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The Crystal Structure of Dibenzoyl Peroxide and the Dihedral Angle in Covalent Peroxides

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The crystals of dibenzoyl peroxide, $C_{14}H_{10}O_4$, have orthorhombic symmetry, space group $P2_12_12_1$, and the unit cell, with dimensions $a=8{\cdot}95$, $b=14{\cdot}24$, $c=9{\cdot}40$ Å, contains four molecules. The crystal structure has been determined by an analysis of three-dimensional X-ray data, which were recorded photographically at 25 °C. The atomic coordinates were derived from the Patterson function and were refined anisotropically by the full-matrix least-squares method. The dihedral angle at the peroxide bond is 91°, which is the structural feature of principal chemical interest. The two phenyl groups of the molecule lie in planes which intersect at an angle of 84° along a line nearly parallel with the O–O bond. The length of the O–O bond is 1·46 Å ±0·015 Å. In the two phenyl carboxyl groups, the average values of the bond angles and distances are the expected ones, within the standard deviations of 1·5° and 0·018 Å. A quantum chemical discussion of the dihedral angle in covalent peroxides is presented which assumes sp^3 hybridization for the bond-forming orbitals of oxygen and takes into account the chemical nature of the substituent groups. A value of 94° is predicted for the dihedral angle in dibenzoyl peroxide.

Introduction

The crystal structure analysis of dibenzoyl peroxide was carried out because specific knowledge concerning the dihedral angle at the peroxide bond and the relative orientation of the acyl groups in this class of compound is of some importance to organic and theoretical chemistry. The detailed molecular structure of a diacyl peroxide had not been recorded previously in the literature. Penney & Sutherland (1934) in the first theoretical discussion of the conformation of molecular peroxide pointed out that if the lone-pair electrons on the adjacent oxygen atoms of H_2O_2 are assumed to be in *p* orbitals, the exchange repulsion forces are least when the dihedral angle is 90°, since the overlap integral between the orbitals vanishes. When electrostatic and dispersion forces are included, the minimum in the energy is estimated to occur at 100°. This work has since stimulated considerable interest in this dihedral angle. Most recently, the coefficients in a three-term potential function for the rotational barrier were determined from an analysis of the far infrared spectrum of gaseous hydrogen peroxide (Hunt, 1965). The minimum in this potential function occurs at 111·5°. From various single-crystal analyses the molecular angle of skew in the solid state has been observed to vary from 90 to 180°. The skewed form was always found, with the single exception of the crystal structure of $Na_2C_2O_4.H_2O_2$ (Pedersen, 1963). The broad range of observed values is a consequence of steric requirements for the formation of strong intermolecular hydrogen-bonded chains, which are surely a larger factor in determining the dihedral angle in the solid state than the exchange repulsion energy in the peroxy group. In *o*-nitroperoxybenzoic acid (Sax, Beurskens & Chu, 1965) and peroxypelargonic acid (Belitskus & Jeffrey, 1965), the dihedral angles are 146 and 132° respectively, and in both crystal structures the hydrogen atom of the peroxycarboxyl group participates in hydrogen bonding. Evidently, crystal structures in which this angle is influenced by hydrogen bonding are not best suited for demonstrating the effect of the lone-pair electrons on the molecular stereochemistry. It seems reasonable to assume that only in crystals without hydrogen bonded peroxide groups will there occur, if at all, molecules in which the substituents on the peroxide group are involved in intermolecular interactions sufficiently weak that the exchange repulsions between lone-pair electrons on adjacent oxygen atoms are the major influence governing the dihedral angle. If this is indeed the case, the angles observed in such crystal structures will fall within a narrow range about a characteristic value. Dibenzoyl peroxide is one such crystal structure, where the molecules are situated in an environment subject to van der Waals type interactions only.

Crystal data

Benzoyl peroxide, $C_{14}H_{10}O_4$, M.W. 242·22, m.p. 103·5 °C,

Orthorhombic, with $a=8{\cdot}95\pm0{\cdot}01$, $b=14{\cdot}24\pm0{\cdot}01$, $c=9{\cdot}40\pm0{\cdot}02$ Å, $V=1210$ Å^3, $D_m=1{\cdot}33$ g.cm^{-3}, $Z=4$, $D_x=1{\cdot}34$ g.cm^{-3}. Space group, $P2_12_12_1$, from the extinctions $h00$ absent for h odd, $0k0$ absent for k odd, and $00l$ absent for l odd.

Experimental

The crystals of dibenzoyl peroxide were supplied to us by Dr L. Silbert of the Eastern Regional Laboratories, U.S. Department of Agriculture. Cell dimensions were measured on the General Electric XRD-3 diffractometer with Cu $K\alpha$ radiation. The three-dimensional intensity data were recorded at room temperature on multifilm equi-inclination Weissenberg photographs with Cu $K\alpha$ radiation. Layers 0 to 9 and 0 to 5 were collected about the b and c axes, respectively, with exposure times ranging from 46 to 97 hours. Photographs taken at 25°C and −100°C showed diffuse scattering which probably indicates both thermal motion and statistical disorder. Only 863 of the 1611 reflections within the limiting sphere could be recorded at 25°C and 101 of these were unobserved above the background. The intensities were estimated visually by comparison with a standard scale. Angle and spot-shape corrections were applied but none were made for absorption or extinction. The interlayer scaling factors were determined by a least-squares method (Rollett & Sparks, 1960), in which the observed intensities were weighted in accordance with the accuracy of the part of the visual scale in which the intensity estimation was made.

Table 1. *Observed and calculated structure factors for dibenzoyl peroxide*

The running index k is listed at the left in each group of reflections having common h and l indices. The other columns are as they follow the k index from left to right: $10F_o$, $10\lvert F_c\rvert$, $10A_c$ and $10B_c$. Those reflections marked with an asterisk were omitted from the least-squares refinement.

