π-ELECTRONIC STRUCTURE OF THE NITROFURAN SYSTEM

IV.* ESR SPECTRA OF ANION RADICALS OF 2-VINYLENE DERIVATIVES OF 5-NITROFURAN

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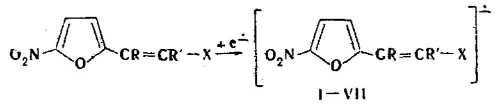
Anion radicals of 2-vinylene derivatives of 5-nitrofuran were obtained by electrochemical generation. The hyperfine structure (hfs) of the ESR spectra of these anion radicals indicates delocalization of the unpaired electron over their entire π-electron system. The effect of the vinylene grouping on the distribution of the unpaired electron in the anion radicals and on the distribution of the unpaired electron in the vinylene grouping itself was examined on the basis of the hfs constants. It was found that the vinylene grouping by localizing more than 10% of the density of the unpaired electron on itself reduces, by a factor of 1.4, the effect of substituents in the 2 position of 5-nitrofuran on the distribution of the spin of the unpaired electron in the nitrofuran framework.

The electrochemical reduction of simple 5-nitrofuran derivatives in dimethylformamide (DMF) proceeds through a step involving the formation of anion radicals of the starting compounds [1, 2]. The presence of a hyperfine structure (hfs) in the ESR spectra made it possible to not only prove the structures of these radicals but also to investigate the distribution of electrons over the π-system and the principles of the interaction of simple substituents with the furan ring [3]. Attempts to obtain this sort of information for more complex compounds, for example, 2-vinylene derivatives of furan, did not give definite results [4-6]. In the present research we therefore made a systematic study of 5-nitrofuran derivatives in which the substituent is separated from the furan ring by a vinylene grouping.

By means of electrochemical reduction in DMF we were able to obtain, in a one-electron step of the process, anion radicals I-VII of vinylene derivatives of 5-nitrofuran that were sufficiently stable for recording by ESR spectroscopy. Consequently, the anion radicals are formed during the following reaction:



I—VII

I $R=R'=H$, $X=COOH$; II $R=Br$, $R'=H$, $X=COOH$; III $R=H$, $R'=Cl$, $X=COOH$;
IV $R=H$, $R'=CH_3$, $X=COOH$; V $R=R'=H$, $X=CHO$; VI $R=R'=H$, $X=COOC_2H_5$;
VII $R=R'=H$, $X=COOCH_3$

For comparison of the hfs constants of the ESR spectra, the hfs constants of anion radicals VIII-XI, which do not contain a vinylene grouping, were determined more precisely under the same experimental conditions.

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*See [1] for communication III.

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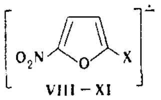

VIII–XI

VIII X=COOH, IX X=COOCH$_3$, X X=COOC$_2$H$_5$; XI X=CHO

The anion radicals of the vinylene series (I–VII) do not differ substantially in stability from anion radicals VIII–XI. The nature of substituent X has the principal effect on the stability of all of the investigated anion radicals. The ESR spectrum of anion radical I (Fig. 1) has splitting of the $3_N \cdot 2_H \cdot 2_H \cdot 2_H \cdot 2_H$ type. The measured hfs constants have the following values: $a_N = 7.95$ Oe, and $a_H = 4.96$, 3.06, 1.37, and 0.93 Oe. Constant a_N is close in value to the a_N values previously obtained for the anion radicals of the nitrofuran series (VIII–XI) [7], and this splitting is due to interaction of the unpaired electron with the nitrogen atom of the nitro group. It is impossible on the basis of only the single spectrum obtained to assign the remaining hfs constants to definite protons. For this, we also studied anion radicals II, III, and IV, in which, in contrast to anion radical I, the individual protons of the vinylene grouping are substituted by other atoms. The absence of a proton attached to the α-atom of the vinylene grouping in anion radical II leads to simplification of the hfs of the ESR spectrum (Fig. 2). Almost all of the spectral lines (the splitting is of the $3_N \cdot 2_H \cdot 2_H \cdot 2H$ type), except for two, are resolved. By comparing the hfs constants of this spectrum ($a_N = 8.6$ Oe, and $a_H = 4.9$, 1.2, and 2.3 Oe) with the values corresponding to anion radical I, we see that in the case of anion radical I the a_H constant of 0.93 Oe is due to the proton of the α-position of the vinylene grouping. Interpretation of the ESR spectrum of anion radical III (hfs of the $3_N \cdot 2_H \cdot 2_H \cdot 2_H$ type), in which the proton in the β-position of the vinylene grouping is replaced by a chlorine atom, led to the following values of the hfs constants: $a_N = 8.3$ Oe, and $a_H = 4.7$, 1.3, and 1.3 Oe. On the basis of a comparison of this set of hfs constants with the hfs constants for anion radical I, it can be asserted that the a_H hfs constant of anion radical I (3.06 Oe) is due to the proton of the β-carbon atom of the vinylene grouping. The remaining two hfs constants of this anion radical are evidently, as usual [7], due to the interaction of the unpaired electron with the protons of the furan ring, namely, $a_H = 4.96$ Oe from interaction with the proton in the 4 position and $a_H = 1.37$ Oe from interaction with the proton in the 3 position.

