

Electric Dipole Moments and Molecular Conformations of Benzophenones, Benzils, Benzhydrols, and Benzoin

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The electric dipole moments of 28 compounds have been measured in benzene solution at 25.0 °C. The results are analysed in terms of the probable conformations of the molecules in solution.

EXCEPT for the benzils it is sterically impossible for both phenyl rings in the molecules studied to be coplanar. Various group moments can be evaluated from the dipole moments of the unsubstituted molecules and those in which both phenyl rings have a *para*-methyl group or chlorine atom as substituent. The results for the *ortho*- and *meta*-substituted compounds are then employed to study their molecular conformations in benzene solution.

EXPERIMENTAL AND RESULTS

The electric dipole moments were determined as described previously.¹ The measured properties of the solutions at 25.0 °C are recorded in Table 1 and the polarisation data and dipole moments in Table 2; the symbols have their usual meanings. The concentrations of the benzhydrol solutions were kept below that at which association becomes significant.²

Preparation and Purification of Compounds.—Each compound was extensively purified immediately before its dipole moment was determined.

Benzophenones.—These were prepared from the appropriate Grignard reagent and acid chloride³ at -10 °C, the intermediate being decomposed with concentrated hydrochloric acid, and the benzophenone isolated by fractionation under reduced pressure and purified by crystallisation to constant m.p. Thus were obtained: di-*o*-tolyl ketone, m.p. 72°; di-*m*-tolyl ketone, m.p. 45°; di-*p*-tolyl ketone, m.p. 95°; 2,2'-dichlorobenzophenone, m.p. 49°; 3,3'-di-

chlorobenzophenone, m.p. 123°; and 4,4'-dichlorobenzophenone, m.p. 148°.

Benzhydrols.—These were prepared by reducing the corresponding benzophenone with aluminium isopropoxide solution.⁴ The benzhydrol was extracted with ether, isolated by distillation, and then recrystallised to constant m.p.; benzhydrol, m.p. 69°; di-*o*-tolylmethanol, m.p. 119°; di-*m*-tolylmethanol, b.p. 134°/0.5 mmHg (Found: C, 84.8; H, 7.6. C₁₅H₁₆O requires C, 84.9; H, 7.6%); di-*p*-tolylmethanol, m.p. 69°; 2,2'-dichlorophenylmethanol, m.p. 90°; 3,3'-dichlorophenylmethanol, m.p. 46°; and 4,4'-dichlorophenylmethanol, m.p. 94°.

Benzoin.—These were prepared by refluxing in a nitrogen atmosphere the appropriate aromatic aldehyde and aqueous alkali-metal cyanide solution.⁴ The benzoin was isolated by extraction with ether followed either by evaporation of the ether or by steam distillation.⁵ The products were crystallised to constant m.p.; benzoin, m.p. 137°; 2,2'-dimethylbenzoin, m.p. 79°; 3,3'-dimethylbenzoin, m.p. 38°; 4,4'-dimethylbenzoin, m.p. 89°; 2,2'-dichlorobenzoin, m.p. 64°; 3,3'-dichlorobenzoin, m.p. 76°; and 4,4'-dichlorobenzoin, m.p. 88°.

Benzils.—These were prepared by oxidising the corresponding benzoin with catalytic amounts of copper(II) salts in ammonium nitrate solution;⁴ benzil, m.p. 95°; 2,2'-dimethylbenzil, m.p. 94°; 3,3'-dimethylbenzil, m.p. 102°; 4,4'-dimethylbenzil, m.p. 104°; 2,2'-dichlorobenzil, m.p. 132°; 3,3'-dichlorobenzil, m.p. 115° (Found: C, 60.1; H, 3.1; Cl, 25.3. C₁₄H₈Cl₂O₂ requires C, 60.2; H, 2.9; Cl, 25.4%); and 4,4'-dichlorobenzil, m.p. 199°.

³ J. W. Cook, *J. Chem. Soc.*, 1930, 1087.

¹ C. W. N. Cumper, A. A. Foxton, J. F. Read, and A. I. Vogel, *J. Chem. Soc.*, 1964, 430.

² A. H. Read, D. Cleverdon, G. B. Collins, and J. W. Smith, *J. Chem. Soc.*, 1955, 3793.

⁴ A. I. Vogel, 'Practical Organic Chemistry,' Longmans, Green and Co., London, 3rd edn., 1956.

⁵ A. Weissberger, *J. Chem. Soc.*, 1935, 223.

