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Radiation damage in thiophene derivatives: ESR and ENDOR studies of x-irradiated 5-nitrothiophene 3-carboxaldehyde single crystals

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The crystal structure of 5-nitrothiophene 3-carboxaldehyde was determined. X-irradiation of these crystals, at 77 K, leads to the formation of a radical pair ($D = -875$ MHz, $E = 49$ MHz) which exhibits hyperfine interaction with two protons. By using the structural information of the crystal structure together with the ESR tensors, it is possible to show that this pair is composed of an allyl-type radical and of a σ radical produced by a C–H homolytic scission. This pair disappears at 155 K. At 290 K a new species is created; the ENDOR analysis shows that this new radical results from a radical addition at the carbon bearing the NO_2 group.

INTRODUCTION

Heteroatoms, in organic chemistry, are often the sites which are the most sensitive to ionizing radiation. This is particularly true for sulfur-containing molecules which give rise to a large variety of sulfur-centered radicals.[1–3] However, when this heteroatom belongs to an aromatic system, e.g., thiophene, the behavior of the molecule on radiolysis seems to be very similar to that of pure benzene.[4] Although many ESR studies have been performed on radicals produced from thiophene at room temperature,[5,6] the primary radical species trapped in crystalline thiophene irradiated at 77 K are only partially known: An allyl type radical has been detected by Nagai and Gillbro[7] and a dimerization reaction has been suggested by these authors. The various steps of the mechanism are, however, unknown, as is the structure of the reaction intermediates.

In the present study we identify one of the primary radical species involved in the radiolysis of a single crystal of 5-nitrothiophene 3-carboxaldehyde. The determination of the crystal stucture allows us to compare the ESR eigenvectors with the bond directions of the undamaged molecule. It appears that, at 77 K, one of the primary products is a pair composed of a σ-type radical and of an allyl radical, while, at higher temperature, an additional isolated allyl-type radical is produced. The structure of these species will also be discussed.

EXPERIMENTAL

5-nitrothiophene 3-carboxaldehyde has been synthesized by nitration of thiophene 3-carboxaldehyde.[8] Single crystals have been grown by slow evaporation of a solution in CH_2Cl_2/hexane.

The crystal structure has been determined at room temperature by using a four-circle Philips PW1100 diffractometer with monochromatic Mo $K\alpha$ radiation.

The x irradiation has been performed at 77 K or at room temperature by using the radiation of a Philips tube having a tungsten anticathode (30 mA, 30 kV).

The ESR spectra have been recorded at 77 K (finger Dewar) and at room temperature on a Bruker 200 D spectrometer (100 kHz field modulation, X band). Variable temperature experiments have been performed by using the Bruker ER 4111 accessory. ^{1}H-ENDOR spectra have been obtained on a Varian E-9 spectrometer equipped with a homemade ENDOR device: The single crystal is oriented in the center of a two-loop copper coil. The radio frequency is produced by a Waveteck frequency generator (model 2000) and the rf power (ENI model 3100) is dissipated in a 50 Ω resistor.

RESULTS

Crystal structure

Crystallographic data: $C_5H_3NO_3S$, Monoclinic, $P2_1/n$, $a = 5.199(1)$, $b = 9.238(3)$, $c = 13.217(3)$ Å; $Z = 4$, $d_c = 1.646$ g cm^{-3}, $F_{000} = 320$, $\mu = 4.27$ cm^{-1}.

The structure has been solved by direct methods (MULTAN 80)[9] and refined by full-matrix least-squares (XRAY 76).[10] All hydrogen atoms have been located from a differ-

TABLE I. Fractional coordinates and, for nonhydrogen atoms, equivalent isotropic temperature factors, U_{eq}, (Å$^2 \times 10^3$) with e.s.d's in parentheses. (U_{eq} is the average of the eigenvalues of U).

