The Triplet Spin-Density Distribution along a Polyene Chain: An Electron-Spin-Echo Study of a Deuterododecapentaenal

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Abstract: We report on the electron-spin-echo decay of triplet [2-^{2}H]dodecapentaenal in stretched polyethylene films. Deuterium nuclear-spin-induced modulations have been observed and analyzed, and a value of 0.12 ± 0.01 is found for the spin density on the carbon atom at position 2. The agreement of this value with that calculated by semiempirical molecular-orbital methods provides the basis for a discussion of the spin-density distribution along the conjugated carbon−carbon chain of polyenes in the lowest triplet state.

Introduction

Triplet states of molecules whose chromophore consists of a linear chain of conjugated carbon−carbon double bonds are notoriously difficult to study because the quantum yield of intersystem crossing is very low. Such states do play a part in photobiological processes where the lowest triplet state of, for example, carotenoids gets populated through excitation transfer rather than intersystem crossing. For model compounds, the lack of triplet population following optical excitation has long hampered their study. A few years ago, we showed that short-chain polyenals, $CH_3(-CH=CH)_n-CHO$, are suited to study the lowest triplet state T_0 of conjugated chains.[1] The spin−orbit coupling on the oxygen atom of the terminal aldehyde group provides the triplet state with a significant transient population upon pulsed laser excitation into the singlet manifold which enabled an investigation of T_0 by electron-spin-echo (ESE) spectroscopy. The T_0 state of such polyenals was found to be a $\pi\pi^*$ excited state. The zero-field splitting of the polyenals with $n = 2-6$ was determined and found to vary inversely proportional to $(n + 1)$.[1,2] This observation was rationalized within a simple Hückel molecular-orbital picture assuming the excitation to correspond to the promotion of an electron from the highest occupied π to the lowest unoccupied π^* orbital (HOMO → LUMO). *Ab initio* MRD-CI calculations on hexadienal and octatrienal corroborated this description and revealed that such a configuration may well account for 85−90% of the wave function of T_0.[3] While this result may seem straightforward at first sight, one should keep in mind that for hexatriene and longer polyenes the lowest excited singlet state does not correspond to the HOMO → LUMO excitation.[4]

Experimental data concerning the electron spin-density distribution along the polyenal chain would provide a critical test of the triplet wave function. In this context we have studied the deuterium hyperfine interaction in *all-trans*-[2-^{2}H]dodecapentaenal abbreviated below as 2D-DP (structural formula in Figure 1). Here we report the result of an electron-spin-echo-envelope-modulation (ESEEM) investigation of this selectively

labeled polyenal which has enabled us to probe the spin density at carbon position 2 along the conjugated chain. The observed spin density of 0.12 is found to agree well with that calculated by the semiempirical modified intermediate neglect of differential overlap (MINDO) method. This suggests that the wave function and spin-density distribution calculated in this way do present an adequate description of T_0 for dodecapentaenal (DP) and thereby paves the way for a discussion of the electron-spin-density distribution in the lowest triplet state of polyenes.

Experimental Section

All-trans-[2-^{2}H]-2,4,6,8,10-Dodecapentaenal was synthesised from *all-trans*-2,4,6,8-decatetraenal and deuterated acetonitrile (Janssen Chimica, 99%). The reaction and procedure are described in ref 5 as part of the synthesis of [15-^{2}H]spheroidene. The synthesis of decatetraenal has been described before.[6] Prior to the experiments 2D-DP was purified by HPLC.

