which do not fall in line with the other compounds as seen in Table III.

TABLE III

INFRARED SPECTRA OF ALKYL NITROSAMINES

Nitrosamine	N=O frequencies of monomer peak			N-N frequency		
	Gas	Liquid	CCl_4	Gas	Liquid	CCl_4
Dimethyl	1493(s)	1475(w, sh)	1470(s, sh)	1017	1049	1042
Diethyl	1485(s)[a]	1470(m, sh)	1470(s)	..	1065	1063
Dipropyl	1487(s)[a]	1456(s)[a]	1460([a])	..	..	..
Diisopropyl	.....	1468(s)	1473(s)	..	..	..
Dibutyl	.....	1460(s, sh)	1465(s)	..	1077	1075
N-Nitroso-morpholine	.....	1450(w, sh)	1465(s)	..	..	..

[a] Taken from Haszeldine's data.[2a]

As the chain length increases, there is a progressive increase in intensity of the N=O band of the liquid relative to the others in the spectrum. This is interpreted as a reduced tendency toward dimerization which is particularly evident for the diisopropyl compound where the bulky nature of the isopropyl group may cause some steric hindrance in the dimer form. The multiplicity of bands in the 1000–1100 cm.$^{-1}$ region of this compound probably arises from both dimer and monomer contributions. A progressive small shift of the N=O frequency in the liquid to longer wave lengths also occurs as the chain length increases.

C. Unsymmetrically Substituted Nitrosamines.—This work has included a brief study of N-nitroso-N-methylaniline, N-nitroso-N-ethylaniline, N-nitroso-N-methyl-*p*-toluidine and benzylmethylnitrosamine. Table IV lists the N=O monomer frequencies, the phenyl frequencies in the 1500–1600 cm.$^{-1}$ region, and the N–N frequencies. In addition, a sharp phenyl band appears in the N–N region which shifts considerably in the benzyl compound. Once again these compounds show a multiplicity of peaks in the 1450–1380 cm.$^{-1}$ region which are believed to arise from the dimer form as well as from CH deformations.

TABLE IV

INFRARED FREQUENCIES OF UNSYMMETRICAL NITROSAMINES

Nitrosamine	Phenyl vibrations	1500 cm.$^{-1}$ region N=O stretching freq. of monomer	N–N stretching frequency	1050 cm.$^{-1}$ region vibrations
N-Nitroso-N-methylaniline (liq.)	1605(m) 1500(s)	1470(s)	1092(s)	1030(m)
N-Nitroso-N-ethylaniline (liq.)	1604(w) 1500(s)	1480(s)	1099(s) 1081(m, sh)	1033(m)
N-Nitroso-N-methyl-*p*-toluidine (60° melt)	1588(vw) 1515(s)	1460(s)	1090(s)	1018(m)
Benzylmethylnitrosamine (liq.)	1610, 1588(vw) 1500(m)	1450(s)	1042(s) 1027(s)	1077(m)
(CCl_4 soln.)	1610, 1588(vw) 1500(w)	1455(s)	1035(m, sh) 1027(s)	1080(m)

The N=O stretching frequency of the monomer is somewhat more intense in phenyl substituted nitrosamines than in the alkyl compounds, suggesting that the tendency toward dimerization is reduced by steric hindrance.

WILMINGTON, DELAWARE

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Microwave Absorption and Molecular Structure in Liquids. XX. Dielectric Relaxation Times and Molecular Shapes of Some Substituted Benzenes and Pyridines[1-3]

