

368. *Physical Properties and Chemical Constitution. Part XL.*¹
The Electrical Dipole Moments of Some Cyclic Diketones

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The electric dipole moments of twelve cyclic diketones have been calculated from measurements of the dielectric constants, specific volumes, and refractive indices of their solutions in pure benzene at 25.00°. The results are discussed in terms of the enolisation and conformations of the molecules.

CYCLIC 1,2-diketones have conformations analogous to those of the corresponding cycloalkanes or cyclo-olefins. Cyclohexane has an unstrained ring, but both smaller and larger cycloalkanes are subject to strain which in the medium rings attains a maximum value in cyclodecane.² Olefins normally exist as *cis*- and *trans*-isomers, the latter being the more stable, but in cyclo-olefins an eight-membered ring is the smallest capable of incorporating a double-bond in the *trans*-configuration; its dipole moment³ (0.8 D) proves that it is still far from being planar. The equilibrium between the *cis*- and *trans*-forms does not favour the latter until an eleven-membered ring is reached.⁴

Information about the conformations of diketones can be obtained from their electric dipole moments. Enolisation in 1,2-diketones complicates the interpretation of the results, but independent evidence for the extent of enolisation is provided by their spectra.

EXPERIMENTAL AND RESULTS

Preparation and Purification of Compounds.—The dipole moment of each compound was measured^{1,5} immediately it had been purified. With the exception of cyclopentane-1,2-dione and cyclohexane-1,3- and -1,4-dione the compounds were examined for purity by vapour-phase chromatography; each gave a single peak. The infrared and ultraviolet spectra of each compound were recorded.

Cyclopentane-1,2-dione. Pure cyclopentanone was brominated in the presence of acetic acid and the crude 2-bromocyclopentanone oxidised⁶ with aqueous ferric chloride at 95°. The solution was saturated with ammonium sulphate, the cyclopentane-1,2-dione extracted with ether, dried, fractionated, and recrystallised from light petroleum (b. p. 40–60°) to a constant m. p. (57°); b. p. 84–86°/8 mm. The dioxime had m. p. 217°.

Cyclohexane-1,2-dione and 3- and 4-methylcyclohexane-1,2-dione. Ethanolic solutions of the corresponding pure ketone at 50° were oxidised by adding a solution of selenium dioxide in 95% ethanol⁷ during 2 hr. The mixture was heated for 6 hr., set aside for 24 hr., the solid filtered off, the solvent removed from the filtrate, and the residue fractionated. Cyclohexane-1,2-dione had b. p. 73–74°/10 mm., m. p. 38°; dioxime m. p. 189°. 3-Methylcyclohexane-1,2-dione had b. p. 76–78°/7 mm., m. p. 63°; dioxime m. p. 164°. 4-Methylcyclohexane-1,2-dione had b. p. 90–91°/19 mm.; dioxime, m. p. 182°.

Cyclohexane-1,3-dione. A commercial sample (Light) was recrystallised from benzene to a constant m. p. (106°).

Cyclohexane-1,4-dione. A commercial sample (Light) was recrystallised from light petroleum (b. p. 60–80°) to a constant m. p. (78°).

Cycloheptane-1,2-dione. Freshly prepared nitrosomethylurea^{8a} was added slowly to a mixture of cyclohexanone and potassium hydroxide in aqueous methanol,⁹ the temperature

¹ Part XXXIX, Cumper, Foxton, Read, and Vogel, *J.*, 1964, 430.

² Kaaremaker and Coops, *Rec. Trav. chim.*, 1952, **71**, 261; Coops, van Kamp, Lambregts, Visser, and Dekker, *ibid.*, 1960, **79**, 1226.

³ Allinger, *J. Amer. Chem. Soc.*, 1958, **80**, 1953.

⁴ Cope, Moore, and Moore, *J. Amer. Chem. Soc.*, 1959, **81**, 3153. See also Leonard and Owens, *ibid.*, 1958, **80**, 6039; Turner and Meador, *ibid.*, 1957, **79**, 4133.

⁵ Cumper, Redford, and Vogel, *J.*, 1962, 1176.

⁶ Acheson, *J.*, 1956, 4232.

⁷ Riley, Morley, and Friend, *J.*, 1932, 1875; Hach, Banks, and Diehl, *Org. Synth.*, 1952, **32**, 35.

⁸ Vogel, "Practical Organic Chemistry," Longmans, Green, London, 1961, (a) p. 869; (b) p. 387; (c) p. 280; (d) p. 493.