Polyethylene film was pressed at 140 °C from polyethylene pellets (low-density polyethylene, Wacker Chemie) and afterward stretched to an extent of about 500%. The dodecapentaenal was incorporated in the polyethylene by soaking the film for 1 h in a saturated solution of 2D-DP in *n*-pentane at room temperature. The samples were irradiated with 2 mJ laser pulses at 355 nm produced by the third harmonic of a Quanta Ray Nd:YAG laser operating at 10 Hz. All experiments were performed at 1.2 K in a home-built homodyne X-band ESE spectrometer.[1]

Two types of ESE experiments were performed. In the first, spin echoes were generated by applying a three-pulse stimulated-echo sequence starting 1 μs after the laser flash, the three $\pi/2$ pulses being separated by a time τ and a time T, respectively. For these experiments the sample was mounted in a Mims transmission cavity operating at 9.579 GHz, with the stretch direction of the polyethylene film making an angle of 90° with the microwave magnetic field. The microwave $\pi/2$ pulses had a typical length of 16 ns, and the minimum time τ between the first two microwave pulses was 180 ns.

In the other type of ESE experiment, we applied a two-pulse-echo sequence 1 μs after the laser flash, the $\pi/2$ and π pulses being separated by a time τ. For these experiments, the sample was mounted in a slotted-tube resonator with a loaded Q of about 1000 at a resonance frequency of 9.357 GHz. With this configuration, the microwave $\pi/2$ pulse had a typical length of 25 ns and the minimum time between the two pulses was 250 ns. The sample was mounted in such a way that

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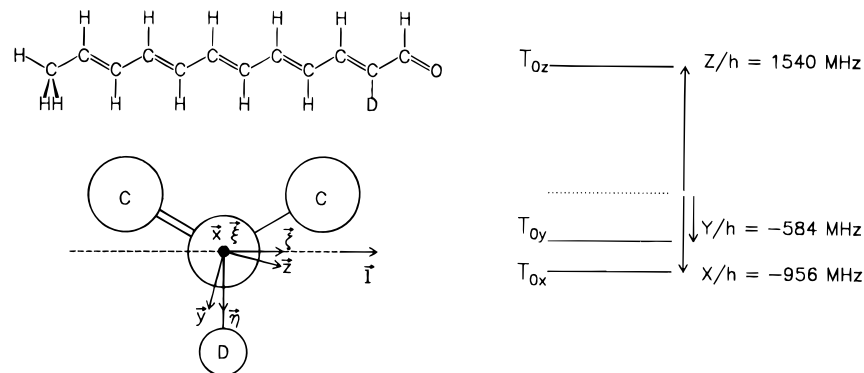
Figure 1. Molecular structure and zero-field triplet sublevel scheme of *all-trans*-[2-^{2}H]-2,4,6,8,10-dodecapentaenal. The directions of the long axis $\vec{l}$ of the molecular chain, of the principal axis $\vec{x}$, $\vec{y}$, $\vec{z}$ of the fine-structure tensor, and $\vec{\xi}$, $\vec{\eta}$, $\vec{\zeta}$ of the deuterium hyperfine tensor are indicated in the enlarged fragment of the polyenal.
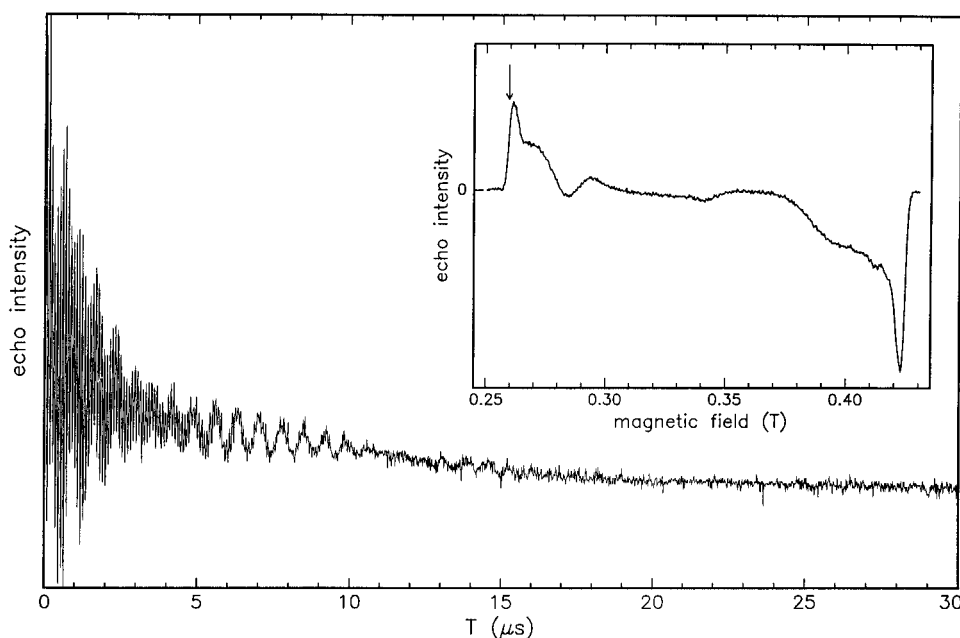