BY ANTHONY J. PETRO[4] AND CHARLES P. SMYTH

RECEIVED JULY 1, 1957

Measurements of dielectric constant and loss at wave lengths of 1.25, 3.22 and 10.0 cm. and 300 m. have been carried out at 20, 40 and 60° on toluene, styrene, ethylbenzene, isopropylbenzene, *o*-xylene, *m*-xylene, *p*-chlorotoluene, α-picoline, 2- and 4-vinylpyridine, and 2- and 4-ethylpyridine in the pure liquid state and on solutions of *p*-chlorotoluene in benzene, *p*-xylene and *p*-dichlorobenzene. The relaxation times and viscosities are examined in relation to molecular size and shape. A regular increase in relaxation time with increasing size of the substituted group is observed for the benzene derivatives with the exception of styrene. The anomalous values for the latter are attributed to planarity of the molecule. The slightly polar hydrocarbons are compared with the polar pyridines after suitable internal field and viscosity corrections have been applied to the latter. The ratios of the molecular relaxation times and viscosities at constant temperature, or equivalently, the molecular relaxation times at constant viscosity, are found to be adequate in most cases for correlation of compounds of different polarity but similar size and shape. A similar correlation is made for *p*-chlorotoluene between the pure liquid and its solutions in non-polar solvents whose molecular sizes and shapes are similar to the solute. Activation energies for viscous flow and dielectric relaxation are compared on the basis of molecular size and shape and the mechanism of each process. The difference between the two quantities is found to be a maximum for the nearly planar molecules and to decrease with increasing bulk and irregularity of the substituted group.

The investigation into the relations between molecular size and shape and dielectric relaxation in liquids has been extended to a group of benzene and pyridine derivatives. Whereas the benzene and pyridine rings are rigid, symmetric and planar structures, substitution of one or more groups into the ring will alter the size and shape of the molecule as well as the planarity and possibly the rigidity. Furthermore, benzene and pyridine are only very slightly different in size and shape but differ markedly in polarity. Consequently, the effects of po-

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(1) This research was supported by the United States Air Force through the Office of Scientific Research of the Air Research and Development Command under Contract No. AF18(600)1331. Reproduction, translation, publication, use or disposal in whole or in part by or for the United States Government is permitted.

(2) This paper represents a part of the work to be submitted by Mr. A. J. Petro to the Graduate School of Princeton University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) Portions of this paper were read before the American Chemical Society, Physical and Inorganic Division, Atlantic City, N. J., Sept. 18, 1956.

(4) Monsanto Fellow in Chemistry, 1956–1957.

TABLE I

DENSITIES, VISCOSITIES, DIELECTRIC CONSTANTS AND LOSSES

				1.25		3.22		10.0 cm.	
t, °C.	d	η(c.p.s.)	ϵ_0	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''
Toluene									
20	0.8669[a]	0.59[a]	2.3837	2.326	0.0564	2.368	0.0352		
40	.8484[a]	.47[a]	2.3390	2.298	.0510	2.330	.0258		
60	.8300[a]	.38[a]	2.2941	2.266	.0412	2.286	.0210		
Styrene									
20	0.9063[b]	0.78[b]	2.4257	2.417	0.0092	2.423	0.0062		
40	.8887[b]	.62[b]	2.3884	2.382	.0084	2.387	.0048		
60	.8712[b]	.49[b]	2.3510	2.347	.0066	2.350	.0036		
Ethylbenzene									
20	0.8670	0.68[a]	2.4042	2.301	0.0541	2.355	0.0565		
40	.8495	.54[a]	2.3587	2.277	.0543	2.327	.0486		
60	.8317	.44[a]	2.3136	2.253	.0540	2.294	.0394		
Isopropylbenzene									
20	0.8619	0.79[a]	2.3833	2.269	0.0424	2.307	0.0555		
40	.8450	.61[a]	2.3386	2.247	.0457	2.289	.0522		
60	.8278	.49[a]	2.2958	2.221	.0465	2.263	.0439		
o-Xylene									
20	0.8800	0.81[a]	2.5872	2.413	0.1247	2.521	0.1047		
40	.8634	.63[a]	2.5315	2.398	.1205	2.489	.9830		
60	.8465	.50[a]	2.4781	2.382	.1106	2.451	.0674		
m-Xylene									
20	0.8647	0.62[a]	2.3684	2.308	0.0412	2.342	0.0366		
40	.8474	.49[a]	2.3268	2.283	.0403	2.311	.0298		
60	.8299	.41[a]	2.2860	2.257	.0364	2.276	.0240		
p-Chlorotoluene									
20	1.0694	0.89[c]	6.25	2.805	0.888	3.702	1.166	5.32	1.49
40	1.0500	.70[c]	5.99	2.873	.975	3.971	1.65	5.56	1.16
60	1.0302	.56[c]	5.66	2.907	1.12	4.181	1.52	5.42	0.889
α-Picoline									
20	0.9443[c]	0.81[c]	10.18	4.288	2.84	7.346	3.372	9.53	1.57
40	.9256[c]	.63[c]	9.30	4.626	2.88	7.519	2.745	9.01	1.21
60	.9076[c]	.51[c]	8.52	4.971	2.83	7.353	2.218	8.48	0.862
2-Vinylpyridine									
20	0.9742	1.13	9.126	3.598	1.97	5.455	2.83	8.01	1.95
4-Vinylpyridine									
20	0.9836	1.22	10.50	3.200	1.70	4.658	3.13	8.47	3.41
40	.9667	0.98	9.77	3.367	1.91	5.369	3.29	8.56	2.57
2-Ethylpyridine									
20	0.9304	0.93	8.33	3.628	2.13	5.732	2.65	7.83	1.62
40	.9126	.71	7.59	3.723	2.08	5.987	2.20	7.39	1.15
60	.8945	.57	7.00	4.048	2.07	5.977	1.73	6.85	0.82
4-Ethylpyridine									
20	0.9413	1.03	10.98	3.450	2.33	5.757	3.95	9.52	2.99
40	.9241	0.78	10.51	3.617	2.76	6.406	3.91	9.52	2.21
60	.9066	0.62	9.82	3.858	2.77	6.867	3.55	9.43	1.60