	X	Y	Z	U_{eq}
S(1)	0.2698(3)	0.210 76(16)	0.635 31(11)	52.0(4)
O(1)	0.2262(10)	0.066 7(5)	0.442 0(3)	71.8(16)
O(2)	0.5160(9)	0.185 4(6)	0.365 5(3)	70.0(16)
O(3)	0.9529(8)	0.580 4(5)	0.633 5(3)	65.3(14)
N(1)	0.3926(9)	0.158 4(5)	0.440 0(3)	50.3(13)
C(1)	0.4476(9)	0.242 3(5)	0.530 1(4)	42.9(14)
C(2)	0.6267(9)	0.345 6(6)	0.543 2(4)	42.2(13)
C(3)	0.6231(8)	0.404 2(5)	0.642 4(3)	41.0(14)
C(4)	0.4418(10)	0.340 8(6)	0.699 3(4)	49.0(14)
C(5)	0.7893(10)	0.521 4(6)	0.681 0(4)	49.9(15)
H(2)	0.763(17)	0.381 (11)	0.484 (7)	
H(4)	0.392(17)	0.352 (11)	0.769 (7)	
H(5)	0.778(17)	0.548 (10)	0.747 (6)	

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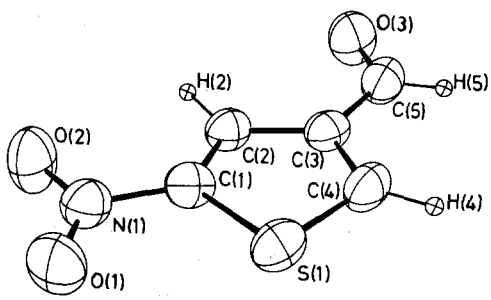
TABLE II. Interatomic distances (Å) and bond angles (deg) with e.s.d's. in parentheses.

S(1)–C(1)	1.730(5)	C(1)–S(1)–C(4)	89.6(2)
S(1)–C(4)	1.700(6)	O(1)–N(1)–O(2)	124.0(5)
O(1)–N(1)	1.212(7)	O(1)–N(1)–C(1)	118.3(4)
O(2)–N(1)	1.225(6)	O(2)–N(1)–C(1)	117.7(5)
O(3)–C(5)	1.210(7)	S(1)–C(1)–N(1)	118.8(3)
N(1)–C(1)	1.438(7)	S(1)–C(1)–C(2)	114.2(4)
C(1)–C(2)	1.339(7)	N(1)–C(1)–C(2)	127.0(5)
C(2)–C(3)	1.420(7)	C(1)–C(2)–C(3)	110.6(4)
C(2)–H(2)	1.13(9)	C(2)–C(3)–C(4)	112.6(4)
C(3)–C(4)	1.365(7)	C(2)–C(3)–C(5)	124.9(4)
C(3)–C(5)	1.463(7)	C(4)–C(3)–C(5)	122.5(4)
C(4)–H(4)	0.97(9)	S(1)–C(4)–C(3)	112.9(4)
C(5)–H(5)	0.91(8)	O(3)–C(5)–C(3)	124.8(5)

ence electron density map and refined with isotropic temperature factors. The final R factor, based on 495 observed reflections [$|F_o| > 3\sigma(F_o)$ and $|F_o| > 6$] is 0.035 {$wR = 0.041$ with $w = \exp[18.0(\sin\theta/\lambda)^2]$}.

The atomic coordinates are given in Table I and the bond lengths and bond angles are shown in Table II.[17]



As expected all the atoms are coplanar (maximum deviation from the mean plane = 0.02 Å) and the C(1)SC(4) angle is close to that measured by rotation spectroscopy for the unsubstituted thiophene.[11]

Low temperature ESR spectra

The ESR reference frame is shown in Fig. 1 together with the crystallographic axes. The ESR spectra obtained at 77 K, directly after x irradiation in liquid nitrogen, are characterized by a central set of broad lines exhibiting a poorly resolved structure (signals A) and by well resolved satellite lines (signals B) (Fig. 2). The ratio "satellite's intensity/central signal's intensity" is not dependent on irradiation time, and all the lines are already detected after only 10 mn of irradiation.

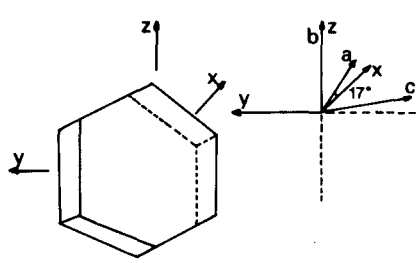


FIG. 1. Idealized single crystal of 5-nitrothiophene 3-carboxaldehyde together with the reference system and the crystllographic axes.

