

# Ion radicals of substituted 2-furylethenetricarbonitriles (an ESR, quantum-chemical, and electrochemical study)

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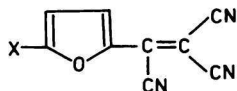
*Dedicated to Academician V Kellö, in honour of his 70th birthday*

Substituted 2-(5-X-2-furyl)-1,1,2-ethenetricarbonitriles acceptors with X = CH<sub>3</sub>, H, Cl, Br, I, and CN cathodically reduced form stable anion radicals with electron spin density distributed over the whole molecule. However, if X = NO<sub>2</sub> the spin density is centred on nitro group ( $a_N = 1.028$  mT) and no spin density is observable on the ethenetricarbonitrile part of radical. The ESR spectra and INDO calculations imply the hindered rotation around the furyl—ethene bond. The reaction products of nitro derivative with arene or heteroarene donors are 2-(5-aryl- or heteroaryl-2-furyl)-1,1,2-ethenetricarbonitriles. Electrochemically they form cation resp. anion radicals with electron spin density centred on aryl resp. furylethenetricarbonitrile part of the molecule. Generally, the reactions are electrochemically reversible with a consecutive chemical reaction. By cyclic voltammetry measured redox potentials correlate well with the Hammett constants of substituents and with INDO calculations.

Замещенные 2-(5-X-2-фурил)-1,1,2-этенетрикарбонитрильные акцепторы с X = CH<sub>3</sub>, H, Cl, Br, I и CN образуют при катодном восстановлении устойчивые радикалы со спиновой плотностью электрона, распределенной по всему скелету молекулы. Однако, при X = NO<sub>2</sub> центром спиновой плотности является нитро-группа с  $a_N = 1,028$  мТ без наблюдаемой спиновой плотности на этенетрикарбонитрильной части молекулы. Спектры ЭПР и вычисления методом INDO свидетельствуют о заторможенности вращения вокруг связи фурил—этен. Продуктами взаимодействия нитро-производных с донорными аренами или гетероаренами являются 2-(5-арил- или гетероарил-2-фурил)-1,1,2-этенетрикарбонитрилы. Из них в результате электрохимического превращения образуются катион- или анион-радикалы с центром спиновой плотности неспаренного электрона на арильной или фурилэтенетрикарбонитрильной части молекулы. В общем

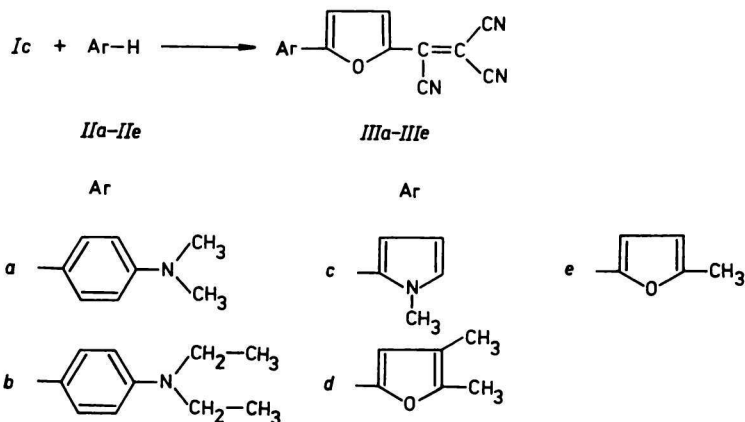
случае, реакции протекают электрохимически обратимо, и за ними следует химическая реакция. Величины окислительно-восстановительных потенциалов, измеренные с помощью циклической вольтамперии, хорошо коррелируют с константами Гамметта и результатами вычислений методом INDO.

Cyanosubstituted ethylenes are widely investigated acceptors. Mostly studied was the ethenetetracarbonitrile [1]. In previous papers [2—5] the preparation of the reactive 2-(5-X-2-furyl)-1,1,2-ethenetetracarbonitrile derivatives *Ia—Ie* was described

*Ia—Ie*

X	X
<i>a</i> H	<i>d</i> CH <sub>3</sub>
<i>b</i> I (Br, Cl)	<i>e</i> CN
<i>c</i> NO <sub>2</sub>	

In the reaction of the most reactive acceptor in group *I*, namely *Ic*, with arene resp. heteroarene donors *IIa—IIe* as products were obtained 2-(5-aryl- resp. heteroaryl-2-furyl)-1,1,2-ethenetetracarbonitriles *IIIa—IIIe* (Scheme 1). The given reaction represents a new way in the preparation of arylfuran derivatives with the electron-donating aryl group in their molecules [5].



