

p,π-Interaction in the Y—C=C< Group

Valentin P. Feshin

Institute of Technical Chemistry, Ural Branch of the Russian Academy of Sciences, 614600 Perm, Russia

The electric field gradient asymmetry parameters for ^{35}Cl nuclei in compounds of the series $\text{Cl}_2\text{C}=\text{CHOR}$, Cl_2CHOCOR etc. do not corroborate a widespread representation of a p,π-interaction between the unshared electron pair of a Cl atom and the π-electron double bond system in these molecules.

In order to describe the peculiarities of the electron distribution in the Y—C=C< group and to explain the experimental data obtained for compounds containing such a group, representations of p,π-conjugation between the unshared electron pair of the Y heteroatom and the π-electron system of the double bond have often been used (e.g., see refs. 1–3). The adequacy of this description and explanation may be experimentally verified. Information on such an interaction in the plane of fragments of molecules is provided by the asymmetry parameters of the electric field gradient (EFG) on halogen atom nuclei (Y = Hal). The quantities η characterize the deviation in the electron density distribution of these atoms from the axial symmetry [eqn. (1)]. Quantities q_{xx} , q_{yy} and q_{zz} are the

$$\eta = (q_{xx} - q_{yy}) / q_{zz} \quad (1)$$

components of the EFG tensor along the corresponding coordinate axes, the Z axis being directed along the C—Hal bond).⁴ In the case of axial EFG symmetry on the halogen atom nuclei, $q_{xx} = q_{yy}$ and $\eta = 0$. When the components q_{xx} and q_{yy} are not identical, the quantity $\eta \neq 0$. The latter situation occurs, for instance, when the unshared electron pairs of halogen atom Y are involved to a varying extent in interaction with other atoms of molecules which contain a Y—C=C< group.

Thus the quantity η gives objective information on the spatial distribution of the halogen atom electron density. This distribution may be related to the participation of the unshared electron pair on the halogen atom in a p,π-interaction with the π-electron system of the neighbouring double bond. In order to study the spatial distribution of the electron density on the Cl atom in molecules containing the planar fragment Cl—C=C<, we measured the EFG asymmetry parameters for ^{35}Cl nuclei in polycrystalline compounds of the series $\text{Cl}_2\text{C}=\text{CHOR}$,^{5,6} $\text{Cl}_2\text{C}=\text{CHOCOR}$, etc. The value η was measured by the beats of the cycling quadrupole spin echo in the external magnetic field.⁷ Table 1 shows some of the data obtained. The assignment of quantities η to Cl atoms in *cis*- and *trans*-positions with respect to the groups OR, OCOR, etc., of the compounds studied was unambiguously performed using the NQR frequencies corresponding to these atoms. The assignment of the ^{35}Cl NQR frequencies in the spectra of these compounds was achieved using the relationship between the ^{35}Cl NQR frequencies of the corresponding *cis*- and *trans*-isomers of ClCH=CHX, and also the regularities in the change in the NQR frequencies of the *cis*-Cl atom of such compounds depending on the character of the X substituent.^{6,8,9} This assignment for compounds of the series $\text{Cl}_2\text{C}=\text{CHOCOR}$ is also supported by the quadrupole spin-lattice relaxation times T_1 of the corresponding Cl atoms.¹⁰ For all the compounds studied, the quantity η for a *trans*-Cl atom is markedly lower

Table 1 ^{35}Cl NQR frequencies (ν^{77}) and EFG asymmetry parameters (η) for ^{35}Cl nuclei at 77 K for compounds containing the Cl—C=C< group

Compound	Cl atom	ν^{77} /MHz	η (%)
<i>cis</i> -ClCH=CHOC ₆ H ₄ Cl-4	<i>cis</i>	34.264	8.2 (± 2.0)
	arom.	35.339	3.0 (± 0.5)
$\text{Cl}_2\text{C}=\text{CHOMe}$	<i>cis</i>	36.904	7.3 (± 1.5)
	<i>trans</i>	37.188	0.0 (± 0.5)
$\text{Cl}_2\text{C}=\text{CHOPh}$	<i>cis</i>	37.146	7.3 (± 1.5)
	<i>trans</i>	37.552	2.7 (± 1.0)
$\text{Cl}_2\text{C}=\text{CHOCH}_2\text{OCHMe}_2$	<i>cis</i>	36.540	8.0 (± 0.6)
	<i>trans</i>	37.433	0.8 (± 0.4)
$\text{Cl}_2\text{C}=\text{CHOCOMe}$	<i>cis</i>	36.876	7.3 (± 1.8)
	<i>trans</i>	38.220	1.2 (± 0.6)
$\text{Cl}_2\text{C}=\text{CHOCOPh}$	<i>cis</i>	37.306	8.1 (± 2.0)
	<i>trans</i>	37.796	1.1 (± 0.2)