In contrast to the anion radicals with COOCH$_3$ and COOC$_2$H$_5$ substituents, in the ESR spectra of which one observes splitting due to the protons of this substituent, the ESR spectra of the free radicals obtained from compounds with a COOH substituent do not have this sort of hfs constant, although quantum-chemical calculations provide evidence for a certain density of the unpaired electron on the oxygen atom of the OH grouping of this substituent [3]. This proves that in the case of compounds with a COOH substituent, the

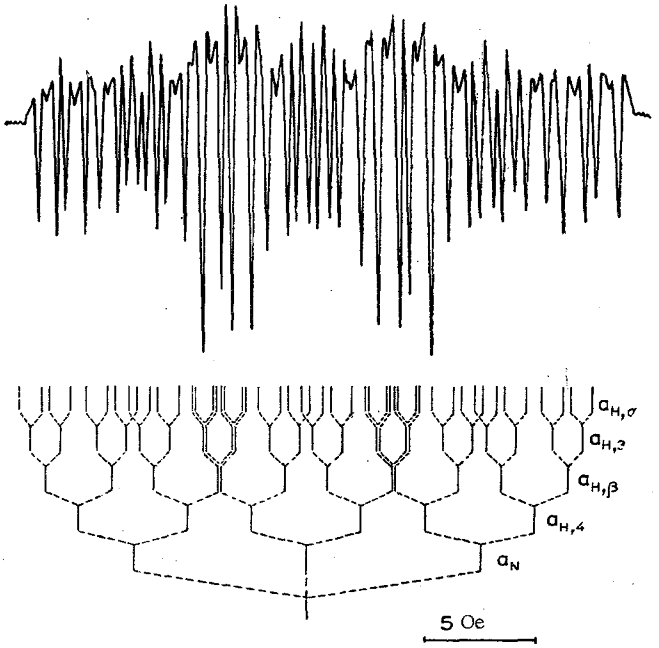

Fig. 1. ESR spectrum of dianion radical I, recorded in the form of the second derivative, and its linear reconstruction.

TABLE 1. Hyperfine Structure Parameters of the ESR Spectra of Anion Radicals of the 5-Nitrofuran Series

Anion radical	R	R′	X	Type of splitting	Spectral length, Oe	Splitting constants, Oe					
						a_N	$a_{H,4}$	$a_{H,3}$	$a_{H,\alpha}$	$a_{H,\beta}$	$a_{H,X}$
I	H	H	COO^-	$3_N \cdot 2_H \cdot 2_H \cdot 2_H \cdot 2_H$	26,38	7,95	4,96	1,37	0,93	3,06	—
II	Br	H	COO^-	$3_N \cdot 2_H \cdot 2_H \cdot 2_H$	25,8	8,6	4,9	1,2	—	2,3	—
III	H	Cl	COO^-	$3_N \cdot 2_H \cdot 2_H \cdot 2_H$	23,9	8,3	4,7	1,3	1,3	—	—
IV	H	CH_3	COO^-	$3_N \cdot 2_H \cdot 2_H \cdot 2_H \cdot 4_H$	34,0	9,0	5,0	1,6	1,6	2,7	—
V	H	H	CHO	$3_N \cdot 2_H \cdot 2_H \cdot 2_H \cdot 2_H \cdot 2_H$	18,72	5,02	3,37	0,89	0,89	3,19	0,51
VI	H	H	$COOC_2H_5$	$3_N \cdot 2_H \cdot 2_H \cdot 2_H \cdot 3_H$	20,89	5,79	3,72	1,20	—	3,72	0,30
VII	H	H	$COOCH_3$	$3_N \cdot 2_H \cdot 2_H \cdot 2_H \cdot 4_H$	21,42	5,80	3,84	1,19	—	3,84	0,34
VIII	—	—	COO^-	$3_N \cdot 2_H \cdot 2_H$	26,03	9,91	5,18	1,02	—	—	—
IX	—	—	$COOCH_3$	$3_N \cdot 2_H \cdot 2_H$	20,72	7,07	4,18	1,08	—	—	0,42
X	—	—	$COOC_2H_5$	$3_N \cdot 2_H \cdot 2_H$	20,40	7,14	4,18	1,07	—	—	0,36
XI	—	—	CHO	$3_N \cdot 2_H \cdot 2_H \cdot 2_H$	17,53	5,65	3,43	0,82	—	—	2,05