Scheme 1

In the paper presented the formation of charge-transfer complexes in the above-mentioned reaction was investigated. Further the ion radical formation of substrates *I* and *III* was studied by means of ESR, cyclic voltammetry, and quantum-chemical calculations.

## Experimental

The ESR spectra were obtained with Bruker SRC 200D spectrometer. The employed flow unit consisted of a flat cell with mixing chamber and two syringes with a maximal flow rate  $2.4 \text{ dm}^3 \text{ h}^{-1}$ . 0.001 M reactants solutions in acetonitrile or dichloromethane were used. The cathodic reduction on platinum in two-electrode arrangement was carried out directly in the cavity of the ESR spectrometer employing 0.001 M solutions of substrate with 0.1 M tetrabutylammonium perchlorate in acetonitrile or dichloromethane. The cyclic voltammograms were measured by means of PA-3 polarograph in the potential range from +1.9 to -1.0 V in 0.001 M substrate and 0.1 M-NaClO<sub>4</sub> acetonitrile solution. As reference served the saturated calomel electrode and as working and auxiliary the platinum electrode. All experiments were carried out under inert argon atmosphere.

The investigated substances were prepared by a modified procedure [2] from original reports [6] for *Ia*, [7] for *Ib*, *Id*, [4] for *Ie*, and [5] for *Ic* and *IIIa*—*IIIe*.

In the quantum-chemical calculations by INDO method in UHF version the parametrization according to *Pople* [8] was employed. The partial annihilation of the higher spin multiplicities from UHF wave function [9] was used by the evaluation of the spin densities. Standard geometries [10] were considered for all studied structures.

## Results and discussion

### *ESR measurements*

By means of flow technique, enabling to determine the radicals with the lifetime in the range of few milliseconds no paramagnetic charge-transfer complexes were observed in the first stage of the reaction even in the case if the strongest donors *IIa* or *IIb* and acceptor *Ic* were employed. Working then in the stop-flow mode the formation of a stable radical was observed. Its concentration increases with the time as shown in Fig. 1. The low value of *g*-factor (2.0035) indicates the elimination of nitro group in the radical product. Limited resolution of the hyperfine structure of ESR spectrum prevents to gain more information on the structure of the observed radical. A similar spectrum is found choosing other reactants from substrates *I* with *II* and also in the reaction of products *IIIa*, *IIIb* with donors *Ia*, *Ib*. Therefore it is probable that the observed radical is a product of consecutive reaction and not an ion radical of

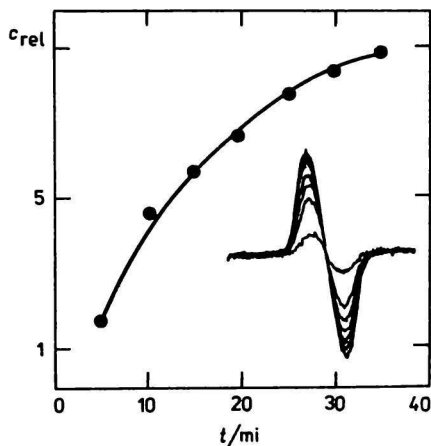


Fig. 1. Time dependence of radical formation in the reaction of 2-(5-nitro-2-furyl)-1,1,2-ethenetricarbonitrile (*Ic*) with *N,N*-diethylaniline (*Iib*) in acetonitrile ( $g = 2.0035$ ); sweep width 10 mT.

the reactants. In the reaction of donors *II* with acceptors *I* on the preparative scale products *III* are obtained in 12–63 % yield.

As a direct observation of the charge-transfer complexes resulting from the formation of the ion radicals of the reactants was not accessible by ESR technique, our attention was focused on the possibility to generate the ion radicals of the investigated donors, acceptors, and their products electrochemically.

