

**787. Molecular Polarisability: The Conformations of Ten Cyclic Dibasic Acid Anhydrides Indicated by their Dipole Moments, Molar Kerr Constants, etc.**

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In the absence of recorded structural information on the ten cyclic anhydrides here considered, "Barton" models have been constructed and intervalency angles measured by hand. From such data, together with known anisotropic bond polarisabilities, dipole moments, etc., the molar Kerr constant expected for each form has been calculated and compared with the value from experiment. Results indicate that maleic, succinic, citraconic, itaconic, phthalic, and naphthalic anhydrides have flat structures, and that glutaric, diphenic, camphoric, and cineolic anhydride have non-planar structures. Where models show alternative conformations to be possible, the measured molar Kerr constant enables the more appropriate to be chosen.

MEASUREMENTS here recorded concern the conformations of cyclic dibasic acid anhydrides as solutes in benzene. They were undertaken because the literature contained no physical evidence relevant to the matter. From various considerations (stabilities, analogies with other multimembered rings, etc.) the probable occurrence of many of these molecules as strain-reduced non-planar structures was obvious. The recognition and specification of such forms, through their molar Kerr constants (which depend upon the spatial arrangements of anisotropically polarisable bonds), is the purpose of the present work.

#### EXPERIMENTAL

*Materials.*—Citraconic anhydride, purified by fractional distillation, had b. p. 213°. Maleic, b. p. 199°, m. p. 52°, and phthalic, b. p. 295°, m. p. 132°, anhydride were B.D.H. "AnalaR" samples, distilled and recrystallised from chloroform. Succinic, m. p. 120°, itaconic, m. p. 68°, and glutaric, m. p. 56°, anhydride were prepared and purified according to Vogel's directions<sup>1</sup> from the corresponding acids by dehydration with acetic anhydride. Naphthalic, m. p. 274°, and diphenic anhydride, m. p. 217°, were extracted with cold sodium carbonate solution to remove the free acid, and the residue recrystallised from acetic anhydride. Camphoric anhydride, m. p. 220°, was prepared by Koenig and Hoerlin's method<sup>2</sup> from ( $\pm$ )-camphoric acid and acetic anhydride and recrystallised from chloroform. Cineolic anhydride, b. p. 160°/ca. 15 mm., was obtained from cineole by oxidation with aqueous permanganate<sup>3,4</sup> to the acid, followed by dehydration<sup>5</sup> with acetic anhydride. The m. p.s or b. p.s of the specimens used as solutes conformed to those found in the literature.<sup>6</sup>

*Measurements and Results.*—Table 1 shows, for solutions each containing weight fractions  $w_2$  of solute in benzene, the differences  $\Delta n$ ,  $\Delta n^2$ ,  $\Delta d$ ,  $\Delta \epsilon$ , and  $\Delta B$  between the refractive indexes, the squares of the refractive indexes, the densities, the dielectric constants, and Kerr effects, respectively, of the solutions and the solvent. Polarisation, molar refractions, dipole moments, and molar Kerr constants at infinite dilution are recorded in Table 2. Since diphenic and naphthalic anhydride are sparingly soluble in benzene and the observed  $\Delta n$ 's therefore so small, refractive index measurements for these two substances were made in quinoline, for which<sup>7</sup>

<sup>1</sup> Vogel, "Practical Organic Chemistry," Longmans, London, 2nd edn., 1951.

<sup>2</sup> Koenigs and Hoerlin, *Ber.*, 1893, **26**, 817.

<sup>3</sup> Rupe and Ronus, *ibid.*, 1900, **33**, 3544.

<sup>4</sup> Rupe and Hirschmann, *Helv. Chim. Acta*, 1933, **16**, 509.

<sup>5</sup> Wallach, *Annalen*, 1890, **258**, 319.

<sup>6</sup> Huntress and Mulliken, "Identification of Pure Organic Compounds, Order I," John Wiley and Sons, New York, 1941.

<sup>7</sup> Timmermans, "Physico-chemical Constants of Pure Organic Compounds," Elsevier, Amsterdam, 1950.

TABLE I.

Increments of densities, refractive indexes, Kerr and dielectric constants, observed with solutions containing weight fractions  $w_2$  of the anhydrides.

<i>Maleic anhydride in benzene</i> *											
$10^5 w_2$ .....	748	2402	2432	3280	4535	5058					
$-10^4 \Delta n$ .....	3	8	8	12	—	—					
$-10^4 \Delta n^2$ .....	8	23	23	35	—	—					
$10^5 \Delta d$ .....	209	760	779	1082	1567	1822					
whence $-\Delta n = 0.030w_2 + 0.158w_2^2$ ; $-\Delta n^2 = 0.081w_2 + 0.726w_2^2$ ; $\Delta d = 0.2781w_2 + 1.577w_2^2$											
$10^5 w_2$ .....	247	442	459	704	828	1233	1342	2190			
$10^4 \Delta \epsilon$ .....	462	762	786	1204	1383	2115	2179	3739			
whence $\sum \Delta \epsilon / \sum w_2 = 16.96$											
$10^5 w_2$ .....	998	1790	2402	3178	3812	4213					
$10^{10} \Delta B$ .....	23	35	57	74	90	93					
whence $\sum \Delta B / \sum w_2 = 2.27 \times 10^{-7}$											
<i>Succinic anhydride in benzene</i>											
$10^5 w_2$ ...	621	858	1135	1403	$10^5 w_2$ ...	485	754	1036	1248		
$10^5 \Delta n$ ...	23	35	45	55	$10^4 \Delta \epsilon$ ...	936	1448	2020	2413		
$10^5 \Delta n^2$ ...	68	104	134	164	whence $\sum \Delta \epsilon / \sum w_2 = 19.35$						
whence $\sum \Delta n / \sum w_2 = 0.039$ ;					$10^5 w_2$ ...	456	759	921	1132	1233	1358
$\sum \Delta n^2 / \sum w_2 = 0.117$					$10^{10} \Delta B$ ...	21	36	44	52	58	63
$10^5 w_2$ ...	492	951	1274	1342	whence $\sum \Delta B / \sum w_2 = 4.68 \times 10^{-7}$						
$10^5 \Delta d$ ...	170	325	446	477							
whence $\sum \Delta d / \sum w_2 = 0.3493$											
<i>Citraconic anhydride in benzene</i>											
$10^5 w_2$ .....	5433	8765	10,280	12,240	14,343	14,489	17,513				
$-10^4 \Delta n$ .....	19	29	33	38	44	46	54				
$-10^4 \Delta n^2$ .....	56	86	97	112	130	136	159				
$10^5 \Delta d$ .....	1440	2359	2790	3073	3951	4000	4878				
whence $-\Delta n = 0.035w_2 - 0.022w_2^2$ ; $-\Delta n^2 = 0.102w_2 - 0.068w_2^2$ ; $\Delta d = 0.2504w_2 + 0.1547w_2^2$											
$10^5 w_2$ .....	1657	2218	3148	4665	5214	6112					
$10^4 \Delta \epsilon$ .....	2602	3476	4911	7221	8040	9395					
whence $\Delta \epsilon = 15.84w_2 - 7.77w_2^2$											
$10^5 w_2$ .....	258	449	591	821	982	1196	1243				
$10^{10} \Delta B$ .....	26	49	63	87	103	128	133				
whence $\sum \Delta B / \sum w_2 = 10.63 \times 10^{-7}$											
<i>Itaconic anhydride in benzene</i>											
$10^5 w_2$ .....	448	628	840	1027	1135	1351	1428				
$-10^4 \Delta n$ .....	3	4	5	6	7	8	—				
$-10^4 \Delta n^2$ .....	9	12	15	18	21	24	—				
$10^5 \Delta d$ .....	108	142	183	225	255	326	—				
$10^4 \Delta \epsilon$ .....	730	1018	1359	1645	1816	2147	—				
$10^{10} \Delta B$ .....	75	109	141	185	200	244	258				
whence $\sum \Delta n / \sum w_2 = -0.061$ ; $\sum \Delta n^2 / \sum w_2 = -0.182$ ; $\sum \Delta d / \sum w_2 = 0.2282$ ; $\Delta \epsilon = 16.34w_2 - 29.30w_2^2$ ;											
$\sum \Delta B / \sum w_2 = 17.68 \times 10^{-7}$											
<i>Glutaric anhydride in benzene</i>											
$10^5 w_2$ .....	342	657	811	1170	1588	1932	2012				
$-10^4 \Delta n$ .....	2	4	5	8	12	—	—				
$-10^4 \Delta n^2$ .....	6	12	15	24	36	—	—				
$10^5 \Delta d$ .....	80	158	204	308	434	543	566				
$10^4 \Delta \epsilon$ .....	548	1042	1278	1823	2440	2933	3038				
$10^{10} \Delta B$ .....	43	83	102	145	195	239	246				
whence $-\Delta n = 0.052w_2 + 1.45w_2^2$ ; $-\Delta n^2 = 0.155w_2 + 4.70w_2^2$ ; $\Delta d = 0.2294w_2 + 2.653w_2^2$ ;											
$\Delta \epsilon = 16.22w_2 - 54.62w_2^2$ ; $10^7 \Delta B = 12.74w_2 - 24.00w_2^2$											