⁹ Kohler, Tishler, Rotter, and Thompson, *J. Amer. Chem. Soc.*, 1939, **61**, 1057; Kaaremaker and Coops, *Rec. Trav. chim.*, 1951, **70**, 1033.

being kept below 5°, and then kept at room temperature for several hours. The mixture was acidified with acetic acid, filtered, and most of the solvent removed by distillation. Crude cycloheptanone separated out as an upper layer and more was extracted from the lower layer with ether. The liquid was dried, the ether removed, and the residue fractionated to give pure cycloheptanone, b. p. 56—57°/13 mm. This was oxidised to cycloheptane-1,2-dione with selenium dioxide¹⁰ as described previously, b. p. 84—85°/2.5 mm.; dioxime, m. p. 179°.

Cyclo-octane-1,2-dione. Cycloheptanone was converted into cyclo-octanone (b. p. 78—80°/15 mm., m. p. 42°) and this was oxidised¹¹ to cyclo-octane-1,2-dione (using aqueous dioxan as

TABLE I

100w ₂	ε ₁₂	v ₁₂	n ₁₂	100w ₂	ε ₁₂	v ₁₂	n ₁₂
<i>Cyclopentane-1,2-dione</i>				<i>Cyclohexane-1,2-dione</i>			
0.1865	2.2861	1.14384	1.49752	0.1597	2.2872	1.14372	1.49765
0.1948	2.2871	1.14382	1.49753	0.3416	2.3022	1.14327	1.49762
0.3323	2.2952	1.14339	1.49755	0.4794	2.3231	1.14261	1.49759
0.5332	2.3064	1.14275	1.49758	0.7242	2.3354	1.14203	1.49762
0.6920	2.3152	1.14221	1.49762	0.9153	2.3496	1.14157	1.49765
0.8791	2.3246	1.14153	1.49765	1.0930	2.3645	1.14116	1.49762
1.0115	2.3327	1.14113	1.49767	1.3047	2.3813	1.14049	1.49765
<i>Cycloheptane-1,2-dione</i>				<i>Cyclo-octane-1,2-dione</i>			
0.1291	2.2881	1.14420	1.49774	0.0917	2.2832	1.14421	1.49775
0.2444	2.3024	1.14389	1.49770	0.2446	2.2975	1.14391	1.49769
0.3163	2.3114	1.14369	1.49769	0.4371	2.3149	1.14353	1.49764
0.4238	2.3238	1.14351	1.49766	0.6428	2.3339	1.14303	1.49761
0.7017	2.3562	1.14289	1.49761	0.7504	2.3446	1.14282	1.49759
0.8202	2.3718	1.14253	1.49758	0.8704	2.3554	1.14256	1.49756
1.0503	2.3987	1.14207	1.49753	1.1477	2.3810	1.14198	1.49747
<i>Cyclononane-1,2-dione</i>				<i>Cyclodecane-1,2-dione</i>			
0.1074	2.2802	1.14394	1.49722	0.2065	2.2837	1.14410	1.49763
0.2233	2.2869	1.14375	1.49717	0.2861	2.2861	1.14398	1.49762
0.3911	2.2963	1.14347	1.49712	0.4882	2.2903	1.14362	1.49761
0.4853	2.3027	1.14325	1.49710	0.6165	0.2939	1.14340	1.49758
0.7189	2.3155	1.14280	1.49704	0.9979	2.3044	1.14261	1.49754
0.9057	2.3262	1.14250	1.49700	1.0726	2.3065	1.14246	1.49752
1.1319	2.3392	1.14201	1.49695	1.3936	2.3162	1.14195	1.49749
<i>Cycloundecane-1,2-dione</i>				<i>Cyclododecane-1,2-dione</i>			
0.1799	2.2789	1.14415	1.49790	0.2261	2.2786	1.14399	1.49747
0.2855	2.2805	1.14401	1.49789	0.2511	2.2796	1.14392	1.49746
0.4333	2.2839	1.14372	1.49785	0.5016	2.2843	1.14349	1.49740
0.7540	2.2900	1.14318	1.49778	0.6110	2.2857	1.14332	1.49737
0.8808	2.2931	1.14290	1.49776	0.9355	2.2921	1.14277	1.49730
1.0597	2.2966	1.14263	1.49772	1.2926	2.2988	1.14219	1.49723
1.4962	2.3051	1.14181	1.49764	1.4373	2.3010	1.14197	1.49718
<i>4-Methylcyclohexane-1,2-dione</i>				<i>3-Methylcyclohexane-1,2-dione</i>			
0.1407	2.2839	1.14413	1.49724	0.1235	2.2829	1.14424	1.49753
0.2716	2.2960	1.14363	1.49718	0.2856	2.2936	1.14385	1.49757
0.3979	2.3035	1.14333	1.49713	0.4502	2.3039	1.14346	1.49761
0.6420	—	1.14268	1.49709	0.5590	2.3113	1.14321	1.49764
0.7477	2.3313	1.14264	1.49705	0.6631	2.3184	1.14293	1.49767
1.0192	2.3508	1.14181	1.49696	0.9387	2.3359	1.14230	1.49773
1.2598	2.3677	1.14120	1.49692	1.1133	2.3485	1.14190	1.49778
<i>Cyclohexane-1,4-dione</i>				<i>Cyclohexane-1,3-dione</i>			
0.2270	2.2780	1.14373	1.49749	0.0838	2.2840	1.14422	1.49779
0.5196	2.2829	1.14292	1.49746	0.0983	2.2854	1.14413	1.49778
1.0769	2.2919	1.14115	1.49744	0.1366	2.2886	1.14399	1.49775
1.2888	2.2957	1.14043	1.49742	0.1693	2.2916	1.14390	1.49774
1.6742	2.3022	1.13922	1.49740	0.2010	2.2944	1.14377	1.49779
2.1106	2.3086	1.13785	1.49736	0.2065	2.2946	1.14376	1.49781
2.2290	2.3148	1.13759	1.49735	0.2087	2.2952	1.14374	1.49785
				0.2358	2.2973	1.14367	1.49780

