	33	39	90
1	24	26	186
2	241	306	8
3	49	40	85
4	105	117	354
5	76	88	43
6	157	183	193
7	60	60	249
8	40	39	127
9	103	101	252
10	127	122	23
11	46	50	330
12	33	39	39
13	-21	28	80
14	70	72	184
15	-21	14	60
16	24	37	200
17	-16	7	292
18	-13	3	119
19	-6	7	260
H	2	4	
0	216	237	0
1	91	82	117
2	103	86	243
3	54	29	54
4	245	274	172
5	67	60	212
6	64	83	147
7	81	94	170
8	224	244	15
9	33	38	67
10	49	62	31
11	-21	22	61
12	73	72	204
13	-21	9	180
14	30	37	153
15	-19	12	246
16	-19	19	39
17	-16	17	321
18	-13	26	5
H	3	4	
0	30	32	90
1	30	34	203
2	332	351	178
3	64	59	93
4	73	73	142
5	100	119	347
6	200	197	356
7	135	141	262
8	87	92	291
9	114	107	265
10	135	125	165
11	57	61	21
12	87	81	167
13	54	58	73
14	46	63	321
15	24	39	86
16	-19	19	313
17	-16	13	115
18	-11	22	196
H	4	4	
0	305	320	180
1	94	89	86
2	64	66	119
3	-19	12	296
4	175	205	10
5	64	68	335
6	111	119	360
7	81	67	29
8	121	102	149
9	-21	24	92
10	51	44	128
11	-21	33	328
12	64	71	5
13	-21	15	9
14	30	31	336
15	-19	12	233
16	-16	32	192
17	-13	8	16
18	-11	13	151
H	5	4	
0	121	123	90
1	33	25	337
2	235	248	358
3	67	65	26
4	67	74	332
5	73	85	77
6	202	227	191
7	67	64	231
8	87	85	212
9	40	38	209
10	81	87	24
11	-21	2	159
12	43	57	326
13	30	39	93
14	51	45	252
15	40	32	128
16	-16	21	168
17	-13	14	158
H	6	4	
0	257	273	0
1	40	35	195
2	132	118	273
3	24	40	238
4	189	212	212
5	54	51	342
6	60	69	86
7	27	21	4
8	151	153	0
9	-21	29	252
10	63	82	297
11	-21	30	54
12	87	81	191
13	-21	26	32
14	21	25	174
15	-16	10	1
16	-13	23	11
17	-11	9	304
H	7	4	
0	167	163	270
1	27	27	258
2	208	202	190
3	46	55	81
4	91	94	113
5	-21	30	245
6	162	181	1
7	43	45	253
8	78	89	329
9	30	31	198
10	63	67	175
11	-21	20	168
12	24	37	144
13	-19	12	79
14	51	41	18
15	-16	16	127
16	-11	24	358
H	8	4	
0	230	240	180
1	70	60	151
2	76	84	165
3	100	121	256
4	132	132	354
5	51	54	259
6	60	59	357
7	49	53	188
8	51	55	180
9	46	53	124
10	-21	18	187
11	-21	30	103
12	76	52	354
13	-16	5	61
14	57	52	316
15	-13	12	358
16	-6	16	229
H	9	4	
0	70	84	90
1	-21	8	15
2	167	160	10
3	46	50	214
4	40	50	282
5	-21	13	129
6	118	88	191
7	-21	21	283
8	60	63	105
9	38	36	256
10	81	71	14
11	-19	19	279
12	30	43	303
13	-16	12	83
14	-13	25	190
15	-8	7	105
H	10	4	
0	111	103	0
1	27	36	138
2	121	104	267
3	27	31	162
4	165	179	181
5	-21	14	81
6	116	113	111
7	-21	23	267
8	121	117	20
9	-19	31	255
10	43	42	337
11	-16	17	167
12	35	35	219
13	-11	8	228
14	-6	12	176
H	11	4	
0	51	45	270
1	30	28	58
2	127	106	179
3	-21	11	84
4	63	55	105
5	30	41	287
6	105	82	22
7	-19	26	268
8	-21	39	338
9	-16	25	238
10	46	41	204
11	-13	19	48
12	-11	24	176
H	12	4	
0	94	95	180
1	24	18	67
2	60	67	100
3	-19	22	303
4	97	86	14
5	21	19	238
6	21	32	304
7	-16	22	88
8	40	35	176
9	-13	20	74
10	54	49	140
11	-6	4	358
H	13	4	
0	57	55	90
1	21	32	315
2	89	77	10
3	40	42	273
4	40	41	296
5	-16	5	141
6	73	72	178
7	-13	13	97
8	-11	29	106
9	8	16	324
H	14	4	
0	49	45	0
1	21	18	230
2	24	30	257
3	-11	14	122
4	63	64	192
5	-8	13	2
6	-3	19	81
H	0	5	
1	130	142	270
2	87	91	90
3	38	36	90
4	81	88	90
5	116	135	90
6	87	98	270
7	-19	9	90
8	30	30	270
9	-38	63	270
10	81	63	90
11	30	21	270
12	-19	5	270
13	21	15	90
14	30	27	90
15	-16	9	90
16	-13	2	90
17	-8	15	270
H	1	5	
0	135	124	90
1	84	83	85
2	30	28	344
3	121	125	52
4	121	141	261
5	89	96	313
6	60	48	218
7	91	90	255
8	64	44	48
9	-19	18	166
10	70	70	43
11	54	46	81
12	27	27	269
13	-19	25	206
14	35	32	235
15	-16	16	224
16	24	15	110
17	-8	2	49
H	2	5	
0	21	20	180
1	87	82	97
2	84	80	258
3	89	73	231
4	54	56	92
5	24	16	243
6	64	70	87
7	91	75	57
8	27	30	90
9	-21	24	150