H= 0 L= 0				
2	94	94	94-	0
4	175	163	163-	0
6	46	45	45	0
8	156	144	144-	0
10	301	295	295-	0
14	171	176	176	0
H= 1 L= 0				
1	596	595	0	595
2	23	19	0	19-
3	267	260	0	260-
4	340	321	0	321
5	314	271	0	271-
6	440	453	0	453
7	61*	26	0	26
8	71	63	0	63
9	96	100	0	100-
10	143	137	0	137-
11	76	77	0	77-
14	59	56	0	56
H= 2 L= 0				
0	479	507	507-	0
1	1000	1036	1036	0
2	124	134	134-	0
3	234	233	233-	0
4	102	99	99-	0
5	186	164	164-	0
6	134	104	104-	0
7	48	44	44-	0
8	96	90	90	0
9	46	38	38	0
10	141	127	127	0
11	71	66	66	0
13	63	58	58-	0
15	42	37	37	0
H= 3 L= 0				
1	43	37	0	37
2	77	76	0	76-
3	20	21	0	21-
4	59*	22	0	22
5	231	221	0	221-
6	94	91	0	91-
7	15*	12	0	12-
8	57	52	0	52-
9	41	39	0	39
10	203	174	0	174-
11	59	48	0	48
15	54	50	0	50
16	35	32	0	32-
H= 4 L= 0				
0	120*	75	75	0
1	121	126	126	0
2	77	70	70-	0
3	76	58	58	0
4	270	273	273-	0
5	206	204	204-	0
6	69	70	70	0
7	18	20	20	0
8	28	25	25	0
9	129	128	128	0
10	254	248	248-	0
H= 5 L= 0				
1	69*	71	0	71
3	165	173	0	173-
4	23	17	0	17-
5	64	59	0	59
6	79	71	0	71-
7	66	59	0	59
8	95	86	0	86
9	121	117	0	117
10	66	63	0	63-
11	176	169	0	169-
12	28	31	0	31
H= 6 L= 0				
0	166	167	167-	0
1	97	93	93	0
3	118	133	133	0
4	148	163	163	0
5	57	50	50-	0
6	24*	2	2-	0
7	36	36	36-	0
9	97	99	99	0
10	154	143	143	0
11	75	62	62-	0
13	41	40	40-	0
14	33	30	30-	0
H= 7 L= 0				
1	27	24	0	24-
4	66	69	0	69-
5	51	52	0	52
7	21	26	0	26
9	80	86	0	86
10	131	147	0	147
H= 8 L= 0				
0	56	54	54	0
1	52	51	51	0
4	37	44	44	0
7	27*	12	12	0
8	31	36	36-	0
9	61	70	70-	0
H= 9 L= 0				
2	34	40	0	40
H=10 L= 0				
0	68	75	75-	0
H= 0 L= 1				
1	413	449	0	449-
2	156	190	190	0
3	453*	602	0	602-
4	70	78	78-	0
5	83	69	0	69
6	25	24	24	0
7	499*	637	0	637-
8	105*	106	106-	0
9	47	51	0	51-
10	36	33	33	0
11	80	74	0	74
13	27	29	0	29
14	31	32	32	0
H= 1 L= 1				
1	367	387	350-	165-
2	137	134	131-	24-
3	274*	314	207-	236-
4	161	161	16	160
5	37	30	0	30-
6	351	395	97	383-
7	239	260	74	249-
8	151	165	155	54
9	20	17	3	17-
10	77	81	68-	45
11	30	27	27-	0
13	36	37	37-	4-
14	27	31	26-	16
16	33	28	28-	6-
17	24	21	1	21-
H= 2 L= 1				
1	653	656	640-	143
2	199	200	196	39-
3	352	376	257-	275
4	73	68	60-	33
5	83	81	45	67
6	253	258	112	233
7	363	362	145	332
8	67	61	5	61-
9	33	29	24	15
10	28	25	2	25
11	92	80	36-	71-
12	44	44	8	43-
13	57	60	55-	25-
16	36	31	22-	21
17	32	32	6	31-
H= 3 L= 1				
0	146	150	0	150-
1	361	356	337	115-
2	236	228	99	205-
3	267	283	114	259-
4	162	159	120-	103
5	20	18	5-	17
6	103	94	76-	56
7	132	123	7	122-
8	72	78	67-	40
9	43	36	30	19
10	89	94	67	66
11	75	67	16-	65
12	68	72	28-	66-
13	49	42	42	2-
16	23	19	11	15
17	32	32	6-	32-
H= 4 L= 1				
0	118	113	0	113
1	119	100	66-	75-
2	156	164	164	3
3	249	236	58	228-
4	50	45	9	44-
5	33	26	26	1-
6	80	79	79	0
7	143	130	118	53-
8	71	67	24-	62
9	51	46	45	10-
10	30	28	6-	28-
11	150	144	4	144
12	43	42	39-	15
13	37	37	13-	34
H= 5 L= 1				
0	54	54	0	54-
1	82	72	72-	7-
2	49	48	18	45-
3	184	181	99	151-
4	81	79	78	12
5	49	53	23-	47
6	84	90	6-	90
8	58	63	0	63
9	23	19	0	19
10	36	27	23-	14
11	126	133	53	122
12	26	19	8-	17-
13	36	26	24-	10
H= 6 L= 1				
0	21	20	0	20-
1	44	41	17	37
2	85	91	63	66
3	150	157	101	119
4	75	79	53	59-
5	30	32	28-	14-
6	27	24	2	24-
7	41	35	33	11
8	42	40	37-	16-
9	24*	2	1	0
10	54	51	34-	37-
11	75	79	31	73-
12	31	35	30-	17
H= 7 L= 1				
1	33*	8	6-	4
2	43	41	21-	35
3	70	73	71-	19
4	31	38	11-	36-
5	26	29	2-	29
6	33	27	27-	3
7	32	26	21-	15-
8	27	28	24	14
9	24	33	29-	16-
10	31	32	13	29-
11	27	27	26-	8
12	23	26	20	16
H= 8 L= 1				
0	29	32	0	32
1	36	34	24-	24-
2	54	52	15-	50-
3	19*	1	0	0
4	18	14	11	9
7	36	29	2-	28-
H= 9 L= 1				
2	19	15	9-	11-
3	18*	29	25	15
H=10 L= 1				
1	24	27	7-	27
2	22	26	23-	11
H= 0 L= 2				
0	207*	267	267	0
1	354	367	0	367-
2	72	70	70-	0
3	153	179	0	179
4	49	49	49	0
5	221	239	0	239
6	160	164	164	0
7	85	83	0	83-
8	36	38	38-	0
9	72	62	0	62
10	129	129	129-	0
12	31	26	26-	0
H= 1 L= 2				
0	1056*	1359	1359	0
1	633*	699	695-	75
2	45	47	31	34-
3	155	166	54	157-
4	231	267	122	237-
5	119	124	119	32
