Dipole Moments of Tropone, 2-Phenyltropone, Tropolone Methyl Ether and their Derivatives*

By Yukio KURITA, Shuichi SETO, Tetsuo NOZOE and Masaji KUBO

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Hitherto we studied the dipole moments of tropolone (or cycloheptatriene-ol-2-one-1) and its derivatives.(1~5) The characteristic feature of the molecules of these compounds is that the electronic structures with a negative charge at the carbonyl oxygen and a positive charge at one of the carbon atoms in the ring contribute appreciably to the normal state. The same situation is expected(6~8) for tropone (or cycloheptatrienone), one of the simplest and the most fundamental compounds with a cycloheptatriene ring. The determination of the dipole moment of tropone made in the present investigation will throw light on the theory of the π-electron problem as applied to the charge distribution in this molecule. We have also carried out measurements on the dipole moments of eleven of its derivatives. All the compounds studied were synthesized* and purified by one of us (T.N.) and his collaborators at the laboratory of organic chemistry, Tôhoku University.

Experimental Method and Results

All the measurements were made in benzene solution at 25° except in one case (compound VII) for which the temperature was varied from 20° to 40°. The apparatus and the method of measurement were the same as used in our earlier works. The Halverstadt-Kumler's method was employed throughout. The moment of tropolone was remeasured, in view of its importance, to get more accurate value from data at various concentrations. The results are shown in Tables 1 and 2, where the same notations are used as those in the previous reports.

Discussion of Results

Tropone.—The value 4.17 D for the moment of tropone is in fair agreement with that of Giacomo and Smyth, 4.30 D.(10) The large

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* Read before the scientific meeting of the Chemical Society of Japan (A Symposium on Tropolone Chemistry) 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) Y. Kurita, T. Nozoe and M. Kubo, ibid., **26**, 242 (1953).

(5) Y. Kurita, T. Mizuno, T. Mukai and M. Kubo, ibid., **26**, 192 (1953).

(6) T. Nozoe, T. Mukai, K. Takase and T. Nagase, *Proc. Japan Acad.*, **28**, No. 9, 477 (1952).

(7) H. J. Dauben and H. J. Ringold, *J. Am. Chem. Soc.*, **73**, 876 (1951).

(8) W. von E. Doering and F. L. Detert, ibid., **73**, 876 (1951).

* See literatures at the end of Table 1.

(10) A. D. Giacomo and C. P. Smyth, *J. Am. Chem. Soc.*, **74**, 4411 (1952).

Table 1

Dielectric Constant and Density Increments, 25°

	Compounds	$w \times 10^5$	$\Delta\varepsilon \times 10^4$	$\Delta d \times 10^5$
I	Tropone[a]	208	439	46
	b. p. 84—85° (6 mm.)	439	862	100
		737	1364	154
		1070	1998	224
II	2-Phenyltropone[b]	225	225	—
	m. p. 85—86°	380	—	79
		804	760	192
		1184	1087	267
III	4-Bromo-2-phenyl-	151	60	21
	tropone[c]	366	99	101
	m. p. 88°	627	195	196
		841	289	290
IV	3,7-Dibromo-	331	156	113
	2-phenyltropone[d]	470	223	182
	m. p. 118°	842	387	351
		1328	611	575
V	2-(*p*-Methoxy-	317	269	73
	phenyl)-tropone[e]	506	416	105
	m. p. 54.5—55.0°	875	670	244
VI	Tropolone methyl	341	538	80
	ether[f]	612	1065	149
	(oil)	1119	1941	278
VII	(Tropolone methyl ether)$_2$·H$_2$O,[f] m. p. 41°			
	20°	253	438	—
		358	650	45
		558	993	105
	30°	253	411	65
		358	608	98
		558	930	142
	40°	253	366	10
		358	555	86
		558	874	168
VIII	*o*-Bromotropolone	160	242	67
	methyl ether A	252	393	107
	(7-Bromo-2-	335	514	141
	methoxy-tropone)[g]	563	876	239
	m. p. 91—91.5°	1077	1670	488
IX	*o*-Bromotropolone	319	187	113
	methyl ether B	613	356	263
	(3-Bromo-2-methoxy-tropone)[g]	1081	589	430
	m. p. 76—77°	1490	867	637
X	α-Thujaplicin	433	430	80
	methyl ether B[h]	694	710	120
	m. p. 72°	1224	1250	210
XI	*m*-Methyltropolone	200	320	48
	methyl ether A	297	543	84
	(6-Methyl-2-methoxy-tropone)[i]	527	891	135
	m. p. 95.5-96°	627	1160	168
XII	Tropolone[j]	471	578	114
	m. p. 51°	864	993	227
		1187	1361	309
		1911	2206	488
		2378	2705	613

