On the Magnetic Susceptibilities of Troponoid System. II : Diamagnetism of Methyl Ether Derivatives

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Diamagnetism of Methyl Ether Derivatives

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Synopsis

The magnetic susceptibiilties of tropolone methyl ether (Ia), 2-methoxy-7-bromo-tropone (o-bromo-tropolone methyl ether) (II) and α-thujaplicin methyl ether (III) have been measured by use of the Gouy balance described in the previous article.[1] The experimental results $(-\chi_M \times 10^6)$ obtained for (Ia), (II) and (III) are 71, 88 and 105 respectively.

The susceptibility of crystalline form of (Ia), i.e., $(C_8H_8O_2)_2 2H_2O$ (Ib), has been also measured, the result being -160×10^{-6} per mole.

It has been shown that the value of ΔK_M, which shows the diamagnetic anisotropy of the tropolone ring belonging to each compound, can be easily derived approximately fromt he experimental value by the application of the empirical additive rule.

The remarkable diamagnetic decrements have been observed in the ΔK_M values, the amounts of which depend upon the kinds of the substituents, i.e., OCH_3, Br and isopropyl groups. The results have shown that the ΔK_M value of (II) is almost zero and that of (Ia) is half the value of tropolone itself.

I. Introduction

In the previous article[1], the diamagnetisms of hinokitiol and α-thujaplicin were reported. The susceptibilities of tropolone methyl ether, 2-methoxy-7.bromo-tropone (o-bromotropolone methyl ether) and α-thujaplicin methyl ether have been measured with the same apparatus as before[1]. From the results obtained in the present experiments, it has been observed, in these substances, that the effects caused by the various substituents which lead to the occurrence of the diamagnetic decrements are larger than those in cases of benzene derivatives, because of the characteristic constitution of the tropolone ring.

II. Experimental results and discussion

1. Tropolone methyl ether (Ia)

By reaction of tropolone with diazomethane in ether, light yellow crystal (m. p., 41°C) was obtained, which was composed of 2 moles of tropolone methyl ether and 1 mole of water of crystallization, having the constitution[2] : $(C_8H_8O_2)_2 \cdot H_2O$.

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* The Chem. Inst., Fac. Sci.

(1) G. Hazato, T. Nozoe, T. Ikenoue, J. Maruha, Y. Kitahara, T. Miura, Sci. Rep. RITU., **A5** (1953), 278.

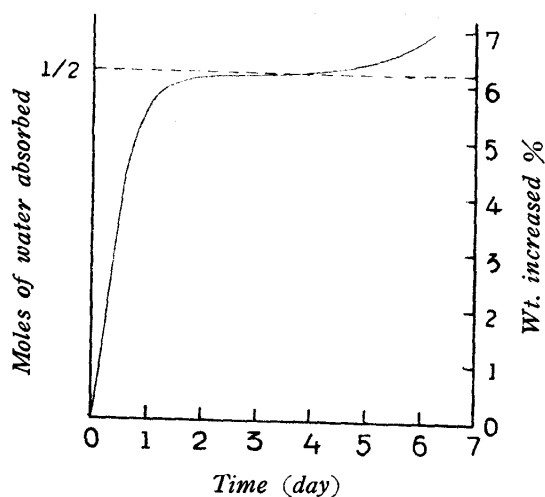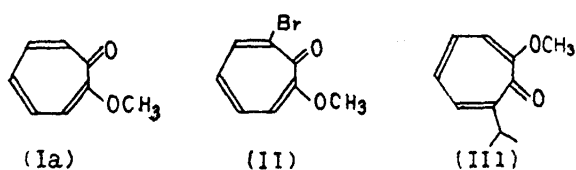(2) T. Nozoe, Sh. Seto, T. Ikemi, T. Arai, Proc. Japan Acad., **27** (1951), 102.

(Ia)   (II)   (III)

Fig. 1

Time (day)

Moles of water absorbed   *Wt. increased %*

By drying in vacuum desiccator or by distillation under reduced pressure (128°C/5 mm), it gave tropolone methyl ether (Ia) itself[2], an oily substance, loosing water of crystallization. On standing in the air, it returned to crystal again, by absorbing half a mole of water, and then it gradually absorbed more water, the process of which being represented in Fig. 1[2].