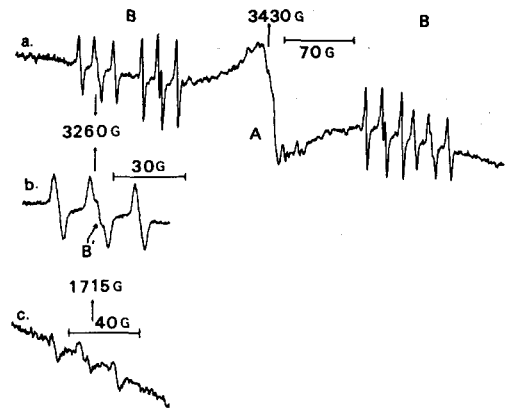


FIG. 2. ESR spectra obtained at 77 K with a single crystal of 5-nitrothiophene 3-carboxaldehyde irradiated at 77 K. (a) ESR lines due to the radical pair (signals B) together with the central part (signals A). The magnetic field is oriented along the direction: 0, 0.044, 0.999. (b) The low field part of the B signals is recorded at an expanded scan range. (c) $\Delta M_s = 2$ transitions (magnetic field along Z axis).

Signals B are very anisotropic and their angular dependencies are shown in Fig. 3. In accordance with the crystal structure two sites are present and the angular variation of the B signals can by analyzed as being due to a radical pair exhibiting hyperfine coupling with two spin $\frac{1}{2}$ nuclei. This interpretation has been confirmed by scanning the field around 1700 G; the weak $\Delta M_S = 2$ signals are effectively detected and the expected hyperfine structure is clearly observed. The large linewidth of the B signals ($\Gamma_{pp} \simeq 4.0$ G) is thought to be due to an unresolved coupling tentatively assigned to ^{14}N. The special pattern which appears for some orientations [e.g., signal B' in Fig. 2(b)] has been simulated by assuming a ^{14}N coupling constant equal to 1.6 G.

The ESR parameters of this system have been obtained using the following Hamiltonian:

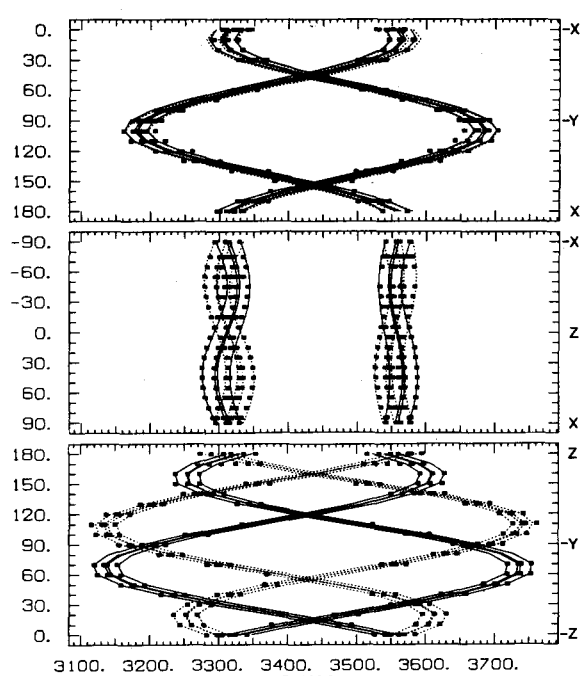


FIG. 3. Angular variation of the ESR signals B (pairwise trapped radical).

TABLE III. ESR tensors for the radical pair.