6	168	180	47	173-
7	64	60	0	60
8	54	51	42-	28-
9	57	57	25-	51-
10	149	161	5-	161
11	67	71	12-	70-
13	47	42	41	11
14	52	51	49	15-
15	34	39	30-	25-
H= 2 L= 2				
0	1307*	1635	1635-	0
1	111	96	35-	90
2	102	63	76	33-
3	72	66	45	48
4	235	242	240	28
5	196	215	207	55
6	252	275	29-	273
7	46	45	21	39-
8	76	70	60	34
9	94	100	74-	67-
10	254	278	259	100
11	48	40	10-	39
14	84	95	76-	56
15	28	26	8-	24-
H= 3 L= 2				
0	453*	503	503	0
1	389	382	217	314-
2	66	61	53-	30
3	221	230	146-	177
4	77	62	0	62-
5	132	118	98	64
6	59	50	3-	50-
8	73	63	14	61-
9	130	129	124-	32-
10	107	119	50	107
11	123	143	44	136
13	31	31	7-	30-
14	38	39	39	0
15	28	27	7	27-
H= 4 L= 2				
0	365*	382	382	0
1	312	315	313-	34
2	105	111	105	36-
3	74	60	7-	59
4	155	132	108-	77
5	173	171	88	147-
6	42	40	10	38
7	35	36	27	24-
8	76	80	43-	67-
9	132	137	103-	91-
10	170	185	147-	112-
11	88	97	5-	97
12	24*	4	1-	4-
13	45	44	39	20-
14	23	30	29	4
H= 5 L= 2				
0	79	75	75-	0
1	74	76	49	57
2	61	59	33-	48
3	68	70	58-	38
4	203*	225	199-	105
5	27	24	19-	14
6	60	57	0	57
8	48	50	46	18
9	72	79	19	77-
10	147	164	141-	83-
11	40	39	39	5
H= 6 L= 2				
0	59*	31	31-	0
1	69	72	72-	3
2	32	25	13	20-
3	65	72	45-	55-
4	42	39	15	36
5	25	19	9	17-
6	41	46	39-	23-
8	23	20	7	19
9	29	32	31	9
10	105	118	45	109-
11	52	38	16	34-
H= 7 L= 2				
1	49	42	41-	6
2	32	30	13	27-
3	51	44	35	27
4	24	18	16-	7
5	41	42	35-	23-
6	18	25	18	16
7	34	39	17-	36-
9	76	84	80	26-
11	36	37	15-	34
H= 8 L= 2				
0	96	90	90	0
1	48	55	52-	16
2	25	27	18-	20-
3	25	29	29-	5-
4	38	45	44-	7-
6	28*	35	29	19
8	22	14	1	14
9	36	36	9-	35
10	39	48	33-	34
11	18*	30	18	24-
H= 9 L= 2				
0	66	77	77	0
1	23	21	12	17
2	17	16	10-	12-
3	17	18	18	0
4	23	22	22	2
5	16	26	22-	13-
7	22*	5	5-	2-
8	21	18	11-	15
9	27	26	12-	23-
H= 0 L= 3				
1	48	53	0	53
2	161	175	175-	0
3	74	63	0	63-
4	206*	262	262	0
5	63	68	0	68-
6	39	34	34-	0
7	51	49	0	49-
8	77	83	83-	0
9	42	43	0	43
10	39	39	39-	0
11	89	100	0	100
12	22	17	17-	0
16	36	38	38	0
17	42	57	0	57
H= 1 L= 3				
0	178	184	0	184-
1	264	279	260	101-
2	129	127	98-	81
3	161	175	173	28
4	106	101	94	38-
5	54	52	1	52
6	38	37	35	11
7	201	224	104-	198-
8	36	39	39	2-
9	53	50	22-	44-
10	91	93	81-	46-
11	86	97	54	80-
12	63	66	15	64
13	31	29	29	1-
14	29	17	6-	16-
16	25	28	12-	25-
H= 2 L= 3				
1	215	228	36-	225
2	210	214	166-	134
3	419	462	196-	418
4	85	83	61	56
5	83	76	48-	59-
6	171	179	11	179-
7	224	238	94-	218
8	75	82	76	31-
9	58	60	60-	4-
10	63	66	64-	15
11	166	169	40-	164-
12	51	52	42	29
13	41	36	4-	36-
14	27*	8	7-	3
16	22	17	0	17-
17	26	33	27	19-
H= 3 L= 3				
0	31	35	0	35
1	63	64	58-	26
2	33	30	29-	8
3	293	299	181-	237
4	72	74	70-	23
5	86	91	11	91
6	112	112	9-	111
7	108	105	64-	83
8	123	120	40-	113-
9	68*	47	31-	35-
10	42	43	38	21
11	134	137	53-	126-
H= 4 L= 3				
0	62	62	0	62-
1	253	274	257	95-
2	152	158	110-	113-
3	145	139	36-	134-
4	141	148	120-	86
5	35	29	3	29-
6	100	103	32-	97-
7	164	170	45-	164-
8	26	24	17	17
9	25*	32	13	28-
10	58	62	48	39
11	36	38	37-	6
13	41	41	40	8
H= 5 L= 3				
0	77	81	0	81
1	107	101	101-	6
2	42	40	3	40
3	60	54	10-	53-
4	14	10	8	6
5	26	24	23	8-
6	86	85	82	22-
7	95	90	31	85
8	37	39	29	25-
9	42*	20	18	7-
11	39	35	4	35
13	33	36	20-	30
H= 6 L= 3				
0	76	79	0	79-
1	56	47	38	28
2	27*	7	1-	6
3	28	21	14	16-
4	44	46	14-	44
5	20	11	0	11
6	27	32	11-	30
7	61	58	11	57
8	23	19	16-	9-
9	40	36	25	26
10	29	27	3	27
H= 7 L= 3				
0	22	20	0	20-
1	70	76	70	28-
2	64	60	34	48
3	27*	11	6-	9
4	18*	25	9-	23-
5	21	16	3	16-
6	40	39	1	39-
7	28	30	20	22
8	30	31	30-	9
9	20	18	11	13-
10	27	24	18-	15-
11	24	22	11-	19-
H= 8 L= 3				
0	25*	0	0	0
1	34	37	19-	31-
2	36	28	28	3
3	51	53	48-	22-
5	21	15	1-	15
8	30	32	0	32
H= 9 L= 3				
1	34	32	21-	25-
2	34	43	22	36-
3	23	19	14	13
H= 0 L= 4				
0	247	277	277	0
1	36	35	0	35
3	29	29	0	29
4	247	273	273-	0
5	69	79	0	79-
6	66	73	73-	0
7	24*	6	0	6-
8	57	65	65-	0
9	104	100	0	100
10	223	252	252-	0
11	36	33	0	33-
12	30	20	20-	0
14	35	29	29	0
15	31	34	0	34
16	18	26	26	0
H= 1 L= 4				
0	200	206	206	0
1	151	161	137	84