Figure 2. Stimulated-echo decay as a function of the time T between the last two $\pi/2$ microwave pulses, measured at a field of 0.259 T with $\angle(\vec{B},\vec{s})$ = 16°. The length of the $\pi/2$ pulses was 16 ns, and the time τ between the first two microwave pulses, 200 ns. The microwave frequency was 9.579 GHz. Inset: ESE-detected EPR spectrum of the lowest triplet state of 2D-DP in a stretched polyethylene film, measured by monitoring the intensity of a two-pulse echo as a function of the magnetic field strength. The direction of the magnetic field and the microwave frequency are the same as in the Figure. The $\pi/2$ amd π pulses had lengths of 24 and 48 ns, respectively, and the time τ between the two microwave pulses was 344 ns. The arrow indicates the position in the spectrum where the ESEEM pattern was measured.

the microwave magnetic field was in the plane of the polyethylene film and made an angle of 45° with the stretch direction.

With the two-pulse-echo sequence, ESEEM patterns were recorded by monitoring the echo intensity while varying the time τ between the $\pi/2$ and π pulses. In the stimulated-echo experiment the time τ was fixed. In this case, ESEEM patterns were recorded as a function of the time T between the last two $\pi/2$ pulses.

Results and Discussion

Previously we have found that for DP the triplet fine-structure principal axes $\vec{y}$ and $\vec{z}$ are in the plane of the molecule with $\vec{z}$ making an angle of 16° with the direction $\vec{l}$ of the polyenal chain (cf. Figure 1), while the principal axis $\vec{x}$ is perpendicular to the molecular plane.[1] A sample of 2D-DP in stretched polyethylene contains a distribution of polyenal orientations around the stretch direction $\vec{s}$, and the ideally oriented molecules have $\vec{l}$ parallel to $\vec{s}$. Consequently, the EPR resonance fields corresponding to maximum emission and absorption become stationary for $\angle(\vec{B},\vec{s})$ = 16°, 74°, and 90°.[1] These orientations are such that

the magnetic field is parallel to, respectively, the principal $\vec{z}$, and $\vec{y}$, and $\vec{x}$ axes of ideally oriented molecules. Two- and three-pulse-echo decays have been investigated for various orientations of the magnetic field with respect to the stretch directions $\vec{s}$ of the film. All decays showed modulations at the hydrogen nuclear Zeeman frequency; for orientations of the magnetic field so that $\angle(\vec{B},\vec{s})$ = 16°, 74°, or 90°, additional modulations were observed.