than that of a *cis*-atom, and in all cases η (*trans*-Cl) is close to zero, i.e. the electron distribution on this atom has essentially axial symmetry. Thus, contrary to widespread opinion, the *trans*-Cl atom of these compounds is practically not involved in the proposed p,π-conjugation. As the ability of *cis*- and *trans*-Cl atoms in molecules of the series $\text{Cl}_2\text{C}=\text{CHX}$ to participate in such conjugation is identical, it should be expected that the *cis*-Cl atom does not participate in any interaction with the C=C double bond. The noticeable quantity η for the *cis*-Cl atom in all the compounds studied (~6–9%) is due to the influence of a vicinal oxygen atom (or all X=OR, OCOR, etc.) directly through the field. Taking into account the importance of the results obtained and the fact that they were obtained for a relatively small number of compounds (15), our investigations will be continued.

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References

- 1 J. March, *Advanced Organic Chemistry*, Wiley, New York, 1985, vol. 1.
- 2 J. D. Roberts and M. C. Caserio, *Basic Principles of Organic Chemistry*, W. A. Benjamin, Inc., New York, Amsterdam, 1964, vol. 1.
- 3 L. V. Vilkov, V. S. Mastryukov and N. M. Sadova, *Opreделение geometricheskogo stroeniya svobodnykh molekul* (Determination of the geometric structure of free molecules), Khimiya, Leningrad, 1978 (in Russian).

- 4 E. A. C. Lucken, *Nuclear Quadrupole Coupling Constants*, Academic Press, New York, London, 1969.
 5 V. P. Feshin and M. G. Voronkov, *Z. Naturforsch., Teil C*, 1990, **45**, 213.
 6 V. P. Feshin, G. V. Dolgushin, M. G. Voronkov, T. I. Bychkova, A. V. Kalabina, Yu. E. Sapozhnikov and Ya. B. Yasman, *Teor. Eksp. Khim.*, 1982, **18**, 378.
 7 Yu. E. Sapozhnikov and Ya. B. Yasman, *Izv. Akad. Nauk SSSR*,

- Ser. Fiz.*, 1978, **42**, 2148.
 8 V. P. Feshin, M. G. Voronkov, G. V. Dolgushin, T. I. Bychkova and A. V. Kalabina, *Dokl. Akad. Nauk SSSR*, 1980, **253**, 192.
 9 V. P. Feshin, M. G. Voronkov, P. A. Nikitin, E. F. Zorina, A. S. Atavin and O. A. Popsui, *Zh. Vses. Khim. Ova im D. I. Mendeleeva*, 1979, **24**, 399.
 10 I. A. Kyutsel, G. B. Soifer and V. V. Shchepin, *Zh. Vses. Khim. Ova im D. I. Mendeleeva*, 1984, **29**, 354.

Copolymerization of Pyrrole with Aromatic Bisdiazonium Salts

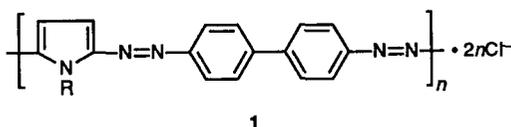
Saule K. Kudaikulova,* Yurii A. Dubnitskii, Otan A. Almabekov and Bulat A. Zhubanov

Institute of Chemical Sciences, Kazakh Academy of Sciences, 480100 Alma-Ata, Kazakhstan. Fax: +7 3272 636634

Pyrrole–azophenylene copolymers have been obtained by spontaneous copolymerization of pyrrole with aromatic bisdiazonium salts.

