

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY, PRINCETON, NEW JERSEY]

# Microwave Absorption and Molecular Structure in Liquids. XLI. The Dielectric Relaxation of Three Substituted Naphthalenes in a Slightly Viscous and a Very Viscous Solvent<sup>1,2</sup>

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The dielectric constants and losses at wave lengths of 1.2, 3.2, 10, 25 and 50 cm. and 575 m. and temperatures of 20, 40 and 60° have been measured for  $\alpha$ -chloronaphthalene and  $\alpha$ -bromonaphthalene in dilute solution in decalin and in Nujol, and for  $\beta$ -methylnaphthalene in dilution solution in Nujol. The data have been used to calculate the relaxation times of the polar solute molecules in the solutions. They all show a considerable distribution of relaxation times, both the distribution and the relaxation times decreasing with rising temperature.  $\beta$ -Methylnaphthalene, the longest molecule of the three, shows the largest distribution parameter and the largest relaxation time. The activation energies and entropies for the dielectric relaxation processes have been calculated.

As a preliminary to the investigation of several series of molecules capable of dipole orientation by intramolecular group rotation, it has seemed desirable to add to our knowledge of the behavior of substituted naphthalenes with fixed molecular dipoles. Dielectric relaxation times have, therefore, been measured in solution in the slightly viscous decalin (viscosity = 2.61 c.p.s. at 20°) and the very viscous Nujol (viscosity = 211 c.p.s. at 20°).

## Experimental Methods

**Apparatus.**—The dielectric constants and losses of several rigid molecules were measured at 1, 3, 10, 25 and 50 cm. and at 575 m. utilizing methods previously described.<sup>3-5</sup>

**Purification.**— $\alpha$ -Chloronaphthalene,  $\alpha$ -bromonaphthalene and  $\beta$ -methylnaphthalene were obtained from the Eastman Kodak Company.  $\alpha$ -Chloronaphthalene and  $\alpha$ -bromonaphthalene were purified by refluxing in a three-foot column for several hours, after which they were fractionally distilled.  $\beta$ -Methylnaphthalene was recrystallized six times from benzene. The resulting material was dried under vacuum in an Abderhalden pistol. The observed melting point was 34.7–34.9°.

Decalin was obtained as the practical grade from Matheson, Coleman and Bell. It was fractionally distilled through a four-foot column. The pure decalin fractions were stored over "Drierite" (W. A. Hammond Drierite Company) until used.

Nujol, purchased from a local drugstore, was placed under vacuum for an hour to remove dissolved gas which might be present and then was used without further purification.

## Experimental Results

Measurements were carried out on decalin and Nujol solutions at 20, 40 and 60°. Refractive index measurements also were made, usually at only one temperature. Slopes  $a_0$ ,  $a'$ , and  $a''$  were obtained by plotting the static dielectric constants  $\epsilon_0$ , the high-frequency dielectric constants  $\epsilon'$ , and the losses  $\epsilon''$  of the solutions against the concentrations. Cole-Cole<sup>6</sup> plots of  $a''$  vs.  $a'$  were made in order to determine<sup>7</sup> the distribution parameter  $\alpha$  and the most probable relaxation time  $\tau_0$ .

Experimental values for  $a_0$ ,  $a'$  and  $a''$  obtained for these compounds are listed after each compound. Concentrations

(1) This research was supported by the Office of Ordnance Research. Reproduction, translation, publication, use or disposal in whole or in part by or for the United States Government is permitted.

(2) This paper represents part of the work submitted by Eugene L. Grubb to the Graduate School of Princeton University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) H. L. Laquer and C. P. Smyth, *J. Am. Chem. Soc.*, **70**, 4097 (1948).

(4) W. M. Heston, Jr., A. D. Franklin, E. J. Hennelly and C. P. Smyth, *ibid.*, **72**, 3443 (1950).

(5) D. A. Pitt and C. P. Smyth, *J. Phys. Chem.*, **63**, 582 (1959).