First consider the orientation of the magnetic field corresponding to $\angle(\vec{B},\vec{s})$ = 16°. The ESE-detected EPR spectrum for this direction of the magnetic field is represented in the inset of Figure 2. The ESE signals at the low- and high-field onsets derive from ideally oriented molecules with $\vec{B}\|\vec{z}$. The three-pulse-echo decay as a function of T for B = 0.259 T, indicated by the arrow in the inset, is represented in Figure 2 and the corresponding FFT spectrum in Figure 3. The signal at 11.0 MHz derives from protons as the frequency corresponds to the proton Zeeman frequency at the applied field. Also the peak at 21.9 MHz (double the Zeeman frequency) and the broader bands centered around 11 MHz with maxima at about 9.3 and
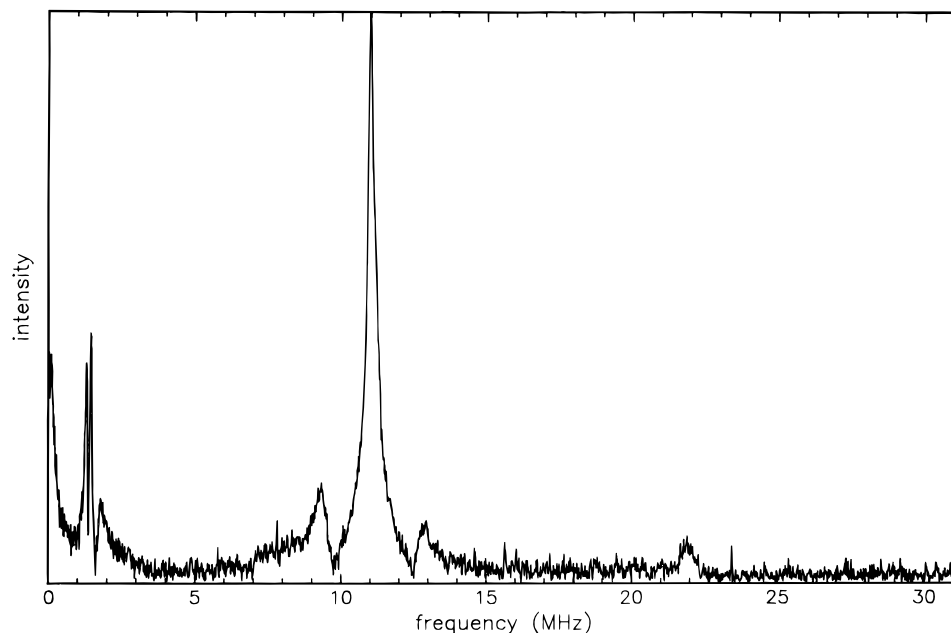
Figure 3. FFT spectrum of the three-pulse-echo decay of Figure 2.

Table 1. Deuterium ESEEM Frequencies from the Experiments with $\vec{B}$ along the Three Canonical Orientations[a]

$\angle(\vec{B},\vec{s})$ (deg)	B (T)	v_z (MHz)	ESEEM frequencies (MHz)			
16	0.259	1.69	1.31	1.45	1.79	
74	0.364	2.38	1.61	2.20	2.98	3.42
90	0.383	2.50	2.44			

[a] B indicates the magnitude of the applied magnetic field and v_z the corresponding deuterium nuclear Zeeman frequency.

12.9 MHz arise from protons coupled to the triplet electron spin. At the applied magnetic field the Zeeman frequency of deuterium amounts to 1.69 MHz. Consequently we interpret the strong bands at 1.31 and 1.45 MHz, and the weaker one at 1.79 MHz as originating from the deuterium nucleus in 2D-DP.

Bands due to the interaction of the triplet electron spin with the deuterium nucleus occur likewise in the Fourier transform of the echo decay at the high-field maxima of the EPR spectra for $\angle(\vec{B},\vec{s}) = 74°$ and $90°$. At the $74°$ orientation, the spectrum shows a broad structure with a maximum at 2.20 MHz and shoulders at 1.61 and 2.98 MHz and a weaker but sharp resonance at 3.42 MHz. For the $90°$ orientation, only one significant low-frequency resonance is observed at 2.44 MHz. The experimental results are summarized in Table 1.