10	40	40	268
11	70	65	284
12	24	18	310
13	49	45	288
14	43	36	104
15	-13	6	44
16	-11	11	109
17	-6	24	39
H	3	5	
0	94	88	270
1	60	53	272
2	97	98	245
3	94	93	295
4	78	70	141
5	57	46	147
6	27	29	165
7	-19	28	124
8	73	71	284
9	33	42	295
10	-19	11	87
11	43	40	246
12	33	24	104
13	-19	13	127
14	-16	7	25
15	30	32	130
16	38	7	134
H	4	5	
0	70	60	180
1	108	126	259
2	157	167	86
3	73	65	127
4	94	87	37
5	114	137	67
6	63	53	293
7	27	32	9
8	70	68	221
9	78	72	265
10	43	34	139
11	-19	6	360
12	27	20	87
13	43	31	61
14	24	23	275
15	-13	9	5
16	-11	25	259
H	5	5	
0	108	99	90
1	108	115	131
2	-19	17	47
3	111	112	79
4	108	100	250
5	54	47	216
6	64	58	203
7	46	45	271
8	63	59	87
9	-19	14	150
10	27	25	59
11	35	34	120
12	43	32	273
13	-16	9	47
14	-13	15	262
15	-11	12	254
H	6	5	
0	-19	0	0
1	54	46	131
2	81	80	246
3	64	59	305
4	-19	32	198
5	38	31	307
6	70	62	92
7	49	47	116
8	27	43	18
9	38	33	73
10	63	50	296
11	-19	16	276
12	38	28	268
13	19	20	239
14	-13	8	345
15	-8	8	181
H	7	5	
0	40	33	270
1	60	49	296
2	81	69	146
3	51	53	268
4	87	78	96
5	40	34	96
6	46	51	22
7	35	35	80
8	43	36	325
9	43	40	262
10	-19	18	237
11	57	43	221
12	-16	17	134
13	43	38	121
14	-11	8	357
H	8	5	
0	76	55	180
1	67	64	222
2	118	81	95
3	97	72	134
4	60	49	44
5	91	66	77
6	94	68	289
7	-19	13	282
8	27	24	213
9	57	47	272
10	51	41	92
11	38	33	216
12	-13	8	9
13	21	14	172
H	9	5	
0	118	95	90
1	63	44	59
2	57	42	7
3	78	56	51
4	108	75	261
5	49	41	330
6	78	59	195
7	70	50	273
8	73	57	100
9	-19	28	217
10	51	46	55
11	19	16	115
12	-11	16	339
H	10	5	
0	70	55	0
1	57	44	90
2	43	31	263
3	60	44	286
4	54	42	159
5	57	42	250
6	57	42	96
7	24	28	116
8	49	41	43
9	30	23	92
10	-11	7	316
11	-8	18	287
H	11	5	
0	91	72	270
1	46	38	315
2	38	33	220
3	21	25	261
4	51	38	106
5	27	17	104
6	24	27	35
7	30	17	61
8	51	39	295
9	27	30	310
H	12	5	
0	63	49	180
1	-13	16	233
2	73	60	99
3	-13	10	186
4	46	35	30
5	24	17	42
6	40	29	280
7	-8	6	20
H	13	5	
0	27	32	90
1	30	33	125
2	30	38	351
3	-8	25	61
H	0	6	
0	-38	69	180
1	-38	41	180
2	-38	17	180
3	54	49	180
4	-38	17	180
5	46	28	0
6	51	22	180
7	-35	59	0
8	-35	7	180
9	-33	17	180
10	-33	7	180
11	-30	2	180
12	-27	28	0
13	-24	5	0
14	-19	10	0
H	1	6	
0	-89	26	270
1	-89	55	214
2	-89	37	218
3	-89	61	323
4	-89	10	190
5	-87	37	0
6	-87	10	121
7	-84	28	169
8	-81	4	64
9	-78	33	172
10	-73	16	147
11	-67	3	282
12	-63	10	247
13	-54	27	326
14	-43	3	360
H	2	6	
0	-94	25	180
1	-94	75	39
2	-94	25	77
3	94	62	19
4	-91	6	290
5	-91	14	161
6	-89	21	185
7	-89	47	157
8	-87	8	227
9	-81	18	353
10	-76	1	305
11	-70	42	349
12	-64	19	30
13	-54	11	294
14	-40	12	313
H	3	6	
0	-121	63	270
1	-121	56	315
2	-121	32	213
3	-118	46	219
4	-118	25	78
5	-116	71	167
6	-114	17	31
7	-111	25	56
8	-108	17	55
9	-103	31	10
10	-97	11	203
11	-89	9	258
12	-78	17	177
13	-67	8	145
14	-43	7	102
H	0	7	
1	-33	19	90
2	-33	28	270
3	-33	18	90
4	-30	7	270
5	-30	2	90
6	-30	14	90
7	-27	7	90
8	-24	11	90
9	-21	7	270
10	-19	4	270
11	-11	3	270
H	1	7	
0	-76	33	270
1	-76	17	115
2	-73	12	244
3	-73	38	46
4	-70	21	144
5	-70	17	339
6	-64	11	192
7	-63	10	235
8	-57	12	255
9	-51	13	141
10	-43	11	199
11	-19	10	88
H	2	7	
0	-78	17	0
1	-78	24	98
2	-78	12	25
3	-76	10	287
4	-73	9	335
5	-73	20	290
6	-67	22	266
7	-64	13	101
8	-60	3	332
9	-51	15	98
10	-43	10	62
H	3	7	
0	-97	5	90
1	-97	14	215
2	-97	16	321
3	-94	7	235
4	-91	26	267
5	-89	11	108
6	-84	9	254
7	-78	15	107
8	-73	9	108
9	-63	12	90
10	-46	9	79
H	0	8	
0	-16	11	0
1	-16	2	180
2	-16	5	0
3	-13	4	180
H	1	8	
0	-38	5	270
1	-35	4	164
2	-33	9	198
3	-27	6	153
H	2	8	
0	-35	9	180
1	-33	2	201
2	-30	4	45