(6) K. S. Cole and R. H. Cole, *J. Chem. Phys.*, **9**, 341 (1941).

(7) C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Company, New York, N. Y., 1955, Chap. II.

are expressed as mole fraction when decalin is used as the solvent and as weight fraction when Nujol is used. Values obtained for  $\alpha$ ,  $a_D$ ,  $a_\infty$  and  $\tau_0$  are listed in Table II.

TABLE I

SLOPES FOR THE DEPENDENCE OF DIELECTRIC CONSTANT AND LOSS ON CONCENTRATION OF SOLUTE

$\lambda$ (cm.)	$a'$ 20°	$a''$	$a'$ 40°	$a''$	$a'$ 60°	$a''$
$\alpha$ -Chloronaphthalene (0–0.030 in Nujol)						
1.25	0.50	0.22	0.53	0.20	0.56	0.21
3.22	0.62	.30	0.69	.37	0.80	.42
10	1.07	.52	1.17	.48	1.26	.43
25	1.34	.48	1.39	.42	1.48	.31
50	1.70	.31	1.68	.23	1.61	.15
575m.	1.88		1.77		1.66	
$\alpha$ -Bromonaphthalene (0–0.030 in Nujol)						
1.25	0.48	0.10	0.50	0.11	0.52	0.12
3.22	.55	.20	.59	.23	.66	.27
10	.72	.35	.79	.35	.85	.34
25	1.09	.39	1.15	.32	1.21	.22
50	1.43	.22	1.38	.18	1.31	.09
575m.	1.51		1.42		1.32	
$\beta$ -Methylnaphthalene (0–0.070 in Nujol)						
3.22	0.325	0.014	0.349	0.042	0.332	0.028
10	.360	.038	.373	.050	.390	.055
25	.385	.044	.405	.052	.428	.048
50	.468	.045	.462	.035	.455	.028
575m.	.537		.503		.478	
$\alpha$ -Chloronaphthalene (0–0.035 in Decalin)						
1.25	0.63	0.37	0.59	0.37	0.61	0.39
3.22	1.08	.62	1.12	.62	1.17	.60
10	1.96	.40	1.89	.35	1.83	.30
25	2.12	.25	2.03	.19	1.96	.12
575m.	2.26		2.11			
$\alpha$ -Bromonaphthalene (0–0.026 in Decalin)						
1.25	0.54	0.31	0.59	0.32	0.63	0.34
3.22	0.97	.61	1.08	.61	1.17	.60
10	1.84	.52	1.78	.43	1.73	.34
25	2.08	.33	2.00	.23	1.94	.15
575m.	2.25		2.09		1.97	

## Discussion of Results

It is profitable to compare the present results with those of previous measurements<sup>8-10</sup> in Table

(8) A. J. Curtis, P. L. McGeer, G. B. Rathmann and C. P. Smyth, *J. Am. Chem. Soc.*, **74**, 644 (1952).

(9) D. H. Whiffen and H. W. Thompson, *Trans. Faraday Soc.*, **42A**, 122 (1946).

(10) A. D. Franklin, W. M. Heston, Jr., E. J. Hennelly and C. P. Smyth, *J. Am. Chem. Soc.*, **72**, 3447 (1950).

TABLE II

SLOPES,  $a_D$ , FOR THE DEPENDENCE OF THE SQUARE OF THE REFRACTIVE INDEX ON CONCENTRATION, WITH INFINITE FREQUENCY INTERCEPTS  $a_\infty$ , RELAXATION TIMES  $\tau_0$ , AND DISTRIBUTION PARAMETERS  $\alpha$

