

Review

# Polyfluoromethine compounds—a new type of conjugated systems

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## Abstract

The methods for synthesis, chemical and physical properties of conjugated  $\alpha,\omega$ -diarylperfluoropolyenes are described. © 1998 Elsevier Science S.A. All rights reserved.

*Keywords:* Perfluoropolyenes; Diarylperfluoropolyenes; Conjugative effect; Polyfluoromethine dyes

## 1. Introduction

Determination of electronic effects through conjugated double bonds is of great importance for theoretical organic chemistry and the theory of the colour of organic compounds. This allows one to elucidate many questions of the reciprocal influence of various atoms and groups, to explain and quantitatively to evaluate the conjugative effect of substituents, to forecast the properties, and to prepare new types of compounds. Of great practical interest is the creation of conjugated polymethine systems, especially, cyanine dyes and  $\alpha,\omega$ -diarylpolyenes.

The size of the fluorine atom is close to that of hydrogen. Therefore one supposes that the transmission of conjugative effects could be possible in compounds with conjugated polyfluoromethine linear chains. The first experiments have not supported this, however, our investigation have shown that  $-(CF=CF)_n-$  groups demonstrate conjugative effects.

Thus, polyfluoromethine compounds may become potential candidates for conjugated systems of a new type. Their peculiarity consists in the fact that only fluorine atoms introduced in place of hydrogen in polymethine systems cannot give strong steric hindrance preventing the transmission of conjugative effects.

To start this investigation it was necessary to develop methods for the synthesis of fluorinated analogues of well-studied polymethine compounds such as  $\alpha,\omega$ -diarylpolyenes, substituted cinnamic acids and their vinyls, substituted cinnamaldehydes, chalcones and cyanine dyes to determine

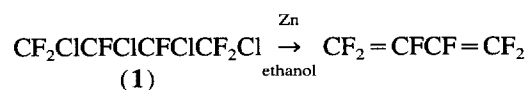
the possibility of the conjugative transmission via the linear polyfluoromethine chain [1].

This report will focus on the methods of synthesis, structure and properties of conjugated aryl- and diarylperfluoropolyenes, their derivatives and polyfluoromethine dyes. We have included a brief review of synthesis and properties of aliphatic perfluoropolyenes such as perfluoro-1,3-butadiene, 1-chloroperfluoro-1,3-butadiene, perfluoro-1,3,5-hexatriene that are the precursors of diarylperfluoropolyenes.

## 2. Aliphatic perfluoropolyenes

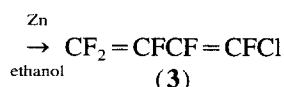
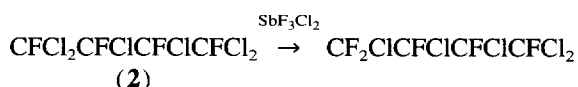
### 2.1. Methods of synthesis and structure of aliphatic perfluoropolyenes

Most methods of perfluorobutadiene synthesis consist in the preparation of 1,2,3,4-tetrachloroperfluorobutane **1** by various routes and its dechlorination with zinc in ethanol [2–6].

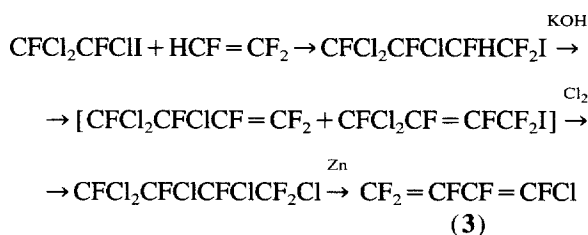


1-Chloroperfluoro-1,3-butadiene **3** has been prepared in 1% yield by chlorine–fluorine exchange between 1,2,3,4-tetrafluorohexachlorobutane **2** and dichlorotrifluoroantimony with subsequent dechlorination of the fluorinated product [7].

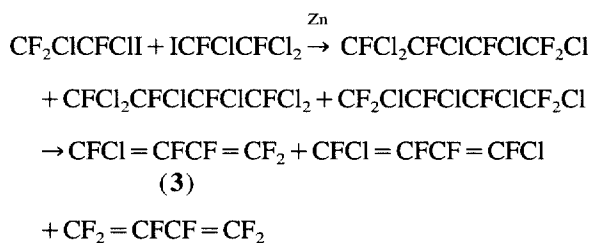
\* Corresponding author.