between the two bonds from the same carbon atom, with carbon–hydrogen bond distances equal to 1·08 Å. The positions of the hydrogen atoms of the methyl groups were not determined.

The quantity minimized in the least-squares calculation was $\Sigma\ w(F_o-|kF_c|)^2$, the weights w being derived from the σ's of each single observation, as determined in the data reduction process. After the final cycle, all the shifts were below the corresponding e.s.d. Unobserved reflexions were assigned a threshold value based on the lowest observable intensity, and included in the refinement only when $|kF_c|$ exceeded this value. The final R index is 9·7% for the observed reflexions.

Table 1 gives the final atomic coordinates with their e.s.d.'s. Anisotropic temperature factors with their e.s.d.'s are listed in Table 2. An isotropic temperature factor $B=6$ Å^2 was assigned to each hydrogen atom. The numbering of the atoms is included in Figs. 1 and 2. Structure factors based on the final parameters are compared with the observed structure amplitudes in Table 3. The average planes in the molecule were determined by the method of Schomaker, Waser, Marsh & Bergman (1959). The equations for the two tolyl planes, including the C(2) atom, are

$$0{\cdot}7555X+0{\cdot}2006Y-0{\cdot}6237Z-1{\cdot}1981=0$$

and

$$0{\cdot}6820X-0{\cdot}6500Y+0{\cdot}3352Z+2{\cdot}5835=0$$

for the ring *trans* and *cis* to the bromine atom respectively; X, Y, Z are coordinates in Å. The equation of the plane of the molecular skeleton C(1), C(2), C(3), C(6), C(15), C(9), C(12), C(16) is

$$0{\cdot}6904X-0{\cdot}2122Y-0{\cdot}6916Z+0{\cdot}9222=0.$$

In all the three cases, no distance exceeding 0·01 Å was found between any atom and the involved plane. The bromine atom is coplanar with the molecular skeleton within 0·012 Å.

Bond distances, bond angles and the averages of their e.s.d.'s (Cruickshank & Robertson, 1953; Darlow, 1960) are reported in Figs. 1 and 2 respectively. All these values are uncorrected for librational effects. In Figs. 1 and 2 the molecule is drawn referred to an orthogonal, right-handed coordinate system $X'Y'Z'$ whose $Y'Z'$ plane is the average plane of the molecular skeleton previously described. The origin is taken at the mass centre of the skeleton. Both the tolyl rings are rotated with respect to the molecular skeleton plane, the rotation angles being $\theta_1=24{\cdot}4°$ and $\theta_2=67{\cdot}9°$ for the ring *trans* and *cis* to the bromine atom respectively.

In Figs. 3 and 4 the packing in the crystal is viewed along the c and b axes respectively.

