

proximately,^{5a} have been obtained recently. Those lead terms which are known exactly are incorporated into the present analysis. Thus, the perturbation series analysis has been applied to Pekeris' data to furnish the material of Table III. For convenience of tabulation a notation is defined such that each correction term has the form $f\Sigma A_n Z^{-n}$. Two points deserve special notice. The present $\epsilon_2^{(2)}$ value clearly shows that the value recently obtained by Hylleraas and Midtdal⁶ has still not converged to the extent they report. Table II compares the further coefficients of their power series fitting with the present higher-order coefficients. Weiss' data are more crude than Pekeris', and the resultant accumulation of contaminants does not allow even $\epsilon_4^{(N)}$ to be reliably recovered. Indeed, it is possible that Weiss' data have $\epsilon_0^{(N)}$ and/or $\epsilon_1^{(N)}$ implicitly incorrect, for he notes that his absolute error increases with increasing Z . This trend must eventually cease for large Z because in the limit of infinite Z his wave functions become exact solutions and must give exact $\epsilon_0^{(N)}$ and $\epsilon_1^{(N)}$ values (but not $\epsilon_2^{(N)}$).

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in conjunction with the theory of Bardeen and Shockley² to calculate the electron mobility in the direction of the chain axis. Taking the electron-free mass as the effective mass, we calculate the change in energy with lattice dilation at the conduction band edge as $E_1 = 7.34$ eV. The elastic constant is taken from the Young's modulus for Nylon 66,³ 0.012×10^{12} dyn/cm². The result for the mobility is $\mu = 1.4$ cm²/V sec at 300°K. Again taking the effective mass of the electron as the free mass, we calculate for the carrier density $n = 5.4 \times 10^{17}$ cm⁻³, leading to a conductivity of 0.12 mho cm⁻¹.

In seeking the reason for the low mobility and conductivity, we note that our calculated E_1 is comparable to that for diamond or silicon.² However, the elastic constant is only 10^{-2} – 10^{-3} as large. The obvious conclusion is that polymers, because of their inherent softness, are going to have relatively low carrier mobilities. Cross linking, etc., might increase the mobility to as much as 10 cm²/V sec, but little more.

Values for conductivities, activation energies, and spin concentrations in polyacetylene pellets are given by Hatano and Kambara.⁴ They find an activation energy of 0.46 eV for a crystalline sample (PA5). Making the same assumptions as before, we calculate a charge carrier density of 1.3×10^{15} cm⁻³. From their observed conductivity of 2.38×10^{-6} mho cm⁻¹, we then calculate a mobility of $\mu = 0.05$ cm²/V sec. In view of the approximate nature of the calculation, and the fact that Hatano and Kambara used unoriented powders of imperfect polymer, this is in satisfactory agreement with the theory.

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Calculated Electron Mobility and Electrical Conductivity in Crystals of Linear Polyenes

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IT is often thought that long-chain conjugated hydrocarbons would function as good electrical conductors, if only they could be prepared as pure single crystals. It is of interest to estimate the probable electrical properties of such a crystal in order to evaluate this idea. We take as a model an array of long-chain, linear polyene molecules, stacked in bundle-of-pencils fashion. Detailed calculation of the band structure of this hypothetical crystal would be a formidable task. However, the calculation along the direction of the chain axes has been made by Tobin¹ who also gives 0.15 eV for the band gap. The conduction band turns out to be about 2 eV wide, so we have to do with a wide-band conductor. Tobin's formulas may be used

Anomalous Alternating Linewidths in ESR Spectra*

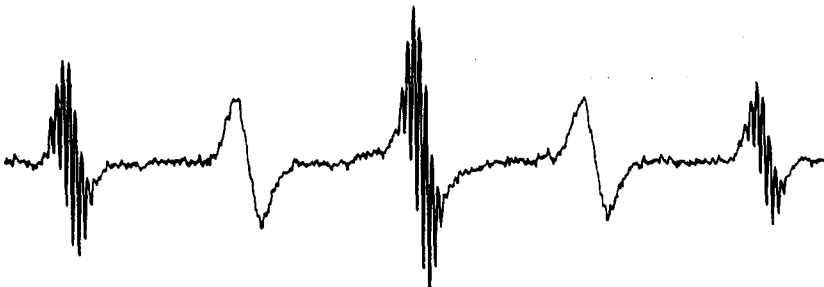
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AN anomalous alternation in the widths of the hyperfine components has been found in the ESR spectrum of the 1,4-dinitrotetramethylbenzene (dinitrodurene) anion radical.¹ The radical was produced by electrolytic reduction of an *N,N*-dimethylformamide solution of dinitrodurene.² The ESR spectrum, Fig. 1, shows a splitting into five major lines corresponding to hyperfine interactions with two equivalent nitrogen nuclei of $a^N = 6.99$ G. The relative amplitudes of these lines clearly deviate from the predicted relative statistical weights of 1:2:3:2:1. The further splitting in the spectrum arises from interactions with the

FIG. 1. Derivative of the ESR spectrum of the dinitroindurene anion radical in DMF at room temperature. Magnetic field increases to the right.