The synthesis of 1-chloroperfluoro-1,3-butadiene **3** in better yield was described in our report [8]. Addition of 1-iodo-1,2,2-trichlorodifluoroethane to trifluoroethene in the presence of benzoyl peroxide at 140–150°C gave 1-iodo-3,4,4-trichloropentafluorobutane. The latter was subjected to the action of potassium hydroxide; chlorination and dechlorination led to 1-chloroperfluoro-1,3-butadiene **3** in 73% overall yield.



1-Chloroperfluoro-1,3-butadiene **3** can also be prepared via dehalodimerization of 1-iodo-1,2-dichlorotrifluoroethane and 1-iodo-1,2,2-trichlorodifluoroethane with zinc in a mixture of acetic anhydride and dichloromethane at 16–20°C [9]. Polyhalogenated butanes obtained by this reaction were converted into a mixture of 1-chloroperfluoro-1,3-butadiene, 1,4-dichloroperfluoro-1,3-butadiene and perfluoro-1,3-butadiene by treating with zinc powder in ethanol. This mixture is easily separated by distillation.



Investigation of fluoro-containing 1,3-dienes have shown decreasing transmission of conjugative effects [10]. Comparison for 1,1,4,4-tetrafluoro-1,3-butadiene [11,12] and perfluoro-1,3-butadiene [13] shown an essential difference between them. The first compound is a planar system like butadiene. The second one is not planar and exists in a cisoid conformation as showed by the electron diffraction. The angle  $\theta$  between the planes of the double bonds in perfluoro-1,3-butadiene was 47–49° [14].

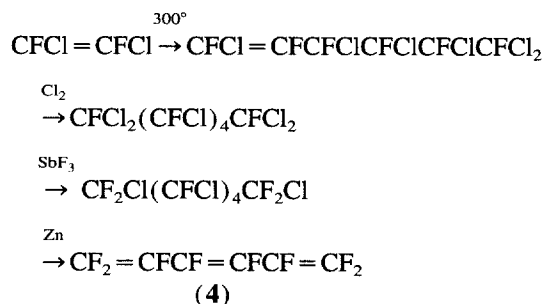


1-Chloroperfluoro-1,3-butadiene **3** is a 1:1 mixture of *Z*- and *E*-isomers as determined by <sup>19</sup>F NMR [8]. The authors of report [8] suppose that 1-chloroperfluoro-1,3-butadiene

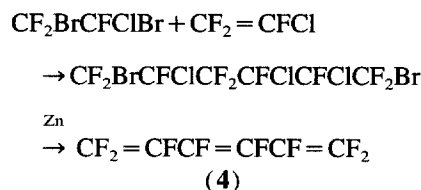
like perfluoro-1,3-butadiene has an *S*-*cis* conformation with similar angle  $\theta$ .



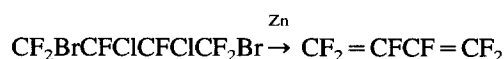
The synthesis of perfluoro-1,3,5-hexatriene **4** was first described in patent [15]. It was obtained from 1,2-dichlorodifluoroethene by several steps.



A new method for perfluoro-1,3,5-hexatriene **4** synthesis was described by Czech chemists [16]. Photolysis of 1,2-dibromo-1-chlorotrifluoroethane in the presence of excess of chlorotrifluoroethene gave a mixture of products of radical-coupling containing perhalohexanes. Dechlorination of the latter with zinc powder produced perfluoro-1,3,5-hexatriene in 66% yield.



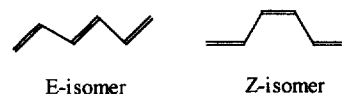
1,4-Dibromo-2,3-dichloroperfluorobutane formed as by-product in this process can be converted into perfluoro-1,3-butadiene.



Authors of Ref. [17] supposed that the perfluoro-1,3,5-hexatriene exists in a twist spiral conformation.



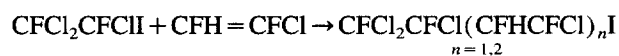
However, other investigators have found that perfluoro-1,3,5-hexatriene obtained by this method was a mixture of *Z*- and *E*-isomers in the approximate ratio 1:9 [18].