The experimental and simulated ESR spectra of the electrochemically generated anion radicals of acceptors *Ia*–*Ic* are shown in Fig. 2 and the assignment of their by simulation obtained splitting constants is summarized in Table 1. The assignment of the splitting constants to furan ring is based on the comparison of the corresponding spectra of structures *Ia*, *Ib*. In *Ib* the hydrogen in position 5 from *Ia* is replaced by iodine. As a result, in the spectrum of *Ib* the interaction with the splitting constant  $a_{H-5} = 0.345$  mT is not observable any more, whereas the other splitting constants remain practically unchanged. From the assignment of  $a_{H-5}$  and the consideration of the alternated distribution of unpaired electron, as well as from the below-described quantum-chemical calculations resulted also the assignment of the remaining splitting constants.

Another distribution of spin density was found by *Ic*. The relatively simple spectrum of *Ic* with high value of  $g$ -factor (2.0055) indicates nitro group centred radical. Taking into account the above given consideration, as well as in the literature [11, 12] described radicals of furan derivatives, the assignment given in Table 1 is suggested. It is remarkable that the well resolved spectrum of *Ic* does not show any indication of hyperfine interaction originating from nitrogen nuclei on the ethenetricarbonitrile skeleton. The same tendency is obvious from INDO calculations.

Simulation of spectra *Ia*, *Ib* in Fig. 2 is satisfactory, although a slight asymmetry of experimental spectra is indicated. This trend is more pronounced in the systems with polyatomic groups ( $-\text{CH}_3$ ,  $-\text{CN}$ ) in position 5 (*Id*, *Ie*). It was not possible to simulate spectra *Id*, *Ie* perfectly, but from a qualitative analysis a similar distribution of spin density was found on radicals *Id*, *Ie* as on *Ia*, *Ib*. An approximative determination of the splitting constants from experiment and INDO calculations for structure *Ie* is given in Table 1. The temperature dependence of spectra *Id*, *Ie* indicates the rotation isomerism, but despite of the intensive modification of the experimental conditions it could not be evaluated quantitatively. In anodic oxidation of substrates *Ia*—*Ie* no formation of their cation radicals was observed.

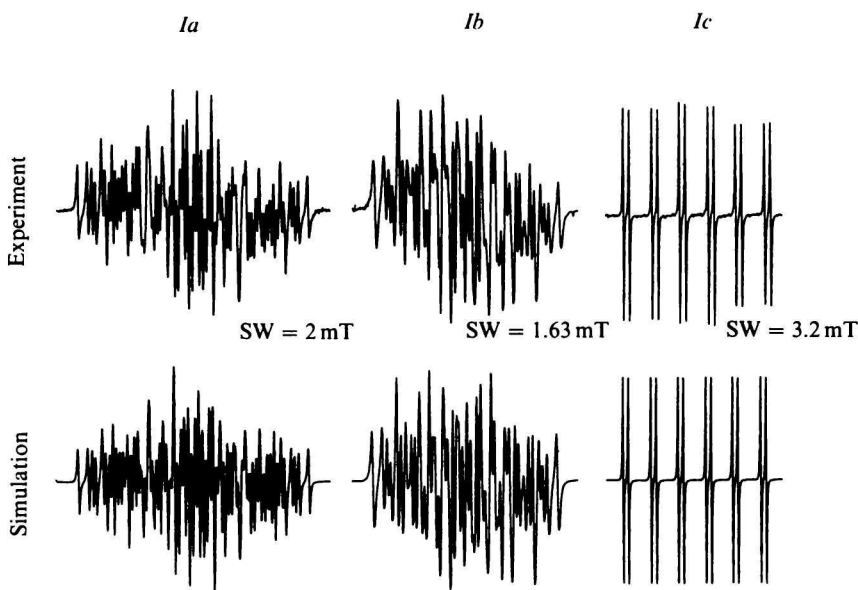
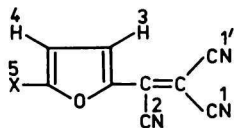


Fig. 2. Experimental and simulated ESR spectra observed in the cathodic reduction of acceptors *Ia*—*Ic* (SW is sweep width).