*Phthalic anhydride in benzene* \*

$10^5 w_2$ ...	420	635	941	1160	$10^5 w_2$	227	560	621	1272	2043			
$10^5 \Delta n$ ...	9	13	19	24	$10^4 \Delta \epsilon$	454	1135	1257	2546	4203			
$10^5 \Delta n^2$	27	39	57	72	whence $\Sigma \Delta \epsilon / \Sigma w_2 = 20.32$								
$10^5 \Delta d$ ...	109	160	235	284	$10^5 w_2$	265	321	378	431	486	586	651	714
whence $\Sigma \Delta n / \Sigma w_2 = 0.021$ ;					$10^{10} \Delta B$	95	113	135	153	176	206	236	251
$\Sigma \Delta n^2 / \Sigma w_2 = 0.062$ ;					whence $\Sigma \Delta B / \Sigma w_2 = 35.62 \times 10^{-7}$								
$\Delta d = 0.2656 w_2 - 1.79 w_2^2$													

*Naphthalic anhydride in benzene*

$10^5 w_2$ ...	88	104	107	115	129	$10^5 w_2$ ...	58	88	104	115	129
$10^5 \Delta d$ ...	18	24	28	30	36	$10^{10} \Delta B$ ...	66	94	116	124	140
$10^4 \Delta \epsilon_1$ ...	178	260	282	271	336	whence $\Sigma \Delta B / \Sigma w_2 = 109.3 \times 10^{-7}$					
whence $\Sigma \Delta d / \Sigma w_2 = 0.2505$ ; $\Sigma \Delta \epsilon / \Sigma w_2 = 24.44$											

*Naphthalic anhydride in quinoline*

$10^5 w_2$ ...	321	556	647
$10^4 \Delta n$ ...	3	5	6
$10^4 \Delta n^2$ ...	9	15	18
$10^5 \Delta d$ ...	82	138	160
whence $\Sigma \Delta n / \Sigma w_2 = 0.092$ ;			
$\Sigma \Delta n^2 / \Sigma w_2 = 0.276$ ;			
$\Sigma \Delta d / \Sigma w_2 = 0.2493$			

*Diphenic anhydride in benzene*

$10^5 w_2$ ...	86	102	113	129	144	163
$10^5 \Delta n$ ...	5	6	7	8	9	10
$10^5 \Delta d$ ...	27	33	36	41	46	52
$10^4 \Delta \epsilon$ ...	65	74	81	98	106	119
$10^{10} \Delta B$ ...	9	11	14	17	18	21
whence $\Sigma \Delta n / \Sigma w_2 = 0.061$ ; $\Sigma \Delta d / \Sigma w_2 = 0.3189$ ;						
$\Sigma \Delta \epsilon / \Sigma w_2 = 7.37$ ; $\Sigma \Delta B / \Sigma w_2 = 12.21 \times 10^{-7}$						

*Diphenic anhydride in quinoline*

$10^5 w_2$ ...	483	562	685
$10^4 \Delta n^2$ ...	3	6	9
$10^5 \Delta d$ ...	121	139	170
whence $\Sigma \Delta n^2 / \Sigma w_2 = +0.104$ ;			
$\Sigma \Delta d / \Sigma w_2 = 0.2486$			

*Camphoric anhydride in benzene*

$10^5 w_2$	764	1120	1881	2821	3788	4593
$-10^4 \Delta n$	1	1	2	3	4	5
$-10^4 \Delta n^2$	3	3	5	8	11	14
$10^5 \Delta d$ ...	154	226	380	568	783	963
$10^4 \Delta \epsilon_1$	1074	1571	2637	4017	5319	6319
$-10^{10} \Delta B$	48	69	116	165	235	288
whence $\Sigma \Delta n / \Sigma w_2 = -0.011$ ; $\Sigma \Delta n^2 / \Sigma w_2 = -0.029$ ;						
$\Sigma \Delta d / \Sigma w_2 = 0.2054$ ; $\Sigma \Delta \epsilon / \Sigma w_2 = 13.99$ ;						
$\Sigma \Delta B / \Sigma w_2 = -6.15 \times 10^{-7}$						

*Cineolic anhydride in benzene*

$10^5 w_2$ .....	234	451	643	749
$-10^5 \Delta n$ .....	6	11	19	23
$-10^5 \Delta n^2$ .....	17	32	56	67
$10^5 \Delta d$ .....	49	93	135	154
$10^4 \Delta \epsilon$ .....	321	598	900	1041
$10^{10} \Delta B$ .....	5	11	15	18

whence  $\Sigma \Delta n / \Sigma w_2 = -0.028$ ;  $\Sigma \Delta n^2 / \Sigma w_2 = -0.083$ ;  $\Sigma \Delta d / \Sigma w_2 = 0.2075$ ;  $\Sigma \Delta \epsilon / \Sigma w_2 = 13.77$ ;  
 $\Sigma \Delta B / \Sigma w_2 = 2.36 \times 10^{-7}$

\* Dielectric polarisation and refractivity measurements by Mr. R. K. Pierens.