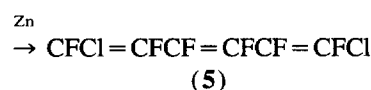
F–F Nonbonded repulsion is presumably present in the two triene isomers, both existing in twist conformations [18].

Another precursor for the preparation of aromatic conjugated perfluoropolyenes could be 1,6-dichloroperfluoro-1.3.5-hexatriene **5**. It can be obtained by the thermal addition

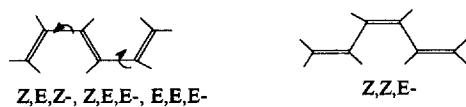
of 1-iodo-1,2,2-trichlorodifluoroethane to 1-chloro-1,2-difluoroethene in the presence of benzoyl peroxide [9].



The polyhalogehexane was converted into 1,6-dichloroperfluoro-1,3,5-hexatriene **5** by consecutive dehydrohalogenation, chlorination and dechlorination.



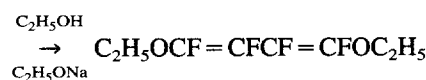
1,6-Dichloroperfluoro-1,3,5-hexatriene **5** is a mixture of *Z,E,Z*-, *Z,E,E*-, *Z,Z,E*- and *E,E,E*-isomers as shown by <sup>19</sup>F NMR. Probably, it also exists in twist conformations just as perfluoro-1,3,5-hexatriene **4**.



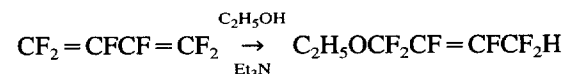
## 2.2. Chemical properties of perfluoro-1,3-butadiene and perfluoro-1,3,5-hexatriene

Perfluoro-1,3-butadiene is similar to fluorinated olefins in its chemical properties which are determined by the presence of fluorine atoms adjacent to the double bond. These atoms withdraw electron density from the  $\pi$ -component of the double bond.

Knunyants et al. [19] discovered that perfluoro-1,3-butadiene in the presence of sodium alkoxide can react with two moles of ethanol. In this reaction terminal carbon atoms underwent nucleophilic attack.

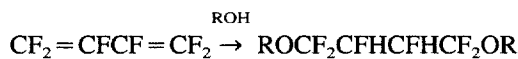


Heating of perfluoro-1,3-butadiene with ethanol in the presence of triethylamine induces 1,4-addition of alcohol.

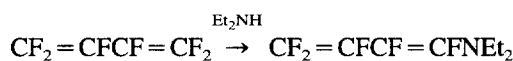


Bubbling of perfluoro-1,3-butadiene through a boiling solution of sodium alkoxide in excess of relevant alcohol

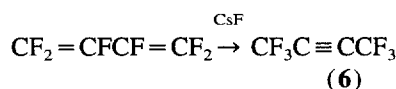
leads to the addition of alcohol to two unsaturated bonds of fluorodiene with following elimination of hydrogen fluoride [20].



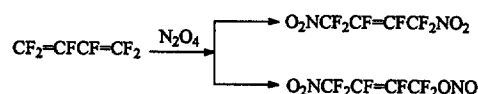
The reaction of perfluoro-1,3-butadiene with primary and secondary amines produces unstable products that are readily hydrolyzed with water.



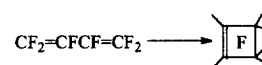
Perfluoro-1,3-butadiene undergoes rearrangement in the presence of cesium fluoride at 150°C to produce hexafluoro-2-butyne **6** in 68% yield [21].



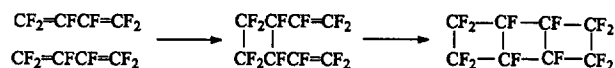
Perfluoro-1,3-butadiene readily reacts with  $\text{N}_2\text{O}_4$  in both liquid and vapour phases at room temperature to give a mixture of products [22].



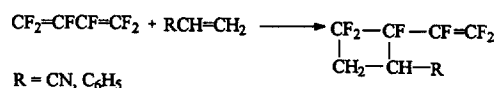
Heating of perfluoro-1,3-butadiene to 400°C gave perfluorocyclobutene [23].



On heating perfluoro-1,3-butadiene to 160°C the 1,2-cycloaddition product was isolated. Higher temperatures lead to further cyclization [24].

