Dipole Moments of Tropolone and Related Compounds(1)

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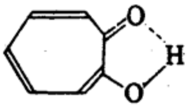
Introduction

One of us(2) carried out extensive studies on the chemical properties of hinokitiol (4-isopropylcycloheptatriene-2, 4, 6-ol-2-one-1) and assumed its structure to be the resonance hybrid among various electronic structures of type A, B and C. He(3) also succeeded in synthesizing this compound and its mother substance, tropolone (cycloheptatriene-2, 4, 6-ol-2-one-1). We measured the dipole moments of some of these compounds in benzene solution. The object of the present work is twofold. The first is to obtain some conclusion concerning the positions of substituents in various substituted tropolone and hinokitiols. The second is to investigate the structure of cycloheptatrienolone ring. This is of interest because the ring has odd number of carbon atoms. Wheland and Mann(4) have measured the dipole moment of azulene, but in general the data on cycloheptatriene ring compounds are very scanty. It will be very desirable to determine whether the cycloheptatrienolone ring is planar like benzene ring or non-planar like cyclooctatetraene ring.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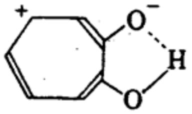
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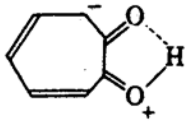
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Experimental Method and Materials

Dielectric constants were measured by heterodyne beat method at the wavelength of 300 m. The sum of P_E and P_A was taken to be equal to the molecular refraction for D-line calculated additively from the atomic refractions of constituent atoms and bonds. This did not cause any serious error because orientation polarizations are very great. The materials used were prepared by one of us(2)(3) and his collaborators. They are :— tropolone, m. p. 51°, tribromotropolone, 126°, hinokitiol, 52°, α-monobromohinokitiol, 56°, α-dibromohinokitiol, 134°, β-dibromohinokitiol, 96°, α-mononitrohinokitiol, 56°, dinitrohinokitiol, 155°.

Experimental Results

The results obtained are shown in Table 1, where w and P denote the weight fraction and molecular polarization respectively. Other notations used have their usual significances.

Table 1

Dipole Moments of Tropolone and Related Compounds

w_2(%)	ε_{12}	d_{12}	P_2(cc.)
Tropolone, 25° and 35°			
0	2.273	0.8733	(317.5)
0.621	2.346	0.8749	295.5
1.332	2.421	0.8764	277.2
1.951	2.487	0.8784	268.7
$P_{2\infty}=317.5$ cc.,	$R_D=32.5$ cc.,	$\mu=3.71$ D	
0	2.253	0.8627	(298.0)
0.621	2.321	0.8645	282.1
1.332	2.395	0.8659	272.3
1.951	2.460	0.8682	265.0
$P_{2\infty}=298.0$ cc.,	$R_D=32.5$ cc.,	$\mu=3.64$ D	
Tribromotropolone, 25°			
0	2.273	0.8733	(125.6)
0.604	2.280	0.8769	122.4
1.145	2.291	0.8800	147.5
1.830	2.305	0.8840	157.5
$P_{2\infty}=125.5$ cc.,	$R_D=55.7$ cc.,	$\mu=1.84$ D	
Hinokitiol, 33°			
0	2.257	0.8651	(375)
2.047	2.467	0.8687	351
3.002	2.573	0.8706	350
3.686	2.628	0.8715	334
$P_{2\infty}=375$ cc.,	$R_D=46$ cc.,	$\mu=4.04$ D	

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(1) Presented at the Annual Meeting of the Chemical Society of Japan on 2 April 1950 and at the General Discussion on Structural Chemistry held by the society on 8 July 1950.

(2) T. Nozoe, *Yakugaku*, **3**, 174(1949).

(3) T. Nozoe *et al.*, *Proc. Japan Acad.*, **26**, 38, 43, 47 (1950).