In order to understand the deuterium ($I = 1$) frequencies and to determine the hyperfine interaction, we have to consider a nuclear spin Hamiltonian including the deuterium Zeeman, hyperfine, and quadrupole interaction:

$$\hat{\mathscr{H}}_N = -g_D\beta_N\hat{I}\cdot B + \langle\hat{S}\rangle\cdot A\cdot\hat{I} + \hat{I}\cdot P\cdot\hat{I}$$

where $\langle\hat{S}\rangle$ represents the expectation value of the triplet electron spin and A and P the deuterium hyperfine and quadrupole tensors, respectively. For a small contribution of the quadrupole term, expected to be on the order of 100 kHz,[7] the nuclear eigenvalues can be found by diagonalizing the matrix of $\hat{\mathscr{H}}_N$ including only the first two terms while treating the last term perturbatively. For $\vec{B}||\vec{z}$, the triplet sublevels correspond to $\langle\hat{S}_z\rangle$

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$= m_s = -1, 0,$ and 1, while $\langle\hat{S}_x\rangle = \langle\hat{S}_y\rangle = 0$. The energies of the nuclear sublevels are given by

$$E^{(j)} = j\{\langle\hat{S}_z\rangle^2(A_{zy}^2 + A_{zx}^2) + (-g_D\beta_NB + \langle\hat{S}_z\rangle A_{zz})^2\}^{1/2} + E_{qz}^{(j)}$$

$$(1)$$

with $j = 0, \pm1$. The quadrupole contribution $E_{qz}^{(j)}$ represents the expectation value of P in the nuclear spin state j for $\vec{B}||\vec{z}$; $E_{qz}^{(1)} = E_{qz}^{(-1)}$. Similar expressions, after cyclic permutation of x, y, and z, hold for $\vec{B}||\vec{x}$ and $\vec{B}||\vec{y}$.

The expression for $E^{(j)}$ allows the assignment of the observed deuterium nuclear spin transitions. First consider the data for $\angle(\vec{B},\vec{s}) = 16°$, i.e., $\vec{B}||\vec{z}$. The low-field EPR signal in the inset of Figure 2 corresponds to the $m_s = 0 \rightarrow m_s = -1$ transition (cf. the principal values of the fine-structure tensor $X/h = -956$ MHz, $Y/h = -584$ MHz, and $Z/h = 1540$ MHz[1]). According to eq 1, the energy differences between the nuclear spin levels in the respective electron-spin states fulfill the relations

$m_s = -1:$ $(E^{(-1)} - E^{(0)}) - (E^{(0)} - E^{(1)}) = 2(E_{qz}^{(1)} - E_{qz}^{(0)})$

$m_s = 0:$ $E^{(1)} - E^{(0)} = g_D\beta_NB + (E_{qz}^{(1)} - E_{qz}^{(0)})$

$E^{(0)} - E^{(-1)} = g_D\beta_NB - (E_{qz}^{(1)} - E_{qz}^{(0)})$ (2)

From these relations we can assign the observed deuterium frequencies to the electron-spin substates. An interpretation consistent with the Zeeman frequency of 1.69 MHz is only obtained if the 1.45 MHz frequency is assigned to one of the transitions within the $m_s = 0$ manifold, and the 1.31 and 1.79 MHz frequencies, to transitions in the $m_s = -1$ manifold. Moreover it follows that $|E_{qz}^{(1)} - E_{qz}^{(0)}| = 0.24$ MHz.

For $\angle(\vec{B},\vec{s}) = 74°$, the magnetic field is along the principal $\vec{y}$ axes of part of the ideally oriented molecules. The interpretation of the EPR spectrum has shown that at the resonance field for these molecules also some other ideally oriented molecules (who have their $\vec{y}$ axis not in the plane spanned by $\vec{B}$ and $\vec{s}$) are in resonance.[1] This explains the broader structure around 2.20 MHz in the ESEEM spectrum for this orientation of $\vec{B}$. For the molecules for which $\vec{B}||\vec{y}$, the high-field EPR signal corresponds to the $m_s = -1 \rightarrow m_s = 0$ transition. The transition

at 2.20 MHz, close to the deuterium Zeeman frequency of 2.38 MHz, belongs to the $m_s = 0$ manifold, and the transitions at 2.98 and 3.42 MHz, to the $m_s = -1$ manifold. It follows that $|E_{qy}^{(1)} - E_{qy}^{(0)}| \approx 0.20$ MHz. The origin of the shoulder at 1.61 MHz is unclear. For $\angle(\vec{B},\vec{s}) = 90°$, the magnetic field is along the principal $\vec{x}$ axis of ideally oriented molecules. The observation of only one frequency close to the deuterium Zeeman frequency will be explained later on.