TABLE 2.

Polarisations, refractions, dipole moments, and molar Kerr constants at infinite dilution in benzene.

Solute	$\alpha \epsilon_1$	$\beta$	$\gamma' n_1^2$	$\infty P_2$ (c.c.)	$R_D$ , obs. (c.c.)	$\mu$ (D) *	$\gamma$	$\delta$	$10^{12} \infty (mK_2)$ obs.
Maleic .....	16.96	0.3183	-0.081	335.6	20.88	3.91	-0.020	5.54	-12.6
Succinic ...	19.35	0.3997	0.117	384.8	22.37	4.20	0.026	11.41	22.1
Citraconic	15.84	0.2866	-0.102	361.2	24.61	4.05	-0.023	25.93	163.2
Itaconic ...	16.34	0.2612	-0.182	372.8	23.86	4.12	-0.041	43.12	307.3
Glutaric ...	16.22	0.2625	0.155	376.8	24.82	4.14	-0.035	31.07	209.3
Phthalic ...	20.32	0.3040	0.062	601.2	36.29	5.24	0.014	86.88	873.8
Naphthalic	24.44	0.2867	0.276 †	959.3	56.56 †	6.63	—	266.6	3834
		0.2287 †							
Diphenic ...	7.37	0.3649	0.104 †	359.3	59.09 †	3.81	0.041	29.78	456.2
		0.2281 †							
Camphoric	13.99	0.2351	-0.029	526.9	45.69	4.84	-0.007	-15.00	-286.2
Cineolic ...	13.77	0.2375	-0.083	564.9	47.50	5.02	-0.019	5.76	1.5

\* The distortion polarisation being taken as  $1.05 R_D$ . † Determined in quinoline.

$d_4^{25} = 1.0900$ ,  $n_D^{25} = 1.62475$ ,  $r_1 = 0.32424$ , and  $D = 0.12785$ . For benzene,<sup>8</sup> when  $w_2 = 0$ ,  $n_D^{25} = 1.4973$ ,  $d_4^{25} = 0.87378$ ,  $\epsilon = 2.2725$ ,  $B = 0.410 \times 10^{-7}$ ,  $r_1 = 0.33506$ ,  $D = 0.19081$ ,  $\bar{H} = 2.114$ ,  $J = 0.4681$ , and  ${}_sK_1 = 7.56 \times 10^{-14}$ . Descriptions of apparatus, procedures, and methods of calculation are in refs. 8 and 9; the symbols used and their definitions have recently been briefly relisted in this *Journal*.<sup>10</sup> Molecular polarisabilities,  $b_1$ ,  $b_2$ , or  $b_3$ , and bond polarisabilities,  $b_L$ ,  $b_T$ , or  $b_V$ , are quoted throughout this paper in units of  $10^{-23}$  c.c.

## DISCUSSION

**Dipole Moments.**—Wesson's Tables<sup>11</sup> give no data for maleic, itaconic, glutaric, naphthalic, camphoric, or cineolic anhydride. An earlier value<sup>12</sup> for diphenic anhydride is inexplicably high and should be replaced by that (3.8<sub>1</sub> D) now reported. Moments of 4.16—4.22 D for succinic anhydride, of 4.23—4.32 D for citraconic anhydride, and of 5.21—5.28 D for phthalic anhydride found in benzene by Rau and Anantanarayanan,<sup>13</sup> agree with those in Table 2, except in the case of citraconic anhydride for which our observation is *ca.* 0.2 D smaller. Longster and Walker's value<sup>14</sup> (3.83 D) for succinic anhydride appears low. Only with cineolic anhydride has the resultant polarity a bearing on the molecular configuration: if the "anhydride" component is taken as 4.84 D (the moment of camphoric anhydride) and the "ether" component as 1.57 D (the moment of cineole<sup>15</sup>), interaction at 92.6° is required to produce  $\mu_{\text{resultant}} = 5.02$  D. This conclusion is used below.

**Molar Kerr Constants and Conformations.**—The standard approach has been to compute the polarisability semi-axes, and thence the molar Kerr constant, expected for likely conformations of each anhydride, and to compare the  ${}_mK$ 's so forecast with those from experiment. Longitudinal, transverse, and "vertical" polarisabilities,  $b_L^{XY}$ ,  $b_T^{XY}$ , and  $b_V^{XY}$ , respectively, of the five bonds involved are:

Bond XY	$b_L^{XY}$	$b_T^{XY}$	$b_V^{XY}$	Bond XY	$b_L^{XY}$	$b_T^{XY}$	$b_V^{XY}$
C-H .....	0.064	0.064	0.064	C-O .....	0.081	0.039	0.039
C-C .....	0.099	0.027	0.027	C=O .....	0.230	0.140	0.046
C=C .....	0.280	0.073	0.077				

Calculations have been made as outlined in ref. 8c or 16; fully described examples (3-halogenocholest-5-enes) may be found in work by Eckert and Le Fèvre.<sup>17</sup> Information on the geometry of these cyclic anhydrides was lacking when this work started; since it was necessary to know the angles which every bond in a given molecule makes with three arbitrarily disposed rectangular axes, X, Y, and Z, "Barton" models<sup>18</sup> were constructed and these angles measured by hand. (Successive reconstructions and remeasurements demonstrated that angle estimates could easily be repeated within  $\pm 0.5^\circ$ .) Angles thus read are recorded for individual anhydrides in the relevant text below. Table 3 summarises the polarisability semi-axes, and the directions in which they are measured, as estimated by using the above bond data, angles, etc.

**Conformations of Maleic, Succinic, Citraconic, and Itaconic Anhydride.**—These related

<sup>8</sup> Le Fèvre and Le Fèvre, (a) *Rev. Pure Appl. Chem. (Australia)*, 1955, **5**, 262; (b) *J.*, 1953, 4041; 1954, 1577; (c) Chap. XXXVI in "Physical Methods of Organic Chemistry," ed. Weissberger, Interscience Publ. Inc., New York, 3rd edn., Vol. I, p. 2459.

<sup>9</sup> Le Fèvre, "Dipole Moments," Methuen, London, 3rd edn., 1953, Chap. II.

<sup>10</sup> Le Fèvre and Sundaram, *J.*, 1962, 1494.

<sup>11</sup> Wesson, "Tables of Electric Dipole Moments," Technology Press, Massachusetts Inst. Technology, 1948.

<sup>12</sup> Le Fèvre and Vine, *J.*, 1938, 967.

<sup>13</sup> Rau and Anantanarayanan, *Proc. Indian Acad. Sci.*, 1937, **5**, A, 185.

<sup>14</sup> Longster and Walker, *Trans. Faraday Soc.*, 1953, **49**, 228.

<sup>15</sup> Freeman, Le Fèvre, and Maramba, *J.*, 1952, 1649.

<sup>16</sup> Le Fèvre, Liversidge Lecture, *J. Proc. Roy. Soc. New South Wales*, 1961, **95**, 1.