Tensor	Eigenvalues	Direction cosines		
$\bar{g}$	2.0068	−0.022	−0.839	∓0.542
	2.0034	0.786	0.319	∓0.525
	1.9984	0.614	−0.437	∓0.656
$\bar{\mathscr{D}}$ (MHz)	340	0.187	0.368	±0.91
	243	−0.971	−0.072	±0.228
	−583	0.150	−0.927	±0.345
$1_{H\text{-}\bar{T}(MHz)}$[a]	59			
	50			
	44			
$1_{H\text{-}T(MHz)}$[a]	50			
	47			
	42			

[a] Due to frequent overlappings of the sites in the *xyz* reference planes, these ^{1}H-hyperfine tensors could not be measured in this frame with a satisfactory precision. The ^{1}H-eigenvalues have been obtained after diagonalization of the tensors measured by rotating the crystal in an arbitrary reference system.

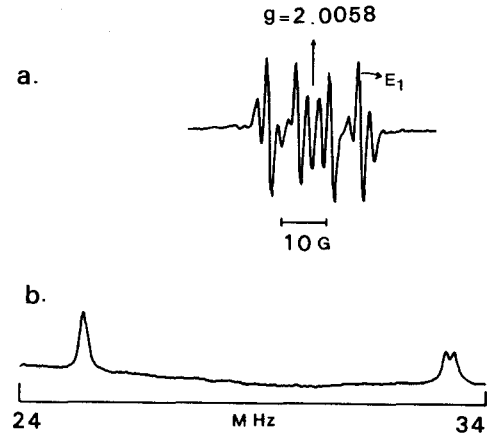


FIG. 4. (a) ESR spectrum obtained for the radical stable at room temperature (H_0 parellel to $0Y$). (b) ENDOR spectrum obtained at 100 K at observing position E_1.

$$\mathscr{H} = H \cdot S\bar{g}h + S\bar{\mathscr{D}}S + S\bar{T}_1 I_1 + S\bar{T}_2 I_2,$$

where $\mathscr{D}$ is the electron–electron dipolar interaction tensor and T_1 and T_2 are the two proton hyperfine tensors. h is the unit vector oriented along the magnetic field direction. An optimization process which calculates the signal positions by using a second order perturbation[12] leads to the g, $\mathscr{D}$, T_1, and T_2 tensors given in Table III.

Room temperature ESR spectra

ESR spectra obtained at room temperature with a single crystal previously irradiated at 77 K are the same as those recorded after irradiation at 298 K. Along the reference axes these spectra are well resolved (e.g., Fig. 4) but the presence of several forbidden lines together with inequivalent sites has prevented us from following their angular variation in the three planes. This problem has been solved by ENDOR (vide infra). The g values measured along the three reference axes are given in Table IV.

Variable temperature ESR spectra

The temperature dependence of the ESR spectra (Fig. 5) obtained with a single crystal of 5-nitrothiophene 3-carboxaldehyde previously irradiated at 77 K shows that the satellite lines suddenly disappear irreversibly at 155 K. The central lines slightly decrease in intensity by heating to 160 K but the structure remains unaffected. Above this temperature a single broad line ($\Gamma_{pp} \simeq 20$ G) is observed until 225 K. At 280 K this broad line further decreases and at 290 K a structure similar with that observed at room temperature is detected. At constant temperature (290 K) the intensity of these signals increases during 1 h.

ENDOR SPECTRA

A single crystal of 5-nitrothiophene 3-carboxaldehyde irradiated at room temperature gives rise to intense ^{1}H-ENDOR spectra (100 K), an example of which is given in Fig. 4(b). The angular dependencies of the high frequency ^{1}H-ENDOR lines are given in Fig. 6 and show that a radical exhibiting hyperfine couplings with two protons is trapped in two crystallographic sites. These hyperfine tensors are given in Table IV and have been obtained by using an optimization program which calculates the position of the ENDOR lines by a first order perturbation theory. Finally, in order to check the consistency of these results, we have used the tensors given in Table IV to simulate the three ESR spectra obtained for the magnetic field aligned along the reference axes. This simulation has been performed by using the perturbation treatment published by McDowell[13] which calculates the probabilities and positions of all the allowed and forbidden transitions, a Gaussian line shape has been

TABLE IV. Proton hyperfine tensors obtained from ENDOR study of the room temperature stable radical.