TABLE I

Increments in electric permittivities ($\Delta\epsilon$), specific volumes (Δv), and refractive indices (Δn) of benzene solutions with weight fractions w_2 at 25.0 °C. $\epsilon_1 = 2.2741$, $v_1 = 1.14445$, $n_1 = 1.49790$

$10^6 w_2$	$10^4 \Delta\epsilon$	$10^5 \Delta v$	$10^5 \Delta n$	$10^6 w_2$	$10^4 \Delta\epsilon$	$10^5 \Delta v$	$10^5 \Delta n$
Benzophenone							
2116	116	-53	20	1424	54	-31	7
5117	312	-111	50	3376	127	-79	21
6837	381	-176	62	4650	175	-108	30
8271	472	-217	76	7566	285	-173	42
9467	540	-248	88	10,526	400	-243	63
10,775	616	-277	100	11,136	413	-255	66
15,453	883	-398	150	14,922	563	-343	94
Di- <i>m</i> -tolyl ketone							
1756	92	-42	13	1452	88	-32	13
3378	182	-76	25	4424	268	-96	39
6176	322	-139	46	6564	397	-143	58
8249	429	-183	60	7563	461	-169	67
9848	510	-223	72	9754	596	-210	86
11,793	614	-265	87	11,730	705	-257	104
15,096	785	-342	111	13,610	830	-296	121
2,2'-Dichlorobenzophenone							
1361	82	-57	13	1569	68	-60	13
2800	169	-112	25	3161	135	-125	27
5479	332	-220	49	5107	217	-201	43
7447	450	-301	66	6819	290	-267	58
8426	509	-342	75	7489	318	-294	64
9156	554	-372	82	9394	399	-368	81
11,021	670	-446	98	11,250	478	-439	96
4,4'-Dichlorobenzophenone							
2202	33	-89	21	1060	89	-34	9
2437	36	-97	23	1734	129	-56	15
4108	64	-164	39	3927	260	-129	33
5996	86	-240	57	5542	412	-179	48
7501	112	-300	71	7766	575	-251	67
8267	126	-333	78	9268	690	-299	79
9924	149	-397	93	9812	730	-316	84
2,2'-Dimethylbenzil							
327	20	-8	4	717	53	-17	7
839	47	-18	7	1737	129	-42	18
1401	86	-29	12	2429	175	-57	25
2311	132	-51	19	3155	226	-75	32
3385	197	-63	28	3713	265	-88	37
3982	229	-87	33	4319	316	-102	44
5326	299	-132	44	5714	413	-135	58
3,3'-Dimethylbenzil							
327	20	-8	4	717	53	-17	7
839	47	-18	7	1737	129	-42	18
1401	86	-29	12	2429	175	-57	25
2311	132	-51	19	3155	226	-75	32
3385	197	-63	28	3713	265	-88	37
3982	229	-87	33	4319	316	-102	44
5326	299	-132	44	5714	413	-135	58
4,4'-Dimethylbenzil							
1004	95	-24	8	571	36	-23	4
2037	174	-49	17	1269	71	-54	9
2547	222	-62	20	2192	123	-92	15
3496	304	-86	27	2972	168	-125	20
4016	347	-98	31	3983	225	-168	27
4804	420	-117	37	5024	282	-213	34
5742	496	-139	44	5520	304	-232	37
3,3'-Dichlorobenzil							
820	38	-39	7	652	146	-28	9
1732	80	-86	15	1502	282	-66	16
2646	121	-126	23	3056	690	-131	32
3117	147	-150	27	3961	853	-174	42
4185	193	-192	36	4712	1043	-207	50
5140	236	-246	45	4874	1097	-212	52
6074	281	-289	52	6581	1477	-286	70
Benzhydrol							
1989	37	-50	18	1537	29	-33	13
5280	87	-137	44	3888	74	-88	32
5684	104	-146	47	5500	105	-119	44
9830	180	-255	81	8314	149	-182	67
10,547	191	-272	86	9315	178	-206	74
12,292	225	-321	102	12,757	243	-280	102
15,365	273	-396	117	17,179	327	-377	139

TABLE I (Continued)

