The Dipole Moments and Molecular Structures of Some Substituted Tropones[*]

By Yukio KURITA and Masaji KUBO

(Received May 12, 1954)

In our previous paper,[1] we have reported the results of measurements of the dipole moments of tropone and some of its derivatives. The high moment of tropone revealed the importance of contribution to the normal state by the electronic structures of dipolar character and the explanation was made in terms of resonance involving cycloheptatrienium oxide structure.[2] This feature was found to be common to all tropone derivatives including tropolone as well as substituted tropolones, giving rise to the quasi-aromatic properties and other characteristic behaviors of these compounds. The purpose of the present investigation is the elucidation of the effect of various substituents on the electronic state of the tropone ring. We have measured the dipole moments of five tropone derivatives having various substituents at a carbon atom or atoms adjacent to the carbon atom of carbonyl group. All of these substituents are π-electron donors. Some of the substituent groups have an axis of free rotation capable of affecting the value of the resultant moment. The present writers have undertaken to determine the geometrical arrangements of these substituents relative to the tropone ring by means of dipole moment measurements.

Experimental Method and Results

All the measurements were made in benzene solution at room temperature. The dielectric constants were measured with the apparatus described in one[3] of our previous reports. The materials used were synthesized and purified by Nozoe and his collaborators in the laboratory of organic chemistry, Tohoku University. The modified Hedestrand's method[4] was employed throughout. The results are shown in Tables I and II, where the same notations are used as those in the previous reports.

Discussion of Results

The dipole moments of 2-bromotropone, 2,7-dibromotropone and other 2-monosubstituted tropones are summarized in Table III, in which the observed moments are compared with calculated ones. These theoretical moments have been calculated with the following assumptions. (1) The cycloheptatrienone ring has a plane regular heptagon form composed of carbon atoms. Hence the angle between C=O direction and the carbon-substituent bond is equal to 51°26′. (2) The interactions between the tropone ring and the substituent groups have been neglected. In other words, the moment of a substituted tropone has tentatively been assumed to be equal to the vector sum of the moment of tropone, 4.17 D,[1] and the bond moment of the substituent. (3) The bond moments of the substituents in cycloheptatriene are equal to the moments of corresponding substituted benzenes. This assumption may be justifiable since the treatment by molecular orbital

---

[*] Read before a symposium on tropolone chemistry held by the Chemical Society of Japan on February 6, 1954.

[1] Y. Kurita, S. Seto, T. Nozoe and M. Kubo, This Bulletin, **26**, 272 (1953).

[2] W. von E. Doering and F. L. Detert, *J. Am. Chem. Soc.*, **73**, 876 (1951).

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

[4] Y. Kurita, T. Nozoe and M. Kubo, This Bulletin, **26**, 242 (1953).

TABLE I

DIELECTRIC CONSTANT AND DENSITY INCREMENTS OF BENZENE SOLUTIONS AT 25°C

	Compounds	m. p.	$w\times10^5$	$\Delta\varepsilon\times10^4$	$\Delta d\times10^5$
I	2-Bromotropone at 30°C	62°(a)	223	339	98
			483	693	—
			665	946	—
			1341	1919	588
II	2, 7-Dibromotropone	170(a)—171°	341	422	143
			558	667	264
			1116	1314	571
			1357	1622	697
III	2-Mercaptotropone	55°(b)	142	235	49
			436	675	129
			742	1133	210
			1231	1886	355
IV	2-Aminotropone	104(c)—105.5°	148	194	—
			161	209	57
			185	255	62
			285	366	88
			358	473	107
V	2-Methylmercaptotropone	43—44°(b)	221	387	57
			536	903	145
			707	1150	199
			714	1160	199

(a) T. Nozoe, S. Seto and S. Matsumura, *Proc. Japan Acad.*, **28**, No, 9, 483 (1952).

(b) T. Nozoe, M. Sato and K. Matsui, *Science Repts. Tohoku Univ.*, I, **37**, 211 (1953).

(c) T. Nozoe, S. Seto, H. Takeda, S. Morosawa and K. Matsumoto, ibid., **36**, 126 (1952).