*N,N*-Dialkylaniline donors oxidize anodically to form stable cation radicals of their dimeric products, namely, 4,4'-(dialkylamino)biphenyls, with similar values of splitting constants as described in the literature [13]. *N*-Methylpyrrole *IIc* forms an unstable radical and no spectra are observable from derivatives *IIId*, *IIe*. In cathodic reduction of *IIa*—*IIe* formation of anion radicals was not detected by ESR.

Table 1

Assignment of splitting constants obtained by simulation of ESR spectra along with their INDO calculated values for anion radicals *Ia—Ic*, *Ie* cathodically generated in dichloromethane (DM) or acetonitrile (AN)



Compound	X	Method	Splitting constants/mT						g-Factor	Note
			$a_{N-1}$	$a_{N-1'}$	$a_{N-2}$	$a_{H-3}$	$a_{H-4}$	$a_{H,N-5}$		
<i>Ia</i>	H	exp.	0.1035	0.127	0.182	0.45	0.0705	0.345	2.0034	in DM, similar in AN
		INDO	0.109	0.133	0.187	0.38	0.093	0.290		
<i>Ib</i>	I	exp.	0.103	0.13	0.174	0.452	0.072	—	2.0035	in AN, similar for X = Br, Cl
<i>Ie</i>	CN	exp.	0.1	0.13	0.17	0.4	0.1	0.06	2.0035	in AN, $a_{H,N}$ exp. (approximative)
		INDO	0.097	0.132	0.166	0.341	0.133	0.043		
<i>Ic</i>	NO <sub>2</sub>	exp.				0.010	0.527	1.028	2.0055	in AN
		INDO				0.084	0.62	1.027		

Electrolytically, products *IIIa*—*IIIe* form cation as well as anion radicals. The tendency to form anion radicals increases from *IIIc* to *IIIe* and cation radicals from *IIIc* to *IIIa*. With *IIIa*, *IIIb* no anion and with *III'd*, *IIIe* no cation radicals are observable. Experimental and simulated spectra of cation radicals *IIIa*, *IIIb* are given in Fig. 3 and by simulation obtained splitting constants in Table 2. From the presented data it is evident that the spin density is centred on the amino group. Thereof resulted the given assignment of the splitting constants to the benzene ring. It was not possible to simulate unambiguously the spectra of anion radicals *IIIc*—*IIIe* due to their partial asymmetry, probably caused by rotamerism. Their qualitative analysis indicates that the majority of electron spin density is localized on the furylene skeleton. The stability of the anion radicals increases from *IIIc* to *IIIe*.

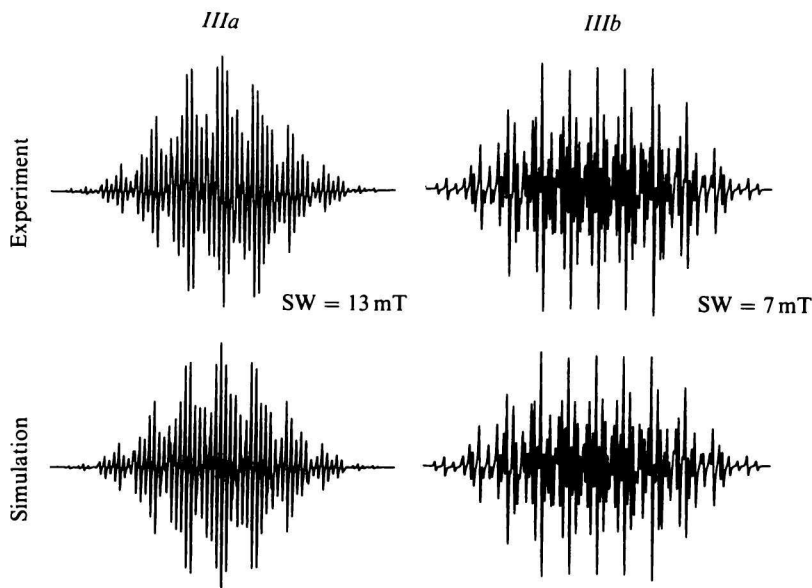
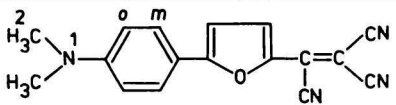
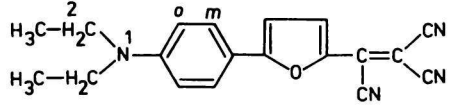


Fig. 3. Experimental and simulated ESR spectra observed in the anodic oxidation of products *IIIa*, *IIIb* in dichloromethane (SW is sweep width).