$10^6 w_2$	$10^4 \Delta\epsilon$	$10^5 \Delta v$	$10^5 \Delta n$	$10^6 w_2$	$10^4 \Delta\epsilon$	$10^5 \Delta v$	$10^5 \Delta n$
Di- <i>m</i> -tolylmethanol							
1573	26	-30	6	1130	15	-22	8
3368	54	-63	24	3743	63	-73	24
4156	66	-84	29	5008	85	-97	36
5958	94	-120	41	8163	136	-159	58
6778	146	-136	48	10,752	181	-191	76
10,004	164	-200	71	12,317	209	-241	87
12,219	195	-245	87	13,456	226	-262	95
Di- <i>p</i> -tolylmethanol							
Di- <i>o</i> -chlorophenylmethanol							
2108	54	-84	19	991	37	-39	8
3847	90	-151	33	3193	102	-127	26
5465	127	-215	47	4669	144	-190	38
8371	194	-330	72	6644	203	-266	54
9388	217	-374	81	7882	243	-312	65
11,463	268	-456	99	10,236	316	-406	84
14,185	329	-562	124	11,190	344	-443	92
Di- <i>p</i> -chlorophenylmethanol							
1332	37	-53	12	1305	84	-42	10
3047	76	-120	26	2225	138	-69	17
4795	118	-190	42	3884	247	-122	30
5985	162	-237	52	5280	338	-163	41
7517	189	-301	65	7110	453	-223	55
8949	225	-356	77	8632	554	-272	67
11,640	293	-469	95	10,621	680	-333	83
2,2'-Dimethylbenzoin							
844	52	-18	4	696	45	-11	2
1539	85	-33	7	1694	108	-24	4
2630	143	-56	12	2448	124	-38	6
3403	190	-70	15	3560	227	-56	8
3703	198	-76	17	3570	227	-58	8
4718	255	-97	21	4674	300	-74	11
5775	314	-119	25	5199	342	-82	12
4,4'-Dimethylbenzoin							
515	39	-14	3	1039	36	-51	10
1610	112	-42	11	1543	47	-75	14
2429	185	-64	17	2558	76	-127	23
2949	223	-77	20	3386	101	-164	31
3680	277	-96	25	4300	123	-209	39
4657	353	-122	32	4467	133	-220	41
4986	372	-133	35	5344	161	-235	44
3,3'-Dichlorobenzoin							
1046	46	-46	9	605	22	-25	6
1562	62	-68	13	1483	33	-57	13
2209	89	-96	18	2598	60	-102	22
3465	135	-150	29	3707	84	-146	32
3960	160	-173	33	3877	79	-155	34
5364	214	-233	44	5111	114	-202	45
5973	240	-259	49	5381	122	-210	47
4,4'-Dichlorobenzoin							

DISCUSSION

Benzophenones.—The 0.24 D difference in dipole moment between benzophenone (3.02 D) and acetone⁶ (2.78 D) must be due primarily to a mesomeric moment. In benzophenone it is impossible for each phenyl ring to display its maximum mesomeric moment since this would require a planar molecule. One suggested conformation has orthogonal rings with one exerting its maximum mesomeric effect which may be equated to the additional moment (0.50 D) in the Ph-C direction (with $\angle \text{PhCC} = 120^\circ$) necessary to increase the dipole moment of acetone to that of acetophenone⁷ (3.06 D). The roles of the two rings would interchange rapidly. A more

⁶ C. W. N. Cumper and P. G. Langley, *Trans. Faraday Soc.*, 1970, **66**, 35.

⁷ A. L. McClellan, 'Tables of Experimental Dipole Moments,' Freeman and Co., San Francisco, 1963.

probable average conformation is one in which each ring is twisted through an angle β and has a small π -electron interaction with the carbonyl group. From an expression by McRae and Goodman⁸ for mesomeric moments $\mu = \mu_{\max} \cos^2\beta$, or $0.24 = 0.50 \cos^2\beta$, and the angle β should be *ca.* 46° .

The dipole moments of *para*-substituted benzophenones are given by equation (1) where 2γ is the

$$\mu = \mu_{\text{Ph}_2\text{CO}} - 2\mu_s \cos \gamma \quad (1)$$

C-C(O)-C bond angle (120°) and the substituent has component moments μ_s of -0.37 D for a methyl group⁹

which this equation predicts the experimental results are as follows: di-*o*-tolyl ketone, 70° ; di-*m*-tolyl ketone, 80° ; 2,2'-dichlorobenzophenone, 94° ; and 3,3'-dichlorobenzophenone, 70° . An error of ± 0.1 D in the calculated dipole moments would change these angles by $\pm 10^\circ$ for the tolyl ketones and by $\mp 2^\circ$ for the chloro-derivatives.

