

argued that the excitations are more like weak binding, or Wannier-type, excitons. We do not believe that this upsets the qualitative validity of the model.

We have also neglected overlap and lattice vibrations. The former would be expected to be of some importance in the solid, especially when the density is increased. This is reflected in our result; f increases with increasing density, whereas experimentally the Lorentz-Lorenz function increases with increasing density after the initial drop when the solid is formed.¹⁵

We therefore conclude that we have described correctly the main qualitative features of the physical situation. A considerably more complicated model would be necessary to handle all the secondary effects which are also operative.

(15) However, recent unpublished results of G. O. Jones and A. Eatwell, Queen Mary College, London, show a short rise in the Lorentz-Lorenz function from about 910 to 925 amagats, followed by a marked decrease extending to about 990 amagats.

The theory may certainly be classed as semiempirical, in that we have used experimental data on nonoptical properties to evaluate parameters in the final result. However, there are no adjustable parameters in the theory.

We conclude with a brief physical discussion of why the main result, eq. 39, is very reasonable. In the true ground state of the crystal, each atom has a certain amplitude for being excited. These virtual excitations are, in fact, the mechanism for producing the London forces which bind the crystal together, when looked at from the point of view of perturbation theory. Now an atom in an excited state has a negative polarizability, which is equal and opposite to the polarizability of an atom in its (unperturbed) ground state in our model. Since there are, on the average, Nf atoms in excited states, $N(1 - f)$ atoms in their ground states, the effective polarizability of an atom should be $(1 - 2f)\alpha$, which is exactly what occurs in eq. 39.

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Microwave Absorption and Molecular Structure in Liquids. LV. Intramolecular Structural Effects in the Dielectric Relaxation of Six Aromatic Compounds^{1,2}

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The dielectric constants and losses, at wave lengths of 1.3, 3.2, 10, and 25 cm. and 575 m. and temperatures of 20, 40, and 60° have been measured for anisole, *p*-dimethoxybenzene, phenylacetonitrile, *p*-xylylene cyanide, 1-(chloromethyl)naphthalene, and 1-naphthaleneacetonitrile in dilute benzene solution. The data have been used to calculate the dielectric relaxation times of the molecules. *p*-Dimethoxybenzene and *p*-xylylene cyanide relax by the rotation of the methoxy and acetonitrile groups, respectively, about their bonds to the ring. The results for anisole have been interpreted in terms of a molecular and an intramolecular relaxation process, while, although more than one relaxation process is evident in the case of phenylacetonitrile, no resolution could be effected. 1-(Chloromethyl)naphthalene and 1-naphthaleneacetonitrile show no evidence of intramolecular group rotation, confirming the steric blocking of group rotation by the hydrogen in the 8-position indicated by molecular models.

Many molecules have been observed to possess short dielectric relaxation times because of the existence of internal modes of relaxation, which are somewhat shielded from the external molecular environment. The present paper presents measurements in the kilomegacycle region on six aromatic compounds containing the CH₂Cl, CH₂CN, and the OCH₃ groups as a means of investigating the intramolecular rotational freedom of polar groups and the effects of steric repulsion.

Experimental

Apparatus.—The apparatus and various methods of measurement have been described in previous papers.³⁻⁵

Purification of Materials.—Anisole, purchased from Eastman Kodak Co., was fractionally distilled under atmospheric pressure. The fraction condensing at 154° gave an index of refraction, n_D^{20} , of 1.5179, which compares with a literature value⁶ of 1.5179.