free radicals recorded in DMF are dianion radicals with a COO^- substituent. Because of the specific hfs, as, for example, in the case of anion radical VII (Fig. 3), the identification of the constant caused by the protons of substituent X is not difficult.

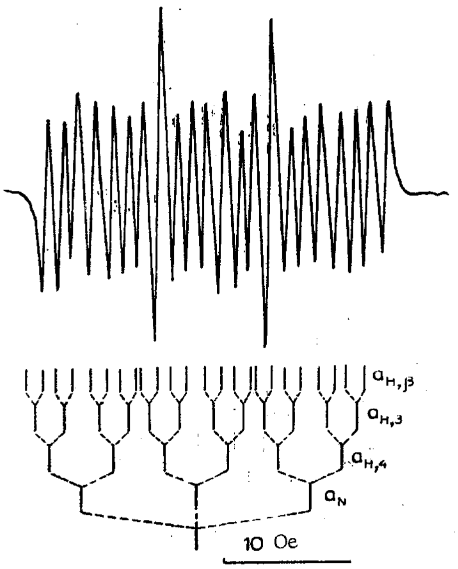

Fig. 2. ESR spectrum of dianion radical II, recorded in the form of its first derivative, and its linear reconstruction.

A similar assignment of the hfs constants was also made for the remaining recorded anion radicals.

From the results presented in Table 1, one can follow the change in the hfs constants and thereby also the redistribution of the density of the unpaired electron in the anion radicals, which characterizes the relative electrophilicity of the various positions of the starting 5-nitrofuran compounds as a function of the character of the substituent. Transition from anion radicals VIII-XI to their analogs with a vinylene grouping in the side chain (I, VII, VI, and V) causes a decrease in the hfs constant due to the nitrogen atom of the nitro group. Inasmuch as the hfs constant and the density of the unpaired electron in the nitro group are interrelated [8], this attests to at least a decrease in the density of the unpaired electron on the nitrogen atom. The same phenomenon is also observed for the $a_{H,4}$ constant; this is a clear indication of a decrease in the density of the unpaired electron in the 4 position of the furan ring. The opposite effect is observed for the $a_{H,3}$ constant; the presence of a vinylene grouping increases the value of the $a_{H,3}$ constant. However, calculations show that in this case the negative spin density of the π-electrons makes the principal contribution, and it is therefore impossible to form a direct judgment regarding the density of the unpaired electron in the first vacant molecular orbital from the value of only this hfs constant.

The hfs constant due to the protons of substituent X also decreases in the presence of the vinylene grouping. This effect is reinforced as the electrophilicity of substituent X increases, and in the case X = CHO in the presence of a vinylene grouping the a_H constant, due to the proton of the aldehyde grouping, decreases by a factor of about four (Table 1, V and XI). The decrease in the density of the unpaired electron in the nitrofuran ring and in substituent X is caused by delocalization of the unpaired electron over the vinylene grouping, within the limits of which the density of the unpaired electron constitutes a considerable value, more than 10% of the electron. The density of the unpaired electron in the vinylene grouping is distributed nonuniformly, and the electrophilicity of the β-position is more than three times that of the α-position. Replacement of the proton in the β-position of the vinylene grouping by a chlorine atom or a methyl group ($R' = CH_3$, Cl) increases the relative electrophilicity of the α-position, but replacement of the proton in the α-position by a bromine atom decreases the electrophilicity of the β-position. Substitutions in the vinylene grouping (in both the α- and β-positions) increase the relative electrophilicity of the nitro group; this is manifested in an increase in the magnitude of the a_N constant. In the examined cases of substitution, the electrophilicity of the 4 and 3 positions of the 5-nitrofuran framework changes only slightly.