Table 1 (*cont.*)

2	103	107	64-	85
3	110	102	28	98-
4	132	146	30	142
5	158	175	161-	69
6	67	68	52	44-
7	34	33	13-	30-
8	40	40	29-	28
9	98	108	98	44
10	157	185	54-	177-
11	111	133	25-	130-
13	27	31	18-	25
14	33	27	0	27-
15	16	10	9	5
H= 2 L= 4				
0	194	205	205-	0
1	194	210	178-	111
2	24	27	20	18-
3	133	149	8	149-
4	158	181	128	128-
5	92	80	80-	2
6	87	96	61-	74-
7	43	39	19-	33
9	133	133	127	40
10	151	161	139	80
11	69	79	0	79-
12	36•	11	7	9-
13	30	21	8	19
14	25	20	16-	12-
15	30	22	20-	9
H= 3 L= 4				
0	468	514	514-	0
1	195	218	216	28-
2	49	52	37-	37-
3	63	62	31	53
4	159	148	135	59-
5	60	52	13	51
6	65	57	5	57
7	63	66	20	62-
8	46	46	3-	46
9	69	66	11	65
10	173	191	134	135
11	36•	6	6-	1-
12	19	16	1	16
13	24	20	19-	6
14	43	48	40-	27
H= 4 L= 4				
0	447•	513	513	0
1	116	114	28	110-
2	41	41	41-	1-
3	35	34	26-	22
4	93	87	49	72-
5	25	19	15-	11
6	103	94	57	74-
7	28	20	5-	19
8	39	34	23-	24-
9	83	75	73-	20
10	91	88	5-	88
13	26	24	0	24-
14	38	34	32	12-
H= 5 L= 4				
0	96	105	105-	0
1	81	75	19-	73
2	52	50	49	11-
3	36	29	29	4-
4	35	28	19	21-
5	42	36	22	28-
6	25	20	10-	17
7	23	16	16	0
8	19•	5	0	5
9	58	57	55-	16-
10	25	22	20-	8-
H= 6 L= 4				
0	198	210	210-	0
1	149	156	155	9-
2	47	54	37-	39
3	20	12	8-	9
5	54	53	38	37
6	31	33	30-	14-
7	26	18	0	18
8	37	37	33	15
H= 7 L= 4				
0	67	58	58-	0
1	61	66	33-	57-
2	31	28	28	1
3	26	23	0	23-
4	30	32	32	5-
5	30	31	30	8-
6	44	47	17-	43-
8	33	30	7-	30-
H= 8 L= 4				
0	40	43	43-	0
1	38	35	33-	12-
2	25	22	22	0
3	18	23	7	21
4	28	33	33-	5
5	18	21	19	9
H= 9 L= 4				
0	22	17	17	0
H= 0 L= 5				
1	71	78	0	78-
2	85	81	81	0
3	282•	362	0	362-
4	118	121	121-	0
5	42	44	0	44-
6	40	36	36-	0
7	55	55	0	55-
8	26	13	13-	0
9	57	47	0	47
10	110	127	127	0
11	179	209	0	209
H= 1 L= 5				
0	86	103	0	103
1	96	96	92-	28-
2	50	47	7	47-
3	163	175	113	133-
4	126	151	141	53-
5	45	41	17	37-
6	32	28	20	19
7	85	100	84	54-
8	37	32	9-	31
9	69	68	40	56
10	53	55	52-	17-
11	84	94	31	89
13	38	33	22-	24
H= 2 L= 5				
0	86	90	0	90-
1	20	20	1-	20
2	106	111	89	66
3	157	150	144	43
4	60	53	13-	52-
5	21	23	23	0
6	19	13	13-	3
7	34	30	24	17
8	30	25	9	23
9	27	21	15	15
10	63	55	23-	49-
11	63	66	61	26-
12	40	32	6-	31
H= 3 L= 5				
0	76	78	0	78
1	100	105	82-	66
2	44	41	6	40
3	95	95	65-	69
4	54	52	50	14-
5	56	53	17-	50-
6	34	29	28-	7
7	75	68	8-	68
8	39	32	28-	15
9	59	51	30-	41
H= 4 L= 5				
0	15	18	0	18
1	79	82	57-	59-
2	73	68	36	57-
4	36	26	24	11-
5	41	39	13	36
6	67	59	15-	57
7	121	117	5-	116-
8	40	33	32-	4-
H= 5 L= 5				
0	32	22	0	22-
1	44	33	0	33
2	89	87	60-	62-
3	43	40	37	16-
5	36	39	3-	39-
6	29	25	4	24-
7	86	85	19-	82-
8	50	41	34	24
H= 6 L= 5				
0	41	33	0	33
1	96	101	73-	69
2	40	31	22-	22
3	40	30	20	22
4	27	22	22	0
5	25•	5	3-	5
6	56	58	35	46
7	67	55	21-	51
8	54	58	24	53-
H= 7 L= 5				
0	45	46	0	46-
1	74	71	65	27
2	40	39	38-	2
3	26•	11	6	9
8	34	24	3-	24-
H= 8 L= 5				
0	18•	2	0	2
1	36•	32	31	7-
2	38	39	20-	33
H= 0 L= 6				
0	120	124	124	0
1	54	53	0	53-
2	41	40	40	0
3	91	98	0	98
4	91	100	100-	0
5	47	51	0	51-
6	34	34	34	0
7	21	22	0	22
9	70	68	0	68-
H= 1 L= 6				
0	105	100	100	0
1	45	46	7-	46
3	16	13	6	11-
4	115	114	114-	4
5	59	60	59	10
6	27	25	14-	20
7	20	18	1-	18
9	89	82	79-	20
H= 2 L= 6				
0	127	122	122-	0
1	30	27	20-	18
2	61	62	1-	62
3	55	60	38	47-
4	83	91	23	88
5	29	25	21-	14
6	31	24	6	23-
7	31	26	20-	15
9	59	58	44	37-
H= 3 L= 6				
0	87	92	92-	0
1	100	108	103-	31-
2	25	22	21	4-
4	40	38	32-	20-
5	21•	9	4-	8-
6	37	39	39-	0
7	22	20	2	20
9	74	72	71	11
H= 4 L= 6				
0	119	126	126	0
2	30	25	24-	6-
3	37	31	7	31
4	44	44	29-	34
6	39	43	25	35
7	37	38	25	28-
8	44	40	38-	13
H= 5 L= 6				
0	254	268	268	0
1	67	65	64-	7
5	55	54	50-	21-
6	25	18	15	10
7	28•	7	0	7
H= 6 L= 6				
0	60	61	61-	0
1	78	79	41	67
6	38	38	25-	28
8	36	34	8	33
H= 7 L= 6				
1	68	67	67	2
2	30	33	32-	8
3	34•	5	3-	4
H= 8 L= 6				
0	22•	3	3	0
1	32	26	22-	12-
H= 0 L= 7				
3	24	17	0	17
4	45	42	42-	0
5	27	30	0	30
7	36	30	0	30-
9	69	75	0	75-
H= 1 L= 7				
0	38	33	0	33-
1	38	37	36	9-
3	109	119	61-	102-
4	33	37	10-	36
5	27	19	19-	1-
7	22	28	26-	11-
H= 2 L= 7				
1	43	44	43	7
3	70	66	42	51
4	34	27	23	14-
5	27	20	7-	19
7	47	51	5	51
H= 3 L= 7				
0	37	37	0	37-
1	77	77	77	8-
2	66	69	27	63
3	29•	13	7-	11
4	57	62	61-	6-
6	37	37	20-	31-
7	57	61	3	61
H= 4 L= 7				
0	60	68	0	68
1	51	48	1-	48-
3	55•	55	48-	26-
8	36	33	23-	24
H= 5 L= 7				
0	35	5	0	5
1	55	53	23-	48-
2	63	48	43	21-
7	56	55	21	51-
H= 6 L= 7				
1	39	33	28-	17
7	18	11	5	9-
H= 7 L= 7				
1	31•	24	24-	1
2	34	25	23	9-
3	31	10	9-	2
H= 8 L= 7				
1	21	22	22	1-
H= 0 L= 8				
0	128	119	119	0
4	34	28	28	0
7	28	28	0	28-
H= 1 L= 8				
0	51	45	45	0
1	52•	54	38	38
4	32	26	23-	13-
5	31	15	8-	12-
H= 2 L= 8				
0	77	77	77-	0
1	58	58	49	31
4	32	23	20	12-
9	39•	46	42-	18
H= 3 L= 8				
0	127	130	130-	0
1	24	7	5	3-
6	28	33	9	32-
H= 4 L= 8				
0	47	49	49-	0
1	46	38	27-	26-
4	42	35	31-	17-
H= 5 L= 8				
0	34	36	36	0
1	23•	23	14-	18-
H= 6 L= 8				
1	22•	21	20-	2-
H= 7 L= 8				
0	33	26	26-	0
3	21	1	1-	1
H= 0 L= 9				
7	35	40	0	40-
H= 1 L= 9				
1	45	47	46-	8
7	33	39	10	38-
H= 2 L= 9				
1	36	36	25-	26
H= 3 L= 9				
1	26•	28	22	17
H= 4 L= 9				
1	31	28	28	5
H= 5 L= 9				
1	34	9	1	8-
H= 0 L=10				
0	40	39	39	0
1	37	42	0	42-
H= 1 L=10				
0	81•	83	83	0
1	22	23	23-	0
H= 5 L=10				
1	17	3	2-	1-