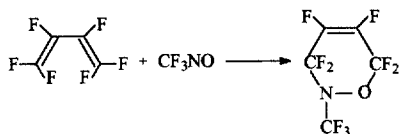


The behaviour of perfluoro-1,3-butadiene in Diels–Alder reactions has been investigated by various groups. Perfluoro-1,3-butadiene does not react with maleic anhydride, acrylonitrile, styrene or 1,4-naphthaquinone. Only 1,2-cycloaddition occurs from the action of perfluoro-1,3-butadiene with acrylonitrile or styrene [25].

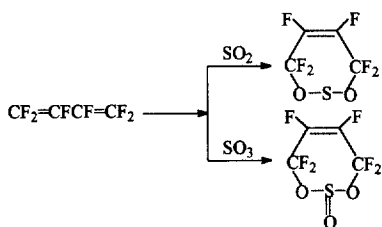


Authors of review [25] explain the low reactivity of perfluoro-1,3-butadiene in Diels–Alder addition by its nonplanar

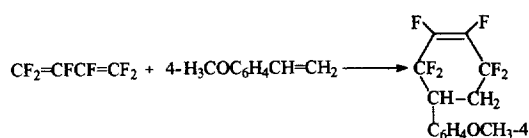
conformation. We would like to note that such a behaviour of perfluoro-1,3-butadiene in diene synthesis can be explained not only by the steric factors but also by a decrease in the electronic density on the terminal carbon atoms due to attraction of electrons by the fluorine atoms. This conclusion is confirmed by the reports showing that perfluoro-1,3-butadiene reacts only with such strong dienophiles as polyfluoronitroso compounds [26,27].



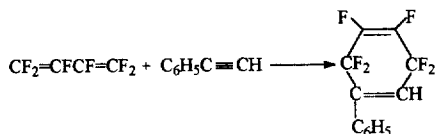
Kazmina et al. [28] have found that perfluoro-1,3-butadiene reacts with  $\text{SO}_2$  or  $\text{SO}_3$  to give the products of diene synthesis.



As a rule, the diene acts as a donor and the dienophile is an acceptor in the classical Diels–Alder reaction. Authors of report [29] investigated the diene synthesis reaction with reversed electronic demands, where the diene was an acceptor and dienophile was a donor. They used perfluoro-1,3-butadiene as diene and styrene with donor substituents in the benzene ring as dienophile. The reaction produced the product of diene synthesis in 11% yield.

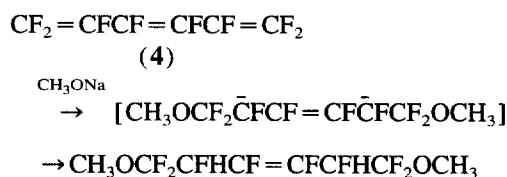


Later a classical Diels–Alder reaction was carried out with phenylacetylene as dienophile and the product of cyclisation was obtained in 8.5% yield [30].

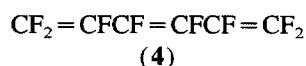


The activity of olefins in polymerization reactions increases from systems with separate bonds to systems with conjugated bonds. However, while polymerization of tetrafluoroethene occurs readily, perfluorobutadiene has less reactivity [31].

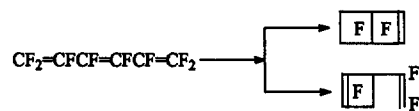
Perfluoro-1,3,5-hexatriene **4**, by its chemical properties, is similar to perfluoro-1,3-butadiene. Methanol in the presence of the sodium methylate adds to 1,2- and 5,6-positions of the perfluoro-1,3,5-hexatriene with the formation of intermediate dianions [17].



The interaction of perfluoro-1,3,5-hexatriene **4** with phenyllithium in ether gives 1,6-diphenylperfluoro-1,3,5-hexatriene [32].



Irradiation of perfluoro-1,3,5-hexatriene in the vapour phase forms two isomers [33].

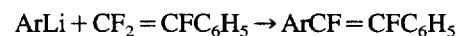


No valence isomers of the perfluoro-1,3,5-hexatriene **4** were detected in the reaction mixture in acetone solution after UV-irradiation. Under these conditions only *cis*–*trans* isomerization occurred.

