Journal of Organometallic Chemistry, 441 (1992) 479–486
Elsevier Sequoia S.A., Lausanne
JOM 22905

Electronic structure of ferrocenylacrylonitrile ion radicals

Z.V. Todres, A.I. Safronov, D.S. Ermekov and R.M. Minyaev

Institute of Organo-Element Compounds of the Russian Academy of Sciences, Moscow (Russian Federation)

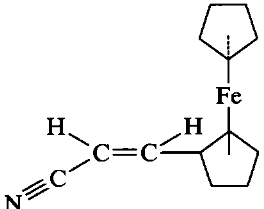
(Received April 29, 1992)

Abstract

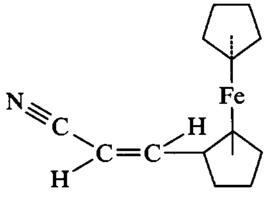
The electronic structure of anion and cation radicals of ferrocenylacrylonitrile was analysed by photoelectronic spectra and extended Hückel molecular orbital calculations. In concordance with the experiments, *cis/trans* conversion is predicted for anion radicals but not for cation radicals. In contrast, *cis/trans* conversion of arylethylenes was found to be possible for anion radicals as well as cation radicals. The difference is explained with marked distinction by the nature of the ion radicals. In homoaromatic ion radicals the molecular orbitals, which are populated by an unpaired electron, embrace all π-orbitals. For the ferrocenylacrylonitrilic system, a molecular orbital occupied by one electron is preferentially constructed by the fragment orbital of the acrylonitrilic fragment in the anion radical and, exclusively, by the atomic orbital of iron in the cation radical. In the latter, one of the next, adjacent orbitals is shown to belong to the acrylonitrilic fragment. If such an orbital is involved in the process of oxidation, rotation around the ethylenic bond is predicted to occur.

Introduction

Ferrocenylacrylonitriles (**1**, **2**) are rather stable and do not interconvert spontaneously. These isomers exist separately in cation radical form, but *cis/trans* (not *trans/cis*) conversion takes place for anion radical forms [1]. In a sense, compounds **1**, **2** differ sharply from stilbenes which are also converted from *cis* to *trans* isomers in anion and cation radical forms as well [2].



(**1**)



(**2**)

This difference ought to be connected with the presence of the ferrocenylic fragment. It is noteworthy that there is effective conjugation between the acryloni-

---

Correspondence to: Professor Z.V. Todres.

trilic group and the ferrocenylic fragment in neutral *cis*-ferrocenylacrylonitrile. The dihedral angle formed by planes of π-systems, which belong to the substituted cyclopentadenylic ligand and the double bond of the acrylonitrilic group, is equal to 23° [3]. This corresponds to 85% conjugation energy, which is maximally possible for the coplanar π-systems [3].

In order to elucidate the molecular orbital difference between the two ion radical forms of ferrocenylacrylonitrile, we have analysed the photoelectronic spectra of isomers **1**, **2** and made quantum-chemical calculations of the appropriate cation or anion radicals.

Photoelectronic spectra (PES)

PES of ferrocene [4], isomeric nitriles **1** and **2** (Figs. 1 and 2) were compared. In the two latter cases, the spectra were non-identical. Hence, *cis/trans* conversion did not take place during recording of the spectra and photoelectronic ionization did not provoke any change in the molecular configuration.

The first band was observed at 6.88 eV for unsubstituted ferrocene, at 7.21 eV for nitrile **1**, and at 7.27 eV for its isomer **2**. Such a shift of potentials for **1**, **2**, compared with ferrocene, is in accordance with the electron acceptor effect of the acrylonitrilic group. This group is characterized by Hammett constants $\sigma_m = 0.24$