It may be added that the generated anion radicals convert with the time to various secondary products. Thus the secondary radical product of *Ic* can be described by the interaction of five equivalent nitrogen nuclei with the unpaired electron ( $a_N = 0.157$  mT and  $g = 2.0034$ ). This product formation is accelerated if cyanides are added into the system. A similar radical product was previously found in the reaction of (5-nitro-2-furyl)phenylsulfone and also 5-nitro-2-furylnitromethane with KCN [14]. The unusual radical structure with five equivalent cyano groups may be attributed to the pentacyanocyclopentadienyl radical.

Table 2

Assignment of splitting constants obtained by simulation of ESR spectra of cation radicals *IIIa*, *IIIb* anodically generated in dichloromethane

Compound	Structures	Splitting constants/mT			g-Factor	
		$a_{N-1}$	$a_{H-o}$	$a_{H-m}$		
<i>IIIa</i>		1.34	1.158	0.555	0.185	2.0040
<i>IIIb</i>		0.694	1.121	0.562	0.188	2.0039

Anion radical of substrate *Ie* converts with the time to the secondary radical product the spectrum of which indicates the opening of furan ring. Also other consecutive products and their mixtures were observed but their analysis and interpretation is not possible at present.

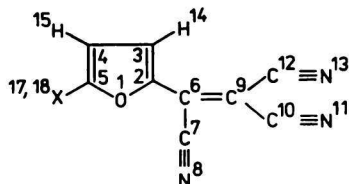
### Quantum-chemical interpretation

The calculated spin densities on the anion radicals of 5-substituted 2-furyl-ethenetricarbonitriles are summarized in Table 3, corresponding splitting constants for *Ia*, *Ic*, *Ie* in Table 1 and ionization potentials in Table 4. The theoretical values of the splitting constants were calculated by the least-square method from the relation  $a_x = Q_x \rho_{sx}$ , where  $a_x$  is the splitting constant,  $\rho_{sx}$  the  $s$ -electron spin density on the  $x$ -th nucleus and  $Q_x$  is the proportionality constant. Its calculated values are  $Q_N = 33.246$  mT and  $Q_H = 61.435$  mT with good correlation coefficients  $\rho_N = 0.9964$  and  $\rho_H = 0.9971$  and  $R$ -factors  $R_N = 0.0189$  and  $R_H = 0.0168$ . Ionization potentials  $I_p$  correlate very well with the half-peak potentials  $E_{p/2}$  obtained by cyclic voltammetry in the cathodic reduction of substrates *I* (Fig. 7). The statistical characteristics for the relation  $I_p = k_1 + k_2 E_{p/2}$  are  $\rho = 0.9974$  and  $R = 0.0191$ .



Table 3

INDO calculated spin densities on *s*-orbitals of individual atoms in anion radicals of 5-substituted 2-furylethenetricarbonitriles



Atom	X					
	H	F	Cl	Br	CN	NO <sub>2</sub>
O-1	0.0008	0.0006	0.0008	0.0009	0.0010	0.0014
C-2	-0.0067	-0.0074	-0.0064	-0.0056	-0.0055	-0.0044
C-3	0.0074	0.0084	0.0076	0.0073	0.0066	0.0060
C-4	-0.0046	-0.0052	-0.0050	-0.0048	-0.0050	-0.0051
C-5	0.0051	0.0058	0.0061	0.0065	0.0049	0.0069
C-6	0.0092	0.0094	0.0084	0.0078	0.0076	0.0059
C-7	-0.0062	-0.0064	-0.0058	-0.0053	-0.0054	-0.0045
N-8	0.0056	0.0057	0.0055	0.0053	0.0050	0.0002
C-9	0.0094	0.0087	0.0099	0.0107	0.0103	0.0108
C-10	-0.0067	-0.0063	-0.0070	-0.0076	-0.0071	-0.0073
N-11	0.0033	0.0036	0.0031	0.0030	0.0029	0.0002
C-12	-0.0068	-0.0070	-0.0071	-0.0072	-0.0072	-0.0074
N-13	0.0040	0.0041	0.0039	0.0041	0.0040	0.0002
H-14	-0.0061	-0.0060	-0.0064	-0.0064	-0.0055	-0.0014
H-15	0.0015	0.0013	0.0016	0.0017	0.0022	0.0101
H-16	-0.0047	0.0001	0.0001	0.0001	-0.0027	-0.0309
X-17	—	—	—	—	0.0013	—
X-18	—	—	—	—	-0.0210	0.0225