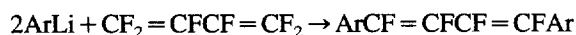
Different behaviours of perfluoro-1,3,5-hexatriene in the vapour and liquid phases could be explained by the multiplicities of the originating excited states. The first singlet state is assumed to control the vapour phase reaction. In contrast, the reaction in acetone, which is known to be an efficient sensitizing agent, can be initiated by the creation of the first triplet state of perfluorohexatriene by energy transfer between acetone molecules in the triplet state and perfluorohexatriene in the ground state [33].

### 3. $\alpha$ -Aryl- and $\alpha,\omega$ -diarylperfluoropolyenes

Methods for synthesis of the first member of conjugated  $\alpha,\omega$ -diarylperfluoropolyenes  $\text{Ar}(\text{CF}=\text{CF})_n\text{Ar}$ – $\alpha,\beta$ -difluorostilbene and its derivatives are well known. The most important of them is the interaction of aryllithium derivatives with tetrafluoroethene or  $\alpha,\beta,\beta$ -trifluorostyrene [34,35].



1,4-Diarylperfluoro-1,3-butadienes with aryl-substituents were first obtained by the reactions of aryllithium compounds with perfluoro-1,3-butadiene [36,37].

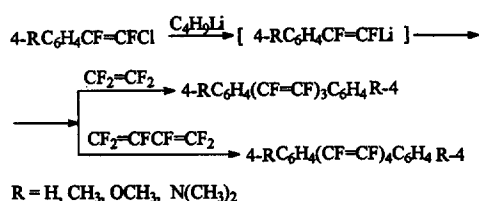


This method for the synthesis of conjugated  $\alpha,\omega$ -diaryl-perfluoropolyenes is not general because perfluoro-1,3,5-hexatriene, synthesized by the Czech chemists [16], readily polymerizes.

We have described a general method for the synthesis of these compounds, and shown that slightly polarized  $\alpha,\beta$ -difluorostyryllithium compounds react with polyfluoroolefins to give conjugated perfluoropolyene systems [38]. It is necessary to synthesize the derivatives of  $\alpha,\beta$ -difluorostyryllithium for the preparation of diarylperfluoropolyenes. The latter can be obtained both from  $\beta$ -chloro- $\alpha,\beta$ -difluoro- and  $\alpha,\beta$ -difluorostyrene by the interaction with butyllithium. The chlorine atom is not replaced with lithium on interaction of butyllithium in ether as solvent [39]. However, using for the metallation a mixture of THF, ether and pentane as solvents, previously employed by Normant for synthesis of vinylithium [40], one can obtain at  $-80^\circ\text{C}$  lithium derivatives not only from  $\beta$ -chloro- $\alpha,\beta$ -difluorostyrene, but also from derivatives with electron donating and electron withdrawing groups [41].

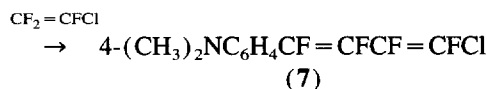
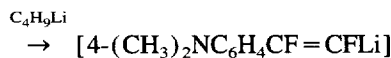
We have investigated the competitive metalation of  $\beta$ -chloro- $\alpha,\beta$ -difluorostyrene and  $\alpha,\beta$ -difluorostyrene with butyllithium to select the best compound for preparation of  $\alpha,\beta$ -difluorostyryllithium [42]. It was found that both compounds were metalated in a similar way.  $\beta$ -Chloro- $\alpha,\beta$ -difluorostyrene and its derivatives are more accessible than  $\alpha,\beta$ -difluorostyrene. Thus,  $\beta$ -chloro- $\alpha,\beta$ -difluorostyrene is preferable for metalation.

$\alpha,\beta$ -Difluorostyryllithium and its derivatives, especially with strong electron donating substituents in the benzene ring that increase the nucleophilicity of the difluorostyryl group, can react with polyfluoroolefins to give diarylpolyfluoropolyene systems [38,43].

