THE DIAMAGNETIC SUSCEPTIBILITIES OF PHTHALIC ACID AND PHTHALIC ANHYDRIDE

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In two previous communications[1,2] we have commented on the values of magnetic susceptibilities of camphoric and succinic acids and their respective anhydrides as recorded by Gray and Birse.[3] It was shown that the mean difference in the values of gram-molecular susceptibilities of optically active camphoric acids and their corresponding anhydrides was $- 12 \cdot 95 \times 10^{-6}$ (as against $- 37 \times 10^{-6}$ found by Gray and Birse)[3] and that the difference between the gram-molecular susceptibilities of succinic acid and its anhydride was $- 13 \cdot 62 \times 10^{-6}$ (Gray and Birse found $- 6 \cdot 92 \times 10^{-6}$). The differences found by us are, however, nearly equal to the gram-molecular susceptibility of water ($- 12 \cdot 96 \times 10^{-6}$). These results are exactly in conformity with Pascal's additivity law and incidentally show that the earlier values of Gray and Birse[3] were erroneous.

We have further examined in this paper the cases of phthalic acid and its anhydride. Gray and Birse[3] found that the gram-molecular susceptibility of phthalic acid was $- 81 \cdot 38$* and its anhydride, $- 66 \cdot 01$. The difference ($- 15 \cdot 37$) between the values of gram-molecular susceptibilities of phthalic acid and its anhydride is thus higher than that for the gram-molecular susceptibility of water ($- 12 \cdot 96$). We have, therefore, repeated this work with carefully purified materials and find that the gram-molecular susceptibility of phthalic acid is $- 81 \cdot 24$ and that of its anhydride $- 67 \cdot 31$: The difference in these values comes to be $- 13 \cdot 93$ which is about one unit higher than the gram-molecular susceptibility of water.

EXPERIMENTAL

Phthalic acid

Phthalic acid was prepared by oxidising naphthalene with concentrated sulphuric acid in the presence of mercuric sulphate as a catalyst.[4] It was purified by repeated crystallisations from hot water when it was obtained as short prisms, m.p. 213° C.

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

Phthalic anhydride

Phthalic anhydride was obtained by heating phthalic acid in a sublimation apparatus. The sublimate which consisted of long needles was pure anhydride, m.p. 128° C.

The measurements of magnetic susceptibility were carried out on a modified type of Guoy's Balance. The working of the balance was checked by making determinations of magnetic susceptibilities of compounds with known values. Special care was taken in the purification of the substances used in these measurements, particularly in avoiding their contamination with any paramagnetic impurity. The compounds were carefully dried in vacuum for several days before use. 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[4])
Phthalic acid	213°	0·4894	81·24	81·38
Phthalic anhydride	128°	0·4548	67·31	66·01
Difference			13·93	15·37

DISCUSSION

We now illustrate the values given in the above mentioned measurements (Table I) by calculating the gram-molecular susceptibilities of phthalic acid and phthalic anhydride using Pascal's corrected values for susceptibility constants and constitutive correction constants (λ) as follows:

1. Phthalic acid, $(C_8H_6O_4)$, $\begin{array}{c}\text{—COOH}\\\text{—COOH}\end{array}$
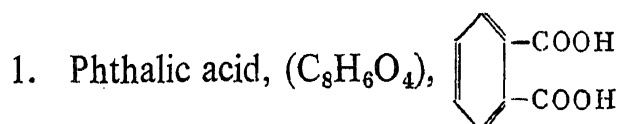
(i) Atomic Susceptibilities:

8 Carbon atoms $= -6\cdot00 \times 8 = -48\cdot00$

6 Hydrogen atoms $= -2\cdot93 \times 6 = -17\cdot58$

2 [= O] $= -3\cdot36 \times 2 = -6\cdot72$

2 [– O –] $= -4\cdot61 \times 2 = -9\cdot22$

(ii) Constitutive correction constants (λ)

one benzene nucleus $= -1\cdot44 \times 1 = -1\cdot44$

Calculated value $= -82\cdot96$

Experimental value (Table I) $= -81\cdot24$

Percentage deviation $= 2\cdot07$

The diamagnetic contribution of the two quaternary carbon atoms on the two functional groups containing oxygen $\left(-C\diagdown\begin{smallmatrix}O\\OH\end{smallmatrix}\right)$ cancels out on account of their symmetrical position with regard to the phenylene group.