On the 2-(5-X-2-furyl)-1,1,2-ethenetricarbonitriles with X = H, Cl, Br, I, and CN the unpaired electron is distributed over the whole molecule. But if X = NO<sub>2</sub> the unpaired electron is centred on nitro group and no spin density is observable on the tricyanovinyl part of the molecule. This can be explained by the change of SOMO orbital (single occupied molecular orbital) which is mainly responsible for the distribution of the spin density. From Fig. 4 it is evident that for X = H and X = CN this MO is nearly equally distributed over the whole molecule. But if X = NO<sub>2</sub> this MO is mainly localized on the furan ring and the nitro group, and only negligibly on the tricyanovinyl part.

Table 4

Cathodic and anodic half-peak potentials  $E_{p/2}$  of 2-(5-X-2-furyl)-1,1,2-ethenetetracarbitriles obtained for various substituents X by cyclic voltammetry along with the INDO calculated ionization potentials  $I_p$

Compound	Anodic $E_{p/2}$ V	Cathodic $E_{p/2}$ V	$I_p$ eV
<i>Ia</i>	0.71	-0.395	0.903
<i>Ib</i>	> 1.90	-0.370	—
<i>Ib'</i>	1.50	-0.360	0.976
<i>Ic</i>	0.620	-0.070	1.553
<i>Id</i>	0.860	-0.490	0.702
<i>Ie</i>	0.99	-0.205	1.228
<i>IIIa</i>	0.820	-0.510	
<i>IIIb</i>	0.780	-0.510	
<i>IIIc</i>	1.080	-0.485	
<i>IIId</i>	1.240	-0.445	
<i>IIIe</i>	1.280	-0.450	

For *Ib'* X = Cl.

ESR spectra of anion radicals indicated a substituent-dependent hindered rotation. Therefore the substituent dependence of rotation barrier of tricyanovinyl group (Fig. 5) was investigated. Whereas if X = H, F, Cl, Br the change of the rotation barrier is very low, but it increases significantly for X = CN and is

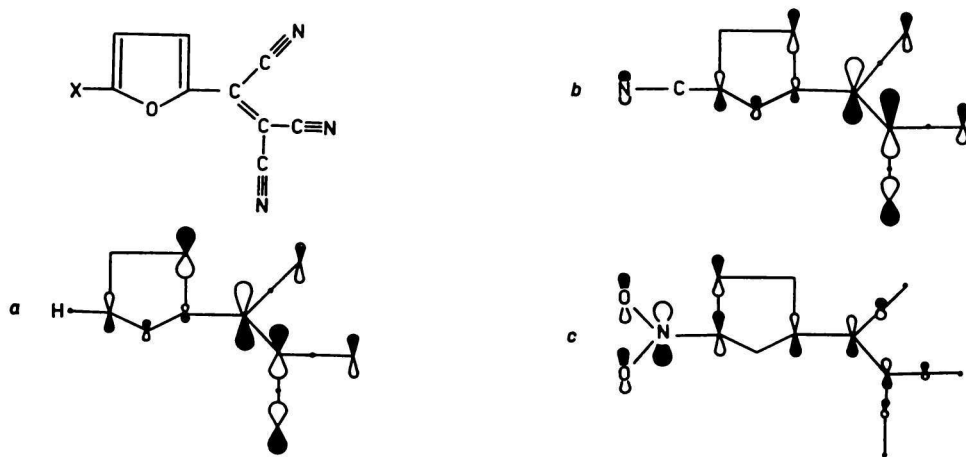


Fig. 4. The shape of SOMO orbitals of 5-substituted 2-furyl-1,1,2-ethenetetracarbitrile anion radicals for various substituents X: a) X = H, b) X = CN, c) X = NO<sub>2</sub>.