π-Electron, bending and steric repulsion energy calculations

The π-electron energy for the molecule with $\theta_1=5$, 15, 25, 35, 45° and $\theta_2=45$, 55, 65, 75, 85° was calculated by the Hückel molecular orbital (HMO) method. For the methyl groups the heteroatom model was used, with $\alpha_{CH_3}=\alpha_C+3\cdot3\beta_0$ and $\beta_{C-CH_3}=0\cdot8\beta_0$ (Favini & Simonetta, 1963) where β_0 is the resonance integral for a carbon–carbon bond at a distance of 1·40 Å. As the σ-bond compression energy was neglected in this calculation, the standard value $\beta_0=-20$ Kcal.mole^{-1} was chosen. The parameters for bromine were $\alpha_{Br}=\alpha_C+\beta_0$ and $\beta_{C-Br}=0\cdot4\beta_0$ (Carrà, Raimondi & Simonetta, 1966; Streitwieser, 1962).

Calculations were performed for all the 25 θ_1, θ_2 combinations by the ω technique, with $\omega=0\cdot625$, the ω value being chosen to give the quickest convergence. At each step of the calculation the bond orders n_{st}

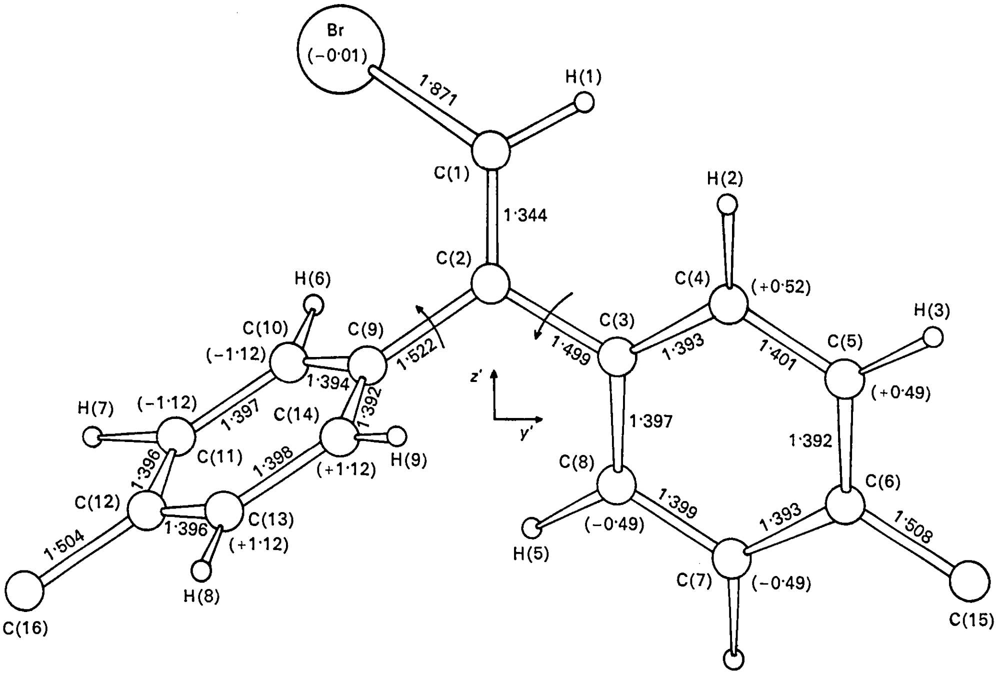

Fig. 1. Bond lengths (Å) in the crystal. The average e.s.d. is 0·016 Å. In brackets, the heights (Å) of non-coplanar atoms are given, with respect to the average plane of the molecular skeleton (see text).