The observed susceptibilities of the oily compound (Ia) and the crystalline one, $(C_8H_8O_2)_2 \cdot H_2O$, are respectively[3];

(Ia) : $\chi_M = -(71\pm2)\times10^{-6}$,

$(C_8H_8O_2)_2 \cdot H_2O$:

$\chi_M = -(160\pm7)\times10^{-6}$.

2. 2-methoxy-7-bromo-tropone (o-bromo-tropolone methyl ether)

The compound having the melting point 90.5~91.5°, was used as the sample, prepared by reaction of o-bromo-tropolone and diazomethane in ether[4], the measured value of which is $\chi_M = -88\times10^{-6}$.

3. α-thujaplicin methyl ether (III)

The compound was prepared by the reaction of α-thujaplicin and diazomethane in ether, as in case of (Ia) and (II), m. p. 71.5－72.5°C[5].

The measured value; $\chi_M = -105\times10^{-6}$.

The measured values and the corresponding calculated ones are shown in Table 1.

Table 1

Sample	$-\chi_M\times10^{-6}$			$-\chi_{\parallel}\times10^6$ (Add.)		α (Contribution of B-Type)
	(Meas.)	(Add.)	(Diff.)	(A-Type)[6]	(B-Type)[6]	
Tropolone methyl ether[3]						
$C_8H_8O_2$(oil) (Ia)	71	86(a)	15	58	64	0.4₆
$(C_8H_8O_2)_2 \cdot H_2O$(crystal)	160	185(aa)	25	130	141	0.5₄
		155(bb)	5			
		170(ab)	10			
		157(Aa)	3			
2-methoxy-7-bromo tropone						
$C_8H_7BrO_2$(II)	88	116(a)	28	88	94	0.0
		101(b)	13			
α-Thujaplicin methyl ether						
$C_{11}H_{14}O_2$(III)	105	121(a)	16	93	99	0.4₂
		106(b)	1			
		112(c)	7			
α-Thujaplicin[1]	100	110(a)	10	82	88	0.6₄

(3) Presented at the 4th Annual Meeting of the Chemical Society of Japan (April 8th, 1951).
(4) T. Nozoe, Y. Kitahara, K. Yamane, A. Yoshikoshi, Proc. Japan Acad., 27 (1951), 18.
(5) T. Nozoe, Y. Kitahara, K. Yamane, T. Ikemi, ibid., 27 (1951), 193.
(6) T. Nozoe, ibid., 26, No. 9 (1950), 30 ; or cf. ref. (1).

The values indicated by (a) are the hypothetical ones calculated additively from the measured value of tropolone[7], the mother substance of these compounds, by use of the values in Table 1 in the previous report[1]; assuming the π-electronic structure of the tropolone ring remains unchanged, even though after the substitution reaction has been performed on the ring skeleton. The values indicated by (b) and (c) were also calculated in the similar way as in case of (a) based on the observed values of (Ia) and α-thujaplicin[1] respectively. $\chi_{\parallel}$ shows the calculated susceptibility per mole of molecule under the assumption that the seven memberec ring of each molecule has a planar structure, and furthermore, the molecular plain and the magnetic field direction are parallel with each other. Speaking more generally, $\chi_{\parallel}$ shows the susceptibility neglecting ΔK_M which is the value of magnetic anisotropy caused by the revolution of π electrons along the closed planar orbits (in this case, the orbits along the seven membered ring). The calculating procedures of the $\chi_{\parallel}$ values, referring to the A and the B types[6], correspond to the formula (5) and (8) in the previous report respectively[8]. α shows the contribution of the B type when the constitution of the tropolone ring is assumed to be expressed by the mesomerism between the A and B types. The values of α were obtained by the conventional additive method which is shown by the following formula, utilizing the values of Table 1 in the present paper.

$$\chi_M \text{(meas.)} = [\Delta K_M + \chi_{\parallel}(B)]\alpha + \chi_{\parallel}(A)(1-\alpha) \qquad (1)$$