In order to derive the spin density at carbon position 2 from the frequencies corresponding to the deuterium nuclear spin transitions, we have to consider the hyperfine interaction of the deuterium nucleus explicitly. The hyperfine interaction contains an isotropic part a_{iso} and an anisotropic part $\mathcal{A}$. The latter is practically determined by the interaction of the deuterium nuclear spin with the π-electron spin density ρ_2 at C_2. This tensor $\mathcal{A}$ is diagonal in the local axes system $\vec{\xi}, \vec{\eta}, \vec{\zeta}$ (cf. Figure 1) with principal values $\rho_2 \mathcal{A}'_{\xi\xi}$, $\rho_2 \mathcal{A}'_{\eta\eta}$, and $\rho_2 \mathcal{A}'_{\zeta\zeta}$. The principal values of $\mathcal{A}'/h$ corresponding to spin density 1, taken equal to g_D/g_H times the values known for hydrogen, are -0.10, 4.81, and -4.71 MHz.[8] For DP, the $\vec{y}$ and $\vec{z}$ axes are rotated by 16° with respect to the $\vec{\eta}$, and $\vec{\zeta}$ axes (cf. Figure 1). Consequently we end up with $A_{xx} = -0.10\rho_2 + a_{iso}$, $A_{xy} = A_{zx} = 0$, $A_{yy} = 4.08\rho_2 + a_{iso}$, $A_{yz} = 2.52\rho_2$, and $A_{zz} = -3.99\rho_2 + a_{iso}$ (in MHz). By rewriting eq 1 for $\vec{B}||\vec{z}$ and its analogue for $\vec{B}||\vec{y}$, expressions are obtained for $|(E^{(-1)} - E^{(1)})/h|$ in the $m_s = -1$ manifold in terms of ρ_2 and a_{iso}. From the frequencies observed for these orientations of $\vec{B}$ we then calculate $\rho_2 = 0.12 \pm 0.01$ and $a_{iso} = 0.31 \pm 0.05$ MHz.

The value of a_{iso} points to a small spin density on the deuterium atom itself. The polarization contribution to a_{iso} from the spin density on C_2 is known to amount to -9.26 MHz for spin density 1.[8] This leads to a negative contribution of -1.11 MHz for $\rho_2 = 0.12$. The remainder, 1.42 MHz, most probably derives from a spin density of about 0.007 on deuterium ($a_{iso} = 218$ MHz for spin density 1[8]) which might hint at a slight nonplanarity of 2D-DP at C_2.

The values of ρ_2 and a_{iso} make A_{xx} small. Consequently we expect only frequencies close to the deuterium nuclear Zeeman frequency in the experiment with $\vec{B}||\vec{x}$ (cf. $\angle(\vec{B},\vec{s}) = 90°$ in Table 1). Besides, since $A_{xy} = A_{zx} = 0$, branching of the nuclear spin states is negligible and so will be the modulation depth.

It is of interest to compare the value of ρ_2 with the spin-density distribution calculated for T_0 of DP by the semiempirical MINDO method, an approach known to yield reasonable results for spin densities. We have considered a planar molecule with strict trigonal and tetragonal bond angles and bond lengths $r(C=O) = 1.32$ Å, $r(C=C) = 1.46$ Å, $r(C-C) = 1.35$ Å (corresponding to a reversed bond order compared to that of the ground state), $r(C-CH_3) = 1.52$ Å, and $r(C-H) = 1.08$ Å.[3] A restricted Hartree−Fock calculation was performed with the MOPAC 93 program followed by configuration interaction including the singly excited configurations made out of the four HOMOs and the four LUMOs. The lowest triplet state proves to be fairly well described by a $\pi\pi^*$ excitation (80% HOMO−LUMO character, consistent with earlier *ab initio* results for smaller chains[3]). The calculated spin-density distribution is represented in Figure 4. The calculated value of 0.135 for ρ_2 is rather close to the experimental value of 0.12. We may extrapolate and conclude that the spin-density distribution along the polyenal chain might well be like that indicated in Figure 4.