¹⁰ Vander Haar, Voter, and Banks, *J. Org. Chem.*, 1949, **14**, 836.

¹¹ Wittig and Krebs, *Chem. Ber.*, 1961, **94**, 3260.

solvent) by the procedure detailed above for cycloheptane-1,2-dione. The cyclo-octane-1,2-dione had b. p. 59—60°/1.5 mm. (Found: C, 68.2; H, 8.8. Calc. for C₈H₁₂O₂: C, 68.5; H, 8.6%); dioxime, m. p. 170°.

Cyclononane-1,2-dione. 2-Hydroxycyclononanone (azeloïn) was prepared by the acyloïn condensation of diethyl azelate^{8b} with sodium in pure xylene.¹² This was converted into cyclononane-1,2-dione by treatment with cupric acetate monohydrate and aqueous acetic acid.¹³ The product was purified by fractionation, b. p. 57—59°/0.6 mm.; dioxime, m. p. 178°.

Cyclodecane-1,2-dione. 2-Hydroxycyclodecane (sebacoïn) was prepared from diethyl sebacate¹² and converted¹³ into cyclodecane-1,2-dione as in the preceding preparation. It had b. p. 69—70°/1 mm., m. p. 42° (Found: C, 71.1; H, 9.6%. Calc. for C₁₀H₁₆O₂: C, 71.4; H, 9.6%); dioxime, m. p. 190°.

Cycloundecane-1,2-dione. This was prepared from azelaic acid which was first esterified¹² and then reduced with lithium aluminium hydride to nonamethyleneglycol¹⁴ (b. p. 136—138°/1.5 mm., m. p. 44°). This was converted successively into 1,9-dibromononane (b. p. 103—105°/0.7 mm.) with hydrobromic acid,^{8c} 1,9-dicyanononane (b. p. 150—152°/1.5 mm.) with potassium cyanide in aqueous ethanol,^{8d,15} nonane-1,9-dicarboxylic acid^{8d,15} (m. p. 111°) by hydrolysis with alkali, and the diethyl ester by esterification (b. p. 146—148°/1 mm.). Cycloundecane-1,2-dione was prepared from this ester by the method used for cyclononane-1,2-dione. The product, b. p. 73—74°/1 mm., solidified on cooling in ice (Found: C, 72.7; H, 9.8. Calc. for C₁₁H₁₈O₂: C, 72.5; H, 9.9%); dioxime, m. p. 207°.