12 equivalent methyl protons of $a^H=0.25$ G. The minor components of the 0 and ± 2 lines³ are comparable in resolution and width but are considerably better resolved and narrower than the ± 1 lines.⁴ These differences decrease with increasing temperature.

We would like to propose the following model to explain this width-alternation phenomenon. The nitro groups in dinitroindurene are influenced by steric interaction with the methyl groups, and therefore a conformation in which they are planar with the benzene ring is highly unlikely. We assume that when one nitro group is planar with the ring, the methyl groups are bent in such a way as to force the second nitro group out of the plane. The pair of nitro groups then undergoes a correlated hindered rotation, one group moving into the plane as the other moves out, while the methyl groups rotate rapidly. We also assume that a^N is a function of the angle of orientation ϕ of the plane of the nitro group with respect to the plane of the benzene ring, and symmetry dictates that $a^N(\phi) = a^N(\phi + \pi)$. From the work of Geske and Ragle,⁵ we know that $|a^N(0)| \neq |a^N(\pi/2)|$.

The rotational modulation of $a^N(\phi)$ causes line broadening by inducing secular and nonsecular relaxation processes determined by the Fourier spectrum of the deviation of the matrix elements of

$$[a^N(\phi_1)\mathbf{I}_1 + a^N(\phi_2)\mathbf{I}_2] \cdot \mathbf{S}$$

from their average value $\langle a^N(\phi) \rangle (\mathbf{I}_1 + \mathbf{I}_2) \cdot \mathbf{S}$. Two simple models have been considered to describe the motion: (1) The position of the nitro groups is determined by a free stochastic rotational diffusion in which the angle between the two nitro groups remains constant. (2) The orientations of the two nitro groups (one planar, the other nonplanar with respect to the ring), interchange by rapid random jumps. Both models predict the same qualitative results. The secular contribution, which is probably the dominant effect, leads to a single line of Lorentzian shape for the $m_I = \pm 1$ and ± 2 lines, and a superposition of two lines of Lorentzian shape but different widths for the $m_I = 0$ line. Our treatment, following the general formulation of Abragam and others,⁶ implies a multiple line must be treated as a superposition of Lorentzian components rather than as a single Lorentzian.⁷ If the two nitro groups are perpendicular to each other, $J_{12}(0) = -J_{11}(0)$,

where $J_{11}(0)$ and $J_{12}(0)$ are, respectively, the secular spectral densities for the motion of one nitro group relative to the plane of the ring, and for the correlated motion of the two nitro groups. The contributions to the width are: $(T_2^{-1})_{\pm 2} = 0$; $(T_2^{-1})_{\pm 1} = J_{11}(0)$; and $(T_2^{-1})_0 = 0$ (statistical weight 1) and $(T_2^{-1})_0 = 4J_{11}(0)$ (statistical weight 2). If $J_{11}(0)$ is large, the $m_I = \pm 1$ lines should be broad, while the $m_I = 0$ line of statistical weight 2 should be so broad that it might not be observed. The amplitudes of the $m_I = \pm 2$ lines and the $m_I = 0$ line would then be nearly the same.

The spectrum of the dinitromesitylene anion radical at 25°C and of the 2,6-dinitrotoluene anion radical at -40°C show similar linewidth alternations which are consistent with the proposed mechanism. The 1,4-dihydroxydurene cation radical also shows an alternation of linewidths, but the effect arises in the methyl proton lines rather than (by analogy with dinitroindurene) in the hydroxyl proton lines.^{8,9} This phenomenon requires the additional assumption that hindered rotations of the hydroxyl group can modulate the methyl proton hyperfine interactions.⁸

We would like to acknowledge assistance in the electrochemical techniques from P. H. Rieger and I. Bernal. The alternating linewidth in dinitroindurene was first observed by these investigators.²

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³ Positions of the major lines will be designated by the quantum numbers $m_I = -2, -1, 0, 1, 2$ for the z component of the total nitrogen nuclear spin angular momentum, and the low-field line will be assumed to correspond to $m_I = -2$.

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