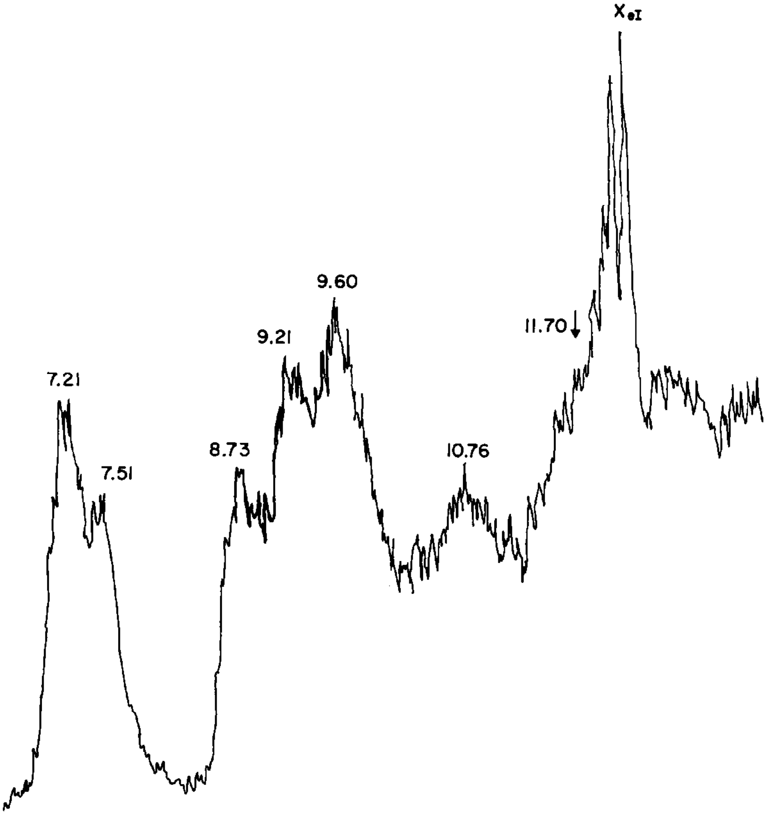


Fig. 1. Photoelectronic spectrum of *cis*-ferrocenylacrilonitrile (**1**) (positions of bands are given in eV).

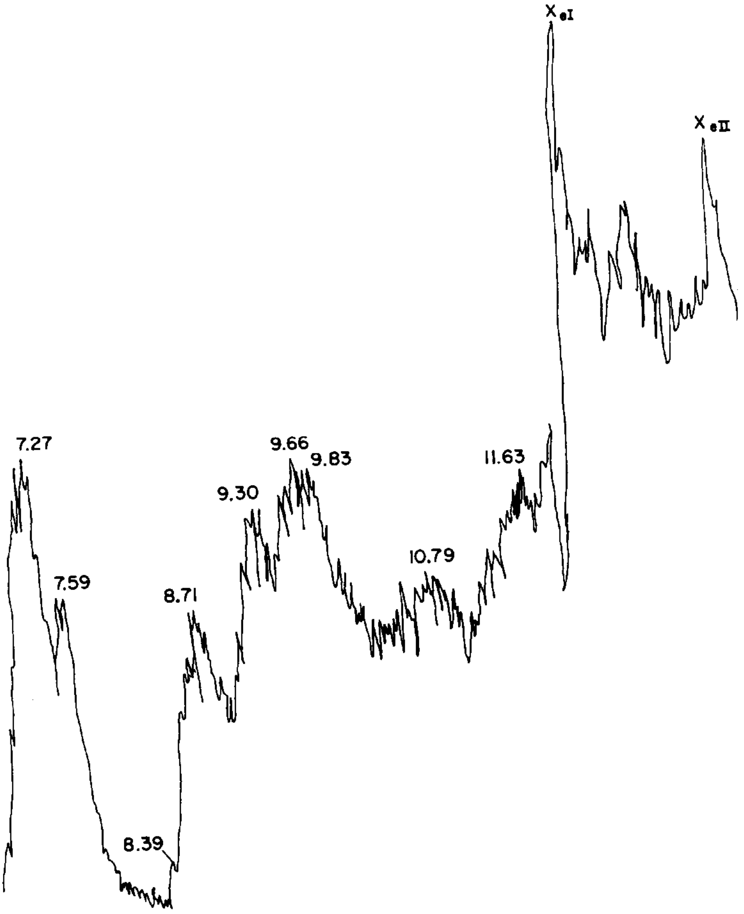


Fig. 2. Photoelectronic spectrum of *trans*-ferrocenylacrilonitrile (**2**) (positions of bands are given in eV).

and $\sigma_p = 0.17$ [5]. For all three objects, the first band was split into two components, which were similar in the sense of their form and intensity. Obviously, the ionization proceeds at the expense of the two *d*-orbitals of iron, which are close in their energetic levels (*cf*. refs. 4 and 6). Because of the greater thermodynamic stability of the *trans* isomer **2** than the *cis* isomer **1**, the first ionization potential is higher for **2** than for **1**.

The next group of bands, in the region 8.73–10.76 eV, corresponds to ionization of the unsubstituted cyclopentadienylic fragment. In the case of ferrocene, such ionization takes place at 8.72 eV [4].

Ionization of the substituted cyclopentadienylic ring $C_5H_4CH{=}CHCN$ is displayed with bands at 9.21, 9.60 and 10.76 eV. Such bands are not naturally observed for ferrocene.