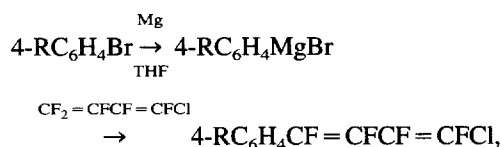


Aliphatic perfluoropolyenes longer than perfluoro-1,3-butadiene are either difficult for preparation or unknown. It was necessary to work out the method for the synthesis of 1-aryl-4-chloroperfluoro-1,3-butadiene derivatives and for the preparation of higher members of the diarylperfluoropolyenes. They are the difluorovinyls of  $\beta$ -chloro- $\alpha,\beta$ -difluorostyrene derivatives. The most convenient route to the preparation of 1-aryl-4-chloroperfluoro-1,3-butadiene derivatives could be the interaction of difluorostyryllithium derivatives with chlorotrifluoroethene.

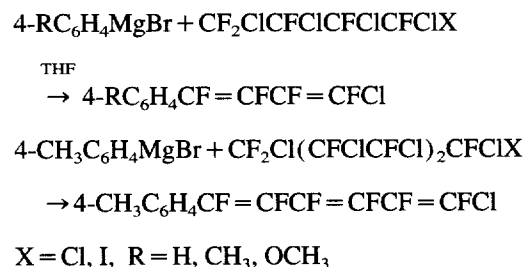
However, 4-dimethylamino- $\alpha,\beta$ -difluorostyryllithium reacts with chlorotrifluoroethene to afford *E,E*-1-(4-dimethylaminophenyl)-4-chloroperfluoro-1,3-butadiene **7** [44].



The other method for the synthesis of 1-aryl-4-chloroperfluoro-1,3-butadienes is the interaction of arylmagnesium species with 1-chloroperfluoro-1,3-butadiene [8,45].



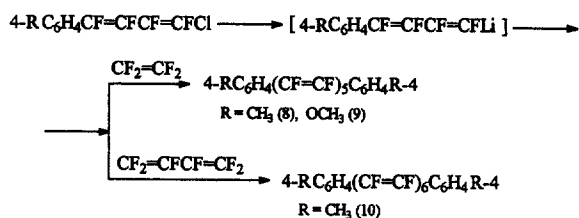
It was found that  $\alpha$ -aryl- $\omega$ -chloroperfluoropolyenes could be obtained in 40–45% yields by the interaction of arylmagnesium reagents with perhalogenoalkanes without prior dechlorination of the latter to unstable  $\alpha$ -chloroperfluoropolyenes [46].



The first stage of this reaction was dechlorination of perhalogenoalkanes with Grignard reagents to  $\alpha$ -chloroperfluoropolyenes. The latter reacted with a further molecule of the arylmagnesium species to form the  $\alpha$ -aryl- $\omega$ -chloroperfluoropolyenes.

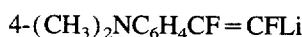
Arylchloroperfluorobutadienes obtained by this method as well as the compounds obtained from 1-chloroperfluoro-1,3-butadiene are a mixture of *E,Z*-, *E,E*- and *Z,E*-isomers [8,45,46]. 1-(4-Methylphenyl)-6-chloroperfluoro-1,3,5-hexatriene is a mixture of *E,E,Z*-, *E,E,E*- and *Z,Z,Z*-isomers as determined by <sup>19</sup>F NMR [47]. Only *E,Z*-1-(4-dimethylaminophenyl)-4-chloroperfluoro-1,3-butadiene was isolated in the pure state [45].

The chlorine atom in 1-aryl-4-chloroperfluoro-1,3-butadienes as well as in  $\beta$ -chloro- $\alpha,\beta$ -difluorostyrene can be replaced with metal in reaction with butyllithium in a mixture of THF, ether and pentane or hexane. Interaction of these lithium derivatives with tetrafluoroethene or perfluoro-1,3-butadiene gives 1,10-diarylperfluoro-1,3,5,7,9-decapentenes **8**, **9** and 1,12-di(4-methoxyphenyl)perfluoro-1,3,5,7,9,11-dodecahexaene **10** with five or six conjugated difluorovinylene links [47].

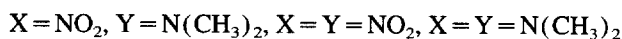
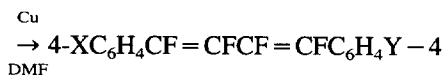
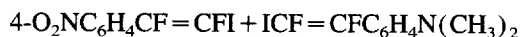


These methods, in principle, can be used only for preparation of symmetrical  $\alpha,\omega$ -diarylperfluoropolyene.