In this case, the value of ΔK_M in the A type is zero[1]. As the value of $\overline{\Delta K_M}$, the theoretical value; -22×10^{-6} was used which has been shown in the formula (7') of the previous report[1]. The sum of the theoretical $\overline{\Delta K_M}$ and the calculated $\chi_{\parallel}(B)$ values is in good coincidence with the measured value[7] of tropolone itself. Now the difference between the calculated values of the A and the B types in $\chi_{\parallel} \times 10^6$ is 6 or its multiple. This is the contribution due to the polarisation of $C-O \rightarrow C^+-O^-$, which being shown by the difference between the values of the formulae (5) and (8) in the previous report[1]. Here, the formula (1) shows that both ΔK_M and $\chi_{\parallel}(B)$ are included in the same bracket referring to the contribution of the B type, i. e., the necessary condition for the occurrence of ΔK_M is the polarization of the carbonyl group. Moreover, in formula (1), χ_M is represented in a linear relation with the two states A and B. Whereas, in view of the quantum mechanical weight, the relation of the formula (1) should stand only with the case of the so-called orthogonality being satisfied between the A and the B types. When this condition were not satisfied, the value of α would show sometimes about 10 per cent deviation from the case of the formula (1). Aside from this fact in the present case, we shall begin with the treatment of the experimental result by use of the formula (1) to obtain the relative values of α in each compound.

In Table 1, we can see a remarkable diamagnetic decrement in the measured

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(7) $\chi_M = -74 \times 10^{-6}$; Presented at the Annual Local Meeting of the Chemical Society of Japan in Sendai, Dec. 4, (1950).

(8) For the value of Br in (III), -33×10^{-6} was adopted, which was derived from the measured values of C_6H_5Br and C_6H_6.

value, in every case, comparing with that derived from the measured one of tropolone which is indicated by (a). Such phenomenon is observed only in case of the quinoid form in the series of benzene derivatives, and it can be considered to be one of the special features in the unsaturated seven membered ring. Namely, the fact shows that the electronic state of π electrons, taking part in the formation of the tropolone ring, is distinctly affected by the ordinary substitution groups. In case of (II), this trend is especially large; the measured value supports almost completely the constitution of the A-type[6], so that it has neither the contribution of $\overline{\Delta K_M}$, nor the polarization of carbonyl group and it is also supposed that (II) will not have the so-called aromatic sharacter. Among the present samples measured, the result of (II) shows the extreme feature.

The difference 15 between the measured value of (Ia) and the additive one can be assumed to be the sum of the two deviations. The one is a fractional change referring to $\overline{\Delta K_M}$ caused by the substitution of the OH group, in tropolone ring, by the OCH$_3$ group, and the other is the deviation between the two $\chi_{\parallel}$'s caused by the fractional transformation from the B tyne to the A one. The contribution of the latter to 15 is $3.2(=15 \times -\frac{6}{28})$ so that $\overline{\Delta K_M}$ is reduced almost by half; 11.8. In consequence of bromine substitution in (Ia) to obtain (II), χ_M value of the latter suffers a loss of 13, a part of which the amount 10.2 has come from $\overline{\Delta K_M}$ and 2.8 from $\chi_{\parallel}$.

Now, in case of (III), 121 (a) $-105=16$. Whereas, the difference between 106(b) and the measured value (105) can be disregarded, so that the effect of the iso-propyl group substituted in (Ia) is almost negligible. On the other hand, starting from the measured value of α-thujaplicin[1], the diamagnetic decrement of about 10 was already perceived by the mere substitution of isopropyl group to the mother body, tropolone, and further decrement of only about 7 was observed in this case by substituting OH by OCH$_3$. Namely, when two or more different substitutions are made in the tropolone ring in succession, it is perceived that each substitution effect on the $\overline{\Delta K_M}$ value depends largely upon the sequence of the substitution process. As the result, it may be concluded, in case of (III), that both methoxyl and isopropyl substituents coexist in the ring and emulate with each other, however, on the average, the former is predominant over the latter in the effect of the diamagnetic decrement.

In a recent paper, the following chemical constitution shown in (Ib), has been proposed for the crystal substance of $(C_8H_8O_2)_2 \cdot H_2O$[2]. The value of χ_M evaluated

(Ib)
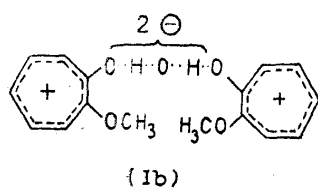
according to this model is too large as shown by (aa) in Table 1, and it is also unreasonable to assign $2\ominus$ to H$_2$O. Although the measured value presented here is an average one of five measurements, there are large deviations between them, perhaps, owing to the discord of water content. As the values indicated by (bb), (ab) and (Aa) lie also within or near the experimental error of the observed one,

we have to expect the further careful measurements to select the most proper model.

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