A closer look at the carbon spin-density distribution reveals a regularity along the chain if we ignore the terminal oxygen
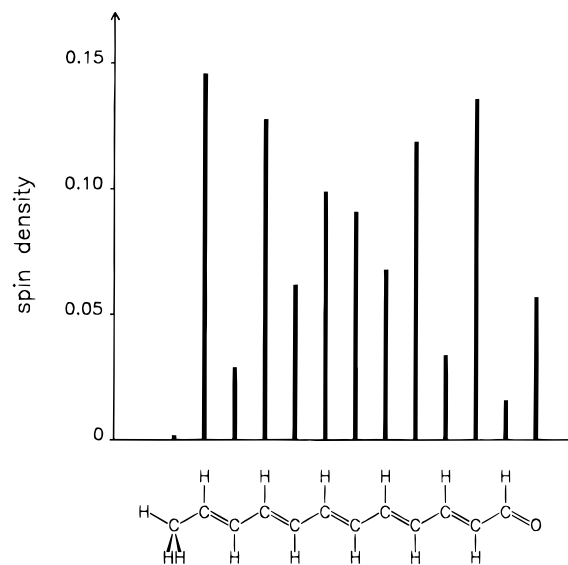

Figure 4. π-electron spin-density distribution over the heavy atoms of dodecapentaenal in the lowest triplet state T_0 as calculated with the MINDO method.

atom. Starting from each end of the chain and considering every other atom, the spin-density increases gradually from 0 to about 0.14. The result is a distribution that shows mirror symmetry around $C_6=C_7$. This can be elegantly rationalized within the Hückel molecular-orbital model for an even alternant hydrocarbon chain.[9] Consider a chain of n carbon atoms, where we take n to be even. The coefficient of the ith atomic $2p_x$ orbital ($i = 1, 2, ..., n$) in the jth molecular orbital ($j = 1, 2, ..., n$) is given by

$$C_{ji} = \{2/(n+1)\}^{1/2} \sin\{ij\pi/(n+1)\}$$

This leads to coefficients $C_{(n/2)i}$ for the HOMO that are equal in magnitude to the coefficients $C_{[(n/2)+1]i}$ for the LUMO (pairing theorem[9]). The spin density on atom i then becomes equal to $|C_{(n/2)i}|^2$ which for odd i becomes

$$\frac{2\cos^2\{i\pi/2(n+1)\}}{n+1}$$

and for even i becomes

$$\frac{2\sin^2\{i\pi/2(n+1)\}}{n+1}$$

Along the polyene chain the argument runs from about 0 up to about $\pi/2$ (for not too small n), which explains the gradual increase (decrease) of the spin density on the even (odd) carbon atoms. This simple model even quantitatively reproduces the spin densities as calculated in the MINDO approach which once again underscores the $\pi\pi^*$, HOMO → LUMO excitation character of T_0. As is clear from the above reasoning concerning a_{iso}, such a simple picture does not account for the isotropic proton couplings along a polyene chain because these are not only determined by the polarization contribution arising from the spin density in the carbon $2p_x$ orbitals.[10]

In summary, we have shown that electron-spin-echo-envelope-modulation studies of selectively deuterium-labeled polyenals enable the determination of the spin-density distribution along

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the conjugated carbon−carbon chain in the triplet state. Well-defined modulations have been observed for [2-^{2}H]dodecapentaenal dissolved in stretched polyethylene films. From the analysis of the hyperfine interaction a spin density of 0.12 has been found at carbon position 2. Comparison of this value with that calculated by MINDO indicates that the description of the triplet state of polyenals in terms of a $\pi\pi^*$, largely HOMO → LUMO excitation is adequate.