1-(Chloromethyl)naphthalene, purchased from Eastman Kodak Co., was fractionally distilled under a reduced pressure of 10 mm. The fraction condensing between 146 and 147° was collected. 1-Naphthaleneacetonitrile, obtained from Eastman Kodak Co., was fractionally distilled under a reduced pressure of 13 mm. The fraction collected between 182 and 183° gave an index of refraction, n_D^{20} , of 1.6205. Phenylacetonitrile, purchased from Eastman Kodak Co., was fractionally distilled under reduced pressure. The distillate gave an index of refraction, n_D^{20} , of 1.5206, which compares with a literature value⁷ of 1.5211. *p*-Xylylene cyanide, obtained from Aldrich Chemical Co., was recrystallized once from ether and twice from benzene and dried in an Abderhalden pistol. The purified material gave a melting point of 98°, which compares with a literature value of 98°. *p*-Dimethoxybenzene, purchased from Eastman Kodak Co., was recrystallized four times from benzene and dried under vacuum in an Abderhalden pistol. The purified material gave a melting point of 56.2°, which compares with a literature value⁸ of 56°. Benzene, purchased from the Allied Chemical Corp., was of reagent grade, thiophene-free quality. It was dried over Drierite and used without further purification.

Results

The experimental results obtained from measurements in benzene solution were treated in the manner previously described.⁹ The dielectric constant and

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

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Discussion

The symmetry of *p*-dimethoxybenzene and *p*-xylylene cyanide is such that there is no fixed moment along the long axis of the molecule and the observed moment is the time average resultant of the components of the two group moments perpendicular to the axis of rotation. Free rotation would be expected to occur if no barrier to internal rotation existed, $\Delta H^* = 0$, that is, if all positions of rotation about the bond to the rest of the molecule were equally probable.

p-Dimethoxybenzene exhibits an unusually short relaxation time for a molecule of such size. The barrier to rotation, ΔH^* , is quite small. The distribution parameter, α , decreases from 0.04 at 20° to 0 at 40 and 60°. Further, a plot of a' vs. $a''\omega$ gives a straight line at 20, 40, and 60°. It is, therefore, concluded that the principal mechanism of relaxation is the rotation of the two OCH₃ groups about their bonds to the ring. The value of the relaxation time at 20° compares well with the value 6.9×10^{-12} sec. measured in benzene solution by Fischer.¹³ Previous measurements in this laboratory¹⁴ gave 9.7×10^{-12} at 20°, 6.4×10^{-12} at 40°, and 4.6×10^{-12} sec. at 60° for the relaxation times. These values at 20 and 40° now appear too long since a 50% drop in the relaxation time occurs over a 40° temperature range indicating a high barrier, ΔH^* .

In the case of anisole in benzene solution, a plot of a' vs. a'' gave a good Cole-Cole arc at 60° with a distribution parameter, α , of only 0.04, which is probably not significant, since a plot of a' vs. $a''\omega$ gave a straight line and relaxation time, 6.6×10^{-12} sec. At 20 and 40° a good Cole-Cole arc could not be drawn and a plot of a' vs. $a''\omega$ showed curvature, which was more marked at 20°. Accordingly, the data were found to be well represented by a superposition of two Debye-type regions. No separation was, of course, attempted at 60°. τ_1 and τ_2 are the relaxation times associated with the over-all and group relaxation processes, respectively, and C_1 and C_2 are their relative contributions. If the assumption of free rotation of the OCH₃ group is a good approximation for *p*-dimethoxybenzene, its most probable relaxation time would be expected to be close to the resolved relaxation time, τ_2 , of anisole. Actually, the resolved relaxation time, τ_2 , of anisole is slightly longer than the values of τ_0 reported in Table II for *p*-dimethoxybenzene at 20 and 40° and slightly shorter than the value found by Fischer¹³ for *p*-dimethoxybenzene in benzene solution at 20°. In decalin, the resolved relaxation times¹⁵ for anisole at 20° were found to be 21.9×10^{-12} and 7.0×10^{-12} sec. for the over-all and internal relaxation mechanisms, respectively, and C_2 was found to be 0.65. At 40°, τ_1 was 18.2×10^{-12} sec., τ_2 , 6.0×10^{-12} sec., and C_2 , 0.68, while in Nujol, at 20°, τ_1 , τ_2 , and C_2 , were 69×10^{-12} sec., 7.2×10^{-12} sec., and 0.60, respectively, and at 40°, 46×10^{-12} sec., 6.6×10^{-12} sec., and 0.60. The values of τ_1 at 40 and 20° for anisole in benzene are slightly lower than those found¹⁵ in decalin, and much lower than those in Nujol, as is to be expected, since the viscosity of decalin is greater than that of benzene,