These angles would be controlled by the competition between the extent of conjugation of the phenyl rings with the carbonyl group and by steric repulsions. The higher value of β for 2,2'-dichlorobenzophenone could be a consequence of neglecting to correct for any interaction between the mesomeric moments of the chlorine

TABLE 2
Polarisation data and dipole moments (μ) at 25.0° C in benzene solution

Compound	α	β	γ	P_T/cm^3	R_D/cm^3	μ/D	Lit./D
Benzophenone	5.70 ₉	-0.258	0.277	243.6	56.95	3.02	2.96 ^a
Di- <i>o</i> -tolyl ketone	3.77 ₂	-0.230	0.179	206.4	63.49	2.64	
Di- <i>m</i> -tolyl ketone	5.20 ₂	-0.226	0.219	263.2	65.43	3.11	
Di- <i>p</i> -tolyl ketone	6.10 ₂	-0.218	0.266	299.3	67.78	3.37	3.45 ^b
2,2'-Dichlorobenzophenone	6.04 ₉	-0.405	0.265	340.9	67.10	3.66	
3,3'-Dichlorobenzophenone	4.23 ₉	-0.391	0.258	256.5	67.78	3.04	
4,4'-Dichlorobenzophenone	1.50 ₃	-0.401	0.281	126.6	68.14	1.69	1.79, ^b 1.72 ^c
Benzil	7.43 ₂	-0.322	0.256	345.2	60.92	3.73	3.79 ^d
2,2'-Dimethylbenzil	5.75 ₃	-0.218	0.248	323.6	75.92	3.48	
3,3'-Dimethylbenzil	7.20 ₄	-0.236	0.302	387.2	77.12	3.89	
4,4'-Dimethylbenzil	8.64 ₆	-0.242	0.228	451.3	73.36	4.30	
2,2'-Dichlorobenzil	5.62 ₉	-0.421	0.201	355.6	69.88	3.74	
3,3'-Dichlorobenzil	4.59 ₄	-0.477	0.255	296.5	68.15	3.34	
4,4'-Dichlorobenzil	2.11 ₆	-0.366	0.249	175.8	79.96	2.20	
Benzhydrol	1.82 ₃	-0.258	0.247	111.8	56.53	1.64	1.60 ^e
Di- <i>o</i> -tolylmethanol	1.90 ₅	-0.219	0.241	134.6	67.28	1.82	
Di- <i>m</i> -tolylmethanol	1.59 ₁	-0.201	0.215	123.2	67.41	1.65	
Di- <i>p</i> -tolylmethanol	1.67 ₇	-0.196	0.212	227.0	67.61	1.70	
Di- <i>o</i> -chlorophenylmethanol	2.31 ₉	-0.395	0.257	166.9	67.99	2.20	
Di- <i>m</i> -chlorophenylmethanol	3.07 ₈	-0.390	0.247	202.8	67.30	2.57	
Di- <i>p</i> -chlorophenylmethanol	2.51 ₄	-0.399	0.257	175.9	67.69	2.30	
Benzoin	6.40 ₈	-0.314	0.233	308.2	61.10	3.48	3.49 ^f
2,2'-Dimethylbenzoin	5.41 ₇	-0.206	0.131	311.9	72.12	3.43	
3,3'-Dimethylbenzoin	6.39 ₂	-0.158	0.068	359.4	72.59	3.75	
4,4'-Dimethylbenzoin	7.56 ₅	-0.262	0.208	404.8	71.66	4.04	
2,2'-Dichlorobenzoin	2.99 ₄	-0.489	0.272	213.1	68.55	2.66	
3,3'-Dichlorobenzoin	4.00 ₆	-0.433	0.244	271.3	71.68	3.13	
4,4'-Dichlorobenzoin	2.25 ₁	-0.393	0.259	182.0	75.84	2.28	

^a N. J. Leonard and L. E. Sutton, *J. Amer. Chem. Soc.*, 1948, **70**, 1564. ^b A. Lutringhans and J. Grohmann, *Z. Naturforsch.*, 1955, **10b**, 365. ^c L. E. Sutton and G. C. Hampson, *Trans. Faraday Soc.*, 1935, **31**, 945. ^d C. C. Caldwell and R. J. W. Le Fèvre, *J. Chem. Soc.*, 1939, 1614. ^e D. Cleverdon and J. W. Smith, *J. Chem. Soc.*, 1951, 2321. ^f O. Hassel, *Z. Elektrochem.*, 1930, **36**, 735.

and 1.59 D for a chlorine atom.¹⁰ This gives a calculated dipole moment for di-*p*-tolyl ketone of 3.39 D, only 0.02 D greater than the observed value, but that for 4,4'-dichlorobenzophenone (1.43 D) is 0.26 D less than determined experimentally. This probably arises from an interaction between the mesomeric moments of the chlorine atoms and carbonyl group.

