THE DIAMAGNETIC SUSCEPTIBILITIES OF SUCCINIC ACID AND SUCCINIC ANHYDRIDE

The Influence of the Anhydride Ring Structure on Molecular Diamagnetism

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IN an earlier communication,[1] it was shown that the magnetic susceptibilities of camphoric acid and its anhydride followed Pascal's additivity law, and that the difference in the values of their gram-molecular susceptibilities was $-13\cdot0 \times 10^{-6}$, which is just equal to the gram-molecular susceptibility of water ($-12\cdot96 \times 10^{-6}$). On the other hand, Gray and Birse[2] found this difference to be $37\cdot0 \times 10^{-6}$, which was considerably more than could be accounted for on the additivity law.

Gray and Birse[2] have also investigated succinic acid and its anhydride, and have found that the difference in the values of their gram-molecular susceptibilities, namely, $-6\cdot9$* is less than the gram-molecular susceptibility of water. It was, therefore, considered desirable to redetermine the magnetic susceptibility of succinic acid and its anhydride. Succinic anhydride is somewhat difficult to prepare in a pure condition, as it becomes contaminated with the free acid during recrystallisation on account of the presence of traces of moisture in the solvent, which brings about partial hydrolysis. We have carried out the magnetic measurements on specially purified material and find that the difference ($-13\cdot6$) between the gram-molecular susceptibilities of the acid and of its anhydride is nearly equal to the gram-molecular susceptibility of water, in conformity with Pascal's additivity law.

Pascal distinguishes three kinds of oxygen as regards its effective atomic susceptibility: when it is singly bound to any two atoms as in alcohols and ethers, it is diamagnetic ($-4\cdot61$); in ketones and aldehydes in

* The unit of magnetic susceptibility is taken throughout this paper as 10^{-6} c.g.s. e.m.u.

which it is doubly bound to a carbon atom, it is feebly paramagnetic (+ 1·71); but when it is doubly bound to a single carbon atom, carrying another oxygen atom, it is again diamagnetic (− 3·71). In acid anhydrides, the atomic susceptibility of the singly linked oxygen atom is the same as in alcohols and ethers: this follows from the concordance in the observed value of χ_M (− 52·73) of acetic anhydride[3] with that calculated (−52·91) on the basis of the singly linked oxygen atom being equal to − 4·61.

Now it has been shown above that the difference in the gram-molecular susceptibilities of a dicarboxylic acid and its inner anhydride is equal to about − 13. But a dicarboxylic acid contains two atoms of hydrogen and one atom of singly linked oxygen more than the corresponding anhydride, and the sum of the susceptibilities of these three atoms, namely, − 10·47, is numerically less than the above-mentioned difference. It, therefore, follows that the change of the acid into its anhydride produces a greater lowering in its diamagnetism than that which simply corresponds to two atoms of hydrogen and one of oxygen. The paramagnetic effect due to ring closure in the heterocyclic structure of an anhydride should, therefore, be equal to −(− 12·96 + 10·47) or + 2·53. This, however, does not take into account any strain which may be associated with rings of different sizes. If the strain factor were absent, or in other words, rings of different sizes were equally stable, the paramagnetic value of the anhydride rings of different sizes would be the same, namely, + 2·53. It is, however, well known that the double bond between two carbon atoms (the ethylenic bond) and other types of unsaturated bonds are in a state of strain caused by the deflection of the carbon valencies from the tetrahedral angle of 109°, 28′. The polymethylenes, according to the Strain theories,[4] are also in a similar state of strain, the amount of the strain depending on the number† of atoms and the nature of attached groups in the ring structure. Any deviation from the above-mentioned difference, − 13·0, between the observed and the calculated values of χ_M of an acid and its anhydride will thus be a measure

† Baeyer's strain theory assumed that the carbon atoms of the ring must lie in a plane and on this basis rings containing six and more carbon atoms involved a negative strain, which was greater as the size of the ring increased. This part of Baeyer's theory has now been discarded: Sachse[4] in 1890 first put forward the idea of stainless rings which was later elaborated by Mohr[4] and has recently been confirmed by experiment. Since stable rings of as many as 32 carbon atoms are now known, there is no necessity of assuming a planar form for any ring of more than five members and the hypothesis of strainless rings of six and higher members in which the atoms forming the ring do not lie in a plane but must take up a multiplanar configuration has been widely adopted by chemists. It should, however, be pointed out that there is evidence that some strain persists even in compounds containing very large rings.[5]

o the strain in rings of different sizes. This point is further elaborated in the discussion.