	T(MHz)	A_{iso}	Anisotropic coupling constant	Direction cosines		
Proton 1	−45.5		$\tau_1 = -16.0$	0.03	+0.751	∓0.659
	−30.9	−29.6	$\tau_2 = -1.2$	0.428	−0.606	∓0.670
	−12.4		$\tau_3 = +17.2$	−0.903	−0.262	∓0.339
Proton 2	−43.0		$\tau'_1 = -15.6$	0.610	−0.342	±0.714
	−28.7	−27.4	$\tau'_2 = -1.2$	0.427	−0.617	∓0.661
	−10.5		$\tau'_3 = +16.9$	0.667	+0.709	±0.232

g values along the references axes: $g_x = 2.006$, $g_y = 2.005$, $g_z = 2.003$

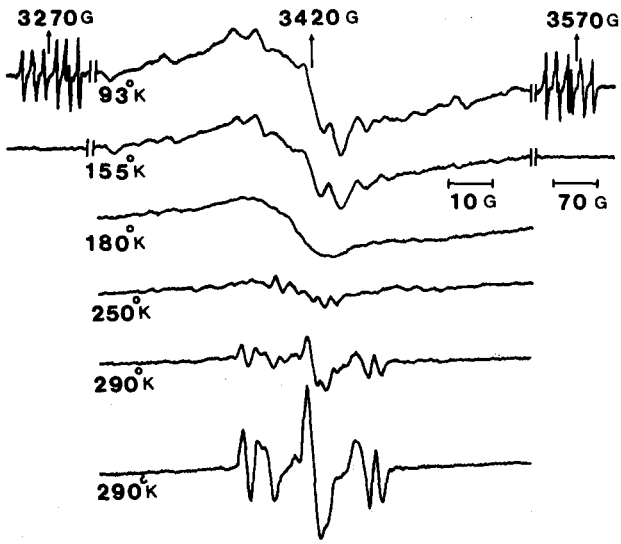


FIG. 5. Temperature dependance for the ESR spectrum obtained with a crystal of 5-nitrothiophene 3-carboxaldehyde irradiated at 77 K. The final spectrum is recorded 30 mn after reaching 290 K.

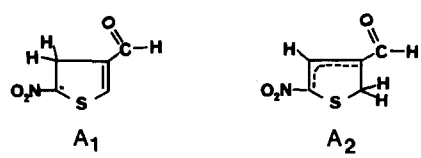
used for the convolution. The simulated spectra are in excellent accord with the experimental spectra.

DISCUSSION

Radical pair

The two hyperfine tensors given in Table III are measured for a radical pair; it is well known that this interaction is half of that which would have been measured on the isolated radical.[14] The corresponding eigenvalues for the isolated species [(118, 100, 88 MHz) and (100, 94, 57 MHz)] are consistent with two protons located in β position from a carbon bearing the unpaired electron or with the methylene protons resulting from the addition of H• to an aromatic system.

The $\mathscr{D}$ tensor given in Table III corresponds to the two following zero field splitting parameters: $D = -875$ MHz, $E = 49$ MHz. This high D value leads—in a rough approximation—to an interdipole distance $\simeq 5$ Å. From the crystal structure it is clear that in the unit cell two molecules only $A(x,y,z)$ and $B(1-x, 1-y, 1-z)$ are separated by such a short distance. Moreover the large E value indicates that, at least for one of the two radicals composing the pair, the unpaired electron is not confined on a single atom. Two radicals derived from the nitrothiophene ring are expected to exhibit a strong delocalization of the unpaired electron: the radical anion and an allyl-type radical. It has been shown[15] that the largest isotropic coupling for nitrothiophene radical anions is due to ^{14}N. As we do not observe any resolved ^{14}N coupling we consider that an allyl radical is the best candidate for one of the two components of the pair (say: the radical located on molecule A). The most probable process giving rise—at 77 K—to an allyl radical is the addition of a hydrogen atom to the thiophene ring. In this mechanism a pair is indeed created if this atom originates from molecule B. Whatever the CH bond that is broken in molecule B, the resulting radical will not present any large ^{1}H hyperfine interaction. The observed ^{1}H couplings are therefore due to the radical located on the A molecule. This radical can be either A_1 or A_2.