ortho- and meta-Substituted Benzophenones.—If each phenyl ring is twisted through an angle β from the sterically impossible structure of a planar molecule (*cf* Figure 1) the resultant dipole moment of a compound with identical substituents in each phenyl ring, obtained by vector addition of component moments, is given by expression (2) where the angle α is 60° for *ortho*- and 120°

$$\mu = \mu_{\text{Ph}_2\text{CO}} + 2\mu_s (\cos \alpha \cos \gamma + \sin \alpha \sin \gamma \cos \beta) \quad (2)$$

for *meta*-substitution. The values of the angle β for

⁸ E. G. McRae and L. Goodman, *J. Chem. Phys.*, 1958, **29**, 334.

atoms and carbonyl group or it could be a genuine increase resulting from an attraction between the

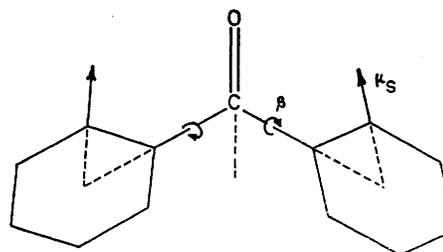


FIGURE 1 Structure of benzophenones

chlorine and *ortho*-hydrogen atoms of different phenyl rings.

With an angle of twist β of 70° or greater the con-

⁹ C. W. N. Cumper, A. I. Vogel, and S. Walker, *J. Chem. Soc.*, 1957, 3640.

¹⁰ C. W. N. Cumper and A. I. Vogel, *J. Chem. Soc.*, 1960, 4723.

jugation effect would be small. If a decrease in conjugation had occurred on introducing substituents into the parent benzophenone this would require a smaller value of β for the chloro-compounds but a greater value for the tolyl ketones.

Similar conformations have been deduced from the dipole moments of the corresponding sulphides,¹¹ the agreement between the values for substituents in the 2-position being closer than in the present case because of the reduced mesomeric effect. In their sulphoxides and sulphones β appears to be greater than 90° . The molar Kerr constant of benzophenone, measured in benzene solution,¹² is consistent with a β value of about 45° and in crystalline 3,3'-dibromobenzophenone¹³ it is 23° .

Benzils.—The dipole moment¹⁴ of biacetyl (1.08 D) has been interpreted as indicating an effective angle of

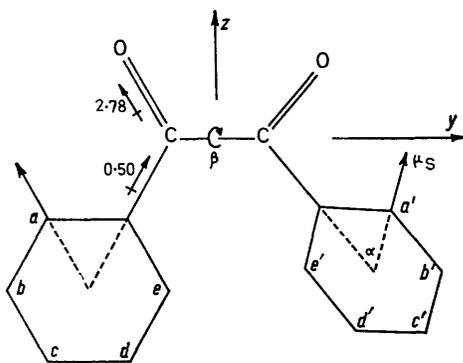


FIGURE 2 Structure of benzils. Position of substituent; (I), a a' ($\alpha = \alpha' = 60^\circ$) or b b' ($\alpha = \alpha' = 120^\circ$); (II), e e' ($\alpha = \alpha' = 300^\circ$) or d d' ($\alpha = \alpha' = 240^\circ$); (III), a e' ($\alpha = 60^\circ$; $\alpha' = 300^\circ$) or b d' ($\alpha = 120^\circ$; $\alpha' = 240^\circ$)

160° between the two C=O directions; in cyclic 1,2-diketones of large ring size this angle¹⁵ is 130 – 140° . The conformations in these aliphatic systems must be determined primarily by the dipolar interaction between the two polar carbonyl groups and the necessity for them to be planar for a maximum mesomeric effect. The u.v. spectrum of benzil¹⁶ proves the presence of strong conjugation between each carbonyl group and its attached phenyl ring, suggesting that the PhCO units are essentially planar. The conjugation between the carbonyl groups is consequently weakened, the tendency for them to be planar is reduced, and the dipole moments of benzils are correspondingly greater.

If the carbonyl moment (μ_{CO}) is taken as 2.78 D and that of C-Ph (μ_{PhC}) as 0.50 D, the experimental dipole moment of benzil requires the two PhCO planes to

* From the electric dipole moment of benzaldehyde¹⁷ (2.75 D) the *cis* and *trans* (with respect to the methyl and carbonyl groups) forms of *o*-tolualdehyde have approximate moments of 2.39 and 2.19 D respectively. The experimental value is 2.80 D. In estimating these dipole moments it is assumed that the PhC moment is 0.50 D giving a C=O bond moment of 2.49 D in aldehydes.

¹¹ C. W. N. Cumper, J. F. Read, and A. I. Vogel, *J. Chem. Soc.*, 1965, 5323, 5860.