Quantum-chemical examination

An extended Hückel molecular orbital (EHMO) approach was used for the calculation. This approach reproduced molecular geometry rather adequately; for

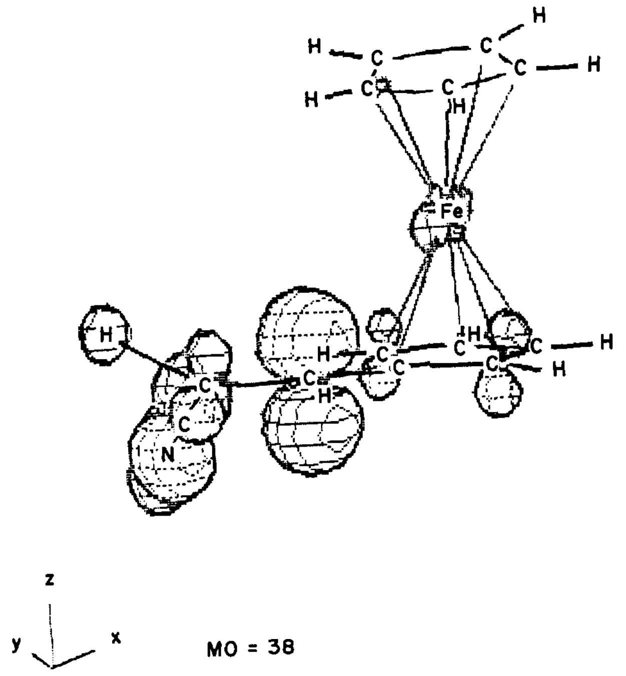


Fig. 3. The highest molecular orbital occupied by one electron, of the anion radical of the nitrile **1**.

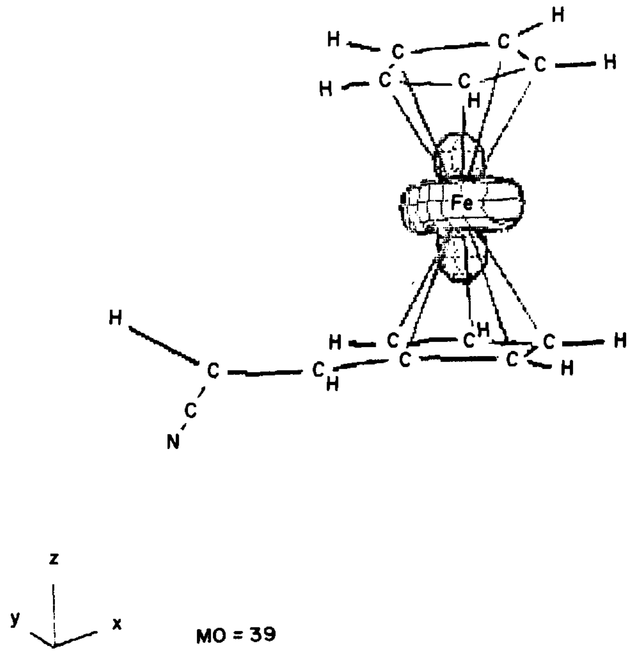


Fig. 4. The highest molecular orbital occupied by one electron, of the cation radical of the nitrile **1**.

instance, the dihedral angle between π-systems of C_5H_4 and of CH=CHCN in compound **1** was obtained as 30°, whereas X-ray datum was determined as 23° [3]. At the same time, numerical accordance was not achieved for MO energetic levels if they were calculated and determined from PES (parameters of the atomic orbital of iron varied within a wide range).

The absence of accordance does not weaken the calculation approach: it has been shown in many works that Koopmanns' theorem cannot be used for interpretation of ionization potentials of ferrocenic molecules (see review, ref. 7). This was the reason why the examination was limited within those orbitals, which were important for the estimation of the stereochemical behaviour of the corresponding ion radical states of *cis* isomer **1**.

After transition of the *cis* isomer **1** into the anion radical state, the lowest MO has to be populated. Calculations show that this orbital is located just on the fragment CH=CHCN (Fig. 3); the order of the CH=CH bond is decreased by almost a quarter. Of course, such a manner of localization can result in decrease of the barrier of rotation around the ethylenic bond, *i.e.* *cis*/*trans* conversion becomes allowable. Hence, *cis*/*trans* conversion of ferrocenylacrylonitrile anion radicals (which is observed in experiments [1]) meets a reasonable explanation within the framework of the EHMO method.