TABLE II

MOLECULAR POLARIZATIONS AND DIPOLE MOMENTS

	t(°C)	ε_1	d_1(g/cc)	α	β(g/cc)	$P_{2\infty}$(cc)	R_D(cc)	μ(D)
I	30	2.2638	0.86670	14.17	0.438	530.5±3.1	38.7	4.94±0.02
II	25	2.2740	0.87102	11.72	0.546	616.8±5.5	46.5	5.27±0.03
III	25	2.2741	0.87093	15.16	0.280	427.0±0.8	38.7	4.36±0.01
IV	25	2.2729	0.87101	13.00	0.256	326.4±7.3	34.4	3.78±0.05
V	25	2.2772	0.87104	15.66	0.290	483.7±4.1	43.4	4.64±0.02

method,[5,6] the results of ultraviolet absorption spectra,[7] and the studies in organic chemistry[8] have revealed that tropone bears resemblance to benzene in regard to the introduction of substituents in their rings and that the conjugation of the ring with Br, OH, SH, NH_2, etc. in substituted tropones is significant as in the case of substituted benzenes.

In the case of substituents other than bromine, one must take into account free rotation about a single bond between the carbon atom of the ring and oxygen, sulfur or nitrogen atom. In the case of oxygen- or sulfur-containing substituent groups, moments have been calculated for three conceivable configurations, viz., *cis*, *trans* and perpendicular forms. We mean by the *cis* form the configuration in which the hydrogen atom or the methyl carbon atom attached to oxygen or sulfur atom is in the plane of the ring and is near the carbonyl oxygen. The configuration in which the hydrogen atom or the methyl carbon atom is at the greatest distance from the carbonyl oxygen is called the *trans* form. The intermediate position resulting from the rotation of freely rotating atoms or groups about the respective axes of rotation through 90° from either *cis* or *trans* form is termed the perpendicular form. In the case of aminotropone, the configuration in which the two hydrogen atoms in question are equally distant from the carbonyl oxygen and are located at the side of the carbonyl group is designated as the *cis*

---

[5] Y. Kurita and M. Kubo, This Bulletin, **24**, 13 (1951).

[6] R. D. Brown, *J. Chem. Soc.*, **1951**, 2670.

[7] M. Tsuboi, This Bulletin, **25**, 366 (1952).

[8] See papers by T. Nozoe and his collaborators published for the most part in the *Proc. Japan Acad. and Science Repts. Tohoku Univ.* Series I since 1950.

form. The rotation of the hydrogen atoms through 180° and 90° gives *trans* and perpendicular forms respectively in the same manner as before.

For the *cis* and *trans* forms of tropolone, mercaptotropone and their derivatives as well as for the perpendicular form of aminotropone, the lone pair orbitals belonging to the substituent groups overlap with the π-orbital of the ring to the highest extent, favoring the conjugation between the ring and the substituents. On the other hand, the perpendicular forms of tropolone and its analogues as well as the *cis* or *trans* form of aminotropone decrease the conjugation between the ring and the substituent groups. Therefore the moments of the substituents will better be approximated by those of alkyl derivatives rather than by those of substituted benzenes. The calculated moments using the former data are given in parentheses in Table III.

TABLE III

DIPOLE MOMENTS OF SUBSTITUTED TROPONES

Substituents	μ_{obs}(D)		μ_{calc}(C)	
Br	4.94		5.3	
Br_2	5.27		6.1	
		cis	Perpendicular	*trans*
OH	3.53(1)	3.1	4.5	5.5
SH	4.36	4.2	4.8	5.4
NH_2	3.78	2.7	3.8	4.7
OCH_3	4.72(1)	3.0	4.1 (4.7)	5.0
SCH_3	4.64	3.6	4.6 (5.0)	5.5
$N(CH_3)_2$	—	2.7 (3.8)	3.6	4.2 (5.0)

In the evaluation of the calculated moments given in Table III, it has been necessary to know the components of the moments of substituents along the direction parallel to the bond between the ring carbon and oxygen, sulfur or nitrogen atom, $\mu_{\parallel}$, and those perpendicular to this direction, $\mu_{\perp}$. These components have been calculated by means of a method similar to that used by Everard and Sutton.[9] These data are given in Table IV. The calculated moments in parentheses in Table III have been obtained using the data given in Table V.

TABLE IV

DIPOLE MOMENTS OF SUBSTITUTED BENZENES

Substituents	μ(D)	$\mu_{\parallel}$(D)	$\mu_{\perp}$(D)
Br	1.57(a)	1.57	0
OH	1.56(a)	0	−1.56
SH	1.19(b)	0.85	−0.83
NH_2	1.52(a)	−1.02	−1.13
OCH_3	1.28(a)	−0.39	−1.22
SCH_3	1.38(b)	0.40	−1.32
$N(CH_3)_2$	1.61(a)	−1.40	−0.79

(a) K. B. Everard, L. Kumar and L. E. Sutton, *J. Chem., Soc.*, **1951,** 2807.