Determination and refinement of the structure

The three-dimensional Patterson function could not be readily interpreted owing to poor resolution, and was therefore recalculated with point-atom sharpening and the origin peak removed, using the formula suggested by Buerger (1959) with scale and temperature factors evaluated by Wilson statistics. The distribution of vectors in this synthesis provided sufficient information to determine the conformation of the molecules and to locate them relative to the screw axes. Structure factors were calculated for the derived model, and the conventional agreement index R was 0·45 for reflections with $\sin\theta < 0{\cdot}4$. The large positional errors in the trial model were first corrected by five cycles of structure factor and Fourier synthesis calculations, limiting the input data in the first two cycles to reflections with $\sin\theta < 0{\cdot}5$. With a uniform isotropic temperature factor of 3·5 Å^2, the agreement was then 0·22. Further refinement by differential Fourier synthesis (Shiono, 1963) with one isotropic cycle and two anisotropic cycles reduced R to 0·15.

The final refinement of the 163 parameters, including a single scale factor, was by full-matrix least-squares (Busing, Martin & Levy, 1962). The quantity minimized was $\Sigma w(F_o - KF_c)^2$, where w was estimated by the Hughes weighting scheme with a value of 6 for $4F_o$min. Of the 762 reflections recorded, 59 of low reliability were omitted in addition to those below the threshhold value. The positional parameters for the hydrogen atoms in this calculation were fixed by assuming a C–H bond of 1 Å in the direction opposite to that of the ring diagonal from the carbon atom to which it was bonded. The thermal parameters were taken to be those of the adjacent carbon atom. The scattering factors of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) were used for the carbon and oxygen atoms, and those of McWeeny (1951) for the hydrogen atoms. For the 703 reflections included in the refinement, the final agreement index was 0·074 and the weighted index was 0·107. With all 863 observed and unobserved reflections, the agreement index was 0·10. The structure factors are listed in Table 1. The atomic parameters and their estimated standard deviations are given in Table 2. The key to the atomic numbering is shown in Fig. 1.

Discussion

The molecule consists of two nearly planar phenylcarboxyl groups associated by a peroxide bond. The phenyl groups lie in planes that intersect at 84° along a line nearly parallel with the peroxide bond (Fig. 2), and in each ring the atoms are coplanar to within

Table 2. *The atomic parameters*

	Fractional coordinates $\times 10^4$ e.s.d. $\times 10^4$			Anisotropic temperature coefficients* $\times 10^2$ e.s.d. $\times 10^2$ (Å^2)					
	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	1227	−2761	3772	264	175	417	−31	10	26
	12	6	13	15	13	24	14	23	15
C(2)	2133	−2311	4703	310	180	340	21	−47	44
	13	6	13	17	13	20	14	22	15
C(3)	2279	−1350	4749	341	195	299	−92	−97	−5
	13	7	12	19	12	20	14	23	15
C(4)	1472	−828	3788	262	168	196	26	−2	30
	10	6	9	15	11	14	11	18	11
C(5)	537	−1284	2808	266	208	301	6	−31	−19
	12	7	12	15	13	17	13	19	15
C(6)	460	−2231	2808	301	184	341	−3	−13	−55
	12	6	12	17	14	20	14	21	15
C(7)	1568	209	3695	240	167	252	7	66	−12
	10	6	11	15	11	16	11	19	14
C(8)	3585	1893	3937	249	176	301	5	−44	−5
	11	6	11	16	12	18	12	20	13
C(9)	4565	4339	2917	314	243	415	−32	11	8
	13	8	15	20	19	22	17	26	19
C(10)	4507	3370	2982	311	169	402	−32	46	16
	12	6	14	18	13	22	13	24	15
C(11)	3585	2921	3918	197	187	287	10	−18	6
	9	6	10	13	12	18	10	18	13
C(12)	2664	3453	4844	281	283	320	−10	−69	−41
	12	8	13	18	19	20	15	22	16
C(13)	2767	4427	4741	393	179	405	7	25	−71
	14	7	15	24	15	24	16	28	15
C(14)	3654	4849	3789	280	165	422	−18	−158	40
	12	6	13	17	12	24	14	25	16
O(15)	2454	535	4780	442	123	346	−67	−42	8
	9	4	8	16	8	14	10	17	8
O(16)	0973	698	2868	277	197	341	12	−21	66
	8	4	8	11	10	13	9	13	10
O(17)	2444	1553	4750	391	191	340	−57	68	−23
	9	4	9	16	11	14	10	17	10
O(18)	4394	1391	3289	278	187	483	20	57	−33
	8	5	10	11	10	18	10	16	11
H(1)	1139	−3457	3774						
H(2)	2701	−2677	5378						
H(3)	2937	−1033	5459						
H(5)	−33	−919	2140						
H(6)	−195	−2549	2105						
H(9)	5253	4660	2219						
H(10)	5136	2993	2342						
H(12)	1985	3131	5534						
H(13)	2138	4804	5374						
H(14)	3682	5543	3743						

* In the form $f^\circ \exp\,[-\tfrac{1}{4}(B_{11}h^2a^{*2}+\ldots+2B_{23}klb^*c^*)]$.