After transition of *cis* isomer **1** into the cation radical state, a single electron remains in the highest occupied MO. The first ionization potential has to give, according to Koopmanns' theorem, the energy of such a highest MO (with the reverse sign). It has already been noticed, however, that the theorem does not work for ferrocenes [7]. That is why several high-lying occupied MOs have to be

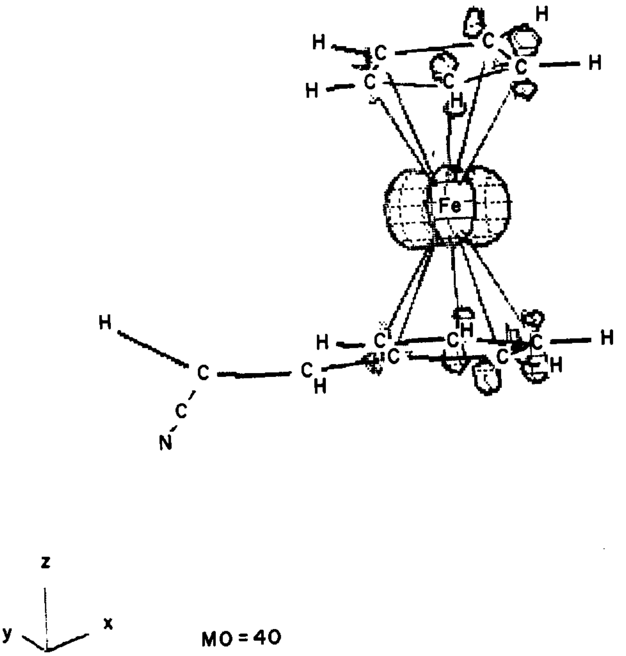


Fig. 5. The highest molecular orbital occupied by two electrons, for the cation radical of the nitrile 1.

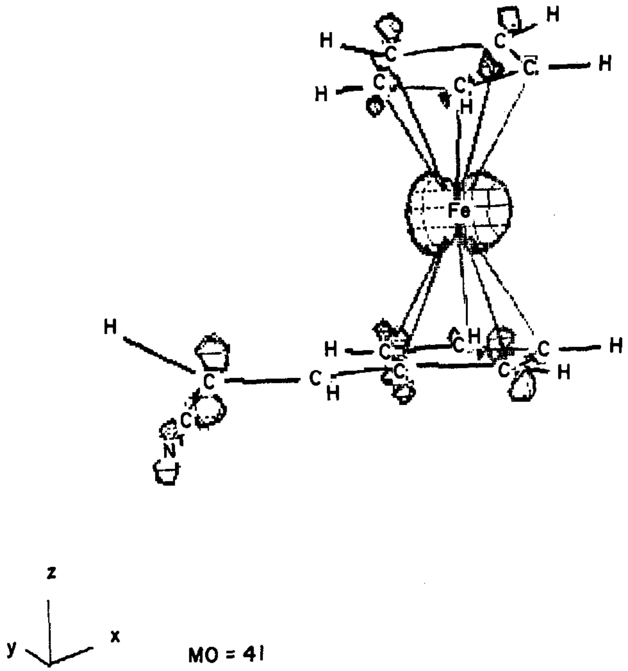


Fig. 6. The molecular orbital, second in energy after the highest occupied orbital, for the cation radical of the nitrile 1.

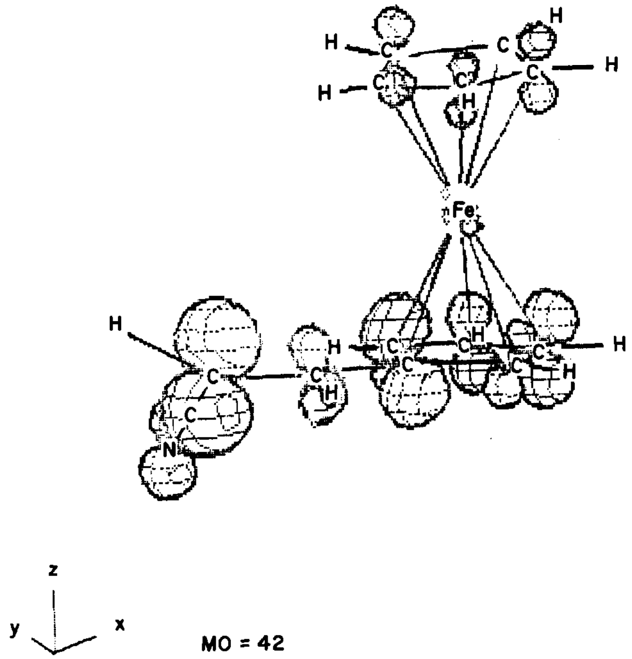


Fig. 7. The molecular orbital, third in energy after the highest occupied orbital, for the cation radical of the nitrile 1.

examined (Figs. 4–7). Evidently, like iron, the acrylonitrilic moiety and the adjoining cyclopentadienilic fragment C_5H_4 of the ferrocenylic moiety can take part in stabilization of the cation radical state.