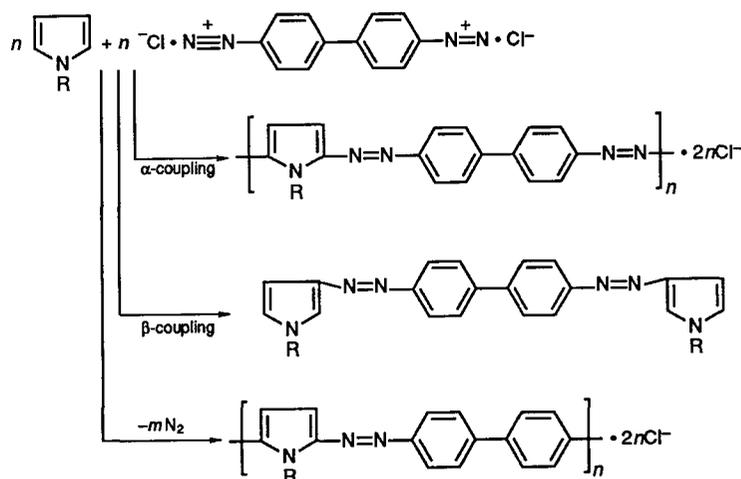
Conjugated polymers have been of interest to many research groups during the past ten years. At the present time polypyrrole is one of the more closely studied polymers of this class and has found practical application as electroactive material.¹ Another type of polyconjugated polymer, polyazophenylene, has demonstrated rather weak conductivity, but is of great interest from the point of view of electrochromic and photochromic properties.² The preparation of pyrrole–azophenylene copolymers thus seemed an interesting and attractive aim in synthetic polymer chemistry.

We report here a method of producing pyrrole–azophenylene copolymers by azo coupling of aromatic bisdiazonium salts (BDS) with pyrrole (py). The reaction of py with phenyldiazonium chloride is well known^{3,4} for the formation of azo dyes. We have found that the addition of py [dropwise, as hot vapour or in solution ($c = 0.5\text{--}1.0 \text{ mol dm}^{-3}$) in a water-immiscible organic solvent] to a cooled (to $0\text{--}5^\circ\text{C}$), freshly diazotized aqueous solution of BDS based on benzidine ($c = 0.5\text{--}1.0 \text{ mol dm}^{-3}$, $\text{pH} = 1\text{--}5$) results in the instantaneous formation of bright, reflective polymeric films on the surface of the BDS solution. Films removed from the surface of the reaction solution were a green–golden colour on one side, on the other side they were smooth black. The films were characterized by good physico-mechanical properties. A process of saturation of the black dispersive powders took place within the reaction mixture itself upon mixing equimolar amounts of the monomers (yield of polymer reached 95%). The other product of the reaction was a violet dye. In order to remove any traces of the dye the film and powder were simultaneously washed with acetone, ethanol and dimethylformamide under reflux.



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Data obtained from elemental analysis, IR spectroscopy and differential thermal analysis (DTA) have shown the identity of the chemical structures of the films obtained by interphase copolymerization on the surface of the reaction system and of the powders obtained in the reaction mixture. The proposed structure of the polymer **1** is as follows.† DTA studies of the polymer have shown: T (beginning of decomposition) 240°C , T (5% weight loss) 350°C , T (19% weight loss) 430°C ; 19% weight loss corresponds to full decomposition of the pyrrole units. The IR spectrum of the copolymer is characterized by well-resolved absorbance bands: ν/cm^{-1} 695w and 760w (C—H



Scheme 1

vibrations of monosubstituted benzene rings), 820, 1002 (C—H of *para*-substituted benzene rings), 1485 and 1600 (aromatic C=C bonds), 1240 and 1540 (pyrrole C=C bonds) and 1170 ($\text{C}_{\text{Ar}}\text{—N}=\text{N}$).⁵ It is known that the azo group —N=N— is very difficult to identify due to the overlap of its absorbance bands with those of the aromatic rings.

Changing the reaction conditions (phase conditions, order of addition of reagents, temperature) led to the formation of other reaction products. Thus, if py is added to the aqueous BDS in a water-miscible solvent ($c = 0.5\text{--}1.0 \text{ mol dm}^{-3}$) such as ethanol or acetone, acetonitrile polymeric films do not form and the main products of the reaction are dyes. Reversing the order of monomer addition also prevents the formation of polymer.

The reaction is thought to proceed as follows (Scheme 1). It is known that diazotization takes place at the α -position of pyrrole at a higher rate than to the β -position. α -Azo dyes are very unstable products in comparison with the β -products.⁴ Hence, we suggest that formation of the polymer takes place due to electrophilic attack by the diazo group at the α -position of pyrrole. The high reactivity of the α -form of diazocoupled py and the bifunctionality of BDS are responsible for the instantaneous character of the copolymerization. Diazocoupling of py in the β -position leads to the formation of a very stable, non-reactive form of β -azo dye. The possible influence of solvent on the correlation of α - and β -forms may be explained by the solvation effect. The stronger nucleophilic centre at the α -C atom of py is solvated by solvent molecules. The diazonium cation, being a weaker electrophilic agent in comparison with inorganic M^{n+} ions or an anode surface (in the case of electrochemical polymerization) reacts with py in the β -position.

† This structure is in good agreement with the elemental analysis data.