Studies on the Dipole Moments of Acenaphthene and its Derivatives

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(Received August 1, 1956)

The dipole moment of acenaphthene was determined in 1949 by Lumbroso[1] as 0.97D, and then in 1950 by Bergmann et al.[2] as 0.85D, both measurements being made in benzene solution. Recently, Chau and Le Fèvre[3] gave the value 0.81D for this substance first determined in the gaseous phase and 0.80D in carbon tetrachloride solution.

Since there is divergence of moment values, it was thought worth while to make an exact measurement on this polar hydrocarbon using the gas-optical method at several temperatures. Measurements were carried out also in benzene solution for the sake of comparison.

Two chlorine derivatives of acenaphthene were prepared for the present work and their dipole moments were also measured in benzene solution at 25°C.

A discussion is given on the polarity of acenaphthene and on related problems.

Experimental Procedure

1. Materials.—(I) *Acenaphthene.*—M.p. 95-96°C. This substance (supplied from Yawata Ironworks) was recrystallized from benzene.

(II) 5-*Chloroacenaphthene.*—M. p. 69.5-70.5°C. Acenaphthene was dissolved in chloroform, and chlorinated by sulfuryl chloride. Then the chlorinated product was distilled twice in vacuo (5 mmHg). The fraction boiling at 145-155°C was recrystallized from ethanol, and then from carbon tetrachloride.

(III) 5, 6-*Dichloroacenaphthene.*—M. p. 166-168 °C. 5-Chloroacenaphthene was dissolved in 1, 2-dichloroethane and chlorinated by sulfuryl chloride in the presence of PCl_5. The product was recrystallized from benzene.

Solvent Benzene.—The solvent benzene was made free from thiophene by anhydrous $AlCl_3$. It was then dried over metallic sodium and distilled.

2. Measurement. — The dielectric constants were measured by the heterodyne double-beat method in the gaseous state[4], and by the resonance method in solution[5].

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[1] H. Lumbroso, *Compt. rend.*, **228**, 1425 (1949).

[2] E. D. Bergmann et al., *J. chim. phys.*, **48**, 356(1951).

[3] J. Y. H. Chau and R. J. W. Le Fèvre, *Australian J. Chem.*, **8**, 562 (1955).

[4] T. Chiba, This Bulletin (to be published).

[5] R. J. W. Le Fèvre and P. Russel, *Trans. Faraday Soc.*, **43**, 374 (1947).

The density d was measured by a pycnometer. The molar polarization of the solute extrapolated to the infinite dilution ($P_{2\infty}$) was calculated by means of the equation proposed by Halverstadt and Kumler[6].

The sum of atomic and electronic polarization (P_E+P_A) was assumed to be equal to MR_D, where MR_D is the molar refraction at D-line.

MR_D of (I) was calculated from refractive index and density obtained for the melted state. MR_D of chlorine derivatives were taken as the sum of MR_D (I) and the atomic refraction of Cl, i. e., $MR_D(\text{II})=MR_D(\text{I})+AR_D(\text{Cl})-AR_D(\text{H})$.

Results

TABLE I

(I) Acenaphthene $MR_D=52.0$ cc.

Gaseous State

T(°K)	p(mmHg)	n	P(cc.)	ΔP(cc.)	μ(D)
464.2	45—63	13	63.8	2.0	0.95
466.3	42—70	11	63.4	1.0	0.93
476.5	57—90	9	63.1	0.8	0.93

Mean value: 0.93D

p: Pressure of the observations
n: Number of the observations
P: Molecular polarization
ΔP: Mean deviation of P

(I) Acenaphthene $MR_D=52.0$ cc.

In benzene at 25°C

w(%)	ε	d	v	
0	2.2720	0.8722	1.1465	
1.2096	2.2868	0.8744	1.1436	$A=0.866$
2.036	2.2898	0.8759	1.1417	$B=-0.232$
3.578	2.3034	0.8787	1.1380	$P_{2\infty}=66.9$ cc.
5.496	2.3187	0.8820	1.1338	$\mu=0.85$D
8.162	2.3421	0.8869	1.1275	

(II) 5-Chloroacenaphthene $MR_D=56.9$ cc.

In benzene at 25°C

w(%)	ε	d	v	
0.6078	2.2920	0.8743	1.1438	$A=4.006$
1.3654	2.3246	0.8763	1.1412	$B=-0.3605$
2.229	2.3607	0.8782	1.1387	$P_{2\infty}=186.4$ cc.
3.098	2.3914	0.8810	1.1351	$\mu=2.50$D

(III) 5,6-Dichloroacenaphthene $MR_D=61.7$ cc.

