THE DIPOLE MOMENT AND STRUCTURE OF SOME CYCLIC ANHYDRIDES : PHTHALIC, SUCCINIC AND CITRACONIC ANHYDRIDES.

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THE cyclic anhydrides form a class of highly reactive compounds which take part in an enormous number of condensation reactions. No moments have been so far measured for any representative cyclic anhydride. In the present investigation the moments of phthalic citraconic and succinic anhydrides have been measured, the first two in benzene as solvent and the last in dioxane. The remarkable values for their moments are discussed in relation to the moments of analogous compounds.

Experimental.

The moments were measured by the method of dilute solutions over a temperature range of 10° to 40°C. with the apparatus and details exactly as given in a previous publication.[1] The dioxane used as solvent was a pure sample which was dried over sodium wire and fractionally distilled also over sodium. Although the fraction collected had boiled steadily at its correct boiling point, its dielectric constant value was much lower than that obtained on a previous occasion[2] for another sample of carefully purified dioxane. As, however, the molecular polarisation of the present sample showed no fall with temperature but a slight rise just as all non-polar liquids do, the experiments were proceeded with this. A search through the literature shows that dioxane does indeed behave erratically, its physical constants depending upon the duration of drying : the dielectric constant values for 20°C. reported during the last four years range from 2·23[3] to 2·35.[4] *Phthalic anhydride* was a Kahlbaum pure specimen, which was resublimed again,

[1] M. A. Govinda Rau, *Proc. Ind. Acad. Sci.* (A), 1936, **4**, 687.

[2] M. A. Govinda Rau and B. N. Narayanaswamy, *Ibid.*, 1935, **1**, 489.

[3] W. D. Kumler and C. W. Porter, *Journ. Amer. Chem. Soc.*, 1934, **36**, 2549.

[4] W. J. Curran and H. H. Wenzke, *Ibid.*, 1935, **57**, 2162.

and fractionally crystallised from pure benzene. *Succinic anhydride* (Kahlbaum pure) was freshly re-crystallised from chloroform in order to further purify it from any succinic acid present. *Citraconic anhydride* (Kahlbaum pure) was fractionally distilled under reduced pressure and a constant boiling fraction collected for use.

Results.

The results are given in Tables I, II and III, the symbols having the usual significance. The values for the electronic polarisation were calculated from atomic refractivities given in Landolt-Bornstein Tables. The values so calculated are in good agreement with the single determinations reported for citraconic anhydride[5] and for succinic anhydride.[6] On account of the high dipole moment values, there is a considerable influence of the dielectric constant of the solvent, and the calculated moments show a slight increase with temperature as is to be expected.

TABLE I.

Succinic anhydride.

Concentra-tion in mol. fraction	10°		20°		30°		40°	
	E	d	E	d	E	d	E	d
0	2·249	1·0441	2·231	1·0331	2·213	1·0221	2·195	1·0112
0·01195	2·532	1·0479	2·501	1·0366	2·470	1·0252	2·440	1·0138
0·01212	2·565	1·0479	2·532	1·0366	2·500	1·0252	2·468	1·0138
0·01795	2·724	1·0500	2·686	1·0385	2·648	1·0270	2·609	1·0155
0·03303	3·124	1·0541	3·070	1·0429	3·015	1·0317	2·961	1·0204

$t°C.$	α	β	$P_{2\infty}$	$\mu \times 10^{18}$
10	26·34	0·305	398·3	4·16
20	25·40	0·300	391·8	4·20
30	24·29	0·295	382·5	4·22
40	23·15	0·285	370·9	4·22

$$P_E = 20·3$$

[5] F. Anderlini, *Gazz. Chim., Ital.*, 1895, 25 (ii), 142.
[6] Knops, *Ann. d. Chem.*, 1888, 248, 175.

TABLE II.
Phthalic anhydride.