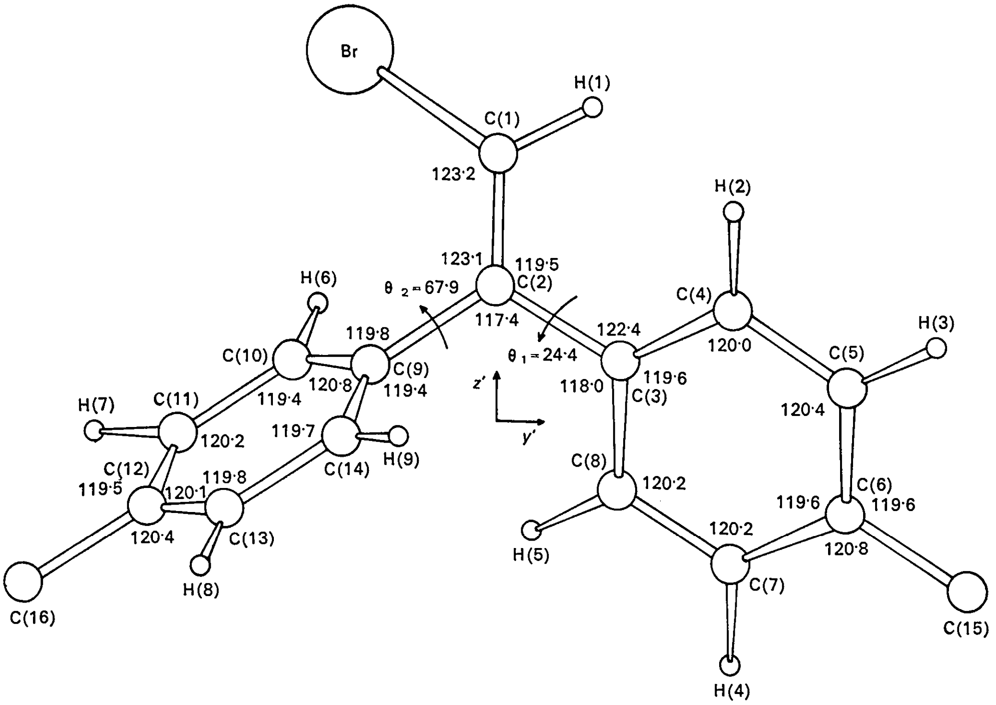

Fig. 2. Bond angles (°) in the crystal. The average e.s.d. is 1·0°. Both the tolyl rings are rotated with respect to the average plane of the molecular skeleton (see text).

were evaluated by the standard HMO formula for all bonds except C(2)–C(3) and C(2)–C(9). For these bonds n_{st} was taken as $\Sigma_i 2c_{si}c_{ti}\cos\theta_j$ ($j=1,2$; i runs over all the occupied orbitals). The C_{sp^2}–C_{methyl} and C–Br distances were kept at the constant values of 1·51 Å (Keidel & Bauer, 1956) and 1·87 Å. This latter value is based on values found in the literature for vinyl bromide (Whiffen, 1958; Howe & Goldstein, 1957) and 1,2-dibromoethylene (Hugill, Coop & Sutton, 1938). The C_{sp^2}–C_{sp^2} distances were calculated from the bond orders with Coulson's formula (Coulson, 1939), as given by Moser (1953). The integral $\beta_{\text{C-C}}$ was varied with the distance R in the following way

$$\beta(R)=\beta_0\exp[2\cdot683(1\cdot40-R)] \qquad (1)$$

(Coulson & Golebiewski, 1961) for all the C–C bonds except C(2)–C(3) and C(2)–C(9). For these bonds the value of β given by (1) was multiplied by $\cos\theta_j$. For each geometry the calculation was repeated to consistency of α's and β's in the second decimal, which corresponds to a consistency to the third decimal for distances. As the final values for all C–C distances in the two aromatic rings for all examples examined were in the range 1·395–1·405 Å, the two rings were assumed to be regular hexagons with a side of 1·40 Å.

At this stage four more degrees of freedom were added to our model: each of the angles φ_1, φ_2, φ_3 and φ_4 (Fig. 5), which lie in the plane of C(1), C(2), C(3), C(9), Br, and H(1), was allowed to assume one of four values, 115, 120, 125 or 130°. With the 25 possible combinations of torsion angles, this makes the total number of possible geometrical models to be considered 6400. For 972 of them bending and steric repulsion energies were calculated and added to the

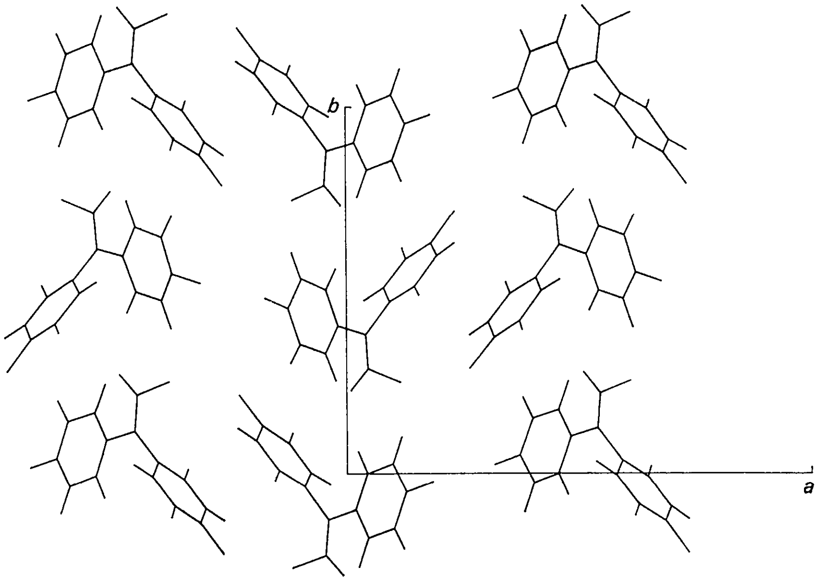

Fig. 3. The crystal structure projected on (001).