Temp., °C.	$a_D$	$a_\infty$	$\tau_0 \times 10^{12}$ sec.	$\alpha$
α-Chloronaphthalene (Nujol)				
20	0.35	0.38	62.4	0.25
40		.41	39.8	.21
60		.44	27.2	.17
α-Bromonaphthalene (Nujol)				
20	0.28	0.44	85.1	0.18
40		.45	53.7	.16
60		.48	35.2	.13
β-Methylnaphthalene (Nujol)				
20	0.31	0.31	148.0	0.46
40		.31	95.1	.36
60		.31	64.8	.25
α-Chloronaphthalene (Decalin)				
20	0.34	0.34	21.0	0.25
40		.34	18.2	.23
60		.34	15.5	.21
α-Bromonaphthalene (Decalin)				
20	0.32	0.35	26.4	0.24
40		.40	21.9	.20
60		.44	17.3	.15

III. The values quoted from reference 9 were calculated on the assumption that the compound gave a Debye-type absorption curve. This assumption may cause a slight error in the calculated relaxation times.

From Table III, it is seen that the relaxation time for a given solvent and temperature is larger for α-bromonaphthalene than for α-chloronaphthalene,

TABLE III

RELAXATION TIMES ( $10^{-12}$  SEC.) OF α-CHLORONAPHTHALENE AND α-BROMONAPHTHALENE IN VARIOUS SOLVENTS

Temp., °C.	Heptane	Decalin	Nujol	Nujol
α-Chloronaphthalene				
20	10.6 <sup>8</sup>	21.0	62.4	63.7 <sup>8</sup>
40	9.0 <sup>8</sup>	18.2	39.8	39.3 <sup>8</sup>
60	7.2 <sup>8</sup>	15.5	27.2	26.5 <sup>8</sup>
α-Bromonaphthalene				
20	16.0 <sup>9</sup>	26.4	85.1	
40	13.5 <sup>9</sup>	21.9	53.7	
60	11.5 <sup>9</sup>	17.3	35.2	

lene, because of the larger size and polarizability of the bromine atom as compared to the chlorine atom. This also has been found in the pure liquid state,<sup>11</sup> where the relaxation times are of almost the same size as those obtained when Nujol is used as the solvent, even though the pure liquid viscosities are much smaller than the Nujol viscosities. It is likely that the dipole-dipole interaction in the pure liquid hinders the relaxation process and consequently gives a larger relaxation time. It also seems probable that the liquid structure of Nujol contains holes which make possible solute molecule

(11) E. J. Hennelly, W. M. Heston, Jr., and C. P. Smyth, *J. Am. Chem. Soc.*, **70**, 4102 (1948).

rotation with much greater ease than would be expected from the resistance to flow evidenced by the high viscosity. The relations between solvent viscosity and relaxation time for the two halonaphthalenes are compared in Table IV, in which  $\tau_D$  is the relaxation time in decalin,  $\tau_N$  is the relaxation time in Nujol and  $\tau_H$  is the relaxation time in *n*-heptane. A similar designation is given for the viscosities.<sup>8,12</sup> In these results the relaxation time is more nearly proportional to the logarithm of the viscosity than to the viscosity itself.

TABLE IV

RATIOS OF RELAXATION TIMES AND VISCOSITIES IN DIFFERENT SOLVENTS AT 20°

$$\eta_N = 211, \eta_D = 2.61 \text{ and } \eta_H = 0.42 \text{ cps}$$

	$\frac{\tau_D}{\tau_H}$	$\frac{\eta_D}{\eta_H}$	$\frac{\tau_N}{\tau_D}$	$\frac{\eta_N}{\eta_D}$	$\frac{\tau_N}{\tau_H}$	$\frac{\eta_N}{\eta_H}$
α-Chloronaphthalene	1.98	6.16	2.97	80.6	5.89	501
α-Bromonaphthalene	1.65	6.16	3.22	80.6	5.32	501