Experimental

Preparation of materials.—Succinic acid was purified by repeated crystallisation from hot water, when it was obtained as colourless prisms, m.p. 185° C.

Succinic anhydride was obtained by refluxing succinic acid with excess of acetyl chloride. It was then poured into a shallow dish and allowed to stand in a soda lime vacuum desiccator until acetyl chloride and acetic acid were cmpletely removed. It was recrystallised from absolute alcohol or anhydrous chloroform as long needles, m.p. 119–20°. It is essential that the solvent should be free from all traces of moisture, otherwise on re-crystallisation succinic anhydride is hydrolysed and the melting point falls.

Magnetic Measurements.—The magnetic susceptibility measurements were carried out on a modified form of Guoy's Balance. The working of the balance was checked by making determinations of magnetic susceptibility of a few standard substances. The same procedure was followed with succinic acid and succinic anhydride. The results of these measurements are recorded in Table I.

TABLE I

Substance	m.p.	$-\chi \times 10^6$ (per gram)	$-\chi_M \times 10^6$ (per gram molecule)	$-\chi_M \times 10^6$ (Gray and Birse[2])
Succinic acid ..	185°	0·487	57·47	54·45
Succinic anhydride	119–120°	(i) 0·438 (ii) 0·439	43·85	47·53
Difference ..	..	..	13·62	6·92

Discussion of Results

The value of succinic acid, calculated on Pascal's additivity law from the atomic susceptibility of the elements, agrees with the experimental value:

Succinic Acid $CH_2.CO.OH$

$CH_2.CO.OH$, Mol. wt. = 118

χ_M (Calc.) $= (4\,C) + (6H) + (2O'') + (2-O-)$

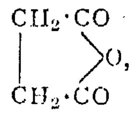
$= -(24{\cdot}00 + 17{\cdot}58 + 6{\cdot}72 + 9{\cdot}22)$

$= -57{\cdot}52$

χ_M (Obs., Table I) $= -57{\cdot}47$

Deviation 0·1 per cent.

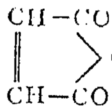
Succinic Anhydride,



Mol. wt.=100

The sum of the atomic susceptibilities of four carbon, four hydrogen and three oxygen atoms, two of which have $(\chi_A)_0 = -3{\cdot}36$ and one has $(\chi_A)_0 = -4{\cdot}61$, is equal to $-47{\cdot}05$ and is greater than the experimental value of χ_M $-43{\cdot}85$ (Table I) by $-3{\cdot}2$. The paramagnetic contribution of the 5-membered heterocyclic ring of the anhydride is, therefore, equal to $+3{\cdot}2$. We have evaluated, as shown in the earlier part of this paper, the paramagnetic effect of anhydride rings as $+2{\cdot}53$, provided no strain factor due to ring structure affecting magnetic susceptibility was involved. It may, therefore, be concluded from these magnetic measurements that the strain involved in the formation of the 5-membered ring in succinic anhydride is very small, as is to be expected.

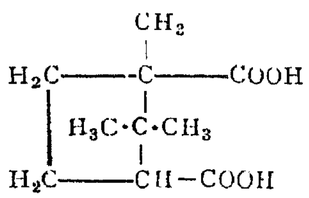
Maleic anhydride



Mol. wt.=98

Similarly the calculated value of the susceptibility of maleic acid is $-49{\cdot}73$, as against the observed value[2] $-49{\cdot}52$, showing a very close agreement. On the other hand, the calculated value of maleic anhydride* agrees with the experimental value only when the effect of the ring-closure is taken into account. Here again the contribution for the ring comes out to be nearly the same as before, namely $+3{\cdot}45$ as against $+3{\cdot}2$ deduced for succinic anhydride. The small difference between the two values is probably within experimental errors. If genuine, it may be attributed to the extra strain due to the presence of a double bond in the ring of maleic anhydride, which is absent in the ring structure of succinic anhydride.

Camphoric Acid



* The sum of the atomic susceptibilities of the elements ($-41{\cdot}19$), the constitutive correction constant due to tertiary carbon atoms in relation to the two functional groups containing oxygen ($-3{\cdot}54$) and the effect of the double bond ($+5{\cdot}47$) add up to $-39{\cdot}26$ as against the observed value[2] of magnetic susceptibility $-35{\cdot}81$, giving a paramagnetic effect of the ring as $+3{\cdot}45$.