<sup>17</sup> Eckert and Le Fèvre, *J.*, 1962, 1080.

<sup>18</sup> Barton, *Chem. and Ind.*, 1956, 1136.

TABLE 3.

Semi-axes, moment components, etc., of cyclic anhydrides.\*

Polarisability principal axes	Direction cosines with			Component moments (D)	Polarisability principal axes	Direction cosines with			Component moments (D)
	X	Y	Z			X	Y	Z	
<i>Maleic anhydride, (a) planar</i>					<i>Citraconic anhydride, planar</i>				
$b_1 = 0.787$	1	0	0	$\mu_1 = 3.91$	$b_1 = 0.985$	0.9925	0.1219	0	$\mu_1 = 3.97_5$
$b_2 = 1.054$	0	1	0	$\mu_2 = 0$	$b_2 = 1.238$	-0.1219	0.9925	0	$\mu_2 = 0.77$
$b_3 = 0.430$	0	0	1	$\mu_3 = 0$	$b_3 = 0.585$	0	0	1	$\mu_3 = 0$
<i>(b) non-planar</i>					<i>Itaconic anhydride, planar</i>				
$b_1 = 0.798_5$	0.9998	0	0.0022	$\mu_1 = 3.91$	$b_1 = 1.004$	0.8300	0.5577	0	$\mu_1 = 3.57$
$b_2 = 1.042$	0	1	0	$\mu_2 = 0$	$b_2 = 1.219$	-0.5577	0.8300	0	$\mu_2 = -2.06$
$b_3 = 0.430$	-0.0022	0	0.9998	$\mu_3 = 0$	$b_3 = 0.585$	0	0	1	$\mu_3 = 0$
<i>Succinic anhydride, planar</i>					<i>Diphenic anhydride, non-planar</i>				
$b_1 = 0.879$	1	0	0	$\mu_1 = 4.2$	$b_1 = 2.568$	0.9457	0.3172	-0.0709	$\mu_1 = 2.32$
$b_2 = 0.992$	0	1	0	$\mu_2 = 0$	$b_2 = 2.402$	-0.3234	0.8965	-0.3027	$\mu_2 = -3.00$
$b_3 = 0.507$	0	0	1	$\mu_3 = 0$	$b_3 = 1.823$	-0.0325	0.3092	0.9505	$\mu_3 = 0.43$
<i>Glutaric anhydride, (a) planar</i>					<i>Camphoric anhydride, form A</i>				
$b_1 = 1.094$	1	0	0	$\mu_1 = 4.14$	$b_1 = 1.945$	0.9622	-0.2706	0.0318	$\mu_1 = -1.31$
$b_2 = 1.158$	0	1	0	$\mu_2 = 0$	$b_2 = 1.860$	0.2666	0.9581	0.1059	$\mu_2 = 4.64$
$b_3 = 0.664$	0	0	1	$\mu_3 = 0$	$b_3 = 1.567$	-0.0591	-0.0934	0.9939	$\mu_3 = -0.45$
<i>(b) boat form</i>					<i>form B</i>				
$b_1 = 1.103$	0.8554	0	-0.5180	$\mu_1 = 4.01$	$b_1 = 1.915$	0.9481	-0.3105	0.0688	$\mu_1 = -1.54$
$b_2 = 0.965$	0	1	0	$\mu_2 = 0$	$b_2 = 1.834$	0.3103	0.9505	0.0131	$\mu_2 = 4.47$
$b_3 = 0.849$	0.5180	0	0.8554	$\mu_3 = 1.02$	$b_3 = 1.624$	-0.0695	0.0090	0.9975	$\mu_3 = -1.04$
<i>(c) chair form</i>					<i>form C</i>				
$b_1 = 1.046$	0.9598	0	0.2807	$\mu_1 = 4.14$	$b_1 = 1.913$	0.9478	-0.3188	0.0066	$\mu_1 = -1.37$
$b_2 = 0.963$	0	1	0	$\mu_2 = 0$	$b_2 = 1.834$	0.3074	0.9081	-0.2842	$\mu_2 = 3.35$
$b_3 = 0.906$	0.2807	0	-0.9598	$\mu_3 = 0$	$b_3 = 1.626$	0.0846	-0.2714	-0.9587	$\mu_3 = -3.22$
<i>Phthalic anhydride, planar</i>					<i>Cineolic anhydride (form: see text)</i>				
$b_1 = 1.578$	1	0	0	$\mu_1 = 5.24$	$b_1 = 2.026$	0.9194	-0.3926	-0.0216	$\mu_1 = -1.56$
$b_2 = 1.638$	0	1	0	$\mu_2 = 0$	$b_2 = 1.860$	0.3839	0.9082	-0.1665	$\mu_2 = 4.57$
$b_3 = 0.832$	0	0	1	$\mu_3 = 0$	$b_3 = 1.651$	0.0850	0.1448	0.9858	$\mu_3 = 1.37$
<i>Naphthalic anhydride, (a) planar</i>					* See text for descriptions of conformations and positions of axes X, Y, and Z				
$b_1 = 2.633$	1	0	0	$\mu_1 = 0$					
$b_2 = 2.253$	0	1	0	$\mu_2 = 6.63$					
$b_3 = 1.127$	0	0	1	$\mu_3 = 0$					
<i>(b) non-planar</i>									
$b_1 = 2.575$	1	0	0	$\mu_1 = 0$					
$b_2 = 2.234$	0	1	0	$\mu_2 = 6.53$					
$b_3 = 1.205$	0	0	1	$\mu_3 = 1.15$					

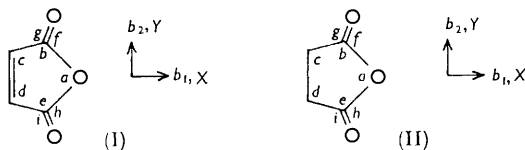
five-membered ring molecules, for which only planar or near-planar structures can be foreseen, are considered first.

A flat maleic anhydride model (I) showed angles as follow:  $a = 104^\circ$ ,  $b = c = d = e = 109^\circ$ ,  $f = g = h = i = 125.5^\circ$ . The resultant moment and the  $b_1$  axis are parallel to the bisector of the angle  $a$ , and  $b_2$  is parallel to the C=C link. Molecular semi-axes are then obtained from bond polarisabilities as  $b_1 = 0.787$ ,  $b_2 = 1.054$ , and  $b_3 = 0.430$  (Table 3). The molecular refraction,  $R_D$ , calculated from Vogel's tables,<sup>19</sup> is 19.76 c.c., which corresponds to a polarisability exaltation,  $\Delta b$ , of 0.133. In the light of experience with conjugated systems,<sup>6,20</sup> this extra polarisability should be added to  $b_2$ . Accordingly we have:  $b_1 = 0.787$ ,  $b_2 = 1.187$ ,  $b_3 = 0.430$ ,  $\theta_1 = 5.11 \times 10^{-35}$ ,  $\theta_2 = -8.63 \times 10^{-35}$ , and

<sup>19</sup> Vogel, *J.*, 1948, 1833; 1952, 514.