Concentra-tion in mol. fraction	10°		20°		30°		40°	
	E	d	E	d	E	d	E	d
0·00	2·299	0·8883	2·279	0·8776	2·259	0·8669	2·240	0·8563
0·00684	2·577	0·8921	2·546	0·8814	2·515	0·8707	2·484	0·8601
0·00966	2·710	0·8936	2·672	0·8830	2·633	0·8725	2·594	0·8620
0·01044	2·732	..	2·693	..	2·654	..	2·615	..
0·01270	2·819	0·8956	2·779	0·8850	2·738	0·8744	2·698	0·8638
0·01850	3·064	..	3·013	..	2·963	..	2·912	..
0·02052	3·144	0·9004	3·088	0·8898	3·032	0·8791	2·976	0·8685
0·02134	3·183	0·9006	3·124	0·9000	3·065	0·8793	3·006	0·8687

$t°C.$	α	β	$P_{2\infty}$	$\mu \times 10^{18}$
10	41·35	0·582	622·9	5·21
20	39·60	0 584	610·0	5·25
30	37·82	0·589	595·4	5·27
40	36·03	0·590	579·9	5·28

$$P_E = 30·2$$

TABLE III.
Citraconic anhydride.

Concentra-tion in mol. fraction	10°		20°		30°		40°	
	E	d	E	d	E	d	E	d
0	2·297	0·8883	2·278	0·8778	2·259	0·8674	2 240	0·8570
0·01601	2·737	0·8946	2·692	0·8841	2·647	0·8736	2·602	0·8632
0·02046	2·858	0·8967	2·815	0·8861	2·771	0·8753	2·728	0·8645
0·04653	3·569	0·9068	3·497	0·8961	3·424	0·8854	3·351	0·8736

$t°C.$	α	β	$P_{2\infty}$	$\mu \times 10^{18}$
10	27·27	0·399	415·5	4·23
20	26·20	0·391	408·2	4·27
30	24·95	0·389	397·7	4·28
40	24·08	0·360	392·9	4·32

$$P_E = 25·0$$

Discussion.

The simplest of the three compounds studied is obviously succinic anhydride, which has no double bonds in the ring, and can be regarded as an $a.a.'$ diketone of tetramethylene oxide. The moment for this compound has been determined by Smyth and Walls[7] as 1·71. In the following discussions we shall neglect the influence of the solvent on the measured dipole moments, and also consider the moment values as significant only to $\pm 0·1 \times 10^{-18}$ e.s.u. as in our present state of knowledge we are not even able to explain completely moments to this order of approximation. Now, the succinic anhydride molecule has a plane of symmetry about the bisectrix of the oxygen angle as shown in Fig. 1 :—
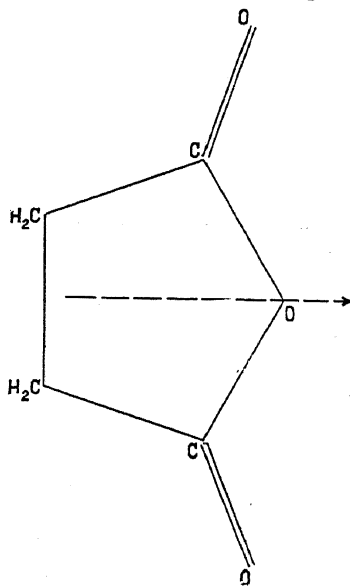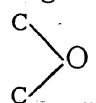
Fig. 1.

and as shown by the geometry of the figure the resultant of the two C = O moments should lie along with the $\overset{C}{\underset{C}{>}}O$ moment on this axis. The value of the latter can be regarded to be the same as that of tetramethylene oxide, *viz.*, 1·7. If tentatively we regard that there are no interaction moments between the components, and that the resultant moment 4·2 is only a vectorial sum of the components, then the contribution of the two C = O moments should be 4·2 — 1·7 = 2·5. Since the value of the C = O moment is on the average 3·0, the inclination of the C = O groups to the axis of the molecule should be given by $2 \times 3·0 \cos \theta = 2·5$, *i.e.*, by $\theta = 65°$. This appears to be a probable value when a pentagon is drawn up with C — C distance as 1·54 Å, C — O distance as 1·43 Å, and the angles

[7] C. P. Smyth and W. S. Walls, *Journ. Amer. Chem. Soc.*, 1932, 54, 3230.