[a] American Petroleum Institute Research Project 44, "Selected Values of Hydrocarbons and Related Compounds." [b] R. H. Boundy and R. F. Boyer (editors), "Styrene: Its Polymers, Copolymers and Derivatives," Reinhold Pub. Corp., New York, N. Y., p. 55. Measured density values: d^{25} 0.9016, d^{40} 0.8885. [c] J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier Publishing Co., Inc., New York, N. Y., 1950.

larity and viscosity on the dielectric relaxation time can be estimated, without consideration of size and shape factors, by comparing the values of the same derivatives of both ring systems. In addition, by measuring the dielectric relaxation time of a polar substance in a non-polar solvent whose molecular size and shape is very nearly the same as that of the solute, all effects except that of viscosity can essentially be eliminated. Accordingly, dielectric constants and losses at microwave frequencies have been measured for a group of substituted benzenes and pyridines in the pure liquid state and also for solutions of *p*-chlorotoluene in benzene, *p*-xylene, and *p*-dichlorobenzene.

Purification of Materials.—The substances studied were obtained from Merck and Company, the Baker and Adamson Company, Union Carbide Corp., Matheson, Coleman and Bell, Inc., the Reilly Tar and Chemical Company, the Eastman Kodak Company, or the Brothers Chemical Company. The sources, methods of purification, and boiling points are listed below.

		B.p., °C.	
	Source	Obsd.	Lit.
Benzene[a]	Merck	79.9	80.1
Toluene[a]	U.C.C.	101.8	110.6
Styrene	Brothers	44–45 (20 mm.)	48 (20 mm.)
Ethylbenzene[a]	Brothers	136.3	136.1
Isopropylbenzene[a]	Brothers	151.6	152.4
o-Xylene[b]	Brothers	144.4	144.4
m-Xylene[a]	Brothers	138.4 (747.8 mm.)	139.1
p-Xylene[c]	Brothers	138.3–138.4	138.4
p-Chlorotoluene[d]	Matheson	162.1	162.4
α-Picoline[d]	Brothers	129.8	129.4
2-Vinylpyridine	Reilly	36 (3 mm.)	80 (29 mm.)
4-Vinylpyridine	Reilly	50 (3 mm.)	54 (7 mm.)
2-Ethylpyridine[d]	Brothers	148.8–149	148.6
4-Ethylpyridine[d]	Eastman	168.2–168.3	166–167
p-Dichlorobenzene	B & A	M.p. 53	M.p. 53

[a] Dried over sodium hydride or calcium hydride and fractionally distilled as needed. [b] Initially purified by the method of Clarke and Taylor,[5] followed by *a*. [c] Fractionally crystallized, followed by *a*. [d] Dried over barium oxide and fractionally distilled as needed.