<sup>20</sup> Bramley and Le Fèvre, *J.*, 1960, 1820.

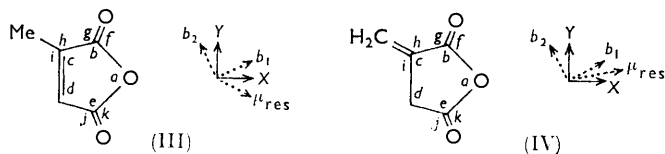
${}_mK$ , calc. =  $-14.8 \times 10^{-12}$ . The observed  ${}_mK$  ( $-12.6 \times 10^{-12}$ ) is less negative than  ${}_mK$ , calc. A slight incorrectness in the interbond angles could easily explain the non-agreement. Professor R. B. Corey (California Institute of Technology), with whom the matter was discussed, kindly arranged an X-ray analysis of crystalline maleic anhydride. He reports<sup>21</sup> the oxygen atom as lying 0.03 Å out of the plane of the remaining atoms, and angles as  $a = 107.5^\circ$ ,  $b = 107.8^\circ$ ,  $c = 108.3^\circ$ ,  $d = 108.8^\circ$ ,  $e = 107.6^\circ$ ,  $f = 121.3^\circ$ ,  $g = 130.9^\circ$ ,  $h = 120.1^\circ$ , and  $i = 132.3^\circ$ ; the two C-O bonds have not quite the same length (1.393 and 1.383 Å). Repetition of our calculations, with these data (cf. Table 3), however, yields an  ${}_mK$ , calc., of  $+13.8 \times 10^{-12}$ , *i.e.*, one of reversed algebraical sign. Mathematically this result is due largely to the smaller angles at  $f$  and  $h$  in the "X-ray" structure. The last, of course, represents the molecule when subjected to lattice forces



and not as a free solute, for which state a greater equality among angles  $f$ ,  $g$ ,  $i$ , and  $h$  seems reasonable. Previously other instances have been noticed where configurations deduced from crystals are manifestly inappropriate to the related solutes (cf. p. 5 of ref. 16).

The model of succinic anhydride (II) had angles as follow:  $a = 106^\circ$ ,  $b = e = 112^\circ$ ,  $c = d = 105^\circ$ ,  $f = g = h = i = 124^\circ$ ;  $R_D$ , calc., is 20.20 c.c.; so that  $\Delta R_D = 2.17$  c.c., and  $\Delta b = 0.258$ . Without addition of this exaltation,  $b_1$ ,  $b_2$ , and  $b_3$  appear as 0.879, 0.992, and 0.507, respectively (Table 3). When  $\Delta b$  supplements  $b_2$ , we have:  $b_1 = 0.879$ ,  $b_2 = 1.250$ ,  $b_3 = 0.507$ ,  $\theta_1 = 4.92 \times 10^{-35}$ ,  $\theta_2 = 0.25 \times 10^{-35}$ , and  ${}_mK$ , calc. =  $21.7 \times 10^{-12}$  (against an observed molar Kerr constant of  $22.1 \times 10^{-12}$ ). Agreement with a flat structure is therefore satisfactory.

In citraconic anhydride (III) the angles were:  $a = 104^\circ$ ,  $b = c = d = e = 109^\circ$ ,  $f = g = h = i = j = k = 125.5^\circ$ . Because of the methyl substituent, neither  $b_1$  nor  $\mu_{\text{resultant}}$  is parallel to  $X$ . From Table 3,  $b_1$  is seen to be inclined at  $7^\circ$  to  $X$  in an anticlockwise sense. If the Me:C:C group has a polarity of 0.3 D, which interacts at  $64^\circ$  with a component equal to  $\mu_{\text{maleic anhydride}}$ , then  $\mu_{\text{citraconic anhydride}}$  itself will be directed *ca.*  $4^\circ$  clockwise from  $X$ ; thus  $\mu_1 = 3.97_5$  D and  $\mu_2 = 0.77_3$  D.  $R_D$ , calc., is 24.41 c.c.; addition to  $b_2$  of the small exaltation so indicated then gives  $b_1 = 0.985$ ,  $b_2 = 1.262$ , and  $b_3 = 0.585$ , whence  ${}_mK$ , calc., becomes  $156.2 \times 10^{-12}$ , which is in fair agreement (in view of the various assumptions) with  ${}_mK$ , obs. =  $163.2 \times 10^{-12}$ .



From the itaconic anhydride model (IV) the following angles were obtained:  $a = 104^\circ$ ,  $b = c = e = 110^\circ$ ,  $d = 106^\circ$ ,  $f = i = k = 126^\circ$ ,  $g = h = j = 124^\circ$ . Bond polarisabilities and these angles, by standard computations, indicate  $b_{\text{max}}$  as situated  $33^\circ 54'$  anticlockwise to the  $Y$  axis. The dipole moment of itaconic anhydride (4.12 D) is less than that of succinic anhydride (4.20 D), and corresponds with the resultant expected when a component of 4.20 D along  $X$  interacts with one of 0.3 D (cf.  $\mu_{\text{Me}_2\text{C}=\text{CH}_2}$  in ref. 11) at an angle of  $107.5^\circ$ ; this resultant should be directed  $4^\circ$  anticlockwise to  $X$ , *i.e.*, practically  $30^\circ$  clockwise from  $b_1$ ; the moment components  $\mu_1$  and  $\mu_2$  then follow as in Table 3.  $R_D$ , calc., for itaconic

<sup>21</sup> Personal communication mentioning unpublished results obtained by R. E. Marsh, E. Ubell, and H. E. Wilcox in the California Institute of Technology.

anhydride is 24.41 c.c., to be compared with  $R_D$ , obs., of 23.86 c.c., *i.e.*, the molecule exhibits a negative exaltation (equivalent to  $-0.065$  polarisability unit) the proper disposal of which is not obvious. If it is ignored, the  ${}_mK$ , calc., is  $358 \times 10^{-12}$  (too large); if it is subtracted wholly from  $b_2$ , the  ${}_mK$ , calc., is  $372 \times 10^{-12}$  (too large); if it is applied entirely to  $b_1$ , the  ${}_mK$ , calc., is  $281 \times 10^{-12}$  (too small); if it is divided equally between  $b_1$  and  $b_2$ , the  ${}_mK$ , calc., is  $326 \times 10^{-12}$ . Its allocation to  $b_1$  and  $b_2$  in the proportions  $\cos^2 30^\circ$  and  $\sin^2 30^\circ$  leads to  $b_1 = 0.955$ ,  $b_2 = 1.203$ ,  $b_3 = 0.585$ , whence  $\theta_1 = 3.45 \times 10^{-35}$ ,  $\theta_2 = 68.65 \times 10^{-35}$ , and  ${}_mK$ , calc. =  $303.2 \times 10^{-12}$  (in reasonable accord with the  ${}_mK$ , obs.,  $307.0 \times 10^{-12}$ ).