¹² R. Bramley and R. J. W. Le Fèvre, *J. Chem. Soc.*, 1962, 56.

intersect at an angle of 98° . The corresponding angle for 4,4'-dimethylbenzil is 94° and that for 4,4'-dichlorobenzil 83° , measured from a planar *cis*-conformation. The slightly lower angle in the last compound may be in error through neglect of mesomeric interaction moments; if these were the same as in 4,4'-dichlorobenzophenone (0.26 D), then the calculated angle between the PhCO planes is increased to 99° .

ortho- and meta-Substituted Benzils.—By reference to Figure 2 the component moments from the left-hand 'half-molecule' are given by equations (3)–(5). The

$$\mu_Z = [(\mu_{CO} + \mu_{PhC} + \mu_s \cos \alpha) \cos 30 + \mu_s \sin \alpha \sin 30] \cos \beta/2 \quad (3)$$

$$\mu_Y = (\mu_{PhC} - \mu_{CO} + \mu_s \cos \alpha) \sin 30 - \mu_s \sin \alpha \cos 30 \quad (4)$$

$$\mu_X = [(\mu_{CO} + \mu_{PhC} + \mu_s \cos \alpha) \cos 30 + \mu_s \sin \alpha \sin 30] \sin \beta/2 \quad (5)$$

components μ_X' and μ_Y' from the other 'half-molecule' have opposite signs and the resultant molecular dipole moment is given by (6).

$$\mu^2 = (\mu_X + \mu_X')^2 + (\mu_Y + \mu_Y')^2 + (\mu_Z + \mu_Z')^2 \quad (6)$$

Three conformations (I), (II), and (III) (Figure 2) will be considered. The values of the angles β at which these equations are in agreement with the experimental results are listed in Table 3, the range quoted being the change in β for a 0.1 D alteration to the calculated dipole moments. Except for 3,3'-dichlorobenzil, which cannot have conformation (II), it is not possible to differentiate between the three structures on experimental grounds. The unsymmetrical conformation (III) may be somewhat less probable and, because in *o*-tolualdehyde the predominant conformation* corresponds to (II), this may be the more likely structure for *ortho*-substituted benzils.

TABLE 3

Values of β at which calculated and experimental dipole moments of benzils agree

Benzil	Conformation		
	(I)	(II)	(III)
2,2'-Dimethyl-	92.5 ± 3.5	104.5 ± 3.5	100.5 ± 3.5
3,3'-Dimethyl-	93.5 ± 1.5	104.0 ± 1.5	100.5 ± 1.5
2,2'-Dichloro-	127.5 ± 1.5	97.5 ± 2.0	137.5 ± 1.5
3,3'-Dichloro-	107.5 ± 1.5		125.0 ± 1.0

In each of these compounds this analysis implies an angle of twist β in the region of 100° . In this respect they have similar conformations to those of hydrogen peroxide and hydrazine¹⁸ but different from the aliphatic

¹³ S. Ramaseshan and K. Venkatesan, *Experientia*, 1958, **14**, 237.

¹⁴ P. H. Cureton, C. G. Le Fèvre, and R. J. W. Le Fèvre, *J. Chem. Soc.*, 1961, 4447.

¹⁵ C. W. N. Cumper, G. B. Leton, and A. I. Vogel, *J. Chem. Soc.*, 1965, 2067.

¹⁶ C. N. R. Rao, 'Ultra-Violet and Visible Spectroscopy,' Butterworths, London, 1961.

¹⁷ S. I. Ahmad, *Indian J. Pure and Appl. Phys.*, 1963, **1**, 434.

¹⁸ C. C. Caldwell and R. J. W. Le Fèvre, *J. Chem. Soc.*, 1939, 1614.

biacetyl and large-ring cyclic 1,2-diketones. The difference is presumably associated with the reduced conjugation between the carbonyl groups in the aromatic compounds not being sufficient to offset unfavourable steric interactions and exchange repulsions.

The Kerr constant of benzil¹⁴ has been interpreted to give an angle of twist β of 97° , the closest agreement between calculated and experimental values being when

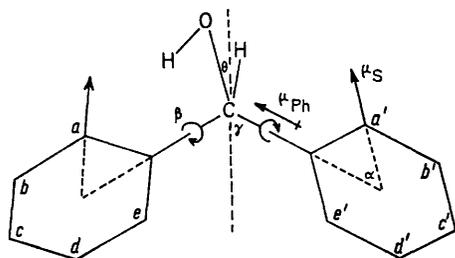


FIGURE 3 Structure of benzhydryl. Position of substituent; (I), a a' or b b'; (II), e e' or d d'; (III), a' e or b' d; (IV), a e' or b d'

each phenyl ring is also twisted about its 1,4-axis by 5° . A skew structure is consistent with the u.v. spectra¹⁹ of benzils.