(a) T. Nozoe, T. Mukai, K. Takase and T. Nagase, *loc. cit.* reference (6).

(b) T. Nozoe, T. Mukai and J. Minegishi, *Proc. Japan Acad.*, **27**, 419 (1951).

(c) T. Nozoe, S. Seto and S. Ito, ibid., to be published shortly.

(d) T. Nozoe, T. Mukai and I. Murata, ibid., **28**, 142 (1952).

(e) T. Nozoe, S. Seto, T. Ikemi and T. Sato, ibid., **28**, No. 8, 413 (1952).

(f) T. Nozoe, S. Seto, T. Ikemi and T. Arai, ibid **27**, 102 (1951).

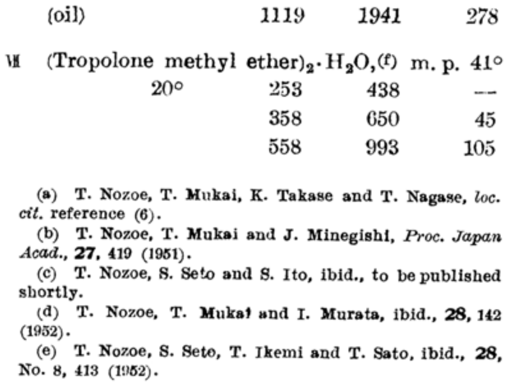
(g) T. Nozoe, Y. Kitahara and S. Masamune, ibid., **27**, 649 (1951).

(h) T. Nozoe, Y. Kitahara, K. Yamane and T. Ikemi, ibid., **27**, 193 (1951).

(i) P. Akroyd, R. D. Haworth and J. D. Hobson, *J. Chem. Soc.*, **1951**, 3427.

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

increase, about 1.1 D, in the moment of this molecule over that of cycloheptanone, 3.04D,(11) indicates the importance of the contribution of polar structure B.



Sutton(12) pointed out that the moments of various unsaturated ketones and aldehydes with conjugated C=C double bonds fit in well with calculated values, if we give mesomeric moments of 0.1 D and 0.2 D respectively to C–C bonds adjacent to the carbonyl group and to the next C=C bonds, each lying along its respective bond. The correction of mesomeric effect can only partly explain the increase of moment of tropone over that of cycloheptanone. The calculated value is 3.5D, still smaller than the observed value by an amount of 0.7 D. This may be attributed to an additional effect due to the formation of cycloheptatrienone ring. In fact, the difference

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(11) Hs. H. Günthard and T. Gäumann, *Helv. Chim. Acta.*, **34**, 39 (1951).

(12) J. B. Bentley, K. B. Everard, R. J. B. Marsden and L. E. Sutton, *J. Chem. Soc.*, **1949**, 2957.