To conclude this section, therefore, we note that while it is possible to reconcile our measurements with planar structures we do not advance them as proofs of flatness. As the example of maleic anhydride shows, the analyses of molar Kerr constants depend critically upon the intervalency angles adopted, and for these we lean heavily on Barton's models, which, of course, suggest planarity as the simplest hypothesis in each of the above cases.

*The Conformation of Glutaric Anhydride.*—Three structures have been considered (Fig. 1): a planar form, and two non-planar forms. In the first, angles at  $a-j$ , in order, were  $114^\circ$ ,  $123^\circ$ ,  $120^\circ$ ,  $120^\circ$ ,  $120^\circ$ ,  $123^\circ$ ,  $118.5^\circ$ ,  $118.5^\circ$ ,  $118.5^\circ$ , and  $118.5^\circ$ . The semi-axes for this form were as in Table 3.  $R_D$ , calc., is 24.86 c.c., whence  $\Delta R_D = -0.04$  c.c. and  $\Delta b = -0.005$  c.c.; if this exaltation operates on  $b_2$ , we have  ${}_mK$ , calc. =  $362 \times 10^{-12}$ ; or, if on  $b_1$ ,  ${}_mK$ , calc. =  $348 \times 10^{-12}$ . The observed  ${}_mK$  (Table 2) is  $209.3 \times 10^{-12}$ , *i.e.*, less than the  ${}_mK$ 's, calc., for these, and other, planar structures, which are therefore rejected.

The two non-planar models examined appeared as almost strainless "boat" and "chair" forms, respectively. In the former, angles were read as:  $a = c = d = e = 109^\circ$ ,  $b = f = 120^\circ$ ; thus the plane of the C=O bonds makes  $80^\circ$  with the plane of the C-O-C triangle. The arbitrary axes  $X$  and  $Y$  lie in the basal C-(CO)  $\cdots$  (CO)-C quadrilateral. Let the moment due to C-O-C be 1.3 D (cf.  $\mu_{Me_2O}$ ); the two carbonyl groups—to produce  $\mu_{\text{resultant}} = 4.14$  D—therefore contribute a component of 3.7 D at  $80^\circ$  to  $\mu_{C-O-C}$ . Since  $\tan \alpha = 1.3 \sin 80^\circ / (3.7 + 1.3 \cos 80^\circ)$ , the angle  $\alpha$ , which  $\mu_{\text{resultant}}$  makes with a centre line between the C=O bonds and in their plane, is  $18^\circ 6'$ ;  $b_1$  is located  $31^\circ 12'$  from  $X$  (Table 3), so that  $\mu_{\text{resultant}}$  and the  $b_1$  direction are inclined at  $14^\circ 18'$ . Thus, adding the exaltation to  $b_1$ , we have  $b_1 = 1.098$ ,  $b_2 = 0.963$ , and  $b_3 = 0.849$ ; these lead to an  ${}_mK$ , calc. ( $322 \times 10^{-12}$ ), which exceeds that found.

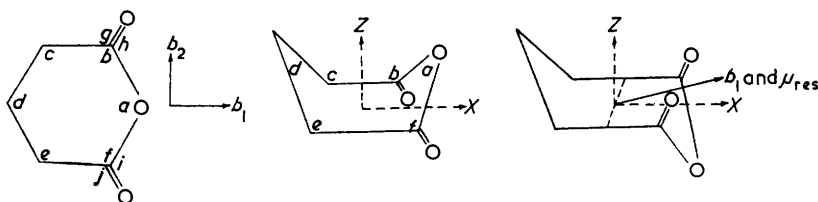


FIG. 1.

The alternative "chair" model has the same interbond angles as the "boat," but  $b_1$  and  $\mu_{\text{resultant}}$  now act as shown (actually calculations give the angle between  $b_1$  and  $\mu_{\text{resultant}}$  as  $0^\circ 36'$ )  $16.3^\circ$  from  $X$  anticlockwise in the  $XZ$  plane. Therefore  $b_1 = 1.041$ ,  $b_2 = 0.963$ ,  $b_3 = 0.906$ ,  $\theta_1 = 0.18 \times 10^{-35}$ ,  $\theta_2 = 47.93 \times 10^{-35}$ , and  ${}_mK$ , calc. =  $202.3 \times 10^{-12}$  (compared with  $209.3 \times 10^{-12}$  from experiment); if the exaltation is applied equally to the three semi-axes,  ${}_mK$ , calc., becomes  $211.8 \times 10^{-12}$ . A "chair" conformation for glutaric anhydride is thus indicated.

*The Conformations of Phthalic and Naphthalic Anhydride.*—A model (Fig. 2a) of the first-named molecule had the following angles:  $a = 104^\circ$ ,  $b = c = d = e = 109^\circ$ , and  $f = g = h = i = 125.5^\circ$ .  $R_D$ , obs.,  $- R_D$ , calc., is 1.23 c.c.; an exaltation of polarisability

of  $+0.146$  has therefore to be added appropriately to the semi-axes computed in Table 3. Adding it to  $b_1$  leads to  ${}_mK$ , calc. =  $\sim 1500 \times 10^{-12}$ . The observed  ${}_mK$  is  $874 \times 10^{-12}$ . On assuming the exaltation to affect  $b_2$  alone, we have  $b_1 = 1.578$ ,  $b_2 = 1.784$ ,  $b_3 = 0.832$ ,  $\theta_1 = 8.94 \times 10^{-35}$ ,  $\theta_2 = 194.67 \times 10^{-35}$ , and  ${}_mK$ , calc. =  $856 \times 10^{-12}$ ; this is 2% lower than the measured value. Identity of  ${}_mK$ , calc. and obs., requires the exaltation to be distributed  $+0.003$  to  $b_1$  and  $+0.143$  to  $b_2$ , but no *a priori* reason for such a division suggests itself.

A planar model (Fig. 2*b*) of naphthalic anhydride showed these angles:  $a = 114^\circ$ ,  $b = f = 123^\circ$ ,  $c = d = e = h = j = 120^\circ$ ,  $g = i = 117^\circ$ . With this molecule the exaltation of refraction appears to be considerable:  $R_D$ , calc., from  $R_{\text{naphthalene}}$ , is 53.28 c.c. or, from Vogel's refractivity for the  $C_{Ar}-C_{Ar}$  bond, is 51.88 c.c.;  $R_D$ , obs., is 56.56 c.c.

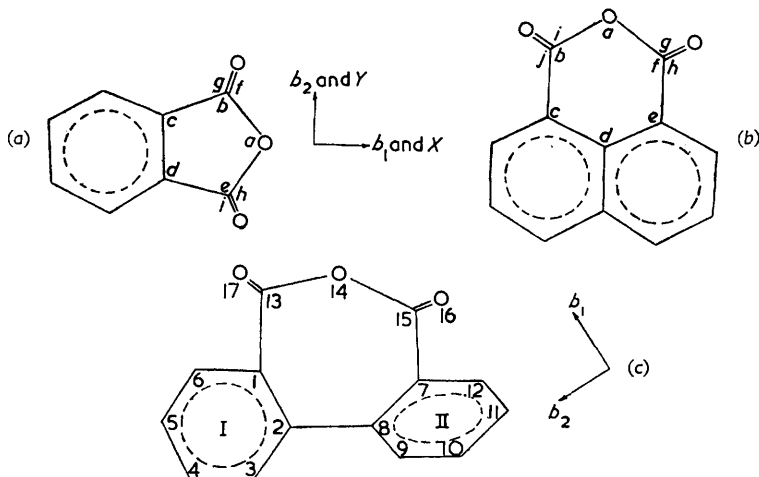


FIG. 2.

