Dipole Moments of Halogen-Derivatives of Hinokitiol

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Introduction

In the previous paper,(1) we reported the results of measurements on the dipole moments of tropolone,(2) hinokitiol(4-isopropylcyclohepta-triene-2, 4, 6-ol-2-one-1)(3) and their derivatives. We arrived at the conclusion that these molecules resonate among various electronic structures contributing to the normal states of these molecules and that the cycloheptatrienolone ring is planar. We found that the dipole moment of hinokitiol is nearly pointing along the line from the center of the ring to the C-atom at 2-position with a positive end at the ring, as shown in the Figure 2 in the next paper.(4)

We have prepared another halogen-derivatives of hinokitiol and carried out, besides investigations in the field of organic chemistry, measurements on the dipole moments of these compounds to determine the position of substituents in these compounds.

Experimental Method and Materials

The dipole moments were measured in benzene solution at 25°. The apparatus and the method of measurements were the same as described in the previous report.(1) The materials used were prepared by one of us and his collaborator. They are: β-monobromohinokitiol, m. p. 42°, α-monochlorohinokitiol, m. p. 117.5-8.5°, β-monochlorohinokitiol, m. p. 47.6-8.5°, γ-monochlorohinokitiol,(5) m. p. 44-46°, and α-dichlorohinokitiol,(6) m. p. 126-7°.

Experimental Results

For the extrapolation of molecular polarization to infinite dilution, Hedestrand's method(7) was used, *i.e.*,

$$\varepsilon_{12} = \varepsilon_1 + \alpha w_2,$$
$$d_{12} = d_1 + \beta w_2,$$
$$p_{2\infty} = p_1\left(1-\frac{\beta}{d_1}\right)+\alpha C,$$
$$C=\frac{3}{d_1(\varepsilon_1+2)^2},$$

where p and w denote specific polarization and weight fraction respectively. Other notations have their usual significances. For benzene at 25°, we have

$$p_1 = 0.3414 \text{ cc./g.},$$
$$d_1 = 0.8727 \text{ g./cc.},$$
$$C = 0.1883 \text{ cc./g.},$$

which can be used throughout the whole calculation. The results are shown in Table 1, in which P and R_D denote molecular polarization and molecular refraction for D-line respectively.

Table 1

Dipole Moments of Halogen-Derivatives of Hinokitiol, 25°

β-monobromohinokitiol		
w_2, %	ε_{12}	d_{12}
0	2.273	0.8727
0.629	2.329	0.8749
1.118	2.374	0.8767
1.382	2.393	0.8777
$\alpha=8.87$, $\beta=0.35$, $P_{2\infty}=455.6$ cc., $R_D=54.1$ cc., $\mu=4.40$ D		
α-monochlorohinokitiol		
0	2.273	0.8727
0.697	2.301	0.8744
1.116	2.319	0.8756
1.957	2.356	0.8778
$\alpha=4.13$, $\beta=0.26$, $P_{2\infty}=202.0$ cc., $R_D=51.2$ cc., $\mu=2.70$ D		
β-monochlorohinokitiol		
0	2.273	0.8727
0.546	2.330	0.8741
1.075	2.389	0.8755
1.855	2.473	0.8776
$\alpha=10.7$, $\beta=0.26$, $P_{2\infty}=447.8$ cc., $R_D=51.2$ cc., $\mu=4.38$ D		

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(1) Y. Kurita, T. Nozoe and M. Kubo, This Bulletin, **24**, 10 (1951).

(2) T. Nozoe, S. Seto, Y. Kitahara, M. Kunori and Y. Nakayama, *Proc. Japan Acad.*, **26** (No. 7), 38 (1950).

(3) T. Nozoe, *Yakugaku* (*Science of Drugs*), **3**, 172 (1949); *Proc. Japan Acad.*, **26** (No. 9), 30 (1950).

(4) Y. Kurita and M. Kubo, This Bulletin, **24**, 13 (1951).

(5) T. Nozoe, T. Mukai and K. Takase, *Proc. Japan Acad.*, **26** (No. 8), 19 (1950).

(6) T. Nozoe, K. Kikuchi and T. Ando, *Proc. Japan Acad.*, **26** (No. 10), 32 (1950).

(7) G. Hedestrand, *Z. physik. Chem.*, **B 2**, 428 (1929).