As follows from PES of molecules **1** and **2**, the minimal difference between the first and the posterior potentials of ionization amounts to 2 eV. That difference is too large to admit closeness between orbital energies of iron and other fragments. According to PES data, the highest occupied MO must be essentially or even exclusively the orbital of iron. It is constructed without participation of the ethylenic fragment, contrary to arylethylene cation radicals (in which all π-orbitals overlap). After one-electron oxidation of ferrocenylethylenes, an unpaired electron and a positive charge are centred at iron, as happens in the cation radical of ferrocene itself, *i.e.* the ferricenium cation. This conclusion, being made for the cation radical of ferrocenylethylene **1**, does not introduce any perturbation in overall view of ferricenium chemistry. The removal of the π-electron cloud of the ethylenic fragment onto the $Fe^{+\cdot}$ centre does not happen. That is why transformation of $\mathbf{1}^{+\cdot}$ into $\mathbf{2}^{+\cdot}$ is not observed in the experiments.

Unexpectedly, the analysis of the MOs of the cation radical of *cis*-ethylene **1** reveals a definite possibility of *cis / trans* conversion of the neutral ethylene as a result of the earlier, probably, two-electron step of oxidation. As seen from Fig. 7, the cation radical of the ethylene has a close, lower, not so deep MO, which is centred on the acrylonitrilic fragment.

Experimental

Photoelectronic spectra were recorded by means of a Perkin–Elmer spectrometer (PES-18) with a helium source of monochromatic 21.22 eV irradiation. The spectra were calibrated with reference to $^2P_{3/2}$ and $^2P_{1/2}$ ionization potentials of Xe (12.13 and 13.43 eV). Independent measurements were made twice or three times during PES recording, and the average calculated. Reproducibility of the measured magnitudes of the ionization potentials, was on average, 0.15 eV. During periodic control estimations of measurement accuracy, the first ionization potential of benzene was 9.24 eV, corresponding to previous data.

Quantum chemical calculations were made by the EHMO method [8] using the CACAO program [9], which was kindly placed at our disposal by D.M. Prosperio (Milan). Geometric parameters of the studied molecule were used according to ref. 3. Ionization potentials and orbital exponents of atoms, which were included in the EHMO calculations, were taken from ref. 10 and are listed in Table 1.

Table 1

Atomic parameters used in EHMO calculations

Atom	Orbital	H_{ii} (eV)	ξ_1	ξ_2	C_1 [a]	C_2 [a]
H	1*s*	−13.60	1.300			
C	2*s*	−21.40	1.625			
	2*p*	−11.40	1.625			
Fe	4*s*	−8.39	1.900			
	4*p*	−4.74	1.900			
	3*d*	−11.46	5.350	1.800	0.5366	0.6678

[a] Contraction coefficients used in the double-ξ expansion.

References

1 Z.V. Todres, T.M. Chernyshova, A.A. Koridze, L.I. Denisovich and D.N. Kursanov, Dokl. Akad. Nauk SSSR, 254 (1980) 902.

2 Z.V. Todres, Tetrahedron, 43 (1987) 3839.

3 Z.V. Todres, A.I. Yanovsky, D.S. Ermekov and Yu.T. Struchkov, J. Organomet. Chem., 369 (1989) 377.

4 S. Evans, M.L.H. Green, B. Levitt, A.F. Orchard and C.F. Pygell, J. Chem. Soc., Faraday Trans. 2, (1972) 1847.

5 C. Hansch and A.J. Leo, Substituent constants for correlation analysis, in Chemistry and Biology, Wiley, New York, 1979, p. 50.

6 J.W. Rabalis, L.O. Werme and T. Bergmann, J. Chem. Phys., 57 (1972) 1185.

7 V.I. Nefedov, in Stroenie Molekul i Khimicheskaya Svyaz' Seriya VINITI "Itogi Nauki i Tekhniki", Moscow, Russia, 3 (1975) 114.

8 R. Hoffmann, J. Chem. Phys., 39 (1963) 1397.

9 C. Mealli and D.M. Proserpio, J. Chem. Educ., 67 (1990) 399.

10 R.H. Summerville and R. Hoffmann, J. Am. Chem. Soc., 98 (1976) 7240.