Dipole Moments of Bromotropolones, Thujaplicins and Related Compounds*

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We have already measured the dipole moments of tropolone and some of its derivatives,(1) (2) (3) and discussed the results in relation to the molecular structure of these compounds and to the electronic structure of tropolone as derived from molecular orbital treatment. The present investigation was undertaken in order to determine the position of substituents in seven new kinds of tropolone derivatives synthesized by one of us (Nozoe) and his collaborators. From the studies on magnetic susceptibility, Hazato and his collaborators suggested that tribromotropolone lacks aromatic properties characteristic of tropolone derivatives.(4) We hoped that the dipole moment measurement would reveal some feature of interest concerning the peculiarity of this compound. Nozoe has reported that unlike other tropolone derivatives α-thujaplicin forms two kinds of crystals of different melting points.(5) It seemed to be interesting to decide whether the difference of the two forms is due merely to the arrangement of molecules in crystals or whether the two crystals are made up of molecules of different molecular structure such that they give different dipole moments in solution.

Experimental Method and Results.—All the measurements were made in benzene solution at 25°C. The dielectric constant was measured with the apparatus reported in the previous paper.(1) The materials used were synthesized and purified in the laboratory of organic chemistry in Tohoku University. The amount of each sample at our disposal was less than 0.3 g. and we were obliged to be satisfied with measurements on solutions of a few different concentrations. As some of these compounds were hygroscopic, we employed a modified Hedestrand method similar to that introduced by Halverstad and Kumler(6) for obtaining specific polarization $p_{2\infty}$ at infinite dilution, differing in the fact that densities were used rather than specific volumes.

$$p_{2\infty}=p_1+C\alpha-\frac{p_1}{d_1}\beta \tag{1}$$

Here p_1 and d_1 denote the specific polarization and density of the solvent, α and β are the rates of change of the dielectric constant ε and density d with weight fraction w,

$$\varepsilon_{12}=\varepsilon_1+\alpha w_2,\quad d_{12}=d_1+\beta w_2 \tag{2}$$

and

$$C=3/d_1(\varepsilon_1+2)^2 \tag{3}$$

where the suffixes 12, 1 and 2 signify the solution, solvent and solute respectively. The crucial data affecting the value of $p_{2\infty}$ were α and β. In evaluating the values for these two constants with equation (2), we used the data on solution alone to minimize the possible effect of moisture content. The probable errors $\delta\alpha$ and $\delta\beta$ estimated by least square method gave for the probable error $\delta p_{2\infty}$ the value

$$\delta p_{2\infty}=C\,|\,\delta\alpha\,|+\frac{p_1}{d_1}\,|\,\delta\beta\,| \tag{4}$$

The probable error $\delta\mu$ in dipole moments was due partly to the assumption that the sum of the electronic and atomic polarization P_E+P_A is equal to the molecular refraction calculated for D-line. Shiratori and Kinumaki(7) reported that the exaltation of molecular refraction is fairly great in these compounds. The atomic polarization of these compounds is supposed to be high owing to the possible vibration of a proton participating in hydrogen bond formation. Fortunately orientation polarization is in general much higher than P_E+P_A in the present case, hence the errors in P_E and in P_A do not affect the value for the moments in an appreciable manner. The results of measurements together with the estimated* errors are given in Tables 1 and 2.

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* Read before the scientific meeting of the Chemical Society of Japan held on July 5, 1952.

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

(2) Y. Kurita and M. Kubo, ibid., **24**, 13 (1951).

(3) Y. Kurita, T. Nozoe and M. Kubo, ibid., **24**, 99 (1951).

(4) G. Hazato, J. Maruha, T. Ikegami and H. Kon, reported at the annual meeting of the Chemical Society of Japan on April 8, 1951.

(5) T. Nozoe, Y. Kitahara, K. Yamane and T. Ikemi, *Proc. Japan Acad.*, **27**, 193 (1951).

(6) I. F. Halverstadt and W. D. Kumler, *J. Am. Chem. Soc.*, **64**, 2988 (1942).