and the viscosity of Nujol is much greater than that of decalin. The benzyl chloride molecule is similar in size and shape to that of anisole. At 20° the relaxation time associated with its over-all relaxation was found¹⁶ to have a value of 21.2×10^{-12} sec. in benzene, which is close to the value 20×10^{-12} sec. for anisole in Table III. Using diphenyl ether and dimethyl ether and taking the oxygen bond angle in the former as 120° and in the latter as 110°, the moments associated with over-all molecular relaxation and group relaxation in anisole were found to be 0.75×10^{-18} and 1.08×10^{-18} , respectively. These values give a calculated moment for anisole of 1.31×10^{-18} , which compares with the experimental solution value¹⁷ 1.25×10^{-18} . The relative amplitude of the over-all dispersion region is then given by

$$C_1 = (0.75)^2 / [(0.75)^2 + (1.08)^2] = 0.32$$

leaving $C_2 = 0.68$. These values for the relative contributions are not far from those found in this research and from those found in other solvents.¹⁵

p-Xylylene cyanide exhibits a relatively large temperature dependence of the relaxation time. The distribution parameter, α , decreases from a value of 0.06 at 20° to 0.03 at 60°. The rotating CH₂CN group sweeps out a cylinder of revolution of radius about 20% larger than that swept out by the OCH₃ group. Although the Stuart-Briegleb models do not indicate much steric hindrance to rotation by the 2,5-hydrogens of the rings, the atomic polarization, which is given by $a_\infty - a_D$, is so large as to indicate a substantial amount of torsional vibration. This is consistent with the large hindering potential barrier observed.

Phenylacetonitrile exhibited behavior which contrasted with that of anisole. At 60° a plot of a' vs. $a''\omega$ gave a straight line of slope corresponding to a relaxation time of 11.3×10^{-12} sec. The distribution parameter, α , is quite small, only 0.06, but, at 20 and 40°, a plot of a' vs. $a''\omega$ gave significant curvature indicative of the presence of more than one relaxation time. The curvature was greater at 20° than at 40°. The experimental data at 40° could almost be described by a Cole-Cole distribution with a most probable relaxation time falling near 17×10^{-12} sec. The data could not be described in terms of two Debye-type regions, as in the case of anisole or benzyl chloride. The value 17×10^{-12} is much longer than 6.8×10^{-12} sec., the value of the relaxation time of *p*-xylylene cyanide at 40°, which indicates that a considerable amount of over-all molecular relaxation takes place. If a moment of 3.5 D. is taken for the CH₂CN group,¹⁷ and the C-C-C bond angle is taken as 110°, and if it is further assumed that the whole moment of the molecule resides in the group CH₂CN, which is not unreasonable, since the moment of CH₃CN¹⁷ is 3.4×10^{-18} and the moment of phenylacetonitrile¹⁷ is 3.5, then a relative contribution of only 10% is calculated for over-all relaxation. A relative amount of over-all relaxation of 10% is too small to give a relaxation time as long as 17×10^{-12} sec., which suggests that the CH₂CN group is not freely rotating. In such a case, the principle of superposition cannot be applied since

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in the presence of substantial barriers to internal rotation the group relaxation would not be expected to be independent of the over-all relaxation process. From the plot of a' vs. $a''\omega$ approximate limiting relaxation times may be estimated. It is found that the longest relaxation time at 20° cannot be shorter than 26×10^{-18} sec. and the shortest relaxation time cannot be longer than 12×10^{-12} sec. Due to the long extrapolation, the arc intercept at infinite frequency, a_∞ , of phenylacetonitrile at 60° should be regarded as approximate. Still, $a_\infty - a_D$ is considerably larger than the corresponding difference for anisole and indicates a substantial amount of torsional vibration.