at the two β-carbon atoms in the ring being taken as 110°. Such a simple explanation, however, does not fit in with many other facts. In the first instance, for the geometric configuration assumed, the oxygen angle comes out as 130°, an angle much too large to account for the observed moment in tetramethylene oxide of 1·7. If on the other hand the oxygen angle is of the order of magnitude to be expected for this moment, *i.e.*, approximately 90°, then a consideration of Fig. 1 will show that the C = O links will be more inclined away from the axis and the contributions of the two C = O moments in succinic anhydride will be far less than 2·5. Secondly, if this difference is really due to the two C = O groups, it should also be the case in succinimide, and the moment of the latter should be about 3·0. Actually, the moment of succinimide as measured by Cowley and Partington[8] is only 1·54, a value which is very nearly the same as that computed by the same authors for the $\begin{smallmatrix} C \\ \diagdown \\ \diagup \\ C \end{smallmatrix}$NH group, thus suggesting that the two C = O group moments cancel each other out. This marked difference between the moments of succinic anhydride and imide is also found in the case of phthalic anhydride and imide whose moments are 5·2 and 2·1 respectively. This characteristic difference thus indicates that the explanation based on a simple vectorial addition of normal group moments does not represent the facts.

It seems more probable that here, as in almost all other compounds containing a C = O group adjacent to $\begin{smallmatrix} C \\ \diagdown \\ \diagup \\ C \end{smallmatrix}$O or separated from it only by a system of conjugate links, there is an electromeric shift of electron density from $\begin{smallmatrix} C \\ \diagdown \\ \diagup \\ C \end{smallmatrix}$O towards the C = O, as a result of resonance between normal and excited states of the molecule. Indeed, it would be a unique case if it were to be postulated that there is no resonance in this system of compounds. A system which is to a certain extent closely analogous to the present case is provided in the diphenyl ethers, where there a $\begin{smallmatrix} \diagup O \\ \diagdown \end{smallmatrix}$ atom directly attached to two carbon atoms in a katio-enoid system. Sutton and Hampson[9] have recently argued from a close analysis of the moments of diphenyl ethers and their substituted compounds, that the oxygen angle in them is 128° ± 4°, and thus definitely more than the
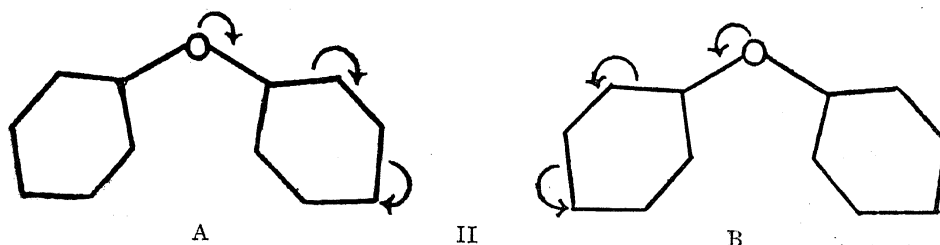
[8] E. G. Cowley and J. R. Partington, *Journ. Chem. Soc.*, 1936, 47.

[9] L. E. Sutton and G. C. Hampson, *Trans. Farad. Soc.*, 1935, **31**, 945.

tetrahedral oxygen angle 109° in other ethers. This increase in angle is explained by them on the ground that there is a resonance of type I
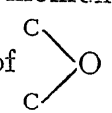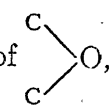
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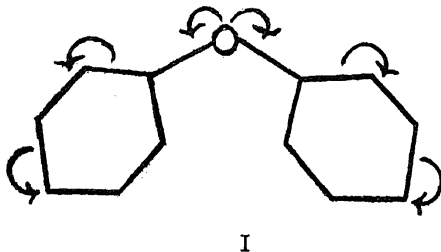
or more probably II A and B.

A   II   B

Further, when the energy of formation of succinic anhydride is computed from the heat of combustion (E = 52·5 e.v.) and compared with the calculated value for the same (E′ = 50·8 e.v.) using Pauling's[10] data for bond energies, there is a difference of 1·7 e.v., representing an appreciable resonance energy. An almost identical value for the resonance energy is also obtained for succinimide : in this compound moreover the imide hydrogen is quite acidic, representing thereby that the nitrogen atom is positively charged on account of the electromeric shift of electrons away from it.