Experimental Results

Dielectric constants, ϵ', and losses, ϵ'', at wave lengths of 1.25, 3.22 and 10.0 cm. and the so-called static dielectric constant, ϵ_0, at 300 m. were measured at 20, 40 and 60° by methods described or referred to in earlier papers of this series.[6] Where necessary, densities were determined with a graduated pycnometer[7] and viscosities were determined with an Ostwald–Fenske viscometer. The values obtained at each temperature of measurement are given in Table I. Data for 2-vinylpyridine at 40 and 60° and for 4-vinylpyridine at 60° were not determined since viscosity measurements indicated that polymerization was taking place at a relatively rapid rate at these temperatures. The measurements on styrene were repeated several times in order to obtain reproducible results. Oxygen was carefully excluded from the liquid both before and during the measurements.

From the dielectric constant data Cole–Cole arc plots were drawn and used to determine the critical wave lengths, λ_m, at which the loss is a maximum. Table II contains the values of the high-frequency dielectric constants, ϵ_∞, the distribution parameters, α, and the critical wave lengths obtained in the usual manner[8] from the arc plots. The macroscopic relaxation times were calculated by the equation

$$\tau_M = \frac{\lambda_m}{2\pi c}$$

TABLE II

HIGH FREQUENCY DIELECTRIC CONSTANTS, DISTRIBUTION PARAMETERS, CRITICAL WAVE LENGTHS, RELAXATION TIMES, MOLAR VOLUMES AND DIPOLE MOMENTS

t, °C.	ϵ_∞	α	λ_m (cm.)	$\tau_M \times 10^{11}$ (sec.)	V (cc.)	μ ($\times 10^{18}$)
			Toluene			0.31[a]
20	2.266	0.03	1.22	0.65	106.3	.31
40	2.232	.02	0.97	.51	108.6	
60	2.198	.03	.78	.41	111.0	
			Styrene			.13[b]
20	2.407	0	1.20	0.64	114.9	.13
40	2.371	0	0.95	.50	117.2	
60	2.336	0	.80	.42	119.5	
			Ethylbenzene			.36[a]
20	2.260	0.12	2.20	1.17	122.5	.37
40	2.228	.09	1.67	0.89	125.0	
60	2.196	.04	1.30	.69	127.6	
			Isopropylbenzene			.37[a]
20	2.243	0.13	3.55	1.88	139.4	.39
40	2.212	.12	2.45	1.30	142.2	
60	2.182	.09	1.85	0.98	145.2	
			o-Xylene			.50[a]
20	2.296	0.08	1.55	0.82	120.6	.52
40	2.264	.07	1.21	.64	123.0	
60	2.234	.04	1.00	.53	125.4	
			m-Xylene			.31[a]
20	2.268	0.11	1.62	0.86	122.8	.31
40	2.237	.06	1.25	.66	125.3	
60	2.205	.04	1.00	.53	127.9	
			p-Chlorotoluene			1.94[c]
20	2.56	0.01	4.85	2.57	118.4	1.60
40	2.52	.01	3.85	2.04	120.6	
60	2.48	.01	3.02	1.60	122.9	
			α-Picoline			1.97[d]
20	2.65	0.06	2.38	1.27	98.6	1.93
40	2.60	.04	1.85	0.98	100.6	
60	2.55	.02	1.51	.80	102.7	
			2-Vinylpyridine			
20	2.58	0.09	3.75	1.99	107.9	1.92
			4-Vinylpyridine			
20	2.74	0.04	5.81	3.08	106.9	2.00
40	2.70	.03	4.27	2.27	108.8	
			2-Ethylpyridine			
20	2.39	0.07	2.78	1.48	115.2	1.96
40	2.35	.06	2.09	1.11	117.4	
60	2.31	.05	1.62	0.86	119.8	
			4-Ethylpyridine			2.66[d]
20	2.52	0.02	4.15	2.20	113.8	2.25
40	2.48	.01	2.35	1.73	116.0	
60	2.44	.01	2.65	1.41	118.2	

[a] A. P. Altshuller, *J. Phys. Chem.*, 58, 392 (1954). [b] A. von Hippel and L. G. Wesson, *Ind. Eng. Chem.*, 38, 1121 (1946). [c] Benzene solution; L. Tiganik, *Z. physik. Chem.*, 13B, 425 (1931). [d] C. W. N. Cumper, A. I. Vogel and S. Walker, *J. Chem. Soc.*, 3621 (1956).

Also included in Table II are the dipole moments, μ, calculated from ϵ_0 and ϵ_∞ values by the Onsager equation,[9] the values obtained for the liquids by other methods being listed in parentheses. Table III contains the slopes, a_0, a', a'', for the dependence of dielectric constants and losses upon the

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(5) H. T. Clarke and E. R. Taylor, THIS JOURNAL, **45**, 831 (1923).