Benzhydrols.—The hydroxy-group in benzhydrol and its *meta*- and *para*-substituted derivatives has sufficient room to rotate about the C—O bond even when the *ortho*-hydrogen atoms are least favourably situated. This rotation is also feasible for *ortho*-substituted compounds but in these cases the conformations may not be symmetrical. The experimental results are analysed in terms of the four conformations illustrated in Figure 3. Except for the contribution from the C—OH group the resultant of the remaining component group moments μ_R are given by equations (7) and (8). Application of

$$(I) \text{ and } (II): \mu_R = 2\mu_{Ph} \cos \gamma + 2\mu_S (\cos \gamma \cos \alpha \pm \sin \alpha \sin \gamma \cos \beta) \quad (7)$$

$$(III) \text{ and } (IV): \mu_R^2 = (2\mu_S \sin \alpha \cos \gamma \cos \beta)^2 + (2\mu_S \sin \alpha \sin \beta)^2 + (2\mu_{Ph} \cos \gamma + 2\mu_S \cos \alpha \cos \gamma)^2 \quad (8)$$

the Eyring formula²⁰ to the free rotation of the moments about the C—O bond gives equation (9) where λ , the angle

$$\mu^2 = \mu_{OH}^2 + \mu_{CO}^2 + \mu_R^2 - 2\mu_{OH}\mu_{CO} \cos 70 + 2\mu_R\mu_{OH} \cos \lambda - 2\mu_{OH}\mu_R \cos 70 \cos \lambda \quad (9)$$

between μ_R and the C—O bond direction, equals θ in conformations (I) and (II) but for (III) and (IV) is given by equation (10). The substituent moments and bond

$$\mu_R \cos \lambda = 2[(\mu_{Ph} \cos \gamma + \mu_S \cos \alpha \cos \gamma) \cos \theta \pm \mu_S \sin \alpha \sin \beta \sin \theta] \quad (10)$$

angles being taken as $\mu_{Ph} = -0.30$, $\mu_{OH} = -1.51$, $\mu_{CO} = 1.40$ D²¹ and $2\gamma = 2\theta = \angle COH = 110^\circ$, the calculated dipole moments are shown in Table 4 and Figure 4. The agreement between the experimental and

theoretical values for benzhydrol and the *para*-substituted compounds provides support for the analysis and group moments employed.

TABLE 4

Values of β at which calculated and experimental dipole moments of benzhydrols agree

Compound	μ/D	Conformation			
		(I)	(II)	(III)	(IV)
Benzhydrol	1.64				
Di- <i>o</i> -tolylmethanol	1.82		$\mu_{calc.} = 1.61$		
Di- <i>m</i> -tolylmethanol	1.65		84		(6)
Di- <i>p</i> -tolylmethanol	1.70		$\mu_{calc.} = 1.70$		
Di- <i>o</i> -chlorophenylmethanol	2.20	78			
Di- <i>m</i> -chlorophenylmethanol	2.57		56	(11)	79
Di- <i>p</i> -chlorophenylmethanol	2.30		$\mu_{calc.} = 2.30$		

Table 4 also lists the values of the angle of twist β , from a conformation in which the phenyl rings are coplanar, for which the calculated and experimental moments for the *ortho*- and *meta*-substituted benzhydrols are in agreement. This approach implies that the average conformations for di-*m*-tolylmethanol and di-*o*-chlorophenylmethanol are ones in which the phenyl rings are approximately orthogonal to the C—CH(OH)—C plane and with the substituents on either side of this plane. Di-*m*-chlorophenylmethanol could also have a symmetrical conformation (II), with a smaller value for β (56°), though the unsymmetrical structure (IV) ($\beta = 79^\circ$) is also consistent with experimental results. These conformations are evidently determined primarily by the steric interactions between the phenyl residues