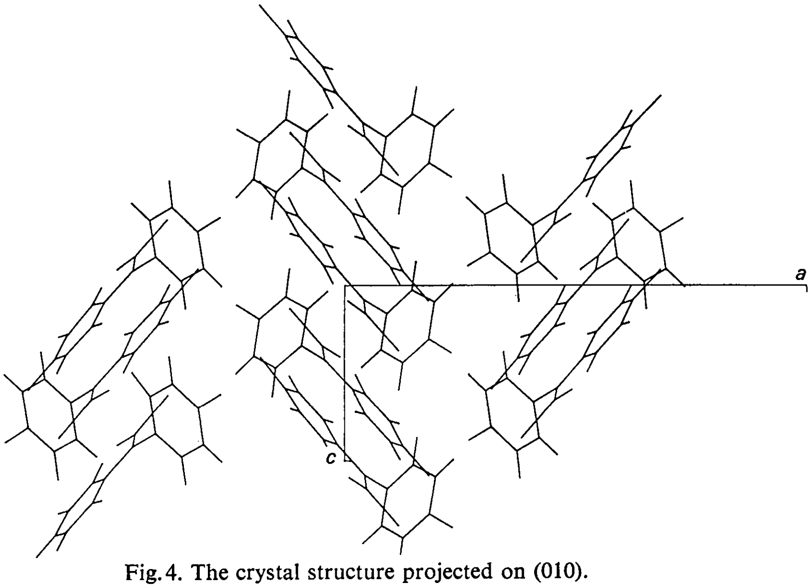

Fig. 4. The crystal structure projected on (010).

appropriate value of the π-electron energy to get a 'total energy' for the isolated molecule. The geometries for which the calculation was actually performed were chosen in such a way as to make possible the identification of the position of the minimum for the function $E=E(\theta_1, \theta_2, \varphi_1, \varphi_2, \varphi_3, \varphi_4)$.

The bending energy in the plane of bonds has been determined by the formula

$$E_{\text{bend}} = \frac{1}{2} \sum_{i=1}^{4} k_i(\varphi_i - \varphi_0)^2 \tag{2}$$

where $\varphi_0 = 120°$ and k is the force constant. The following values for the force constants were used: $k_1 = k_2 = 1{\cdot}35 \,.\, 10^{-11}$ erg.rad^{-2} (Favini & Simonetta, 1963), $k_3 = 0{\cdot}79 \,.\, 10^{-11}$ erg.rad^{-2} (Dowling, Puranik, Meister & Miller, 1957), $k_4 = 0{\cdot}68 \,.\, 10^{-11}$ erg.rad^{-2} (Westheimer, 1956). The compression energy for pairs of atoms at distances smaller than the 'touching distance' was calculated by the formula

$$E_s = -0{\cdot}721(r_0/r)^6 + 2{\cdot}11 \,.\, 10^4 \exp(-10{\cdot}88r/r_0)\,, \tag{3}$$

where E_s in Kcal.mole^{-1} is the interaction energy, r the actual distance and r_0 the 'touching distance', obtained by adding van der Waals atomic radii. The values of these radii have been taken from standard tables (Pauling, 1960) and corrected when the line joining the two atoms and the direction of the nearest bond make an angle smaller than 90° (Dostrovsky, Hughes & Ingold, 1946). In this calculation the methyl group was considered as a single atom with van der Waals radius equal to 2·0 Å. Equation (3) is an extension of the one given by Kitaygorodsky (1961). This was originally given to calculate carbon and hydrogen interactions and has been here adapted to include methyl groups and bromine atoms. For 12 of the 25 possible sets θ_1 and θ_2 the minimum of energy, with respect to φ_1, φ_2, φ_3, φ_4, is given in Table 4, the absolute minimum of energy being indicated by an asterisk. The corresponding molecular geometry is also given in Table 4.

However, in the crystal each molecule experiences the strain of the surrounding molecules which causes a distortion of the molecules so that the crystal reaches the minimum of free energy. We know from X-ray data the position and orientation of the real molecules in the crystal and we put our model molecules in the same places. Considering a reference molecule, we make the C(2) atom, the C(1)–C(2) axis and the C(1), C(2), C(3), C(9) plane of the model coincident with the same atom, axis and plane of a real molecule in the crystal. We then calculate the coordinates of all the atoms in the model molecule, and by symmetry operations we can also get the coordinates of the atoms of all the model molecules in the crystal. We assume that the thermal energy and the entropy of the real crystal and of crystals made from any one of our model molecules are approximately the same. Also the attractive van der Waals forces are about the same, so what we need to do to find the theoretical geometry of the molecules in the crystal is to add to the 'total energy' of the isolated molecule the repulsion energy from the surroundings and then to find the minimum.

Table 4. '*Total energy*' (Kcal.mole^{-1}) *for the isolated molecule*

The most stable conformation, indicated by an asterisk, has bond lengths C(1)–C(2) = 1·35, C(2)–C(3) = 1·48, C(2)–C(9) = 1·52 Å.