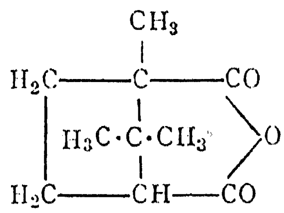
Similarly the molecular susceptibility of camphoric acid may be calculated on the basis of the additivity law, as follows:—

(*a*) Sum of the atomic susceptibilities of 10 carbon, 16 hydrogen and 4 oxygen atoms—2 of the oxygens are doubly bound and the other two singly bound $= -122 \cdot 74$

(*b*) Diamagnetic contribution of quaternary and tertiary carbon atoms on two* functional groups containing oxygen $= -6 \cdot 62$.

(*c*) The contribution of the cyclopentano ring containing a *gem*-di-methyl group (λ) is obtained as $+4 \cdot 16$, when the sum of *a*, *b* and *c* factors is equated with the observed value[1] of gram-molecular susceptibility of camphoric acid ($-125 \cdot 2$).

It is found that in camphoric anhydride,



in order to get a fit between the calculated and the observed value[1] ($-112 \cdot 2$) of susceptibility, the effect of the six-membered heterocyclic ring, formed on passing from the acid into the anhydride, has to be taken as $+2 \cdot 61$,† which is nearly the same as in the other two anhydrides referred to above.

In Table II, the paramagnetic effect of the 5- and 6-membered anhydride rings is shown.

TABLE II

	Contribution due to the heterocyclic ring
1. Succinic anhydride (5-membered) ..	+ 3·2
2. Maleic anhydride (5- „) ..	+ 3·45
3. Camphoric anhydride (6- „) ..	+ 2·61
	Mean + 3·09

* In a previous communication,[1] where a similar calculation was made, the effect of the tertiary and quaternary carbon atoms on only *one* of the two functional groups containing oxygen was taken into account. The neglect of the effect of the tertiary and quaternary carbon atoms on the other functional group and also of the effect of the cyclopentane ring, on the susceptibility, both due to oversight, almost cancel each other.

† In a previous communication,[1] already referred to, it was stated that the ring closure in camphoric anhydride had no effect on its magnetic susceptibility, unlike on optical activity. This is not correct as the value of the paramagnetic effect ($+2 \cdot 61$) above calculated for the 6-membered anhydride ring shows. At the same time, it is to be admitted that whereas optical activity in camphoric anhydride is phenomenally depressed, ($\alpha = 0$), ring closure has not this marked effect on its susceptibility.

In calculating the value of the gram-molecular susceptibility of camphoric anhydride, the paramagnetic effect of the cyclopentane ring with a *gem*-dimethyl group (+ 4·16) taken in the calculation was deduced from the susceptibility value of camphoric acid which also contains this ring. It may, however, be noted that it is lower than Pascal's value (+ 7·2) for the cyclopentane series.

The observed differences in the gram-molecular susceptibilities of camphoric, maleic and succinic acids and their corresponding anhydrides are given in Table III.

TABLE III

	$-\chi_M \times 10^6$	Difference
Camphoric acid[1]	125·20	12·95
Camphoric anhydride[1]	112·25	
Maleic acid[2]	49·52	13·71
Maleic anhydride[2]	35·81	
Succinic acid (Table I)	57·47	13·62
Succinic anhydride (Table 1)	43·85	

We thus see that the observed difference between the susceptibilities of dicarboxylic acids and the corresponding anhydrides, which in all the three cases is nearly equal to the susceptibility of water (− 13·0), can be explained on the additivity law, if the anhydride ring is taken to contribute about + 3 to the molecular susceptibility. The small variaion in this contribution observed in the different anhydrides is well within experimental error, and is also of the same order as may be expected from the different amounts of strain in the rings in the three anhydrides.

SUMMARY

(1) Measurements have been made on the magnetic susceptibilities of succinic acid and its anhydride.

The susceptibilities are:

$$\chi_M = -57\cdot47 \times 10^{-6} \text{ for the acid;}$$

$$\chi_M = -43\cdot85 \times 10^{-6} \text{ for the anhydride.}$$

(2) The difference between the gram-molecular susceptibilities of succinic acid and its anhydride is that of a molecule of water. This is to be expected, both from considerations based on the additivity law, and from observations on other acids and their anhydrides, namely camphoric acid, maleic acid and their corresponding anhydrides.

(3) The difference of about 13 is numerically more than can be attributed to two atoms of hydrogen and one of singly linked oxygen, which will give only 10·47.

(4) The extra effect is attributed to the formation of a ring in the anhydride, the paramagnetic contribution of which may be taken as about + 2·5.

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