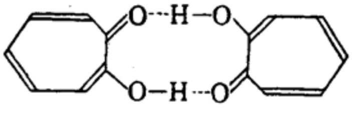
(4) G. W. Wheland and D. E. Mann, *J. Chem. Phys.*, **17**, 264(1949).

w_2(%)	ε_{12}	d_{12}	P_2(cc.)
α-Monobromohinokitiol, 33°			
0	2.257	0.8651	(430)
2.047	2.420	0.8724	411
2.448	2.454	0.8738	404
3.055	2.505	0.8762	402
$P_{2\infty}=430$ cc., $R_D=54$ cc., $\mu=4.32$ D			
α-Dibromohinokitiol, 33°			
0	2.257	0.8651	(430)
1.208	2.329	0.8710	409
2.334	2.391	0.8756	393
3.941	2.486	0.8832	386
$P_{2\infty}=430$ cc., $R_D=62$ cc., $\mu=4.27$ D			
β-Dibromohinokitiol, 20°			
0	2.283	0.8790	(269)
0.4351	2.302	0.8809	317
0.6964	2.317	0.8821	342
0.9113	2.332	0.8832	368
$P_{2\infty}=269$ cc., $R_D=62$ cc., $\mu=3.14$ D			
α-Mononitrohinokitiol, 25°			
0	2.273	0.8733	(847.3)
0.558	2.387	0.8753	824.3
1.212	2.522	0.8769	807.5
1.526	2.582	0.8777	788.7
$P_{2\infty}=847$ cc., $R_D=53$ cc., $\mu=6.19$ D			
Dinitrohinokitiol, 20°			
0	2.283	0.8790	(537)*
2.450	2.534	0.8874	506
$P_{2\infty}=537$ cc., $R_D=59.5$ cc., $\mu=4.63$ D			

* Hedestrand's method of extrapolation (*Z. physik. Chem.*, B, **2**, 428(1929).) was used for this as well as for others giving values consistent with those extrapolated graphically.

Discussion

The dipole moments of these compounds are high. Hence the existence of dimers with a vanishing moment such as (I) cannot be conceivable. The normal dependence of molecular polarization upon concentration also denies such association. The bonds of high moments in the molecules of tropolone and hinokitiol are located in the part of -CO-C(OH)-. Assuming the bond moments of C=O, C-O and O-H to be equal to 2.5 D, 0.86 D and 1.53 D respectively, the valency angle ∠C-O-H to be 110° and that of ∠C-C-C at the C-atom of carbonyl group to be 130° as in benzophenone,⁽⁵⁾ the resultant moment is calculated as 2.1 D, if the valency angle ∠C-C-O at the C-atom of C-OH is equal to the tetrahedral angle. The resultant moment is fairly insensitive to the assumed value of the ∠C-C-O angle. In fact, it is 2.0 D if the latter angle is equal to 115.7° which corresponds to the regular heptagon form of the ring and 1.85 D if the angle is assumed to be 120°. The difference between these and the observed values are too great to be attributable to the solvent effect or induction effect. We must take into account the hydrogen bond between the H-atom in OH and the O-atom in C=O and resonance among various electronic structures of the type B with a formal positive charge at one of the seven C-atoms in the ring. There will be fourteen such electronic structures if the two O-atoms can interchange their role. Each of these structures, to be sure, corresponds to an excited state with smaller number of double bonds. Hence its contribution to the normal state will be small. But the number of these dipolar-ionic structures are great and each of these structures has very high moment. These two factors will be sufficient to account for the observed moments. Furthermore the fact that tropolone and its derivatives show fairly strong acidic character and that they are readily attacked by electrophilic reagents giving substitution products suggests the possibility of resonance involving the electronic structures of type C. Their contribution, however, will be small. The rather small contribution of the electronic structures of type C is in agreement with our results concerning the direction of dipoles in the molecules as will soon be evident.