θ_1	θ_2	φ_1	φ_2	φ_3	φ_4	Total energy
5	55	125	120	120	125	−674·15
15	45	125	120	125	120	−673·44
15	55	125	120	120	120	−673·83
15	65	125	120	120	120	−673·26
25	45	120	120	125	120	−671·28
25	55	120	120	120	120	−674·18*
25	65	120	120	120	120	−673·27
25	75	120	120	120	120	−673·03
35	45	120	120	125	120	−672·89
35	55	120	120	120	120	−673·39
35	65	120	120	120	120	−673·00
45	55	120	120	120	120	−672·55

We used again formula (3), this time without correction of the van der Waals radii for the angular distance from the nearest bond. This simplification was made necessary by the need of keeping the program of the calculation to a size that the computer could accept and was justified by the fact that, in general, the direction from an atom of the reference molecule to an atom in surrounding molecules makes an angle larger than 90° with the direction of the nearest bond. We made first a trial calculation including all molecules for which C(2) lay within a sphere of radius 20 Å centered on C(2) of the reference molecule. It was recognized that most of the molecules had all the atoms at distances larger than the 'touching distance' with any of the atoms in the reference molecule. It was seen that the appropriate radius for the sphere to include all the molecules between which repulsion may exist was 10 Å, and ten surrounding molecules were partially inside this sphere. This calculation however could not be performed for all the geometries we had considered before. We kept $\varphi_1 = \varphi_4 = 120°$ and allowed for φ_2 and φ_3 the 120 and 125° values. For the four possible combinations of these φ_i values, the same θ_1, θ_2 combinations as before were considered and the 'total energies' for the model molecule in the crystal were calculated. The more interesting results are summarized in Fig. 6 and Table 5. In Table 5, the approximate geometry corresponding to the minimum calculated energy of the molecule in its crystalline environment is given.

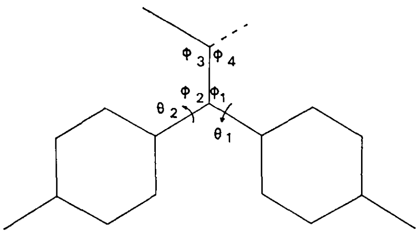

Fig. 5. Degrees of freedom allowed for the model molecule.

Table 5. *Minimum energy geometries in the model molecule after packing*

Angles are in degrees and energy in Kcal.mole^{-1} (see Fig. 6). For the most stable conditions (case *A*) the bond distances are C(1)–C(2) = 1·35, C(2)–C(3) = 1·48, C(2)–C(9) = 1·53 Å.

θ_1	θ_2	φ_1	φ_2	φ_3	φ_4	Energy	Case
25	69	120	120	120	120	−673·13	*A*
25	69	120	120	125	120	−672·62	*B*
25	65	120	125	120	120	−673·08	*C*
25	65	120	125	125	120	−672·57	*D*

Discussion

The crystal structure of the molecule reveals the existence of three planes containing the two tolyl groups and the ethylenic group. The e.s.d.'s of the bond lengths and bond angles are probably underestimated, owing to the fact that the absorption correction was not allowed for. It seems that this effect is partially compensated by the values assumed by the thermal parameters. In any event, the thermal motion in the crystal appears to be very large, especially for the bromine atom and the two methyl groups. The carbon–bromine, the ethylenic and the two C_{sp^2}–C_{methyl} bond distances are in the expected range. The C(2)–C(3) and C(2)–C(9) bond lengths also show normal values; the difference between them, even if scarcely significant, is in the correct sense, considering the different amount of rotation of the connected ring with respect to the ethylenic plane. The two dihedral angles are 24·4 and 67·9° (see Fig. 2).

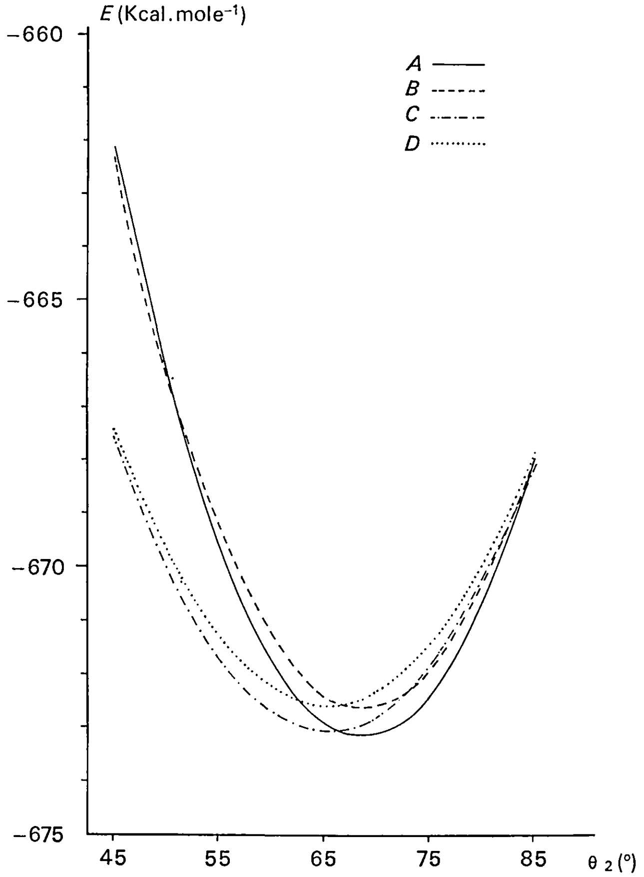

Fig. 6. 'Total energy' of the model molecule after packing (see Table 5).