(6) R. S. Holland and C. P. Smyth, *J. Phys. Chem.*, **59**, 1088 (1955).

(7) G. R. Robertson, *Ind. Eng. Chem.*, *Anal. Ed.*, **11**, 464 (1939).

(8) C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., Inc., New York, N. Y., 1955, pp. 69–70.

(9) L. Onsager, THIS JOURNAL, **58**, 1486 (1936).

TABLE III

SLOPES (a) FOR DEPENDENCE OF DIELECTRIC CONSTANT AND LOSS ON MOLE FRACTION OF *p*-CHLOROTOLUENE IN NON-POLAR SOLVENTS

			1.25		3.22 cm.	
t, °C.	ϵ_1	a_0	a'	a''	a'	a''
			Solvent, benzene			
20	2.2836	5.36	1.08	1.45	2.67	2.14
40	2.2436	4.88	1.29	1.59	3.07	1.91
60	2.2036	4.53	1.70	1.62	3.24	1.62
			Solvent, *p*-xylene			
20	2.2699	3.84	0.825	1.21	1.81	1.56
40	2.2368	3.49	0.905	1.21	2.10	1.31
60	2.2034	3.19	1.06	1.21	2.21	1.22
			Solvent, *p*-dichlorobenzene			
60	2.3826	3.35	0.64	1.07	1.74	1.32

mole fraction of *p*-chlorotoluene in the indicated non-polar solvents, whose dielectric constants ϵ_1 are also listed. The relaxation times of *p*-chlorotoluene in the solutions were calculated from arc plots drawn by plotting a' *vs.* a''.[10] The results are listed in Table IV.

TABLE IV

SLOPES OF HIGH FREQUENCY DIELECTRIC CONSTANT *vs.* MOLE FRACTION (a_∞), DISTRIBUTION PARAMETERS AND CRITICAL WAVE LENGTHS OF *p*-CHLOROTOLUENE IN NON-POLAR SOLVENTS

t, °C.	a_∞	α	λ_m (cm.)	$\tau \times 10^{11}$ (sec.)
		Solvent, benzene		
20	0.33	0.10	3.67	1.95
40	.30	.11	2.63	1.40
60	.27	.11	1.96	1.04
		Solvent, *p*-xylene		
20	0.07	0.12	3.46	1.84
40	.06	.12	2.54	1.35
60	.05	.12	1.94	1.03
		Solvent, *p*-dichlorobenzene		
60	−0.18	0.18	2.93	1.56

Discussion of Results

The dipole moments measured for the hydrocarbons listed in Table II are seen to be, for the most part, in good agreement with the literature values obtained for pure liquids. For *p*-chlorotoluene and 4-ethylpyridine, however, there is a considerable discrepancy between the observed and the literature values. The ϵ_∞ values for these substances, as well as for the other substituted pyridines, are somewhat higher than the corresponding n^2_D values, a discrepancy frequently observed in previous measurements in this laboratory. Poley[11] has found a similar difference between ϵ_∞ and the square of the refractive index measured in the far infrared for a group of polar substituted benzenes and has attributed the difference to the presence of a second high-frequency dispersion region of dipolar origin.

The relaxation time of pyridine in benzene solution[12] at 20°, 0.36 × 10^{-11} sec., can be taken as roughly approximating the value for benzene since the two molecules are similarly shaped and nearly the same in size. Substitution of a methyl group to yield toluene decreases the viscosity from 0.65 to 0.59 at 20°, but nearly doubles the relaxation time. The protrusion of the methyl group out of the plane of the ring, therefore, causes looser packing of the molecules, resulting in the decrease in viscosity, but has a stronger effect in reducing the ease of rotational orientation of the molecule. Substitution of a second methyl group to give *o*-xylene and *m*-xylene causes the viscosity to increase by 37 and 5%, respectively, and the relaxation time by 26% and 32% over the values for toluene. Axial ratios measured on Stuart–Briegleb models indicate that *o*-xylene approaches a circular shape more closely than does *m*-xylene. The slightly smaller molar volume of the former indicates closer packing and a correspondingly higher viscosity, but, because of the more symmetrical shape of the molecule, does not result in a correspondingly greater relaxation time. This interpretation is supported by the slightly higher values of the distribution parameter for *m*-xylene at 20°. However, since the τ_M values are nearly equal and become equal at 60°, it appears that most of the dipolar relaxation takes place by rotation in the plane of the ring, the greater free volume present at 60° minimizing the effects of a difference in shape.