Table 2

Dipole Moments of Tropone and Related Compounds in Benzene Solution at 25°

Compounds		ε_1	d_1(g./cc.)	α	β(g./cc.)	$P_{2\infty}$(cc.)	R_D(cc.)	μ(D)
I		2.2788	0.87121	17.98	0.204	387± 4	30.9(a)	4.17±.03
II		2.2751	0.87144	9.01	0.234	355± 8	55.1	3.82±.05
III		2.2719	0.87075	3.36	0.387	215±12	62.9	2.73±.11
IV		2.2732	0.87078	4.54	0.461	346±12	70.7	3.67±.01
V		2.2772	0.87084	7.15	0.316	332± 9	61.4	3.63±.05
VI		2.2668	0.87127	17.92	0.254	494± 1	37.2	4.72±.01
VII	20°	2.2816	0.87605	18.06	0.300	1045±29	78	6.81±.10*
	30°	2.2617	0.86616	16.88	0.246	1005±26	78	6.78±.10*
	40°	2.2384	0.85443	16.55	0.502	980±26	78	6.80±.10*
VIII		2.2721	0.87124	15.56	0.458	666± 2	45.0	5.51±.01
IX		2.2724	0.87112	5.71	0.436	269±11	45.0	3.31±.08
X		2.2716	0.87156	10.34	0.165	397± 4	51.1	4.11±.02
XI		2.2683	0.87131	18.67	0.272	565±21	41.7	5.06±.10
XII		2.2759	0.87113	11.26	0.258	289± 3	32.5(b)	3.53±.02

(a) R_D observed is 33.9 cc.(8)

(b) R_D observed is 37.46 cc. and the value extrapolated to infinite wavelength is 34.30 cc.(9)

* Apparent moments.

of 0.7 D is very close to the moment of 0.85D calculated theoretically for heptafulvene.(13) The magnetic susceptibility measurements by Maruha and Hazato(14) also indicate the importance of the electronic structures of the type B.* If we assume that the structure A has a moment 3.0 D and the structure B has 16.8 D, the contribution x of the polar form B can be calculated from

$$3.0(1-x)+16.8\,x=4.17$$

as $x=0.082$. There are six individual structures for B. Hence the contribution of each polar structure is 0.014, giving an effective positive charge 0.014 e to each of the six ring carbon atoms. Brown(15) in his molecular orbital treatment gave an effective charge of 0.06—0.11 e. This is not surprising, since the neglect of mutual repulsion between electrons, made in simple molecular orbital method, will always give too high value for the theoretical moment.

2-Phenyltropone and its derivatives.— The moment of 2-phenyl-tropone is smaller than that of tropone, due to the induction effect. Presumably the benzene ring is nearly perpendicular to the plane of cycloheptatriene ring to minimize steric hindrance. The absorption spectra studied by Tsuboi(16) also indicate that the degree of conjugation between the two rings is not great. With the assumption that the cycloheptatriene ring has a regular heptagon form, that the moment of 2-phenyltropone, 3.82 D in magnitude, lies along the C=O bond direction and that the value of C—Br bond moment is 1.5 D, the moment of 4-bromo-2-phenyltropone was calculated to be 2.6 D, a little lower than the observed value of 2.73 D. Actually owing to induction effect, the moment of 2-phenyltropone makes an angle of a few degrees with the C=O direction towards phenyl-group. This with C—Br moment gives a greater resultant moment in agreement with experiment. The moment calculated for 3,7-dibromophenyltropone in a similar manner is 4.4 D to be compared with the observed value of 3.67 D. The difference of this order of magnitude may be attributed to the induction and steric effects.

The position of methoxy-group in 2-(p-methoxyphenyl)-tropone has already been determined by us(17) from evidences in organic synthesis. Hoping to confirm the conclusion, we calculated the moment for p-position with reasonable assumptions. The calculated value of 3.9 D agrees fairly well with the observed value of 3.63 D.**

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(9) T. Shiratori and S. Kinumaki, private communication.

(13) E. D. Bergmann, E. Fischer, D. Ginsberg, Y. Hirshberg, D. Lavie, M. Mayot, A. Pullman and B. Pullman, *Bull. Soc. Chim. France*, **1951**, 684.

(14) J. Maruha and G. Hazato private communication.

* See also the literature (a) of Table 1.

(15) R. D. Brown, *J. Chem. Soc.*, **1951**, 2670.

(16) M. Tsuboi, private communication.

(17) T. Nozoe, S. Seto, T. Ikemi and T. Sato, *loc. cit.* reference (e) of Table 1.