Cyclododecane-1,2-dione. Decamethylene dibromide (commercial sample from Schuchardt, b. p. 150°/5 mm., m. p. 28°) was treated¹⁶ as detailed above for 1,9-dibromononane. The dinitrile had b. p. 158°/0.5 mm., decane-1,2-dicarboxylic acid had m. p. 129°, and its diethyl ester had b. p. 156°/1 mm. Cyclododecane-1,2-dione had b. p. 99—101°/1.5 mm., m. p. 43° (Found: C, 73.5; H, 10.2. Calc. for C₁₂H₂₀O₂: C, 73.4; H, 10.3%); dioxime, m. p. 214°.

The apparatus, experimental techniques, and method of calculation and of presenting the results are as described in previous Parts^{1,5} of this series. The measured properties of the benzene solutions at 25.00° are presented in Table 1 and the slopes of the linear graphs of their dielectric constants (α) and of their specific volumes (β) against weight fraction, together with the polarisation data and dipole moments (μ), are collected in Table 2.

TABLE 2

Compound	α	β	∞P_2 (cm. ³)	R_D (cm. ³)	${}_0P$ (cm. ³)	μ (D)
Cyclopentane-1,2-dione	5.44 ₅	-0.328 ₀	124.3	24.48	99.8	2.21
Cyclohexane-1,2-dione	8.24 ₁	-0.281 ₉	202.5	28.36	174.2	2.92 *
Cycloheptane-1,2-dione	11.9 ₇	-0.228 ₄	318.2	32.45	285.7	3.74
Cyclo-octane-1,2-dione	9.23 ₉	-0.212 ₈	282.9	36.30	246.6	3.47
Cyclononane-1,2-dione	5.76 ₉	-0.187 ₉	211.2	41.01	170.2	2.89
Cyclodecane-1,2-dione	2.62 ₄	-0.189 ₉	131.0	46.15	84.9	2.04
Cycloundecane-1,2-dione	2.00 ₉	-0.178 ₄	121.3	49.61	71.7	1.87
Cyclododecane-1,2-dione	1.81 ₁	-0.166 ₄	124.0	53.70	70.3	1.86
4-Methylcyclohexane-1,2-dione	7.45 ₈	-0.254 ₈	210.3	30.89	179.4	2.96
3-Methylcyclohexane-1,2-dione	6.62 ₈	-0.236 ₈	191.3	35.38	155.9	2.76
Cyclohexane-1,4-dione	1.63 ₈	-0.310 ₀	62.4	26.99	35.4	1.32 †
Cyclohexane-1,3-dione	8.71 ₆	-0.356 ₁	210.0	27.64	182.4	2.99

* 2.80 D at 46.1° (Srivbely and Lander, *J. Amer. Chem. Soc.*, 1950, **72**, 3756). † 1.29 D at 25° (Lé Fèvre, *J.*, 1935, 1696).

DISCUSSION

The bond angles in cyclic 1,2-diketones are presumably similar to those in the cyclic olefins but there are no stable geometric isomers. Molecular models show that the angle between the planes containing the two $\cdot\text{C}\cdot\text{CO}\cdot\text{C}\cdot$ groupings is zero in cyclopentane-1,2-dione but can have any value from 0 to 180° in cyclodecane-1,2-dione and in larger rings. Repulsion between the carbonyls would favour a large angle but it cannot exceed 90° until

¹² Alliger, *Org. Synth.*, 1956, **36**, 79.

¹³ Blomquist, Liu, and Bohrer, *J. Amer. Chem. Soc.*, 1952, **74**, 3643; Blomquist and Goldstein, *Org. Synth.*, 1956, **36**, 77.

¹⁴ Nystrom and Brown, *J. Amer. Chem. Soc.*, 1947, **69**, 1197.

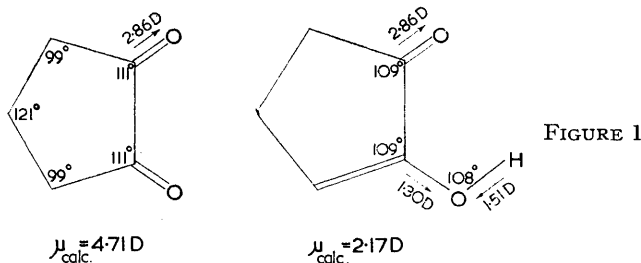
¹⁵ Brann and Danziger, *Ber.*, 1912, **45**, 1970.

¹⁶ Chuit, Boelsing, Hausser, and Malet, *Helv. Chim. Acta*, 1926, **9**, 264.

the ring contains at least seven atoms. A large torsional oscillation is present in the larger rings.