The effect of molecular size and shape on the relaxation time is more striking when the size of the substituent group is increased. For ethylbenzene, a 15% increase in viscosity over the value for toluene is accompanied by an increase of 83% in relaxation time and for isopropylbenzene the corresponding increases over the values for toluene are 34 and 190%. In these two substances the larger bulk and irregularity of the substituent groups cause more interference between molecules than in the case of toluene.

The relaxation time of styrene appears to be anomalous. In spite of the fact that the vinyl group is larger than the methyl group and also that styrene has a 32% larger viscosity than toluene, the relaxation times of the two molecules are practically identical. Such a result would be consistent with the existence of styrene in a planar configuration as a result of resonance. Closer packing of the molecules would then be allowed with a corresponding increase in viscosity and density over the values for toluene, as observed. The relaxation process could then occur with less interference from molecules in adjacent planes and an increase in relaxation time paralleling the viscosity increase would not be realized. The zero value of α for styrene is not inconsistent with this description.

The relaxation times of *p*-chlorotoluene and the substituted pyridines are larger than for the hydrocarbons because of their larger polarities, smaller molar volumes and, hence, higher viscosities. In comparing the benzenes and pyridines, therefore, account must be taken of the effect of viscosity and of the internal field on the relaxation time. These two factors can be considered separately. It may be expected intuitively that the relaxation time of a molecule should depend on the

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[10] A. D. Franklin, W. M. Heston, Jr., E. J. Hennelly and C. P. Smyth, THIS JOURNAL, **72**, 3447 (1950).

[11] J. Ph. Poley, Thesis, Technische Hogeschool, Delft, 1955.

[12] R. C. Miller and C. P. Smyth, THIS JOURNAL, **79**, 308 (1957).

Table V

Effect of Viscosity and Internal Field on Relaxation Times

	Constant viscosity				Constant temp.			
	t, °C.	η	τ_η	τ_μ	t, °C.	η	τ_μ	τ_μ/η
Toluene	20	0.59	0.65	0.64	20	0.59	0.64	1.09
α-Picoline	46		.93	.70		.81	.95	1.17
γ-Picoline[6]	55		.91	.67		.94	1.02	1.09
Ethylbenzene	20	0.68	1.17	1.17	20	0.68	1.17	1.72
2-Ethylpyridine	45		1.04	.79		.93	1.13	1.21
4-Ethylpyridine	33		1.53	1.16		1.03	1.64	1.59
Styrene					20	0.78	0.64	0.82
2-Vinylpyridine						1.13	1.51	1.34
4-Vinylpyridine						1.22	2.32	1.90
p-Chlorotoluene	38	0.72	2.05	1.64	20	0.89	2.06	2.31
Pure liquid					60	.56	1.30	2.32
In p-xylene	11		2.15	2.15	20	.64[a]	1.95	3.00
					60	.42[a]	1.04	2.67
In benzene	13		2.22	2.22	20	.65[a]	1.84	2.88
					60	.39[a]	1.03	2.45
In p-dichlorobenzene	60		1.56	1.56	60	.72	1.56	2.17

[a] Ref. *a*, Table I.

free volume in which the molecule may rotate. Since, according to the Debye equation[13]

$$\tau = \frac{4\pi\eta a^3}{kT}$$

τ is proportional to the viscosity, and the latter, in turn, is dependent on the free volume,[14] it may further be expected that two molecules of the same size and shape should have the same relaxation time when the free volumes are equal, *i.e.*, when the macroscopic viscosities are equal. The explicit temperature dependence of τ is ignored for the moment but the attempt will be made later to justify this procedure. The macroscopic relaxation times at constant viscosity, τ_η, interpolated from plots of the temperature dependence of each process, are listed in Table V. The correlation of relaxation times is better at constant viscosity than at constant temperature (*cf.* Table II) but still inadequate.