If  $\Delta R_D$  is taken as 3.28 c.c., an extra polarisability of 0.390 unit has to be incorporated; addition of this to  $b_2$  provides  $b_1 = 2.633$ ,  $b_2 = 2.643$ ,  $b_3 = 1.127$ ,  $\theta_1 = 27.13 \times 10^{-35}$ ,  $\theta_2 = 880.8 \times 10^{-35}$ , and  ${}_mK$ , calc. =  $3818 \times 10^{-12}$ , in adequate agreement with  ${}_mK$  observed =  $3834 \times 10^{-12}$ . Various non-planar models have also been examined. Table 3 includes data for a form having an angle at  $a$  of  $112^\circ$  and angles  $b-j$  all of  $120^\circ$ ;  ${}_mK$ , calc., however is only  $3120 \times 10^{-12}$  even when  $\Delta b$  supplements  $b_2$ . With neither planar nor non-planar structures can  ${}_mK$ 's, which harmonise with the  ${}_mK$  measured, be predicted if the exaltation be applied as in phthalic, maleic, or citraconic anhydride.

To conclude, therefore, the present work is best interpreted if these two anhydrides have flat structures.

*The Conformation of Diphenic Anhydride.*—The model (Fig. 2*c*) constructed for this 7-ring anhydride had angles of  $120^\circ$  at all carbon atoms and one of  $110^\circ$  at the oxygen atom. The arbitrary axes  $X$ ,  $Y$ , and  $Z$  were chosen so that  $X$  and  $Y$  are in the plane of ring I with  $X$  passing through  $C_{(13)}$  and  $C_{(8)}$ . The phenyl group II is twisted at  $35^\circ$  to the phenyl group I, about a common axis joining atoms nos. 5, 2, 8, 11;  $C_{(15)}$  is in plane II. The C=O group (15, 16) is at right-angles to plane I, and the other C=O group is similarly disposed to plane II. The C-O (14, 15) and C-C (15, 7) bonds both make angles of  $30^\circ$  with their projections on to plane I. The resultant moment acts from the mid-point of the C-C bond (2, 8) through the oxygen atom 14, *i.e.*, at  $17.5^\circ$  to the plane I.  $R_D$ , calc., from  $R_{\text{benzene}}$  is 59.17 c.c. (or, with Vogel's refractivity for the  $C_{Ar}-C_{Ar}$  link, 59.19 c.c.);  $R_D$ , obs., is 59.09 c.c. If the small negative exaltation of polarisability thus indicated is divided equally between  $b_1$  and  $b_2$ , we have  $b_1 = 2.563$ ,  $b_2 = 2.397$ ,  $b_3 = 1.823$ ,  $\theta_1 = 5.38 \times 10^{-35}$ ,  $\theta_2 = 109.0 \times 10^{-35}$ , and  ${}_mK$ , calc. =  $481.1 \times 10^{-12}$ . This estimate of  ${}_mK$  is *ca.* 5.5% higher



than the value from experiment. The discrepancy can easily be removed by a slight variation of the model whereby the interplanar angle is raised above  $35^\circ$ ; as a consequence,  $b_3$  is increased at the expense of  $b_1$  and  $b_2$ , *i.e.*, the anisotropy diminishes, and with it the  ${}_mK$ , calc. Actually, with the models used, larger interplanar angles could easily be realised without notable strain in the whole structure.

*The Conformation of Camphoric Anhydride.*—Three models appear possible: 3(a), in which both C=O groups and the anhydride oxygen atom are in the same plane; 3(b), in which the carbonyl bonds are *trans* and the anhydride oxygen is *cis* to the *gem*-dimethyl bridge; and 3(c) the reverse of 3(b).

In 3(a), angles are:  $a = 114^\circ$ ,  $b = c = 123^\circ$ ,  $d = f = 117^\circ$ ,  $e = g = 120^\circ$ ,  $h = i = 105^\circ$ ,  $j = 98^\circ$ ,  $k = l = 109^\circ$ . The axes  $X$  and  $Y$  are placed in the plane of ring II with  $Y$  bisecting the oxygen valency angle. Planes I and II are mutually at  $110^\circ$ , II and III at

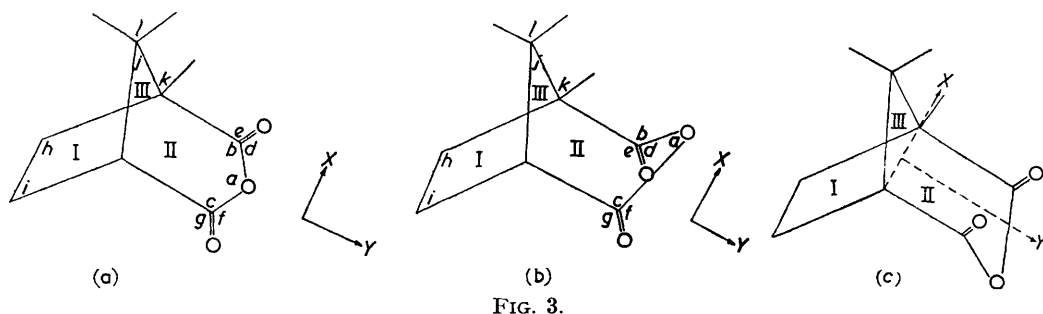


FIG. 3.

$115^\circ$ , and I and III at  $135^\circ$ . Polarisability semi-axes and their locations within the  $XYZ$  framework emerge as in Table 3.  $R_D$ , calc., is 45.91 c.c.;  $R_D$ , obs., is 45.69 c.c.; the small negative exaltation thus indicated is added algebraically to  $b_2$ . The molar Kerr constant computed emerges as  $+230 \times 10^{-12}$ , in strong discord with the negative value ( $-286.2 \times 10^{-12}$ ) from experiment.

In 3(b) angles  $a = k = l = 109^\circ$ ,  $b = c = d = e = f = g = 120^\circ$ ,  $h = i = 107^\circ$ , and  $j = 100^\circ$ . Interplanar angles are as in 3(a). The plane containing the carbonyl groups is defined by a  $26^\circ$  clockwise rotation from plane II, and that containing the C-O-C triangle by an anticlockwise rotation of  $32^\circ$ ; calculation (cf. glutaric anhydride) then indicates that  $\mu_{\text{resultant}}$  acts in a direction  $13^\circ$  clockwise from the  $Y$  co-ordinate in the  $YZ$  plane,  $\mu_Y$  and  $\mu_Z$  are therefore 4.72 and  $-1.09$  D, so that  $\mu_1 = -1.54$ ,  $\mu_2 = 4.47$ , and  $\mu_3 = -1.04$  D. The  ${}_mK$ , calc., from these data is  $111.9 \times 10^{-12}$ , *i.e.*, incorrect both in sign and magnitude.