Having thus postulated resonance in these molecules, the immediate question is, as to the relative orientation of the moment of the excited structures. In succinic anhydride and imide the moment of the excited states must be in the opposite direction to that of $\begin{matrix} C \\ C \end{matrix}\!\!>\!\!O$ moment. On account of the symmetry of the molecule about the axis of $\begin{matrix} C \\ C \end{matrix}\!\!>\!\!O$, the resultant moment of the excited states must also be along this same axis, and

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[10] L. Pauling and J. Sherman, *Journ. Chem. Physics*, 1933, 1, 605.
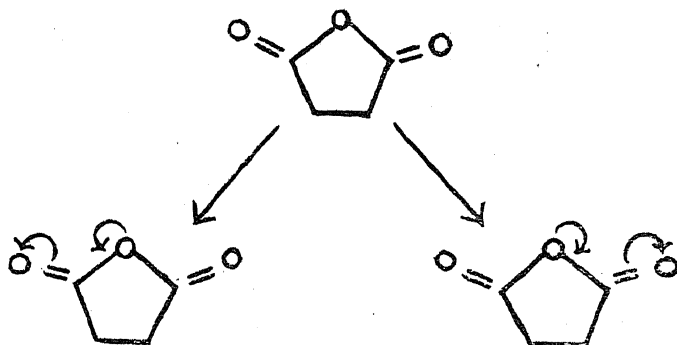
according to scheme II. From these considerations the magnitude of this excited moment comes out as $4 \cdot 2 + 1 \cdot 7 = 5 \cdot 9$, a remarkably high value. In succinimide, the value for this moment does not appear to be so large. The calculations are a little complicated here as the resultant moment of the imide group $\overset{C}{\underset{C}{\diagdown}} N - H$ is not in the plane of the ring.

Partington's calculation of the moment of this group as $1 \cdot 6$ is not very convincing inasmuch as the observed moment for piperidine[11] and also for diethyl amine are both $1 \cdot 2$, and in either of these compounds there is very little strain or resonance. As the observed moment for succinimide is $1 \cdot 5$, which is nearly the same as that for $N - H$ bond, it is probable that whatever normal moment there is along the axis of $\overset{C}{\underset{C}{\diagdown}} N$, *i.e.*, approximately $1 \cdot 0$, it is compensated by the " excited " moment.

The difference between the moments of phthalic anhydride and succinic anhydride is of the same order of magnitude as that between phthalimide and succinimide, the latter being the smaller. The rise in moment on the fusion of the phenyl to the anhydride ring is $1 \cdot 0$ in the former case, and $0 \cdot 6$ in the latter. Since in both cases the moment has increased, the additional moment must be in the same direction, that is, towards the phenyl nucleus. This would mean in other words that there is an electromeric shift of electrons towards the phenyl nucleus. Such a postulate is in consonance with the increased anionoid reactivity of the benzene nucleus in phthalic anhydride towards kationoid reagents such as halogens, nitric acid and sulphuric acid. It is interesting to note in this connection that although the predominant sense of electromeric shift in benzoic acid is away from the ring, there is also a weak shift towards the

[11] M. A. Govinda Rau and B. N. Narayanaswamy, *Zeit. Physikal Chem.*, (B), 1934, **26**, 42.

ring as is evidenced by the formation of *ortho* and *para* derivatives. In the dibasic phthalic acid the nucleus should be even less reactive than in benzoic acid and indeed, sulphonation is very difficult in this compound, while nitration and other reactions are also considerably hindered as compared with the reactivity in phthalic anhydride.

The moment of citraconic anhydride was measured as an intermediate case between succinic and phthalic anhydrides. Maleic anhydride would be the ideal substance to work with, but as a sample of citraconic anhydride was readily available, measurements were made on this substance in the hope that the presence of a methyl substituent would not produce any marked difference. As expected the moment is between the values for the other two compounds, but very much nearer to that of succinic anhydride. This is in agreement with our thesis that there is an electromeric shift away from the $\overset{\text{C}}{\underset{\text{C}}{\diagdown}}\!\!\diagup\text{O}$ grouping, as otherwise the moment of citraconic anhydride would be appreciably more and nearer to that of phthalic anhydride.

Summary.

1. The moments of phthalic, citraconic and succinic anhydrides have been measured, the first two in benzene as solvent and the last in dioxane. The moment values at 20° C. are respectively 5·25, 4·27, and $4\cdot20 \times 10^{-18}$ e.s.u.

2. The moment values are considerably high compared with the moments of the corresponding compounds phthalic and succinic imides.

3. The moments are interpreted as due to a strong resonance structure, which reverses the normal direction of moment to be expected from vectorial addition.