γ-monochlorohinokitiol

0	2.273	0.8727
0.465	2.332	0.8739
0.919	2.386	0.8750
1.467	2.457	0.8764

$\alpha=12.5$, $\beta=0.25$, $P_{2\infty}=515.9$ cc.,
$R_D=51.2$ cc., $\mu=4.74$ D

α-dichlorohinokitiol

0	2.273	0.8727
0.610	2.331	0.8745
1.196	2.388	0.8765
1.675	2.430	0.8779

$\alpha=9.50$, $\beta=0.31$, $P_{2\infty}=468.3$ cc.,
$R_D=56.1$ cc., $\mu=4.46$ D

Discussion

We have already measured the dipole moment of hinokitiol and determined the direction of the moment in the molecule. The conceivable position of substituent in bromohinokitiol are 3 (ortho), 5 (para) or 7 (ortho') as justified by molecular orbital treatment,(4) which have shown that π-electron distribution is concentrated at C-atoms 3, 5 and 7. The cycloheptatrienolone ring is planar. We may, as a first approximation, assume that the ring has a regular heptagon form. Assuming the bond moment $\mu(\mathrm{C-Br})=1.48$ D as before, we can calculate the theoretical moments for 3-bromo-, 5-bromo- and 7-bromohinokitiol to be 4.8 D, 2.6 D and 4.32 D(8) respectively. Comparing these values with the observed one, it is concluded that the position of substituent in β-monobromohinokitiol is 3 (ortho).

The bond moment $\mu(\mathrm{C-Cl})$ is 2.0 D in aliphatic compounds and 1.5∼1.7 D in benzene derivatives. Assuming $\mu(\mathrm{C-Cl})=1.7$ D, we can calculate the theoretical moments for monochloro- and dichlorohinokitiols. The results are: 3-monochlorohinokitiol, 4.95 D; 5-monochlorohinokitiol, 2.4 D; 7-monochlorohinokitiol, 4.4 D; 3, 5-dichlorohinokitiol, 3.6 D; 3, 7-dichlorohinokitiol, 4.8 D; and 5, 7-dichlorohinokitiol, 2.8 D. Comparing these values with the observed ones, it is concluded that the position of substituents in α-monochlorohinokitiol is 5 (para), in β-monochlorohinokitiol 7 (ortho'), in γ-monochlorohinokitiol 3 (ortho) and α-dichlorohinokitiol is 3, 7-dichloroderivative. The results are summarized in Table 2.

Table 2
The Position of Substituents in Halogenated Hinokitiols

Hinokitiol derivatives	$\mu_{\mathrm{obs.}}$	$\mu_{\mathrm{calc.}}$	Position of substituents
α-monobromo-	4.32 D	(4.32 D)	7 or *o'*
β-monobromo-	4.40 D	4.8 D	3 or *o*
γ-monobromo-	—	2.6 D	5 or *p*
α-dibromo-	4.27 D	4.7 D	3, 7 or *oo'*
β-dibromo-	3.14 D	2.9 D	5, 7 or *o'p*
dibromo-	—	3.7 D	3, 5 or *op*
α-monochloro-	2.70 D	2.4 D	5 or *p*
β-monochloro-	4.38 D	4.4 D	7 or *o'*
γ-monochloro-	4.74 D	4.95 D	3 or *o*
α-dichloro-	4.46 D	4.8 D	3, 7 or *oo'*
β-dichloro-	—	2.8 D	5, 7 or *o'p*
dichloro-	—	3.6 D	3, 5 or *op*

These conclusions are in conformity with and supported by the results of structural determinations in organic chemistry carried out by one of us (Nozoe) and his collaborators.(5),(6),(9)

Summary

The dipole moments of halogen-derivatives of hinokitiol (4-isopropylcycloheptatriene-2, 4, 6-ol-2-one-1) were measured in benzene solution at 25°. The values obtained are: β-monobromohinokitiol (3-bromo-), 4.40 D; α-monochlorohinokitiol (5-chloro-), 2.70 D; β-monochlorohinokitiol (7-chloro-), 4.38 D; γ-monochlorohinokitiol (3-chloro-), 4.74 D; α-dichlorohinokitiol (3, 7-dichloro-), 4.46 D. By analysing the results obtained, the position of substituents in the halogenated hinokitiols were determined and are given immediately after each name of these compounds in parentheses.

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(8) α-Monobromohinokitiol (μ=4.32 D) was assigned to 7-mono-bromohinokitiol from considerations in organic chemistry.(3),(5)

(9) T. Nozoe, Y. Kitahara and K. Doi, *Proc. Japan Acad.*, **26** (No. 10), 25 (1950).