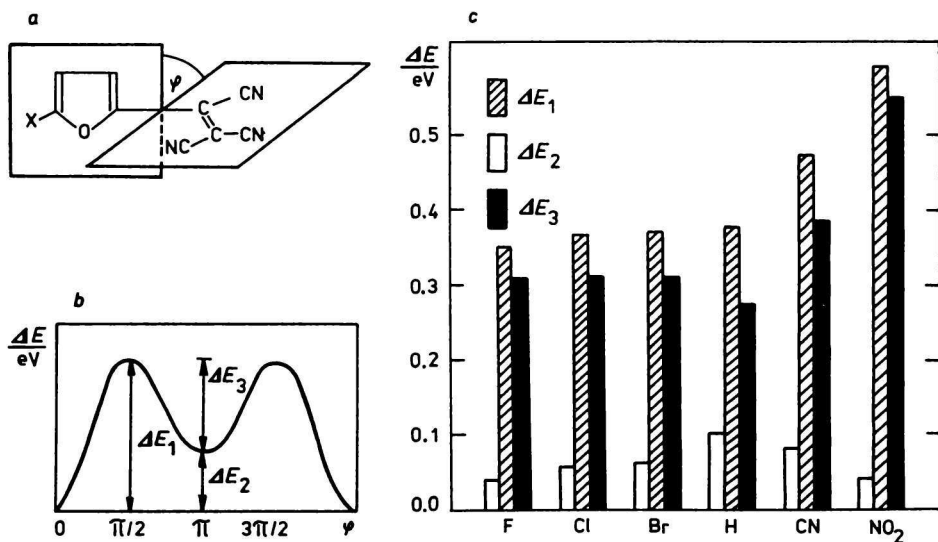


Fig. 5. INDO calculated energies of rotation barriers.

Definition of rotation angle (a); angle dependence and definition of rotation barrier (b); values of rotation barrier for various X (c).

maximal for  $X = \text{NO}_2$ . This indicates that the substituents with a negative mesomeric effect increase the  $\pi$ -electron population on the furan—tricyanovinyl bond, *i.e.* they increase its double-bond character and consequently increase the energy of the rotation barrier around it. In contrast to that the negative induction effect of substituents X over the three  $\sigma$ -bonds is negligible. This is confirmed here by our calculations of Wiberg indices [15] of the furan—tricyanovinyl bond for various substituents ( $W = 0.99$  for  $X = \text{F}$ , 1.01 for Cl, 1.02 for Br, 1.03 for H, 1.15 for CN and 1.27 for  $X = \text{NO}_2$ ).

### Cyclic voltammetry

By cyclic voltammetry investigated substrates *I* and *III* are summarized in Table 4. The cyclic voltammograms in the range (+ 1.9; -1) V show cathodic peaks without their corresponding reversible counter-peaks. Exception is substrate *Ic*, where after cathodic reduction at the scan rate  $0.2 \text{ V s}^{-1}$  also anodic counter-peak was observed. Characteristic cyclic voltammograms with the cathodic and anodic parts are illustrated on substrate *IIIc* in Fig. 6a. A special behaviour of *Ic* at various scan rates is shown in Figs. 6b, c. The obtained half-peak potentials  $E_{p/2}$  for cathodic reduction and anodic oxidation at the scan rate  $0.2 \text{ V s}^{-1}$  are given in Table 4.

$E_{p/2}$  Values for anodic oxidation of substrates *III* correlate very well with the observed stability of their cation radicals. Substrates *IIIa*, *IIIb* with  $E_{p/2}$  0.820 V and 0.780 V form stable radicals, *IIIc* with  $E_{p/2}$  1.080 V less stable one and no radical formation is observed for *III d* and *III e* with  $E_{p/2}$  values 1.280 V and 1.240 V. Otherwise in anodic oxidation of *III* all  $E_{p/2}$  values are nearly the same within the span of 0.060 V. This is in accord with the ESR observation indicating the localization of the electron spin density on the furylethenetricarbonitrile skeleton. The small changes in  $E_{p/2}$  as well as their trend (maximal for *III d*, *III e*, minimal for *III a*, *III b*) can be attributed to the influence of substituent X.