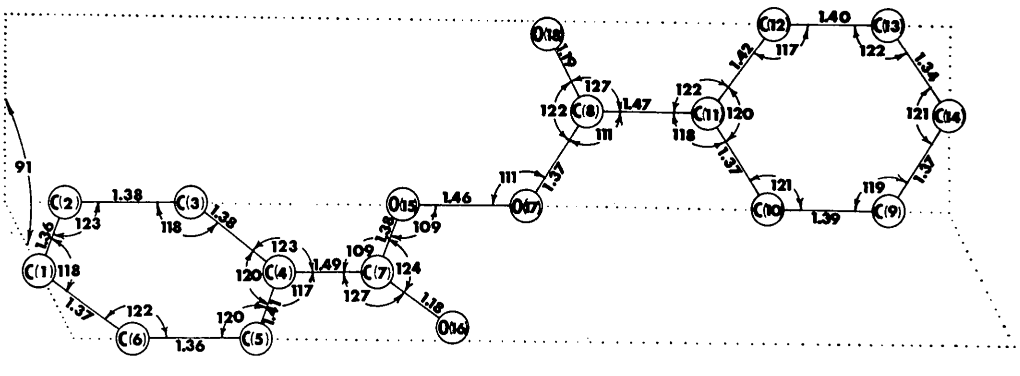

Fig. 1. Some interatomic distances and angles in dibenzoyl peroxide.

$\frac{1}{2}\sigma$ (0·01 Å). Neither the O(16)C(7)O(15)O(17) nor the O(18)C(8)O(17)O(15) group is planar, but they exhibit a slight torsional displacement of 2·5 and 4·2° respectively about the C(7)–O(15) and C(8)–O(17) bonds (Table 3). In *o*-nitroperoxybenzoic acid, the corresponding displacement is 5°. The equations to some of the atomic planes in the molecule are given in Table 3, together with the angles subtended at their lines of intersection. The most interesting of these is the dihedral angle of 91° at the peroxide bond. Although this value agrees with the theoretical estimate of the angle in the isolated molecule, the question of the extent to which it may have been perturbed by the lattice forces cannot be ascertained from a single analysis alone. Supporting evidence that this perturbation is small is provided by the work of Caticha-Ellis & Abrahams (1965), who have found a dihedral angle of approximately 90° in 4,4′-dichlorodibenzoyl peroxide, although the molecular packing in the two crystal structures is different. The conformation of these two molecules also differs at single bonds other than the peroxide bond owing to variations in certain other dihedral angles. However, structure analyses of molecular peroxides of more diverse geometry are needed to determine how sensitive is the dihedral angle to molecular environment. The molecular packing, the dihedral angle at the peroxide bond and the two dihedral angles between the phenyl groups and the carboxyl groups to which they are bonded are shown in Fig. 2. The closest contacts between molecules are the expected van der Waals interactions. In view of the mode of molecular packing and qualitative observations on the distribution of the X-ray diffuse scattering at different temperatures, the suggestion is made that this crystal may contain both D and L molecules and is composed of micro-domains, each containing molecules of the same sense and separated by stacking faults. The enantiomorphism of organic peroxides has been discussed recently (Jeffrey, 1964).

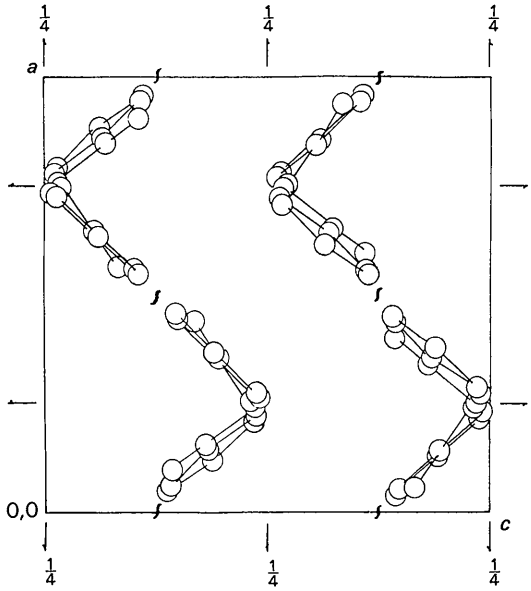

Fig. 2. The (010) projection of dibenzoyl peroxide showing the molecular packing, the dihedral angle at the peroxide bond, and the angle of torsion at the single bonds between the phenyl and carboxy groups.

The bond lengths and valence angles with their standard deviations are shown in Fig. 1, where the σ's are 0·02 Å in the bond lengths and 2·0° in the valence angles. The C–C distances in the benzene rings vary from 1·34 to 1·42 Å, but do not differ by more than 3σ from the mean of 1·379 Å. The C–C distances external to the ring are 1·49 and 1·47 Å. The C=O distances are 1·18 and 1·19 Å, the C–O distances are 1·38 and 1·37 Å and the O–O distance is 1·46 Å. The angles in the benzene rings average 119·4°. The three angles at carboxyl carbon atom (7) are 109, 127 and 124°, and the corresponding angles at atom (8) are 111, 127 and 122°. The average C–O–O angle is 110°, implying that the bonding orbitals on the oxygen atoms are sp^3 hybrids. Within the accuracy of the analysis these values are in agreement with comparable parameters reported for *o*-nitroperoxybenzoic acid. The rather large standard deviations in the parameters are a consequence of the cut-off in the data, which, in view of the comparatively high melting point, is only partially due to thermal motion. Since some preliminary calculations indicated that the rigid-body approximation was not applicable to this molecule, no correction to the bond lengths for the thermal motion was attempted. However, the directions and magnitudes of the principal axes of the apparent vibration ellipsoids of the atoms as given by the least-squares refinement are shown in Table 4.