(I)

As a result of resonance among these structures, it is supposed that each bond in the ring has a certain amount of double bond character and the cycloheptatriene ring takes a plane form. The valency angle of carbon must deviate from its normal value and consequently internal energy will increase. We calculated the hybridization of $2s$, $2p_x$ and $2p_y$ orbitals giving three hybrid orbitals ψ_1, ψ_2, ψ_3 the latter two of which are equivalent and make an angle θ with each other. It was found that, as shown in Table 2, the bond strengths for θ equal to the angle of a regular heptagon 128°34′ are weakened about 0.6% in

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(5) N. L. Leonard and L. E. Sutton, *J. Am. Chem. Soc.*, **70**, 1564(1948).

Table 2

Bond Strengths of sp^2-Hybrid Orbitals

θ	ϕ_1	ϕ_2, ϕ_3
109°28′	1.932	2.000
120°	1.991	1.991
128°34′	1.999	1.979

the two equivalent orbitals ψ_2, ψ_3 to be assigned to the bonds in the ring and strengthened about 0.4% in a non-equivalent orbital ψ_1 for the bond to a substituent as compared with the benzene ring. Though in total the bond strengths become weak, the small increase of energy of this magnitude will be overcompensated by high resonance energy(6) due to a great number of resonating structures stabilizing the molecules. It should be noted that if instead of bond strength, the dependence of bond energy, calculated by Penney(7) from resonance integrals, upon the angle θ is considered, the formation of heptagon ring becomes more favorable.

Finally the position of substituents in various derivatives must be determined. A difficulty arises because, though the magnitude of dipole moment of hinokitiol has been measured, the direction of dipole in the molecule cannot be obtained experimentally. The approximation is reasonably adequate that the moment of monobromohinokitiol is the vector sum of that of hinokitiol μ_0 and C-Br bond moment (μ(C-Br)=1.48 D). It is highly probable from the consideration on the course of formation(1) of α-monobromohinokitiol that Br-atom is in the position 7. Therefore, a plane heptagon form of the ring being assumed, the C-Br moment points along a line from the center of the ring to the C-atom at the position 7. The angle between this and μ_0 can be determined since their vector sum is known. There are two possibilities in the direction of μ_0, one to each side of C-Br bond moment. Considering various resonating structures of type B, μ_0 pointing in the direction nearly coincident with the line from the center of the ring to the middle point of two O-atoms with positive end at the ring(8) is taken to be correct. The other possibility with the dipole nearly pointing in the opposite direction must be rejected.(9) The magnitude and the direction of the dipole moment of hinokitiol being known, the moment of tropolone can be calculated by subtracting vectorially the bond moment of isopropyl group, which is assumed to be equal to that of isopropylbenzene(10) (μ(C-i-C_3H_7)$-\mu$(C-H)=0.65 D). The calculated moment is 3.8 D in agreement with the observed value 3.7 D. For bromo- and nitro-derivatives, the conceivable position of substitution are 3, 5 and 7 in analogy to benzene derivatives such as phenol or aniline.(11) The calculated moments of dibromohinokitiols are 3.7 D, 4.7 D and 2.9 D for 3,5-, 3,7- and 5,7-dibromohinokitiol respectively. Comparing these values with the observed ones, it is concluded that the position of substituents in α-dibromohinokitiol is 3,7 while in β-dibromohinokitiol it is 5,7.(12) Assuming the bond moment of nitro-group to be μ(C-NO_2)$-\mu$(C-H)=3.0 D, the moment of mononitrohinokitiol is calculated to be 6.0 D, 1.3 D and 5.1 D for 3-, 5- and 7-nitrohinokitiol. Comparing these values with the observed one, the probable positions of a substituent group in α-mononitrohinokitiol is supposed to be 3 or 7. The calculated moments of dinitrohinokitiols are 4.1 D, 5.4 D and 2.6 D for 3,5-, 3,7- and 5,7-dinitrohinokitiol respectively. Comparing these values with the observed one, it is supposed that dinitrohinokitiol under investigation is 3,5- or 3,7-derivative. The reason for the indefinite conclusions are partly connected with the magnitude of C-NO_2 bond moment that must be assumed.(13) For tribromotropolone, all the three positions 3, 5 and 7 must be substituted by Br-atoms. The moment calculated from that of tropolone and three C-Br bond moments is 2.8 D, which is much higher than the observed value. If, however, the moments of C=O, C-OH are added vectorially together with three C-Br and two C-H moments in accordance with the electronic structure of the type A without