The values of the distribution parameter  $\alpha$  for α-chloronaphthalene in Nujol, like those of the relaxation time, agree closely with the results of a previous measurement.<sup>8</sup> There is only a slight difference in  $\alpha$  values for the two halonaphthalenes in a given solvent, as might be expected. However, in decalin the values of  $\alpha$  are much larger than the low values previously<sup>8</sup> obtained in *n*-heptane. β-Methylnaphthalene has  $\alpha$  values much larger than those for the α-halonaphthalenes in Nujol. In the pure liquid, β-methylnaphthalene shows a larger distribution parameter than that found for the α-compound.<sup>13</sup> These observations can be explained by considering the dipole moment direction in these molecules. In β-methylnaphthalene the dipole moment lies in the plane of the two rings, not along the short axis of the molecule, but between the long and the short axes in such a manner that rotation around both axes is expected to take place. The fact that rotation can take place about two axes leads to the expectation of a larger distribution of relaxation times, especially

TABLE V

ACTIVATION ENERGIES (KCAL./MOLE) AND ENTROPIES (E.U./MOLE)

	Temp., °C.	$\Delta F^*$	$\Delta H^*$	$\Delta S^*$
α-Chloronaphthalene in Nujol	20	3.46	3.62	0.55
	40	3.46	3.58	.38
	60	3.47	3.54	.21
α-Bromonaphthalene in Nujol	20	3.64	3.70	.20
	40	3.65	3.66	-.03
	60	3.65	3.62	-.09
α-Chloronaphthalene in Decalin	20	2.83	0.81	-6.80
	40	2.97	.77	-7.02
	60	3.09	.73	-7.08
α-Bromonaphthalene in Decalin	20	2.96	1.33	-5.56
	40	3.09	1.29	-5.75
	60	3.17	1.25	-5.76
β-Methylnaphthalene in Nujol	20	3.97	3.39	-1.98
	40	4.01	3.35	-2.11
	60	4.04	3.31	-2.19

(12) O. F. Kalman and C. P. Smyth, *ibid.*, **82**, 783 (1960).

(13) R. W. Rampolla and C. P. Smyth, *ibid.*, **80**, 1057 (1958).

in Nujol solution, for the  $\beta$ -substituted naphthalenes than for the  $\alpha'$  substituted. It was found<sup>13</sup> that the  $\alpha$  value at 40° for  $\alpha$ -methylnaphthalene is 0.08 and for  $\beta$ -methylnaphthalene, 0.16. The relaxation times of  $\beta$ -methylnaphthalene in Nujol are larger than those of the  $\alpha$ -halonaphthalenes in Nujol because, due to the more elongated structure of  $\beta$ -methylnaphthalene, it will experience more resistance to rotation and thus have a higher relaxation time.

The free energies  $\Delta F^*$ , heats  $\Delta H^*$  and entropies  $\Delta S^*$  of activation for dielectric relaxation, calculated in the usual manner,<sup>11</sup> are given in Table V.

It is evident that the  $\Delta F^*$  values in Table V increase with increasing viscosity and molecular size, as has been observed for a number of other liquids.<sup>8,11,12</sup>  $\beta$ -Methylnaphthalene is effectively larger than the two  $\alpha$ -halonaphthalenes, because the direction of the dipole moment in the molecule causes the molecular rotation to sweep out a greater volume than that swept by the other two molecules in rotating around their long axes. The  $\Delta H^*$  values obtained for  $\alpha$ -bromonaphthalene in several solvents decrease as the solvent complexity and viscosity decrease. A large decrease in entropy of activation occurs when measurements are carried out in decalin or *n*-heptane as compared to Nujol.

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## Synthesis of Arylphosphonous Dichlorides by Reduction of Diazonium Fluoroborate-Phosphorus Trichloride Reaction Products<sup>1,2</sup>

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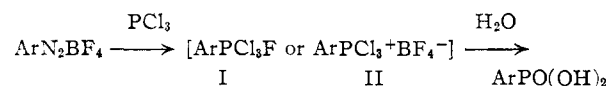
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Products of the reaction of diazonium fluoroborates with phosphorus trichloride have been reduced with magnesium to form phosphonous dichlorides. Although the yields are in the 20–35% range, the reaction serves as a source of phosphonous dichlorides unobtainable by other methods. Several new structures have been made. The reaction also has given access to new phosphinic acids, since these compounds are prepared readily by hydrolysis of the dichlorides.