** The theoretical value is rather insensitive to the presumed position of methoxy-group (3.9 D for *para*, 3.9 D for *meta* and 3.4 D for *ortho*-substitution). It is therefore impossible from the dipole moment data alone to determine the position.

Table 3

Dipole Moments of Methyl Ethers of Tropolone Derivatives

2-Methoxy-tropones	*cis*-Position	Perpendicular form	*trans*-Position	Observed (D)
3-Bromo-	3.4—4.4	4.1—4.9	4.7—5.4	3.31
7-Bromo-	4.0—4.6	5.3—5.7	6.3—6.7	5.51
6-Methyl-	3.3—4.2	4.3—5.0	5.1—5.7	5.06
7-Isopropyl-*	2.9—3.8	3.8—4.6	4.6—5.2	4.11

Tropolone methyl ether and its derivatives.—The moment of tropolone methyl ether was estimated from those of tropone and methoxy-group with due regard to the mesomeric moments of O—C (ring) bond. The calculated moment is 3.1—3.9 D for *cis*-configuration, i.e., for methyl group near the oxygen atom of C=O in the ring plane, 5.1—5.6 D for *trans*-configuration and 4.2—4.8 D for the structure in which the methoxy-group lies in a plane perpendicular to the ring. The possible explanation of the observed moment, 4.72 D, is either that the methoxy-group is out of the ring plane to minimize steric hindrance or that both *cis*- and *trans*-configurations are present to give an intermediate moment. A similar conclusion can also be derived for substituted methoxytropones as shown in Table 3.

In particular, the moment of 3-bromo-2-methoxytropone is very close to the theoretical value for *cis*-configuration. Probably the methoxy-group is repelled by the great steric repulsion of bromine atom at 3-position. This will render the molecule less stable than that of 7-bromo-2-methoxytropone in good agreement with the fact that the former is more liable to aromatization than the latter.(18) Mills and Tyrell(19) in their preliminary measurements gave for the moment of *m* (β in their notation)-methyltropolone methyl ether A the value of 4.9 D in agreement with ours. Sutton and Saxby(20) also measured the moment** of this compound and supported the constitutions proposed by Akroyd and others.

The moment of tropolone methyl ether hydrate is independent of temperature and the dependence of the dielectric constant and density of the solution upon concentration is normal. This fact suggests no association taking place. The observed apparent moment of 6.80 D agrees within experimental errors with

$$\bar{\mu}=[2\mu^2(\text{trop. meth. eth.})+\mu^2(\mathrm{H_2O})]^{1/2}$$
$$=(2\times4.72^2+1.75^2)^{1/2}=6.9\ \mathrm{D}.$$

Hence we conclude that in benzene solution the hydrate dissociates into three separate *molecules*.

Summary

The dipole moments of tropone, 2-phenyltropone, tropolone methyl ether and their derivatives were measured in benzene solution at 25°. The increase of moment of tropone over that of cycloheptanone was adequately explained by mesomeric effect and an additional effect due to the formation of cycloheptatriene ring. The latter effect was supported by the theoretical moment for heptafulvene. The moments of various derivatives were compared with the theoretical data. The agreement between them confirmed the correctness of the position of substituents in these compounds already determined or inferred from the standpoint of organic syntheses. The apparent moment of tropolone methyl ether hydrate indicates that in benzene the hydrate dissociates into three separate molecules.

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Chemical Institute, Faculty of Science,
Nagoya University, Nagoya
Chemical Institute, Faculty of Science,
Tôhoku University, Sendai

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* The position of isopropyl-group was determined by T. Nozoe, S. Seto, T. Ikemi and T. Sato from evidences in organic chemistry, the details of which will be published shortly.

(18) T. Nozoe, Y. Kitahara and S. Masamune, *loc. cit.* reference (g) of Table 1.

(19) R. D. Haworth and J. D. Hobson, *J. Chem. Soc.*, **1951**, 561.

(20) P. Akroyd, R. D. Haworth and J. D. Hobson, *loc. cit.* reference (i) of Table 1.

** Unfortunately their value is not given in the paper.