The dielectric constant and loss data for 1-naphthaleneacetonitrile and 1-(chloromethyl)naphthalene fit well on Cole-Cole arcs showing only one relaxation time for the former and a slight distribution of relaxation times for the latter. The relaxation times of the rigid α -chloronaphthalene,¹⁸ α -bromonaphthalene,¹⁹ α -nitronaphthalene,²⁰ and α -naphthyl isocyanate²¹ molecules in benzene solution at 20° are, respectively, 15.8×10^{-12} , 18×10^{-12} , 22.8×10^{-12} , and 31.5×10^{-12} sec. The relaxation times found for 1-(chloromethyl)naphthalene and 1-naphthaleneacetonitrile fit in well

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with the series given above and should, therefore, be interpreted as arising from over-all relaxation. The effect of the steric repulsion of the 8-hydrogen has been observed¹⁴ previously in the considerably longer relaxation times of the methoxy- and ethoxynaphthalenes with the substituent group in the 1-position as compared to those with the group in the 2-position.

The Stuart-Briegleb molecular models indicate strong steric repulsion between the 8-hydrogen and the methoxy or ethoxy group in the 1-position, but somewhat less hindrance to group rotation than in the cases of the CH_2Cl and CH_2CN groups, the complete rotation of which appears to be impossible without great distortion of the bond angles. The absence of any detectable contribution from group relaxation confirms the existence of the steric blocking indicated by the molecular models for the 1-naphthaleneacetonitrile and 1-(chloromethyl)naphthalene molecules, but the contributions from hindered group rotation found for 1-methoxy- and 1-ethoxynaphthalene show a degree of molecular flexibility not inherent in the models. The short and practically identical relaxation times found^{22,23} for the hydroxyl group in the 1- and 2-positions are consistent with the smallness of steric hindrance to rotation shown by the models for the 1-position and its absence for the 2-position.

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Theory of Line Widths in Electron Spin Resonance Spectra: Motion of Methyl Groups¹

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The relaxation-matrix theory of line widths in electron spin resonance spectra has been employed to analyze the line-width effects arising from the motions of methyl groups in π -electron free radicals. Broadening of the lines can result because the methyl-proton hyperfine splittings are a function of the angle of orientation of the methyl group, and thus the splittings fluctuate as this angle varies. The motion of the methyl groups is treated by a Brownian motion model assuming a free rotatory diffusion about the C-C bond between the methyl group and the aromatic system to which it is bonded, and also by a jump model in which the group can undergo transitions from one to another of three different equilibrium orientations. Radicals with several methyl groups are analyzed as having either completely correlated or completely uncorrelated motions. The correlated motions are approximated by assuming a gear-like interleaving without slip of the hydrogen atoms on methyl groups substituted at adjacent positions on an aromatic ring. When the motions of the methyl group cause large contributions to the line width, the central pair of lines from the splittings by one methyl group are predicted to be broad and the end lines narrow. When there are two or four methyl groups in the radical, large line-width contributions lead to a spectrum in which every third line is narrow while the remaining lines are broad, an effect which is analogous to the alternating line-width phenomenon. For very rapid rotations, nonsecular as well as secular line-width contributions are important, and consequently the nondiagonal relaxation matrix for the case of one methyl group has been analyzed in detail. None of these effects of methyl-group rotations has been observed in the e.s.r. spectra of aromatic radicals, and from the negative results it is possible to estimate that the relaxation time τ_c for the rotation of the methyl groups is less than 10^{-8} sec. The predicted effects are most likely to be found by low-temperature studies on radicals which have large methyl-proton hyperfine splittings and highly hindered methyl groups.

I. Introduction

In a number of recent studies³⁻¹¹ on the electron spin resonance spectra of aromatic free radicals in solution, anomalous line-width variations have been found

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that are attributable to modulations of the isotropic hyperfine interactions. Some of the effects observed

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