A complication with 1,2-diketones is that enolisation can occur. The mono-enol form would be most stable, relative to the diketo-form, when its remaining carbonyl is able to conjugate with the double bond in the ring and when the dipole and exchange interactions between the two carbonyl groups in the keto-form are least favourable. In other words, enolisation should be most extensive when the carbonyl groups are in a planar *cis*-configuration (*e.g.*, cyclopentane-1,2-dione) and decrease as the ring increases in size and becomes more flexible.

Cyclopentane-1,2-dione.—The bond angles in 3,3,5,5-tetramethylcyclopentane-1,2-dione have been determined in the solid state by X-ray analysis¹⁷ and are shown in Figure 1. If the bond angles are assumed to be the same in the unsubstituted molecules and the carbonyl-group moment is taken as 2.86 D (as in cyclopentanone¹⁸), then the keto-form of cyclopentane-1,2-dione has a calculated moment of 4.71 D. In the enolic form the C—O and O—H bond moments may be taken as 1.30 and 1.51 D, respectively (derived from the dipole moments of aliphatic alcohols and water). If free rotation occurred about the C—O bond then from the Eyring¹⁹ formula its dipole moment should be 2.94 D. The observed value of 2.21 D agrees well with the calculated value (2.17 D) for the fixed conformation shown in Figure 1. Intramolecular hydrogen bonding in the enol form may be discounted as the



enolic hydrogen and carbonyl oxygen atoms are about 2.5 Å apart. The deciding factor holding the OH group in the plane of the ring must be a weak π -electron conjugation between the oxygen atom of the hydroxyl group and the unsaturated carbon atom, as is also the case in carboxylic acids and esters.²⁰

No allowance has been made for induced or mesomeric moments nor for the effect of the solvent on the relevant group moments and upon the experimental value of 2.21 D for this compound. Nevertheless, this analysis is consistent with cyclopentane-1,2-dione's existing almost exclusively in the enolic form.

Cyclohexane-1,2-dione.—The ring in this molecule is not planar. If the bond angles are assumed to be 120 and 109.5° for sp^2 - and sp^3 -hybridised atoms,¹⁷ respectively, then, in the most likely conformation of the keto-form, the planes which contain the three atoms bonded to each carbonyl carbon atom are inclined at about 25°. With a carbonyl-group moment of 3.08 D, as in cyclohexanone,¹⁸ the calculated dipole moment of the diketone is 5.21 D. In the enol form the polar carbon—oxygen bonds are virtually co-planar and the calculated moment is 2.68 D. The experimental value of 2.92 D is therefore consistent with the compound's existing largely, but not entirely, in the enolic form in benzene solution.

Cyclic 1,2-Diketones With Larger Rings.—As the size of the ring is increased the two carbonyl groups can approach more closely to a planar *trans*-conformation. The enol content is markedly reduced. This is supported by a sharp reduction in the intensity of

¹⁷ Goaman and Grout, *Tetrahedron*, 1963, **19**, 1531.

¹⁸ Günthard and Gäumann, *Helv. Chim. Acta*, 1951, **34**, 39.

¹⁹ Eyring, *Phys. Rev.*, 1932, **39**, 746.

²⁰ Zahn, *Phys. Z.*, 1932, **33**, 730; Marsden and Sutton, *J.*, 1936, 1383; O'Gorman, Shand, and Schomaker, *J. Amer. Chem. Soc.*, 1950, **72**, 4222.

the infrared O-H absorption at $3\ \mu$ when the ring size is increased from six to seven atoms and its complete disappearance in cyclodecane-1,2-dione.²¹ Further evidence is provided by the ultraviolet absorption spectra in ethanol (Table 3). The intense absorption in cyclopentane- and cyclohexane-1,2-diones is typical of enolised 1,2-diketones²² and the much weaker absorption with larger rings is consistent with the predominance of the keto-form in these systems.²³

TABLE 3

Diketone	$\lambda_{\max.}$ (m μ)	$\epsilon_{\max.}$	Diketone	$\lambda_{\max.}$ (m μ)	$\epsilon_{\max.}$
Cyclopentane-1,2-dione ...	253	9410	Cycloundecane-1,2-dione ...	269	162
Cyclohexane-1,2-dione	267	7440	Cyclohexane-1,4-dione	283	30
Cycloheptane-1,2-dione ...	267	129	Cyclohexane-1,3-dione	258	13,040
Cyclo-octane-1,2-dione ...	272	148			

If the enolic content is ignored the mean angle between the planes containing the two $\cdot\text{C}\cdot\text{CO}\cdot\text{C}\cdot$ groups required to give the observed dipole moment of each compound may be computed and these are given in the last column of Table 4; the same carbonyl-group moments as in the corresponding monoketones¹⁸ have been used.