In benzene at 25°C

w(%)	ε	d	v	
0.492	2.3118	0.8741	1.1440	$A=7.649$
0.996	2.3488	0.8757	1.1419	$B=-0.429$
1.395	2.3812	0.8769	1.1404	$P_{2\infty}=369$ cc.
1.929	2.4243	0.8786	1.1382	$\mu=3.85$D

w: Concentration
ε: Dielectric constant
d: Density
v: Specific volume
A, B: Rates of change of the dielectric constant ε and specific volume v with weight fraction $w/100$.

Discussion of Results

In agreement with the results of the preceding workers, a dipole moment of acenaphthene 0.93D as vapor was found in the present measurement.

This marks high polarity as a hydrocarbon. It is to be noted in this connection that the moment of acenaphthene is approximately equal to, or slightly larger than, twice of that of toluene, that is, 0.37D×2=0.74D.

Further, the existence of an abnormal solvent effect as suspected from the previous data[*1,2] can be definitely ruled out both from the work of Chau and Le Fèvre[3] and from the present research.

The dipole moments of acenaphthene, 5-chloroacenaphthene and 5,6-dichloroacenaphthene are compared with those of naphthalene, 1-chloronaphthalene and 1,8-dichloronaphthalene[8] (see Fig. 1). Almost equal increases in moment upon the successive substitution of Cl atoms are found both in acenaphthene and naphthalene. The increase 1.31–1.35D on the introduction of the second Cl atom is lower than the increase on the first substitution 1.51–1.65D. The apparent reduction is due to the mutual induction of the two C–Cl dipoles.

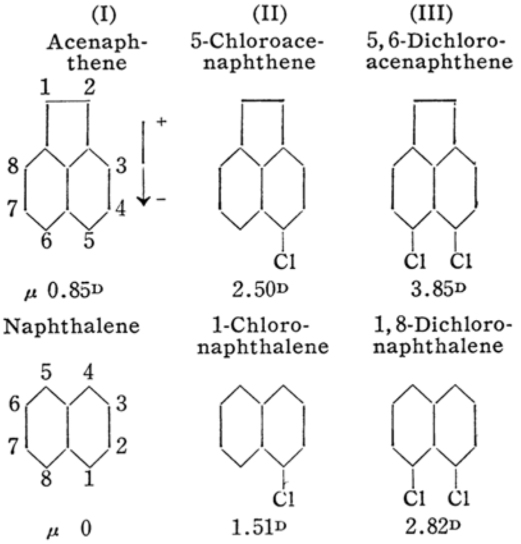

Fig. 1

From the above comparison, it will be seen that the electron displacement in an acenaphthene molecule caused by the substitution of Cl atoms is essentially not

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

[7] v. Auers and Frühling, *Ann.* **422**, 200 (1921).

[*] Lumbroso's value in 1947 was 1.57D.

[8] G. C. Hampson and A. Weissberger, *J. Chem. Soc.*, **1936**, 393.

much different from that in naphthalene. In other words, no special change occurs which might be expected from the existence of the linkage C_1–C_2. Therefore, the dipole moments of Cl-derivatives of acenaphthene can be calculated by the simple rule of vector addition.

The moment of 5-chloroacenaphthene is larger by 0.99D than that of 1-chloronaphthalene while 5,6-dichloroacenaphthene is larger by 1.03D than 1,8-dichloronaphthalene. It can be concluded, therefore, that the dipole moment of acenaphthene of about 0.9D has the direction shown by the arrow head in Fig. 1.

This fact may deserve special attention, since it has been reported⁽⁹⁾ that the most reactive positions of acenaphthene in the substitution reactions are its 5 and 6 positions.

Summary

The dipole moment of acenaphthene (I) was measured in the gaseous phase as 0.93D. Measurement in benzene solution at 25°C gave the following moment values: acenaphthene (I) 0.85D; 5-chloroacenaphthene (II) 2.50D; and 5,6-dichloroacenaphthene (III) 3.85D. By the comparison with the moments of naphthalene derivatives it was shown that the moments of (II) and (III) are approximately equal to the sums of the moment of (I) and the moments arising from one and two C–Cl bonds, respectively.

The authors wish to express their sincere thanks to Prof. K. Higasi for the helpful suggestion and discussion on this subject, and to Prof. Y. Nagai, to Prof. Y. Morino, and to Dr. I. Miyagawa for the kind guidance and valuable advice through this study.

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9) H. E. Nürsten and A. T. Peters, *J. Chem. Soc.*, **1950**, 729; N. Gotoh and Y. Nagai, *J. Chem. Soc. Japan*, (Ind. Chem. Sec.) **58**, 50 (1955).