(7) K. Shiratori and S. Kinumaki, reported at the annual meeting of the Chemical Society of Japan on April 4, 1952.

* Excluding errors due to P_E and P_A.

Table 1

Dielectric constant and density increments of benzene solutions at 25°C.

	Compounds	Melting points	$w \times 10^5$	$\Delta\varepsilon \times 10^3$	$\Delta d \times 10^4$
I	Bromotropolone	190°^{ab}	429	12	15
			781	21	32
II	Bromotropolone	108°^{ab}	329	26.3	10.8
			568	46.3	—
			1090	89.0	45.5
			1682	141.3	73.5
III	Dibromotropolone	161°^{b}	227	15	8
			856	45	43
			1250	69	66
IV	Tribromohinokitiol	90.5°^{c}	371	10	16
			836	21	41
			1057	29	52
V	α-Thujaplicin A	34°^{d}	344	26.6	6.2
			657	49.8	11.1
			1023	77.9	18.3
VI	α-Thujaplicin B	25.5°^{d}	347	26.7	7.9
			788	61.2	15.8
			1284	97.1	24.5
VII	Dibromo-α-thujaplicin	80–1°	309	8	13
			633	17	26
			1113	30	46

(a) T. Nozoe, S. Seto, Y. Kitahara, M. Kunori and Y. Nakayama, *Proc. Japan Acad.*, **26**, No. 7, 38 (1950).
(b) T. Nozoe, Y. Kitahara, K. Yamane and A. Yoshikoshi, ibid., **27**, 18 (1951).
(c) T. Nozoe, T. Mukai, K. Takase and A. Matsukuma, ibid., **27**, 152 (1951).
(d) T. Nozoe, Y. Kitahara, K. Yamane and T. Ikemi, ibid., **27**, 193 (1951).

Table 2

Molecular polarizations and dipole moments at 25°C.

	ε_1	d_1, g./cc.	α	β, g./cc.	P, cc.	R_D, cc.	μ, D
I	2.274	0.8709	2.56	0.483	128	40.3	2.07
II	2.2705	0.87069	8.48	0.463	354.2± 2.8	40.3	3.91±.02
III	2.2753	0.87100	5.23	0.566	309 ±14	48.1	3.57±.10
IV	2.2725	0.87117	2.72	0.525	260 ±16	69.6	3.05±.13
V	2.2730	0.87133	7.55	0.179	278.5± 2.0	46.3	3.37±.02
VI	2.2736	0.87153	7.51	0.177	279.6± 3.9	46.3	3.37±.03
VII	2.2726	0.87153	2.74	0.411	224.6± 1.7	61.9	2.82±.02

Discussion.—In order to determine the position of substituents in these molecules, we calculated the values of the moments for various possible isomers with the following assumptions. (1) The tropolone ring has a regular heptagon form. Hence the bond monents lie along the lines from the center of the ring to their respective carbon atoms. This assumption is supported by an electron difraction experiment by Heilbronner and Hedberg(8) and that carried out in our laboratory.(9) (2) The bond moment was assumed to have the same value as in the corresponding benzene derivative, i. e., $\mu(\text{C-Br})=1.5\,D$, $\mu(\text{C-}i\text{-C}_3\text{H}_7)=-0.65\,D$, $\mu(\text{C-NO}_2)=4.0\,D$. (3) The substitution by electrophilic atoms and groups such as bromine and nitro-group are most liable to take place at carbon atoms 3(ortho), 5(para) and 7 (ortho′). This was derived from our molecular orbital treatment(2) and is in conformity with the results in organic synthesis.* (4) The moment of tropolone, 3.5 D** in magnitude, lies along a line pointing from the center of the ring to the middle point of two oxygen atoms with its positive end at the ring. That this assumption holds approximately is supported by our previous conclusion from dipole moment measurement.(1) The calculated moments were compared with the experimental data and the position of substituents was determined as shown in Table 3.