Two factors make the structure A_1 to be very improbable: (i) The localization of the unpaired electron on C(1) does not agree with the experimental E value; (ii) no resolved ^{14}N hyperfine coupling is observed. In accord with the experimental spectra additional couplings for the structure A_2 are expected to be unresolved when this radical belongs to a pair: the H(5) coupling constant must be weak since this proton is located close to the nodal plane of the allyl system, the ^{14}N constant must be small since this nucleus is in α position from a carbon whose spin density is less than 0.5.

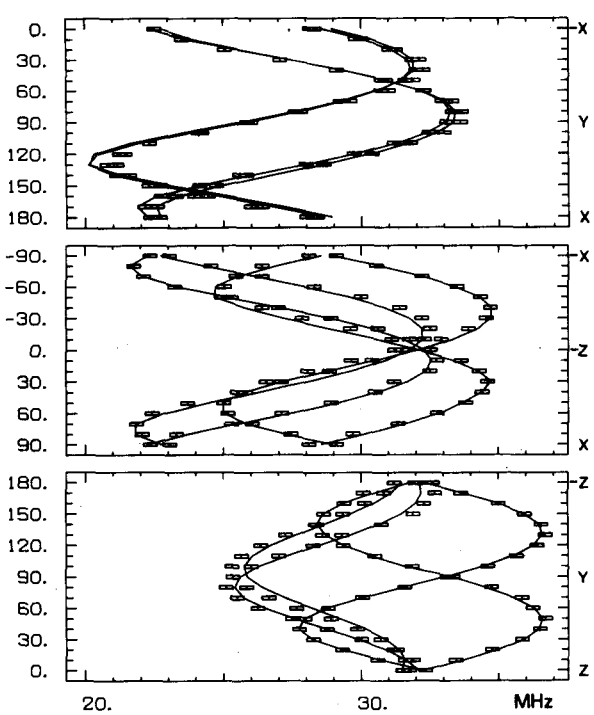


FIG. 6. Angular variation of the ENDOR signals obtained with the radical stable at room temperature.

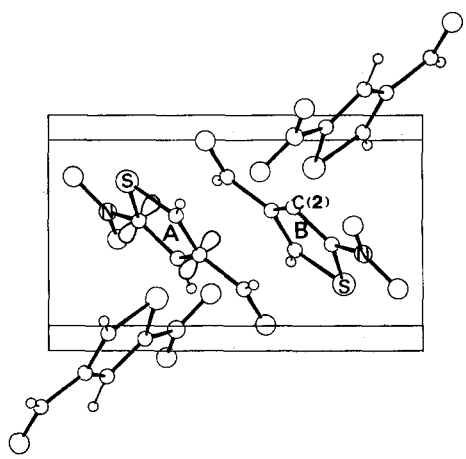


FIG. 7. Projection of the crystal structure on the *ab* plane. A and B represent the two components of the radical pair.

TABLE V. INDO spin densities for the radical resulting from the addition of H• at C(1) of 5-nitrothiophene 3-carboxaldehyde.

	C(1)	C(2)	C(3)	C(4)	C(5)
$2p_x$	− 0.018 15	0.016 3	− 0.013 6	0.015 5	0.006 87
$2p_y$	− 0.017 28	0.018 12	− 0.019 78	0.013 69	0.003 71
$2p_z$	− 0.028 4	0.498 04	− 0.205 8	0.459 6	0.073 46

Assumed geometry: S–C(1) = 1.81, C(1)–C(2) = 1.52, C(2)–C(3) = 1.366, C(3)–C(4) = 1.365, C(4)–S = 1.7, C(3)–C(5) = 1.5, C(5)–H = 0.88, C(5)–O = 1.17 Å, SC(1)C(2) = 105.8, C(1)C(2)C(3) = 111.5, C(2)C(3)C(4) = 116.7, C(3)C(4)S = 112.9, C(4)SC(1) = 93, HC(1)N = 101°.

If a hydrogen addition specifically occurs on C(4) it is probable that a B molecule's hydrogen atom is located near this carbon atom. From the crystal packing we find the following distances:

$$C(4)_A\text{---}H(5)_B = 6.05\ \text{Å}, \quad C(4)_A\text{---}H(4)_B = 6.8\ \text{Å},$$
$$C(4)_A\text{---}H(2)_B = 3.6\ \text{Å}.$$

It is therefore reasonable to conclude that the radical pair is formed by a σ-type radical localized on C(2) of molecule B and an allyl radical of structure A_2.