In form 3(c) the angles are as in 3(b), but the carbonyl and the C-O-C planes are now located by anticlockwise and clockwise rotations of  $41^\circ$  and  $39^\circ$ , respectively, from the plane II;  $\mu_{\text{resultant}}$  now acts in the  $YZ$  plane  $15^\circ$  clockwise from the plane containing the C=O bonds;  $\mu_Y$  and  $\mu_Z$  are therefore 4.35 D and 2.12 D., and  $\mu_1 = -1.37$ ,  $\mu_2 = 3.35$ , and  $\mu_3 = -3.22$  D units. The calculated molar Kerr constant follows as  $-177 \times 10^{-12}$ , which is correct as to sign but numerically about 110 units too positive. If the direction of  $\mu_{\text{resultant}}$  in the  $YZ$  plane is *ca.*  $7^\circ$  (instead of  $15^\circ$ ) clockwise from the carbonyl plane, then  $\mu_X = 0$ ,  $\mu_Y = 4.01$ ,  $\mu_Z = 2.71$ ,  $\mu_1 = -1.26$ ,  $\mu_2 = 2.87$ ,  $\mu_3 = -3.69$ ,  $\theta_1 + \theta_2 = -66.59 \times 10^{-35}$ , and  ${}_mK$ , calc. =  $-279.6 \times 10^{-12}$  (observed,  $-286.2 \times 10^{-12}$ ). Such an amendment in the disposition of  $\mu_{\text{resultant}}$  seems permissible since vectorial addition of components for C=O and C-O links, which provided the first estimate of  $15^\circ$ , is itself speculative. It should be mentioned that a parallel alteration in the argument for form 3(b) above reduces the  ${}_mK$ , calc., to *ca.*  $+60 \times 10^{-12}$  but fails to produce the high negativity displayed by  ${}_mK$  expt.

We conclude that camphoric anhydride as a solute adopts a conformation close to that specified here as 3(c).

*The Conformation of Cineolic Anhydride.*—In view of the smallness of  ${}_mK$ , obs., only the model likely to be least anisotropic has been considered (Fig. 4); in this angles were measured

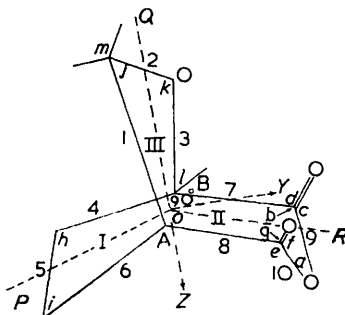


FIG. 4.

as follow:  $a = 111^\circ$ ,  $b = c = d = e = f = g = 120^\circ$ ,  $h = i = 109^\circ$ ,  $j = k = l = m = 110^\circ$ . The lines  $OP$ ,  $OQ$ , and  $OR$  bisect the planes I, III, and II and meet at  $120^\circ$ . The arbitrary axes  $X$ ,  $Y$ , and  $Z$  are fixed by  $Y$ 's being perpendicular to plane III and  $Z$  parallel to  $QO$ , *i.e.*, at  $60^\circ$  to plane II. The four hydrogen atoms at  $h$  and  $i$  are staggered, so that, when viewed at the model along the line  $AOB$ , bond 1 is  $10^\circ$  anticlockwise and bond 3  $10^\circ$  clockwise to  $QO$ , bond 6 is  $10^\circ$  anticlockwise, and bond 4 is  $10^\circ$  clockwise to  $PO$ ; bonds 8 and 7 are similarly related to  $OR$ . Bonds 2 and 5 are twisted  $20^\circ$  to the line  $AB$ . The angle between the resultant moment of the ketonic groups and that of the two C-O bonds (9 and 10) appears as  $65^\circ$ ; the moment of the anhydride group (taken as  $4.84$  D, the moment of camphoric anhydride) therefore acts *ca.*  $14^\circ$  clockwise from the plane containing the C=O bonds. The angle of interaction of this anhydride moment and that of the ether (cineole) unit has already been computed. Accordingly the resultant moment of the whole molecule acts at  $18^\circ$  from the component of magnitude  $4.84$  D, *i.e.*,  $5^\circ$  from the  $Y$  axis and  $85^\circ$  from the  $X$  axis. Thus  $\mu_X = 0.43$ ,  $\mu_Y = 4.96$ , and  $\mu_Z = 0.61$  D; semi-axes and  $\mu_1$ ,  $\mu_2$ , and  $\mu_3$  follow as in Table 3.  $R_D$ , calc.,  $-R_D$ , obs., is  $0.27$  c.c.; the corresponding small negative exaltation is applied to  $b_2$ , giving  $b_1 = 2.026$ ,  $b_2 = 1.828$ ,  $b_3 = 1.651$ ,  $\theta_1 = 1.25 \times 10^{-35}$ ,  $\theta_2 = -1.17 \times 10^{-35}$ , and  ${}_mK$ , calc.  $= 0.34 \times 10^{-12}$ , in fair agreement with the value from experiment ( $1.15 \times 10^{-12}$ ).

*Conclusion.*—For convenience the calculated and found molar Kerr constants (in  $10^{-12}$  units) are assembled in Table 4. On the whole, the agreement is satisfactory and

TABLE 4.

Molar Kerr constants, calculated and found.

Anhydride	Calc.	Found	Anhydride	Calc.	Found
Maleic .....	-14.8	-12.6	Phthalic .....	856	874
Succinic .....	21.7	22.1	Naphthalic .....	3818	3834
Citraconic .....	156	163	Diphenic * .....	481	456
Itaconic .....	303	307	Camphoric * .....	-280	-286
Glutaric * .....	212	209	Cineolic * .....	0.34	1.5

\* Calc. value shown is that for the selected non-planar conformation.

strengthens confidence in the methods used. The discrepancies are understandable since for them four possible causes are obvious. First, the determination of  ${}_mK_2$  is usually subject to an uncertainty of a few per cent and the smaller the  ${}_mK_2$  the larger does this percentage appear; secondly, excellent as the Barton models are, small errors in the angles between adjacent bonds can, especially in large constructions, be cumulative, so

that the angles made by more distant bonds with the  $X$ ,  $Y$ ,  $Z$  axes may be read incorrectly; thirdly, the calculation of  ${}_mK$  is sensitive to the direction of action of the resultant dipole moment and, for this, dependence must often be placed on the vectorial additivity of component moments. Relatively minor alterations of angles and/or the location of  $\mu_{\text{resultant}}$  would markedly improve the comparisons in Table 4. Lastly, the proper allocation of exaltations of polarisability to the three molecular semi-axes is sometimes not clear either from theory or analogy. Nevertheless, and despite these difficulties, we submit that the conformations adopted above for the planar anhydrides, or selected from alternatives for the non-planar anhydrides, are reasonable, and in accord with structural principles now current.

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