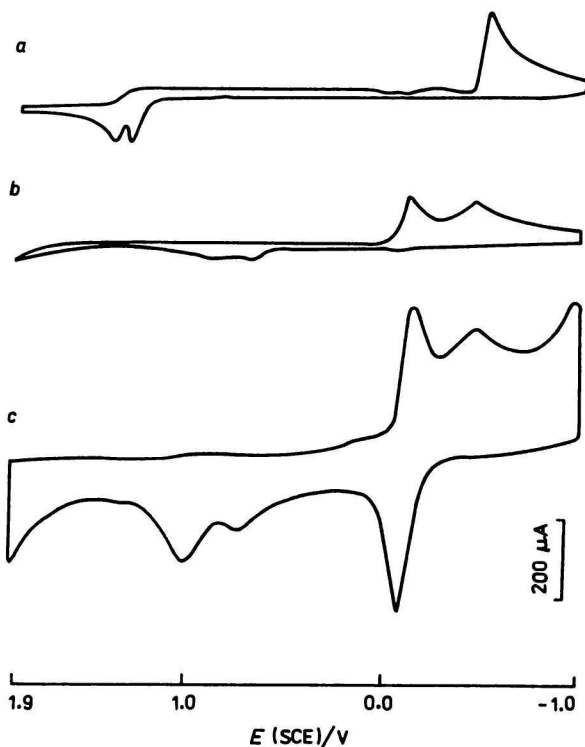


Fig. 6. Cyclic voltammograms of 0.001 M substrates and 0.1 M- $\text{NaClO}_4$  solution at various scan rates  $v$ .

- a) Characteristic voltammogram for substrate *I*, *III* (*IIIc*,  $v = 0.02 \text{ V s}^{-1}$ ); b)  $I_c$ ,  $v = 0.02 \text{ V s}^{-1}$ ;  
c)  $I_c$ ,  $v = 0.2 \text{ V s}^{-1}$ .

In anodic oxidation of substrates *I* no cation radicals were observed and it is difficult to comment the observed changes of  $E_{p/2}$ . Otherwise in the cathodic reduction of *I* stable anion radicals were found. The changes of  $E_{p/2}$  values correspond well to the INDO calculated ionization potentials (Table 4, Fig. 7).

$E_{p/2}$  Values correlate also well with the Hammett constants [16]  $\sigma_p^-$  for *para* position of benzene ring (Fig. 7) with correlation coefficient  $\rho = 0.9817$  and factor  $R = 0.0312$ .

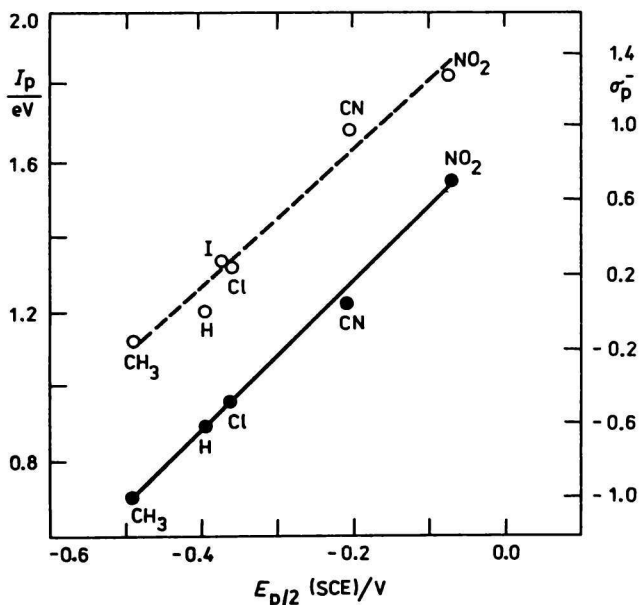


Fig. 7. Dependence of INDO calculated ionization potentials  $I_p$  (●—) and Hammett constants  $\sigma_p^-$  (○—) on the cathodic half-peak potentials  $E_{p/2}$  of substrates *I* (Table 4).

A further evaluation of cyclo-voltammetric results according to [17] characterizes the oxidation and the reduction as approximately reversible electrochemical reactions with a consecutive chemical reaction. The classification of the substrates according to their consecutive reactions is out of the scope of this contribution.

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