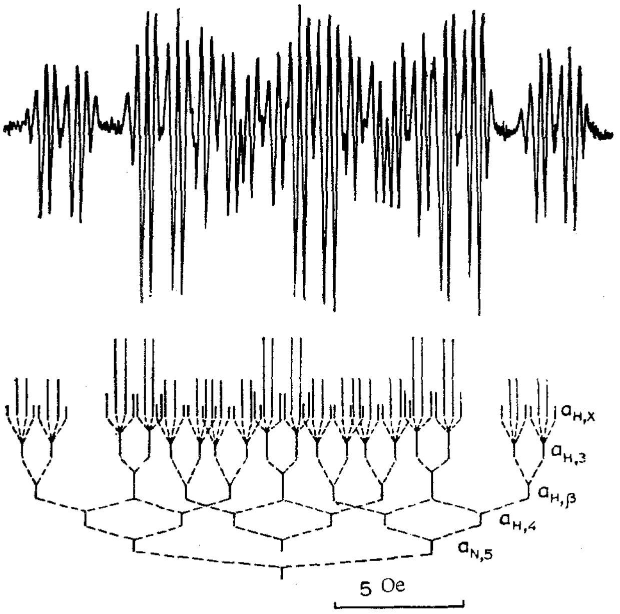

Fig. 3. ESR spectrum of anion radical VII, recorded in the form of the second derivative, and its linear reconstruction.

It has been shown that the a_N and $a_{H,4}$ hfs constants of anion radicals decrease regularly as the electrophilicity of the substituent in the 2 position of 5-nitrofuran increases [7]. It follows from a comparison of these hfs constants for anion radicals I and V-VII that when there is an intermediate grouping in the substituent of the vinylene type this sort of general principle of the effect of substituent X is retained. This is confirmed, for example, by the linear interrelationship between the a_N^{vin} and $a_{H,4}^{vin}$ constants of anion radicals I and V-VII and the corresponding a_N and $a_{H,4}$ constants of their analogs, VIII-XI: $a^{vin} = 0.92 + 0.71a$ ($r = 0.993$).

It follows from the value of the reproducibility coefficient ($Z = 0.71$) in the equation that the inclusion of a vinylene grouping decreases the effect of substituent X on the hfs constants caused by the nitrogen atom of the nitro group and the proton of the 4 position of the 5-nitrofuran framework by a factor of 1.41. This sort of estimate for the starting 5-nitrofuran molecules was previously made in [9], in which the potentials of the polarographic reduction of these compounds were compared, and it was found that the vinylene grouping reduces the effect of substituent X on the reaction center by a factor of 1.67. It should be emphasized that in our case the attenuation was determined from the steric characteristics of the unpaired electron in the anion radicals, whereas in [9] it was determined from the energy characteristics of the first vacant orbital of the starting compounds. The closeness of the found values of the "electronic conductivity" of the vinylene grouping indicates that the parameters of the π-electron system and the interrelationship between them do not change significantly with the addition of one electron to the starting molecules.

EXPERIMENTAL

The anion radicals of the investigated compounds were obtained by electrochemical generation on the surface of a mercury drop in a microcell [10] mounted in the resonator of an ESR spectrometer. When the rectangular resonator (H_{102}) of an ER 9 ESR spectrometer (Karl Zeiss, Jena) was used, the reactor of the cell [10] was flat in the near-cathode portion with a test-solution layer thickness of ~ 0.4 mm. The solutions of the investigated substances were prepared in DMF (concentrations of 10^{-3} to $5 \cdot 10^{-3}$ M) and contained an inert salt $[(C_3H_7)_4NBr]$ in a concentration of 0.1 M. The electrochemical generation of the anion radicals was realized at potentials of the plateau of the limiting current of the first polarographic wave at -0.6 to -1.0 V relative to the anode – mercury sludge. The ESR spectra of the anion radicals were recorded with RÉ-1301 (with a cylindrical resonator and a resolution of ~ 0.4 Oe) and ER 9 (Karl Zeiss, Jena) (with a rectangular resonator and a resolution of better than 0.3 Oe) spectrometers. The magnetic field scan was calibrated from the ESR spectrum of nitrobenzene anion radicals [11].

The samples of the starting compounds from which anion radicals I-XI were obtained by electroreduction were given to us by K. K. Venter, for which we sincerely thank him. According to the PMR data, starting compounds I-VII are the trans isomers.

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