The dihedral angle in covalent peroxides

The Penney–Sutherland discussion of the dihedral angle in the peroxide groups is limited specifically to the H_2O_2 molecule and makes the assumption that the oxygen $2s$ orbital is not used in bonding. A more general theoretical treatment is needed as a basis for discussing the other covalent peroxide structures. Essentially this must show how the exchange repulsion energy changes in its dependence upon the dihedral angle as the chemical nature of the substituent atoms on the peroxide group is varied. For this purpose the exchange integrals between the electrons in filled orbitals must be evaluated as functions of the dihedral angle and the bonding parameters. If, for simplicity, the overlap rather than the exchange integrals is used in the evaluation, comparative estimates of the configurational energy of the molecule can be deduced, the stable configurations being those for which the overlapping is a minimum. It is the latter method which is followed here.

In these calculations, the bonding electrons of oxygen are assumed to be in sp^3 orbitals, whereas the lone-pair electrons are assigned to sp and p orbitals. In order to define the dihedral angle θ, the orbital directions of oxygen atom 1 are fixed while those of atom 2 are rotated about the O–O bond, where $\theta=0°$ is taken to be the *cis* conformation. The x axis is chosen to coincide with the peroxide bond with the positive sense from O(1) to O(2). The subscript on ψ designates the oxygen atom; the Roman numerals (I) and (II) indicate atomic orbitals used respectively in the peroxide bond and in the bond to the substituent atom; numerals (III) and (IV) indicate orbitals of the lone-pairs.

$$\psi_1(\mathrm{I}) = \frac{1}{2}s + \frac{\sqrt{3}}{2}p_x$$

$$\psi_1(\mathrm{II}) = \frac{1}{2}s - \frac{1}{2\sqrt{3}}p_x + \sqrt{\frac{2}{3}}p_y$$

$$\psi_1(\mathrm{III}) = \frac{1}{\sqrt{2}}s - \frac{1}{\sqrt{6}}p_x - \frac{1}{\sqrt{3}}p_y$$

$$\psi_1(\mathrm{IV}) = p_z$$

Table 3. *Some planes of atoms in dibenzoyl peroxide*

Atomic planes	Coefficients in $AX+BY+CZ+D=0$			
	A	B	C	D
Phenyl C(1) to (6)	0·7603	−0·0531	−0·6474	−1·244
Phenyl C(9) to (14)	0·7285	0·0096	0·6849	4·923
C(7), O(15), O(17)	0·7905	−0·0065	−0·6124	−1·024
O(15), O(17), C(8)	0·5934	0·0192	0·8047	4·951
C(7), O(15), O(16)	0·8007	−0·0560	−0·5973	−0·96876
C(8), O(17), O(18)	0·6135	−0·0498	0·7881	4·768

Dihedral angles in dibenzoyl peroxide

Planes	Dihedral angle
C(7)–O(15)–O(17) and C(8)–O(15)–O(17)	91°22′
Phenyl group [C(1) to C(6)] and O(15)–C(7)–O(16)	3 42
Phenyl group [C(9) to C(14)] and O(17)–C(8)–O(18)	9 30
C(7)–O(15)–O(17) and C(7)–O(15)–O(16)	2 26
C(8)–O(17)–O(18) and C(8)–O(15)–O(17)	4 14

Table 4. *R.M.S. displacements and directions of principal axes of vibration**

	$U(i)\times10^2$	$\theta(i,a)$	$\theta(i,b)$	$\theta(i,c)$		$U(i)\times10^2$	$\theta(i,a)$	$\theta(i,b)$	$\theta(i,c)$
C(1)	22 Å	74°	17°	85°	C(10)	22	77	14	96
	29	163	74	84		30	157	76	72
	36	86	97	8		35	71	89	19
C(2)	22	102	20	106	C(11)	23	123	34	97
	30	148	108	116		25	146	124	96
	33	120	82	31		30	99	87	9
C(3)	21	61	33	75	C(12)	26	50	60	55
	29	109	63	146		30	53	143	89
	36	36	109	119		33	118	110	36
C(4)	21	101	32	120	C(13)	22	91	16	74
	25	78	117	150		34	155	98	66
	28	16	74	85		36	65	104	29
C(5)	25	92	11	80	C(14)	22	91	9	99
	28	154	87	116		25	150	96	119
	31	116	100	29		39	120	83	31
C(6)	22	88	18	72	O(15)	18	79	11	90
	30	171	85	97		32	106	87	164
	33	99	107	19		37	20	101	106
C(7)	22	106	23	74	O(16)	23	99	24	111
	24	134	113	53		29	168	101	93
	30	48	92	42		33	97	70	22
C(8)	23	93	3	89	O(17)	23	76	14	87
	26	153	92	117		30	60	95	149
	31	117	93	27		36	34	104	60
C(9)	26	69	21	93	O(18)	23	105	17	82
	31	159	69	87		29	161	106	80
	35	86	88	5		39	79	95	13

* The r.m.s. displacement $U(i)$ is directed along the ith axis of the ellipsoid, where $\theta(i,a)$, $\theta(i,b)$ and $\theta(i,c)$ are angles between the ith axis and crystallographic axes a, b, c.

$$\psi_2(\mathrm{I}) = \frac{1}{2}s - \frac{\sqrt{3}}{2}p_x$$

$$\psi_2(\mathrm{II}) = \frac{1}{2}s + \frac{1}{2\sqrt{3}}p_x + \sqrt{\frac{2}{3}}\,(p_z \sin\theta + p_y \cos\theta)$$

$$\psi_2(\mathrm{III}) = \frac{1}{\sqrt{2}}s + \frac{1}{\sqrt{6}}p_x - \sqrt{\frac{1}{3}}\,(p_z \sin\theta + p_y \cos\theta)$$

$$\psi_2(\mathrm{IV}) = p_z \cos\theta - p_y \sin\theta$$

The localized m.o.'s for the σ bonds are

$$\psi(\mathrm{O{-}O}) = \frac{1}{\sqrt{2}}\,[\psi_1(\mathrm{I}) + \psi_2(\mathrm{I})]$$

$$\psi[\mathrm{O(1){-}R(1)}] = \lambda_1\psi_1(\mathrm{II}) + (1-\lambda_1^2)^{\frac{1}{2}}\psi[R(1)]$$

$$\psi[\mathrm{O(2){-}R(2)}] = \lambda_2\psi_2(\mathrm{II}) + (1-\lambda_2^2)^{\frac{1}{2}}\psi[R(2)]$$

where R(1) and R(2) are atoms bonded to O(1) and O(2) respectively. The values for λ are estimated from bond moments (Coulson, 1952). The other bonding parameters λ_π are estimated from bond orders (Pauling, 1960) and are defined by the relation

$$\lambda_\pi^2 = C_1^2 + \ldots\ldots C_n^2$$

where the C_i^2 are the coefficients of ψ(IV) in the filled orbitals of a π electron system involving oxygen and a substituent group. The overlap integrals can now be expressed as functions of the dihedral angle, the bonding parameters, and overlap integrals between the atomic basis functions, as in the integral

$$\langle \lambda_1\psi_1(\mathrm{II})|\lambda_{\pi_2}|\psi_2(\mathrm{IV})\rangle = -\lambda_1\lambda_{\pi_2}\langle p_{1y}p_{2y}\rangle \sin\theta\,.$$