The internal field effect arises from the fact that the reaction field of the dipoles influences the orientations of the molecules. Relaxation must, therefore, occur by a coöperative effect which involves a group of molecules rather than a single one. The net result is to observe a macroscopic relaxation time which must be corrected to give a microscopic value. Various equations for the effect of the internal field have recently been evaluated by Miller and Smyth.[15] These authors found that the approximate expression given by Powles[16] and derived more rigorously by O'Dwyer and Sack[17] as a first-order approximation was the most nearly adequate for calculating the molecular relaxation time from the directly measured or macroscopic value. Powles obtained a molecular relaxation time, τ_μ, given by

$$\tau_\mu = \frac{2\epsilon_0 + \epsilon_\infty}{3\epsilon_0}\,\tau_M$$

τ_μ values at constant viscosity and at constant temperature are also listed in Table V. The agreement among the τ_μ values at constant viscosity is generally better than that among the values at constant temperature, which are comparable, in agreement, to the macroscopic values at constant viscosity. The correlation of τ_μ values at constant η is equivalent to the correlation of τ_μ/η values at constant T which has been previously[15] employed. These values also have been included in Table V for the purpose of correlating the data for the vinyl compounds. For p-chlorotoluene in solution the values are calculated from the viscosities of the solvents. Good agreement is obtained for the three methyl-substituted compounds and also for ethylbenzene and 4-ethylpyridine. The lack of agreement in the case of the three vinyl-substituted compounds and the discrepancy for 2-ethylpyridine may be ascribed to any or all of the following factors: the inadequacy of the Debye relationship, the approximate nature of the internal field correction, the presence of a distribution of relaxation times, or, in the case of the vinyl compounds, the presence of a small amount of polymer. The discrepancy between the solution and pure liquid values of p-chlorotoluene may be due to the possibilities mentioned above as well as the fact that the solvent viscosity has been used to calculate the solution value instead of the true parameter for the viscous interaction between solvent and solute molecules. Since the correct η value is probably intermediate between those of pure solvent and pure solute, the τ_μ/η ratios for the benzene and p-xylene solutions would be lowered and that for the p-dichlorobenzene solution would be increased, resulting in closer agreement with the ratio for the pure liquid. The better correlation of the solution results in Table V is obtained at 60° where the greater free volume present would tend to minimize slight differences in size between solute and solvent molecules. The relative constancy of τ_μ/η values of a compound at different temperatures indicates that the ratio a^3/T in the Debye equation is constant with temperature. This would imply that, for these molecules, a^3 would better be interpreted in

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[13] P. Debye, "Polar Molecules," Chemical Catalog Co., New York, N. Y., 1929, Chap. V.

[14] S. Glasstone, K. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, pp. 486–487.

[15] R. C. Miller and C. P. Smyth, This Journal, **79**, 3310 (1957).

[16] J. G. Powles, *J. Chem. Phys.*, **21**, 633 (1953).

[17] J. J. O'Dwyer and R. A. Sack, *Australian J. Sci. Research*, **A5**, 647 (1952).

terms not of the volume of a molecule but rather of the volume occupied by a molecule, which would be given by V/N instead of $4\pi a^3/3$. The omission from consideration of the temperature dependence of τ, therefore, appears to be justified by the results.

The activation energies calculated according to Kauzmann[18] from the temperature dependence of the viscosity and the relaxation time are listed in Table VI. Also included for comparison are the values for pure pyridine,[6] pyridine in benzene solution (*i.e.*, benzene[12]), and γ-picoline.[6] For the planar molecules of benzene and pyridine, $\Delta H_v^{\ddagger}$ is relatively much larger than $\Delta H_\epsilon^{\ddagger}$, indicating that viscous flow involves greater interference by neighbors than does dielectric relaxation. This is to be expected since dielectric relaxation takes place by rotation of the molecule with little or no translation, whereas viscous flow may involve both forms of motion. With increasing dissymmetry and consequently greater mutual interference of the molecules during relaxation, the difference in activation energies decreases nearly to zero as in ethylbenzene and becomes negative in isopropylbenzene. The $\Delta H_\epsilon^{\ddagger}$ and $\Delta H_v^{\ddagger} - \Delta H_\epsilon^{\ddagger}$ values for styrene appear comparable to those of the planar molecules rather than to that of ethylbenzene which has a molecule close to that of styrene in size. This is in accord with the previous indication of the planarity of styrene. The relatively lower value of $\Delta H_\epsilon^{\ddagger}$ for *o*-xylene is also consistent with the previous description of its dielectric behavior. The values for 4-ethylpyridine, however, must be considered anomalous. Free energies and entropies of activation for each process also have been calculated. The values for $\Delta F_\epsilon^{\ddagger}$ lie between 2 and 4 kcal./mole and those for $\Delta S_\epsilon^{\ddagger}$ lie between −1 and −4 e.u. The negative entropy values indicate that the relaxation occurs by the coöperation of nearest neighbors, the molecules maintaining a relatively highly ordered arrangement.