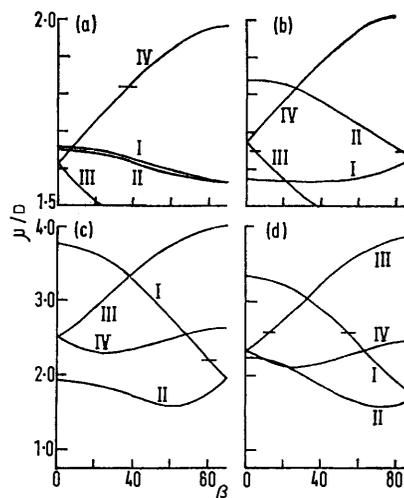


FIGURE 4 Calculated dipole moments of substituted benzhydrols as a function of the angle β ; (a) *o*-tolylmethanol; (b) *m*-tolylmethanol; (c) *o*-chlorophenylmethanol; and (d) *m*-chlorophenylmethanol

and the necessity for adequate space for the rotating hydroxy-group. In di-*o*-chlorophenylmethanol some tendency to intramolecular hydrogen bonding could partially invalidate the conclusions but the sharpness of its i.r. absorption at 3630 cm^{-1} in dilute carbon tetra-

¹⁹ N. J. Leonard, R. T. Rapala, H. L. Herzog, and E. R. Blout, *J. Amer. Chem. Soc.*, 1949, **71**, 2997.

²⁰ H. Eyring, *Phys. Rev.*, 1932, **39**, 746.

²¹ C. W. N. Cumper, *Tetrahedron*, 1969, **25**, 3131.

chloride solution does not confirm the presence of hydrogen bonding. In the corresponding methyl compound, di-*o*-tolylmethanol, Figure 4 indicates that only the unsymmetrical conformation (IV) is possible with a β value of *ca.* 35°; this conformation, and possibly (I), allows free rotation of the hydroxy-group. In (IV) the magnetic environments of the methyl groups would not

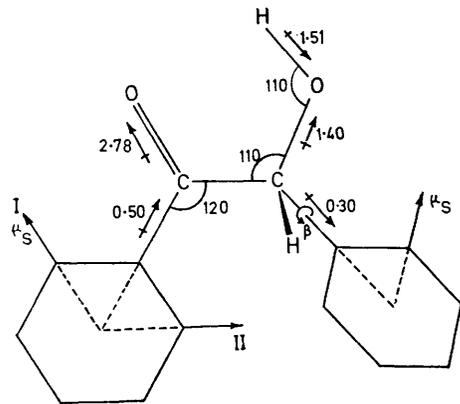


FIGURE 5 Structure of benzoin

be equivalent unless their situations were being interchanged by rotation about the Ph-C bonds. Only a single n.m.r. absorption peak was observed in benzene and chloroform solutions of over an 80 °C temperature range extending down to -40 °C.

Benzoin.—From the u.v. spectra of benzoin¹⁶ it appears that the carbonyl group interacts strongly with the π -electrons in its attached phenyl ring. Also, these molecules exhibit a strong i.r. absorption band at 3480—3490 cm^{-1} characteristic of intramolecular hydrogen bonding; this is in spite of the rather long O...H-O distance. We therefore assume that the Ph·CO·COH

part of the molecule is planar and that the bond angles and component moments are as in Figure 5.

The dipole moments calculated on this basis for benzoin and 4,4'-dimethyl- and -dichloro-benzoin are 3.10, 3.60, and 1.79 D respectively, in poor agreement with the experimental values of 3.48, 4.04, and 2.28 D. The discrepancies could arise (a) from the Ph·CO·COH part of the molecule not being strictly planar but oscillating about this as an average situation or (b) from altered component moments caused by the hydrogen bonding and with contributions from structures such as

Ph($\ddot{\text{O}}\text{H})-\text{C}(\ddot{\text{O}})\text{HPh}$. Reasonable agreement with the experimental results is obtained if the above effects are considered to produce a rather large extra component moment of 1.20 D acting in the direction of the C(O)-C(OH) bond; the calculated moments then being benzoin 3.52 D, 4,4'-dimethylbenzoin 4.00 D, and 4,4'-dichlorobenzoin 2.29 D.

If the moments of the 2,2'- and 3,3'-dimethyl- and 3,3'-dichloro-benzoin are calculated on the above basis for various values of an angle of twist β about the Ph-CHOH bond then agreement with experiment is obtained (a) with the substituent of the first phenyl ring either in position (I) or (II) (Figure 5), the latter being more likely as it would then be *trans* to the carbonyl group, and (b) with the second phenyl ring twisted through an angle of *ca.* 160 or 330° from its position in Figure 5 where the CH-Ph atoms are coplanar; *i.e.*, the two phenyl rings are at an angle of *ca.* 65°.

The calculated dipole moment of 2,2'-dichlorobenzoin is 0.7—3.4 D greater than measured. This might be due to a mesomeric moment between the chlorine atom and carbonyl group but is more likely to arise from an interaction between the hydroxy-hydrogen atom and a chlorine atom.

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