In order to check the validity of this model we have calculated the zero field splitting parameters for this radical pair by using the structural information given by the crystal x-ray determination (Fig. 7). A unit spin density is placed on C(2) of molecule B. $\rho_1/2$ and $\rho_3/2$ electrons are located in each lobe of the p orbitals at a distance $r = 0.645$ Å[16] from the nucleus C(1) and C(3), respectively (molecule A). These orbitals are perpendicular to the crystallographic thiophene plane. The electron–electron dipole interaction between the point dipole centered on C(2) and the other four fractional electrons ($\rho_1 = \rho_3 = 0.45$) give rise to four $\mathscr{D}$ tensors which are summed up. Diagonalization of the resulting tensor leads to $D = 1275$ MHz and $E = 72$ MHz.

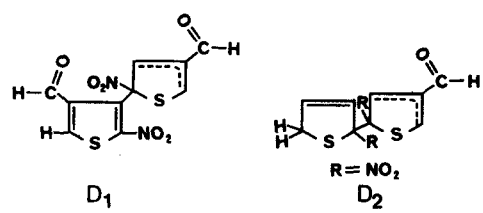
In this model we did not consider, however, the structural modifications involved by the hybridization change in C(4) (molecule A). This change is likely to be accompanied by atomic displacements in molecule A and will affect the calculated $\mathscr{D}$ tensors. For example, an elongation of 0.6 and 0.2 Å for the vector $C(2)_BC(1)_A$ and $C(2)_BC(3)_A$, respectively leads to $D = -872$ MHz, $E = 50$ MHz (with $\rho_1 = 0.42$ and $\rho_3 = 0.45$) which totally agree with the experimental values.

Radical species stable at room temperature

The ^{1}H hyperfine coupling tensors (Table IV) which characterize the radical stable at room temperature have been decomposed in isotropic and anisotropic coupling constants (Table IV). These two sets of coupling constants are in good accord with those expected for two protons located in α positions from radical carbons bearing, respectively, 46% and 43% of the total spin in their $2p_\pi$ orbital. We have carried out an INDO calculation in order to check the consistency of this spin population with a species resulting from the addition of a radical at the carbon C(1) of 5-nitrothiophene 3-carboxaldehyde. These results, obtained for the addition of H•, are given in Table V and are in good accord with this identification. The eigenvectors associated with the intermediate eigenvalues τ_2 and τ_2'—expected to be aligned along the $2p_\pi$ direction—are almost parallel (angle = 3°) and make an angle of 9° with the normal to the crystallographic C(2)C(3)C(4) plane. The eigenvectors τ_3 and τ_3' make, respectively, an angle of 13° and 11° with the C(4)H(4) and C(2)H(2) crystallographic bond directions. These angular parameters together with the experimental spin densities are in excellent agreement with an allyl-type radical formed by addition of a radical at the carbon C(1). The hybridization change of this carbon is certainly the cause of the $\sim 10°$ value found for the above-mentioned angles.

Radiation mechanism

From the variable temperature study it appears that one of the primary radiation effects is the homolytic scission of a C(2)H(2) bond. The resulting H• can be trapped by the C(4) carbon of the nearest molecule to give the radical pair (satellite lines) or can add to an other thiophenic carbon to give a variety of thienyl radicals (central lines). The pair vanishes at 155 K and at 160 K some of thienyl radicals disappear. It is probable that some of the isolated σ radicals or allyl-type radicals are still stable between 260 and 290 K (broad line without any structure), this temperature is then sufficient to allow diffusion of these radicals which can thus add to the C(1) carbon of a neighbor undamaged molecule and give rise to D_1 or D_2:



D_1 D_2

which is the single radical observed at room temperature.

This mechanism is in accordance with previous observations about the radiogenic dimerization of thiophene. This is, however, the first time—to our knowledge—that the allyl–σ radical pair is detected.

ACKNOWLEDGMENT

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