TABLE VI

ACTIVATION ENERGIES FOR VISCOUS FLOW ($\Delta H_v^{\ddagger}$) AND DIELECTRIC RELAXATION ($\Delta H_\epsilon^{\ddagger}$) (KCAL./MOLE)

	$\Delta H_v^{\ddagger}$	$\Delta H_\epsilon^{\ddagger}$	$\Delta H_v^{\ddagger} - \Delta H_\epsilon^{\ddagger}$
Benzene	2.5	(1.4)	(1.1)
Pyridine	2.5	1.4	1.1
Styrene	2.3	1.4	0.9
Toluene	2.2	1.6	.6
α-Picoline	2.2	1.6	.6
γ-Picoline	2.5	1.8	.7
o-Xylene	2.3	1.5	.8
m-Xylene	2.0	1.7	.3
p-Chlorotoluene	2.3	1.7	.6
Ethylbenzene	2.1	1.9	.2
2-Ethylpyridine	2.4	2.0	.4
4-Ethylpyridine	2.5	1.5	1.0
i-Propylbenzene	2.3	2.5	−0.2

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[18] W. Kauzmann, *Rev. Mod. Phys.*, **14**, 12 (1942).

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Dipole Moment and Steric Strain in Hexaaryldisilanes[1,2]

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The dipole moments of 1,1,2-triphenyl-1,2,2-tri-*p*-tolyldisilane, 1,1,1-triphenyl-2,2,2-tri-*p*-tolyldisilane and 1,1,1-triphenyl-2,2,2-trimethyldisilane have been determined in dilute benzene solution. The measured values 0.80, 0.77 and 0.64×10^{-18}, respectively, have been used to calculate a value of 115° for the aryl–silicon–silicon bond angle. Failure to detect free radicals in solution indicates that the distortion does not lead to measurable dissociation of these compounds. On the basis of available data and the measured moments, the following approximate maximum group moment magnitudes and their directions have been assigned: phenyl^{-}–$^{+}$Si $= 0.84 \times 10^{-18}$ and tolyl^{-}–$^{+}$Si $= 0.25 \times 10^{-18}$.

The gift of three substituted disilanes by Professor Henry Gilman of the Iowa State College has made possible the investigation of their molecular dipole moments and of the group moments and bond angles in the molecules. Steric hindrance might be expected among the aryl groups in hexaaryldisilanes analogous to that found in hexaarylethanes.[4] In the case of the latter compounds so much steric hindrance is present between the aryl groups across the ethane linkage that dissociation takes place in solution.[5] Since silicon has a 50% larger covalent radius than carbon[6] it is to be expected that such steric hindrance, if present at all, would be greatly reduced. Dipole moment measurements have been carried out on 1,1,2-triphenyl-1,2,2-tri-*p*-tolyldisilane and 1,1,1-triphenyl-2,2,2-tri-*p*-tolyldisilane, which will hereafter be referred to as I and II, respectively. These two substances form an ideal pair for determining such steric effects, since they contain the same groups but with a different arrangement, allowing the valence angles to be calculated from measured dipole moments without knowledge of the individual group moments.

The phenyl–Si and *p*-tolyl–Si group moments could be determined by measuring the moment of a compound containing either of the above groups

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[2] This paper represents a part of the work to be submitted by Mr. A. J. Petro to the Graduate School of Princeton University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[3] Monsanto Fellow in Chemistry, 1956–1957.

[4] W. A. Waters, "The Chemistry of Free Radicals," 2nd ed., Oxford University Press, London, 1948.

[5] W. A. Waters, ref. 4, pp. 59–60.

[6] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940, p. 164.