The angle in cyclodecane-1,2-dione, and in larger ring systems, might have been expected to be nearer to 180° (planar *trans*-conformation), but there must be a considerable oscillation occurring in these molecules. Even butane-2,3-dione has a dipole moment²⁴ of 1.22 D at 55° , corresponding to an angle of about 150° between the planes containing the carbonyl groups; it is more probable that they are oscillating through an angle on either

TABLE 4
Dipole moments

Number of ring atoms	Monoketone *	1,2-Diketone †	Angle between $\cdot\text{C}\cdot\text{CO}\cdot\text{C}\cdot$ planes
5	2.86	2.21	‡
6	3.08	2.92	‡
7	3.04	3.74	89.5°
8	2.93	3.47	93.7°
9	2.82	2.89	107.5°
10	2.72	2.04	128.7°
11	—	1.87	133.2°
12	2.72	1.86	133.5°

* Literature values. † Experimental values; this Paper (see Table 2). ‡ Exist largely in the enolic form.

side of the planar *trans*-arrangement. For completely free rotation of two carbonyl groups the calculated moment is about 2.0 D.

Methylcyclohexane-1,2-diones.—The enolic content of methylcyclohexane-1,2-diones is probably large, as in the unsubstituted compound. In the enolic form of 4-methylcyclohexane-1,2-dione, models indicate that the C-Me bond could be either virtually in the same plane as the carbon-oxygen bonds and cause a small increase in the dipole moment of the molecule, or it could be inclined at 60 – 80° to this plane, where it would reduce the total moment slightly. The experimental value (2.96 D) is 0.04 D greater than the moment of the unsubstituted cyclohexane-1,2-dione.

The methyl substituent in 3-methylcyclohexane-1,2-dione could be on the carbon either adjacent to the hydroxyl, or to the carbonyl group. In either case, the effect upon the dipole moment would be very small. The observed dipole moment (2.76 D) is 0.16 D less than that of the unsubstituted compound and this could imply a slightly increased enolic content.

Cyclohexane-1,3- and -1,4-dione.—With a carbonyl-group moment of 3.08 D (as in cyclohexanone), the experimental dipole moment of cyclohexane-1,4-dione (1.32 D) corresponds to an effective angle of 155° between the two polar bonds. This assumes that the

²¹ G. B. Leton, Ph.D. Thesis, London, October 1963.

²² Woodward and Blout, *J. Amer. Chem. Soc.*, 1943, **65**, 563; Gillam, Lynas-Gray, Penfold, and Simonsen, *J.*, 1941, 60; Heywood and Kon, *J.*, 1940, 713.

²³ Leonard and Mader, *J. Amer. Chem. Soc.*, 1950, **72**, 5338.

²⁴ Bloom and Sutton, *J.*, 1941, 727.

molecule is entirely in the keto-form which is supported by its ultraviolet spectrum (Table 3). Microwave absorption in benzene solutions²⁵ of cyclohexane-1,4-dione indicates that the carbonyl groups are directed in the opposite sense and X-ray analysis²⁶ of the solid material shows that the angle between the polar bonds in this phase is 152° . The corresponding spectrum of the other isomer, cyclohexane-1,3-dione, however, indicates a very large enol content. The calculated moment for the structure shown in Figure 2 is 1.42 or 4.16 D with the polar groups planar.

For free rotation of the hydroxyl group, or for an equal distribution of the molecules

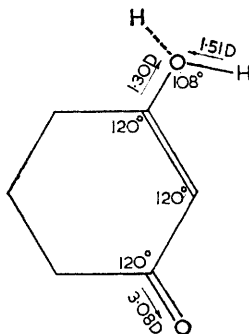


FIGURE 2

between the two extreme planar forms, the calculated moment is 3.11 D, which is only a little larger than the experimental value of 2.99 D.

In analysing the dipole moments of these diketones no allowance has been made for the effect of the solvent. Since the reference carbonyl-group moments have been taken from the dipole moments of the corresponding monoketone an allowance for this effect could not affect the general conclusions reached in the discussion.

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²⁵ Aihara, Chitoku, and Higashi, *Bull. Chem. Soc. Japan*, 1962, **35**, 2056.

²⁶ Groth and Hassel, *Proc. Chem. Soc.*, 1963, 218.