Table 3

The position of substituents in tropolone derivatives

Compounds	μ_{obs}	μ_{calc}	Position of substituents
Bromotropolone	2.07	2.00	5 or *p*
Bromotropolone	3.91	4.10	3 or *o*
Dibromotropolone	3.57	4.16	3,7 or *oo′*
Tribromohinokitiol	3.05	3.10	3,5,7 or *oo′p*
α-Thujaplicin A	3.37	3.42	3 or *o*
α-Thujaplicin B	3.37	3.42	3 or *o*
Dibromo-α-thujaplicin	2.82	3.03	5,7 or *po′*

In general the agreement between the observed and the calculated moments is good, considering the approximations made in the calculation. The slight dscrepancy in the case of *oo′*-dibromotropolone may be due to the strong steric and induction effects between oxygen and bromine atoms, as was also the case in *oo′*-dibromohinokitiol.(3) In tribromohinokitiol, the agreement is as good

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(8) E. Heilbronner and K. Hedberg, *J. Am. Chem. Soc.*, **73**, 1386 (1951).
(9) M. Kimura and M. Kubo, This Bulletin, **26**, 250 (1953).
* Cf. reference (a) and (b) of Table 1.
** Recalculated using Halverstadt-Kumler's method.

as can be expected, while such was not the case in tribromotropolone.⁽¹⁾ We recalculated the moment for the latter using the Halverstadt-Kumler's method instead of graphical extrapolation and obtained the moment value 2.46 *D*, which is close to the theoretical value of 2.66 *D*. Hence we can conclude that the successive substitution by bromine in tropolone or hinokitiol do not affect the structure or the electronic state of tropolone ring, though Hazato⁽⁴⁾ reported the peculiarity of tribromotropolone. Our conclusion is in conformity with Kimura's result on electron diffraction that in tribromotropolone the structure of tropolone ring is nearly identical with that of tropolone.⁽⁹⁾

In view of the fact that the Halverstadt-Kumler's method gives better results than the ambiguous graphical extrapolation, we have recalculated the data on α-dinitrohinokitiol (m. p. 155°),⁽¹⁾ for which we could not get a definite conclusion. The observed value recalculated is 4.79 *D* and this is in good agreement with the theoretical value of 4.5 *D* for 5, 7(or *po'*)-dinitrohinokitiol. This assignment can explain the results in organic synthesis⁽¹⁰⁾ adequately.

The two crystal forms of α-thujaplicin gave an identical moment. The conceivable two molecular forms of α-thujaplicin, i. e., 3-isopropylcycloheptatriene-2, 4, 6-ol-2-one-1 and 3-isopropylcycloheptatriene-2, 4, 6-ol-1-one-2 are expected to have values for their moments different from each other by an amount of about 0.4 *D* due to the induction effect. This should surely be detectable by experiment. The absence of such a difference indicates that the two crystal forms give identical molecules in solution. Probably the molecules in the two crystal forms are the same with each other, the difference being attributable to the arrangement of molecules in crystals.

Summary

The dipole moments of seven tropolone derivatives were measured in benzene solution at 25°C. The values obtained are: bromotropolone (m. p. 190°C., 5-bromo-), 2.07 *D*; bromotropolone (108°C., 3-bromo-), 3.91 *D*; tribromohinokitiol (90.5°C., 3, 5, 7-tribromo-), 3.05 *D*; α-thujaplicins, both A (34°C.) and B (25.5°C.) form, 3.37 *D*; dibromo-α-thujaplicin (80°C., 5, 7-dibromo-), 2.82 *D*. By analysing the results obtained, the position of substituents in these molecules were determined and are given immediately after each name of these compounds in parentheses. The two crystal forms of α-thujaplicin with different melting points give an identical moment in solution. α-Dinitrohinokitiol of m. p. 155°C. is 5, 7 (or *po'*)-dinitrohinokitiol.

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(10) T. Nozoe, Y. Kitahara, K. Yamane and K. Yamaki, *Proc. Japan Acad.*, **26**, 14 (1950).