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(6) We (Y. Kurita and M. Kubo, this Bulletin, **24**, 13 (1951)). have carried out molecular orbital treat ment on tropolone and obtained high resonance energy.

(7) W. G. Penney, *Proc. Roy. Soc.*, A, **146**, 223 (1934).

(8) The molecular orbital treatment on tropolone also gives a moment in the direction along the line from the center of the ring to the middle point of the two O-atoms, with a positive end at the ring.

(9) It can be shown that the latter possibility gives resultant moments for dibromo-derivatives that never agree with experiments.

(10) J. W. Baker and L. G. Groves, *J. Chem. Soc.*, **1939**, 1144.

(11) By the molecular orbital treatment already mentioned, it is found that in the molecule of tropolone, π-electron distribution is concentrated at C-atoms 3, 5 and 7, which justifies that only these positions are liable to be attacked by electrophilic reagents.

(12) 3,5-Dibromo derivative can be excluded also from considerations in organic synthesis. Both α- and β-dibromohinokitiol can be obtained from α-monobromohinokitiol by bromination(3).

(13) Considering the neglection of possible formation of hydrogen bond between the H-atom in OH and the O-atom in the neighboring nitro-group and the consequent existence of tautomers and taking into account the investigations on the rearrangement product of this compound(2), we should like to reserve, for a while, definite conclusions concerning the positions of substituent groups. Final decision must be given after investigations are extended to cover wider scope of compounds of related structure.

considering resonance effect, the calculated value is 1.8 D in close agreement with experiment. Probably unshared electron pairs of Br-atoms in competition with that of O-atom decrease the resonance effect and consequently diminish the localization of positive charge on the ring, which is characteristic to tropolone. Furthermore, the electron withdrawal by three electronegative Br-atoms decreases the electron density in the ring, rendering the contribution of the electronic structure of type B more difficult or that of type C more important in conformity to the experimental observations that Br-substituted tropolone and hinokitiol are more strongly acidic than their mother substances.

Summary

The dipole moments of tropolone (cycloheptatriene-2,4,6-ol-2-one-1) and related compounds were measured in benzene solution. The values obtained are:— tropolone, 3.71 D (25°) and 3.64 D (35°); tribromotropolone (3,5,7-tribromo-), 1.84 D(25°); hinokitiol(4-isopropylcycloheptatriene-2,4,6-ol-2-one-1), 4.04 D (33°); α-monobromohinokitiol (7-bromo-), 4.32 D (33°); α-dibromohinokitiol (3,7-dibromo-), 4.27 D (33°); β-dibromohinokitiol (5,7-dibromo-), 3.14 D (20°); α-mononitrohinokitiol (3- or 7-nitro-), 6.19 D (25°); dinitrohinokitiol (3,5- or 3,7-dinitro-), 4.63 D (20°). The high dipole moments of tropolone and hinokitiol were explained adequately by taking into consideration the contribution of various resonance structures with a formal positive charge at the ring C-atoms. The resonance was supposed to give a certain amount of double bond character to each bond in the ring, causing plane cycloheptatrienolone ring. The position of substituents in the substituted tropolone and hinokitiols were determined and are given immediately after each name of these compounds in parentheses.

We wish to express our cordial thanks to Prof. S. Seto, Mr. Y. Kitahara and Mr. T. Mukai of Tohoku University for collaborating with us in the syntheses of these new compounds and to Prof. A. Kotera for lending us his experimental apparatus. Our thanks are also due to the Ministry of Education in aid of this research.

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