2. Phthalic anhydride, $C_8H_4O_3$,
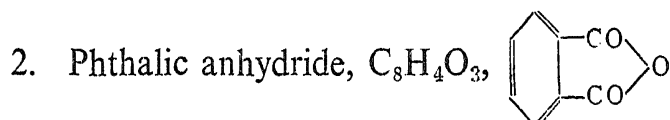
(i) Atomic susceptibilities:

8 Carbon atoms	$= -6 \cdot 00 \times 8 =$	$- 48 \cdot 00$
4 Hydrogen atoms	$= -2 \cdot 93 \times 4 =$	$- 11 \cdot 72$
2 [= O]	$= -3 \cdot 36 \times 2 =$	$- 6 \cdot 72$
1 [- O -]	$= -4 \cdot 61 \times 1 =$	$- 4 \cdot 61$

(ii) Constitutive correction constant (λ)

one benzene nucleus	$= -1 \cdot 44 \times 1 =$	$- 1 \cdot 44$
Calculated value ..		$= -72 \cdot 49$

There is no constitutive correction for oxygen due to symmetry.
Experimental value (Table I) .. $= -67 \cdot 31$

The difference between the calculated and experimental values ($+5 \cdot 18$) must be attributed to the ring structure of phthalic anhydride.

The observed difference in the gram-molecular susceptibilities of dibasic acids and their anhydrides are given in Table II.

TABLE II

	$- \chi_M \times 10^6$	Difference
Camphoric acid[1] ..	125·20	12·95
Camphoric anhydride[1] ..	112·25	
Succinic acid[2] ..	57·47	13·62
Succinic anhydride[2] ..	43·85	
Phthalic scid ..	81·24	13·93
Phthalic anyhydride ..	67·31	

It will be observed that the difference between the susceptibilities of dicarboxylic acids and their corresponding anhydrides (Table II) is nearly equal to (-13), the gram-molecular susceptibility of water. This is in exact accordance with Pascal's law as these anhydrides are formed from the acids by the loss of a molecule of water.

CONSTITUTIVE CORRECTION CONSTANT FOR WATER

The observed gram-molecular susceptibility of water is $-12 \cdot 96$, whereas on Pascal's additivity law, it should be $-10 \cdot 47$. The difference ($-2 \cdot 49$) is thus the constitutive correction constant (λ) for a gram-molecule of water.

In Table III, the paramagnetic effects of the 5- and 6-membered rings are shown.

TABLE III

Name of the anhydride		Contribution due to the heterocyclic ring
Camphoric anhydride (6-membered)[2]	..	+ 2·61
Succinic anhydride (5-membered)[2]	..	+ 3·21
Phthalic anhydride (5-membered)	..	+ 5·18

The 6-membered ring in camphoric anhydride contains a *gem*-dimethyl group; it is, therefore, under the least strain. The 5-membered anhydride ring in phthalic anhydride would appear to be under the greatest strain on account of its conjugation with a benzene ring. The 5-membered ring in succinic anhydride would occupy an intermediate position. The paramagnetic effects of the different rings given in Table III are thus qualitatively proportional to the strain in them.

ACKNOWLEDGEMENT

SUMMARY

1. The gram-molecular susceptibilities of carefully purified samples of phthalic acid and its anhydride are determined.

The susceptibilities are:

$$\text{Phthalic acid, } \chi_M \quad .. \quad .. = -81\cdot24 \times 10^{-6}$$
$$\text{Phthalic anhydride, } \chi_M .. \quad .. = -67\cdot31 \times 10^{-6}$$

It is found that whereas the value of the gram-molecular susceptibility of phthalic acid found by Gray and Birse and ourselves is nearly equal, that for the anhydride is higher in our case.

2. The difference in gram-molecular susceptibilities of dibasic acids and their anhydrides is nearly equal to that of water with minor variations, possibly due to different structures attached to the anhydride rings.

3. The constitutive effect of the rings in the anhydrides of different dibasic acids has also been discussed.

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