Arylphosphonous dichlorides have been known almost since the beginnings of organophosphorus chemistry, but remain relatively rare compounds. The majority of the presently known phosphonous dichlorides were prepared by two methods developed by early workers.<sup>3</sup> One method involves the aluminum chloride-catalyzed reaction between phosphorus trichloride and certain aromatic compounds. Early difficulties with product isolation have been largely overcome,<sup>4</sup> but this method remains limited in scope. Thus, *meta*-directing groups present in the aromatic compound prevent substitution; ring-activating substituents lead to a mixture of *ortho* and *para* isomers, predominantly the latter. The other method involves the arylation of phosphorus trichloride with aryl mercury compounds. Two recent publications have reported the use of other organometallic compounds in this reaction. Yakubovich and Motsarev<sup>5</sup> used aryl aluminum chlorides, while Weil, Prijs and Erlenmeyer<sup>6</sup> have used aryl zinc chlorides. The versatility of these arylations, however, is impaired by limitations on the nature of substituents permissible on the aromatic nucleus.

For many years, most syntheses of arylphosphonic acids started with phosphonous dichlorides

or derivatives, and thus these compounds also remained relatively rare. In 1951, Doak and Freedman<sup>7</sup> opened up this field with a synthesis based on the cuprous halide-catalyzed reaction of phosphorus trihalides with dry diazonium fluoroborates in organic solvents. The reaction products are not isolated but are hydrolyzed to give phosphonic acids. Yields of 30–50% or more are common, and very few failures have been recorded. In the years since 1951, a large number of new structures have been made by this general reaction, which may be expressed as



The intermediate has never been subjected to study, although structures I or II<sup>8</sup> seem reasonable. Whatever its precise structure, the intermediate appeared to us to be chemically similar to the tetrahalophosphoranes ( $\text{ArPX}_4$ ), also readily hydrolyzed to phosphonic acids.<sup>9</sup> This suggested the possibility that the intermediate might be reduced to the phosphonous dichloride, a reaction well-known for the tetrahalophosphoranes.<sup>10</sup> Such a reaction would then make available many new structures presently unobtainable. In a somewhat similar manner, Komkov, Karavanov and Even<sup>11</sup> and Parshall<sup>12</sup> have reduced structures of

(1) Some of this work was the subject of a preliminary communication; L. D. Quin and J. S. Humphrey, Jr., *J. Am. Chem. Soc.*, **82**, 3795 (1960).

(2) Supported by the Duke University Research Council and in part by Research Grant No. E-3624 of the National Institute of Allergy and Infectious Diseases, U. S. Public Health Service.

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(4) W. T. Dye, *J. Am. Chem. Soc.*, **70**, 2595 (1948).

(5) A. Y. Yakubovich and G. V. Motsarev, *Zhur. Obshch. Khim.*, **23**, 1543 (1953).

(6) T. Weil, B. Prijs and H. Erlenmeyer, *Helv. Chim. Acta*, **35**, 1412 (1952); **36**, 1314 (1953).

(7) G. O. Doak and L. D. Freedman, *J. Am. Chem. Soc.*, **73**, 5658 (1951).

(8) P. C. Crofts, *Quart. Revs.*, **12**, 341 (1958).

(9) Reference 3, Chapter 4.

(10) L. D. Quin and C. H. Rolston, *J. Org. Chem.*, **23**, 1693 (1958), and other references cited therein.

(11) E. P. Komkov, K. U. Karavanov and S. Z. Even, *Zhur. Obshch. Khim.*, **28**, 2963 (1958).

(12) G. W. Parshall, *J. Inorg. Nucl. Chem.*, **12**, 372 (1960).