The values used for these integrals are listed in Table 5 and are taken from tables of normalized Slater A–O overlap integrals by Mulliken, Rieke, Orloff & Orloff (1949). Overlap between non-bonded atoms is neglected. The sum of the squares of the θ-dependent overlap integrals are then examined for minima and these are expressible as functions of the λ's.*

Table 5. *Overlap integrals between peroxide oxygen atoms separated by* 1·48 Å

Atomic orbitals	S_{ij}
$2s\sigma$, $2s\sigma$	0·157
$2s\sigma$, $2p\sigma$	0·193
$2p\sigma$, $2p\sigma$	0·22
$2p\pi$, $2p\pi$	0·071

The sp^3 hybridization of the oxygen bonding orbitals increases the angle of minimum overlap over the value calculated by Penney & Sutherland assuming p bonding, as shown by the first entry in Table 6. The effect of altering the electronegativity of the substituent atom in the absence of either π bonding or interfering steric groups is illustrated by the first four entries of Table 6. If the substituent is more electronegative than oxygen, the angle decreases and moves closer to 90°, because the centroid of charge distribution in the σ bond is shifted away from the oxygen atom which diminishes the magnitudes of the overlap integrals that contain this σ bonding orbital. These are the overlap integrals that are sensitive to sp^3 hybridization of the bonding orbital and as they are necessarily decreased, the effectiveness of hybridization for increasing the angle is reduced. As the last three entries in the table show, the largest effect on the angle is produced when the lone pair electrons engage in π bonding with a substituent group, which obviously lowers the overlap between the lone pair p electrons.

Table 6. *The dihedral angle of minimum overlap and its dependence upon the chemical bonding parameters* λ_Σ, λ_{π_1} *and* λ_{π_2}

θ_0	$\lambda_\Sigma{}^2$	$\lambda_\pi{}^2{}_1$	$\lambda_\pi{}^2{}_2$	μ_{bond}*	Type O–R
92° 37′	0·5	1	1	0	Non-polar
92 44	0·55	1	1	0·7	O–C
93 08	0·65	1	1	1·5	O–H
92 34	0·47	1	1	0·4	F–O
95 22	0·50	0·83	1	0	
101	0·50	0·83	0·83	0	
93 50	0·55	0·95	0·95	0·7	$(\mathrm{O{-}}\underset{\Phi}{\mathrm{C}}\mathrm{{=}O})$

* Bond moments of the Σ bonds in Debye units. The O–F moment was calculated from electronegativities by the method of Pauling (1960). The others were taken from Table 10–7 of Barrow (1961). In this calculation λ_Σ was assumed to be the same for both substituents and to apply to symmetrical peroxides such as ROOR, with the exception of the fifth case which refers to an unsymmetrical peroxide where one of the oxygen atoms is involved in π bonding.

These results permit a qualitative estimate to be made of the relative magnitudes of the dihedral angles in different covalent peroxides, if it is possible in addition to predict the relative effect of the electrostatic, van der Waals, and steric interactions upon the angle. As an example, a larger angle would be estimated for H_2O_2 than for F_2O_2 because (1) from the preceding discussion the more electronegative F leads to an angle closer to 90°; (2) the electrostatic repulsion between the OH bonds is greater than in the case of OF bonds; (3) π bonding between the substituents and the peroxide group is not a factor; and (4) steric effects are negligible at the interatomic distances between the substituents at values of the angle being considered. In F_2O_2 the angle is 87°30′ (Jackson, 1962). These results emphasize the potential importance of the electrochemical nature of the substituent groups upon the stereochemistry of the covalent peroxides. In particular the last entry in the table refers to a dicarboxylic substituent on the peroxide moiety as for example in dibenzoyl peroxide and predicts a dihedral angle near 94°.

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* The sum of the squares of the θ-dependent overlap integrals is given by the expression

$$S^2 = \sum_X \sum_Y \sum_i \sum_j \langle \psi_i(X)\psi_j(Y)\rangle^2 \lambda^2\alpha_i\lambda^2\beta_j\,,$$

where i and j assume the values 1 and 2; X and Y assume values II to IV; and either $\lambda\alpha$ or $\lambda\beta$ can be $\lambda_\pi\lambda_\Sigma$ or 1 depending upon the wave functions in the overlap integral.

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Structure des Deux Formes Cristallines de l'Acide Azélaïque, $COOH[CH_2]_7COOH$

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The structure of the two polymorphic modifications of azelaic acid has been determinated by least-squares refinement on three-dimensional data. Bond lengths and angles are calculated and discussed. A study of the bond distances and angles indicated that the two carboxylic groups of the same molecule are very different.

Les diacides aliphatiques saturés à chaine normale et à nombre impair d'atomes de carbone présentent un dimorphisme avec un point de transition situé entre 70 et 90°C (Caspari, 1928–1929; Dupré La Tour, 1932). On obtient des plaquettes de la forme β par évaporation lente à température ordinaire d'une solution d'acide azélaïque dans l'acétone. Par clivage on peut avoir des prismes allongés suivant la direction [010]. Nous avons employé la technique de Bridgman pour cristalliser, à partir du produit fondu, de fines aiguilles cylindriques de forme α, allongées suivant [001]. On a pu facilement réaliser tous les clichés de diffraction de cette forme, sa stabilité étant suffisante à température ordinaire.

Données cristallographiques

Maille et groupe spatial

Tous les clichés ont été réalisés avec la radiation $K\alpha$ du cuivre. Nous avons rapporté dans le Tableau 1 les données cristallographiques caractéristiques des deux formes:

Tableau 1. *Données cristallographiques des deux formes de l'acide azélaïque*

	Forme α	Forme β
Maille	$a=5,67\pm0,01$ Å	$a=22,75\pm0,02$ Å
	$b=9,61\pm0,02$	$b=4,78\pm0,01$
	$c=27,39\pm0,05$	$c=9,83\pm0,02$
	$\beta=136°50'$	$\beta=111°50'$
Densité		
mesurée	1,235 g.cm^{-3}	1,245 g.cm^{-3}
calculée	1,255	1,260
Z	4	4
Groupe spatial	$P2_1/c$	$C2/c$

Mesure des intensités

Pour la forme α, les intensités des taches de diffraction sont obtenues directement par comptage à l'aide d'un diffractomètre automatique à monocristal.

Pour la forme β, nous avons employé une méthode de comparaison visuelle des taches de diffraction obtenues sur un rétigraphe avec les taches d'une échelle d'intensité.