(b) H. Lumbroso and C. Marschalk, *J. chim. phys.*, **49,** 385 (1952).

TABLE V

DIPOLE MOMENTS OF ALKYL DERIVATIVES

Substituents	μ(D)	$\mu_{\parallel}$(D)	$\mu_{\perp}$(D)
OCH_3	1.24	0.62	−1.07
SCH_3	1.57	1.01	−1.20
$N(CH_3)_2$	0.86	0.29	−0.81

The moments calculated for 2-bromotropone and 2,7-dibromotropone are greater than the observed values. Presumably this is due to ortho effect, i. e., to the mutual electrostatic induction of bond moments and to the bond deflection caused by steric repulsion of bulky atoms in ortho position, both decreasing the resultant moments. If the correction is made for the effect of electrostatic induction in the same way as Sutton and his coworkers[10] have done, the moments of these two bromoderivatives are calculated as 5.1 D and 5.6 D respectively in fair agreement with the observed values. Mention should be made here that a similar behavior due to ortho effect has also been recognized in many of the brominated tropolones, phenyltropones and alkyltropolones having a bromine atom or atoms at ortho position to carbonyl carbon.[1,3,4,11]

The observed moments of tropolone and mercaptotropone are nearly equal to the values calculated for the *cis* form, while the moment of aminotropone is close to that of the perpendicular form. In these geometrical configurations, the conjugation between the ring and the substituent groups can attain its maximum possible extent. Moreover a hydrogen bond can be formed between the carbonyl oxygen and the substituent. The hydrogen bond formation will increase the

---

[9] K. B. Everard and L. E. Sutton, *J. Chem. Soc.* **1951,** 2818.

[10] J. B. Bentley, K. B. Everard, R. J. B. Marsden and L. E. Sutton, *J. Chem. Soc.*, **1949**, 2957.

[11] Y. Kurita, T. Mizuno, T. Mukai and M. Kubo, This Bulletin, **26**. 192 (1953).

trend of electron attraction of carbonyl oxygen, giving rise to the increase of the contribution of cycloheptatrienium oxide structure. This is in conformity with the fact that the observed moment of tropolone is slightly higher than the calculated moment in contradistinction to the case of bromo-derivatives. The magnetic susceptibility measurements by Maruha and Hazato[12] have also indicated that the contribution of the cycloheptatrienium oxide structure is greater in tropolone than in tropone.

The moments of methoxytropone and methylmercaptotropone can adequately be explained either by the perpendicular form or by the mixture of *cis* and *trans* forms. Although the dipole moment data are incapable of settling the problem of the alternative, we think the former viewpoint is nearer the truth on the basis of the following considerations. (1) The fact that the absorption spectra[7] of methoxytropone bear some resemblance to the spectra of tropone rather than to those of tropolone indicates that conjugation taking place between the tropone ring and the methoxy group is weak. (2) The plane configurations are unlikely in view of the steric hindrance acting between the methyl group and carbonyl oxygen or between the methyl group and the hydrogen atom at the position 3 of the tropone ring.

Summary

The dipole moments of *ortho*-substituted tropones were measured in benzene solution at room temperature. The values obtained are as follows: 2-bromotropone, 4.94 D; 2,7-dibromotropone, 5.27 D; 2-mercaptotropone, 4.36 D; 2-aminotropone, 3.78 D; 2-methylmercaptotropone, 4.64 D. These values together with those of tropolone and methoxytropone were compared with the calculated moments and the following conclusions were derived. The moments of the bromotropones are lower than those calculated by simple vector addition owing to ortho effect. In tropolone, mercaptotropone and aminotropone, the substituent groups take such configurations that these groups are conjugated with the cycloheptatriene ring in the highest degree and that an intramolecular hydrogen bond is formed between the carbonyl oxygen and the hydrogen atom of each of the substituent groups. In methoxytropone and methyl mercaptotropone, on the other hand, the conjugation is weak and each of the substituent groups lies in a plane nearly perpendicular to the ring.

We wish to express our thanks to Prof. Nozoe and his collaborators in Tohoku University, who kindly provided us with samples used in this experiment. Our thanks are also due to the Ministry of Education in aid of this research.

Chemical Department, Faculty of Science,
Nagoya University, Nagoya

---

[12] J. Maruha and G. Hazato, reported at the annual meeting of the Chemical Society of Japan on April 3, 1953.