The φ_2 and φ_3 angles are larger, at a 3σ level, than 120°, while φ_1 is not significantly different from 120°. The φ_4 angle has not been determined experimentally. No non-bonded distances significantly smaller than the corresponding 'touching distance' were found. On comparison with experimental values, the configuration of maximum stability for the isolated molecule (Table 4) shows a nice agreement of C–C bond lengths and φ_i angles; the θ_1 angle is also very close but the calculated θ_2 angle is significantly smaller than the observed one. A possible explanation of this discrepancy might be the interaction with neighbour molecules after packing in the crystal. This point was checked in the calculation of the energy of a crystal made of model molecules. The allowed degrees of freedom were chosen so that the energy needed for distortion is a minimum. The result is in good agreement with experiment (see Table 5); there is an increase of the calculated θ_2 angle to 69° with all the φ_i angles equal to 120° (case *A*), or to 65° with an increase of the φ_2 angle to 125° (case *C*). This suggest that the minimum lies between $\theta_2 = 65°$ and 69°, with φ_2 between 120° and 125°.

The constancy of θ_1 in the isolated molecule and all the model crystals is particularly significant (see also Simonetta & Carrà, 1963). The agreement must not be overestimated owing to the many assumptions and approximations involved in the method of calculation and to the fact that small differences in energy are dealt with. There is no doubt, however, that the packing is responsible for the disagreement between the isolated and the real molecule geometries; we may have some confidence that the magnitude of the distortion due to packing is correct and that the geometry given for the isolated molecule can be considered calculated with a good approximation.

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Structure Cristalline du Dichlorure de Cadmium Diformamide, $CdCl_2.2HCONH_2$

Par André Mitschler, Jean Fischer et Raymond Weiss

Laboratoire de Chimie Structurale, Institut de Chimie, Université de Strasbourg,
1, *rue Blaise Pascal,* 67 *Strasbourg, France*

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The crystal structure of bisformamide cadmium chloride has been determined and refined with three-dimensional data using Cu $K\alpha$ X-radiation. $CdCl_2.2HCONH_2$ is triclinic with $a=8{\cdot}37\pm0{\cdot}02$, $b=7{\cdot}26\pm0{\cdot}02$, $c=3{\cdot}77\pm0{\cdot}01$ Å, $\alpha=93°41'\pm20'$, $\beta=109°07'\pm20'$ and $\gamma=113°48'\pm20'$. $Z=1$. Space group: $P\bar{1}$.

Fourier and least-squares methods were used to determine positional coordinates. The molecules of formamide are bonded to the metal by the oxygen atoms. The structure is built up from chains of octahedral $CdCl_4O_2$ polyedra, linked along the [001] axis. The two O atoms belong to two molecules of formamide lying opposite to the plane containing the Cd atom and the four Cl atoms.

Introduction

Par la détermination des structures cristallines des composés d'addition moléculaire $CdCl_2.2OC(NH_2)_2$ et $CdCl_2.2C_2H_5N_3O_2$ Nardelli, Cavalca & Fava (1957) et Cavalca, Nardelli & Fava (1960) ont montré que la liaison Cd–X est généralement assurée par l'atome d'oxygène dans les composés du type $CdCl_2.2X$, X désignant une molécule organique possédant des groupements C–O et C–N donneurs de paires d'électrons.

Le spectre d'absorption infra-rouge d'un composé d'addition moléculaire permet souvent de déterminer la nature de l'atome donneur lié au métal; l'existence d'une liaison métal–oxygène ou métal – azote entraîne généralement une diminution de la constante de force de la liaison C–O ou C–N et par là, une diminution de la fréquence ν(C–O) ou ν(C–N) par rapport à la molécule organique libre.

Pour $CdCl_2.2HCONH_2$, le spectre d'absorption infra-rouge, enregistré en suspension dans le Nujol, ne permet pas de déterminer avec certitude si le formamide est lié au cadmium par l'atome d'oxygène ou par l'atome d'azote. En effet, la fréquence de la vibration d'élongation ν(C–O) ne change pas par rapport à celle du formamide pur, à l'état liquide (Suzuki, 1960); la fréquence de la vibration ν(C–N) augmente, au lieu de diminuer. Le Tableau 1 donne les fréquences des vibrations ν(C–O) et ν(C–N), du formamide lié au

Tableau 1. *Fréquences des vibrations* ν(C–O) *et* ν(C–N) *du formamide engagé dans* $CdCl_2.2HCONH_2$ *et du formamide non lié*

Fréquences observées	$CdCl_2.2HCONH_2$	$HCONH_2$
υ(C–O)	1690 cm^{-1}	1690 cm^{-1}
υ(C–N)	1350 cm^{-1}	1309 cm^{-1}