One can obtain asymmetrical 1,4-diaryl substituted perfluoro-1,3-butadienes from difluorostyryllithium or its derivatives and  $\alpha,\beta,\beta$ -trifluorostyrene. However, only 4-dimethylamino- $\alpha,\beta$ -difluorostyryllithium was found to react with  $\alpha,\beta,\beta$ -trifluorostyrene [44]. It is likely that the dimethylamino substituent activates the nucleophilic centre.



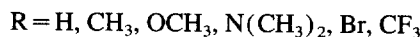
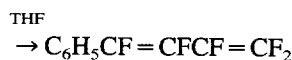
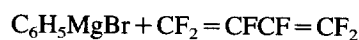
Asymmetrical derivatives of 1,4-diphenylperfluoro-1,3-butadiene like  $\alpha,\beta$ -difluorostilbene and its derivatives can be obtained by Ulmann type reactions of substituted  $\beta$ -iodo- $\alpha,\beta$ -difluorostyrenes with nitro- and dimethylamino-groups in the 4-position of the aromatic ring. Three substances were obtained in this reaction, one was an asymmetrical product and two were symmetrical compounds. The pure compounds were separated by crystallization [35].



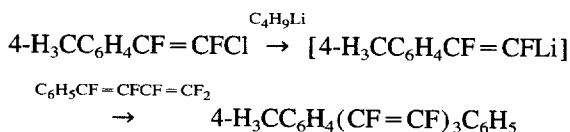
The interaction of iododifluorostyrene derivatives (one of them has a nitro-group) with copper leads mainly to 4,4'-dinitro compounds ( $\text{X} = \text{Y} = \text{NO}_2$ ). This is in accord with the greater activity of compounds having withdrawing substituents in the Ulmann type reaction due to activation of halogen atoms in these compounds by electron withdrawing substituents. The influence of the nitro-group in this case is transferred through the difluorovinylene fragment to the iodine atom, which is similar to activation of the chlorine atom in 4-nitro- $\beta$ -chlorostyrene [48].

The longer asymmetrically conjugated  $\alpha,\omega$ -diarylperfluoropolyenes can be obtained by the reaction of 1-arylperfluoro-1,3-butadiene, which is a difluorovinyllog of  $\alpha,\beta,\beta$ -trifluorostyrene, with  $\alpha,\beta$ -difluorostyryllithium or 1-aryl-4-lithio-perfluoro-1,3-butadiene. The interaction of methylmagnesium bromide or phenylmagnesium bromide with perfluoro-1,3-butadiene in ether was claimed to give 1-methyl-2,3,4,5,5-pentafluoro-2,4-pentadiene or the 1,4-diphenylperfluoro-1,3-butadiene isomers [32]. We failed to reproduce these reactions in ether but in THF phenylmag-

nesium bromide reacts with perfluoro-1,3-butadiene and 1-phenylperfluoro-1,3-butadiene is obtained in 63% yield [49].

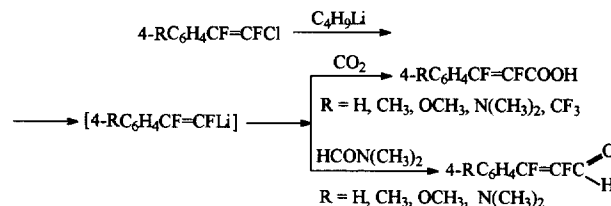


Asymmetrical derivatives of 1,4-diarylperfluoro-1,3-butadiene can be obtained by the reaction of 1-arylperfluoro-1,3-butadiene with the aryllithium reagents. The interaction of 1-arylperfluoro-1,3-butadiene with various derivatives of  $\alpha,\beta$ -difluorostyryllithium or 1-aryl-4-lithio-perfluoro-1,3-butadiene lead to longer asymmetrically conjugated  $\alpha,\omega$ -diarylperfluoropolyenes [49].



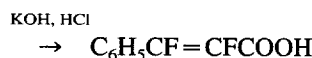
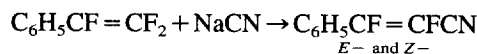
#### 4. $\omega$ -Carboxyl and $\omega$ -carbonyl derivatives

The lithiated  $\alpha,\beta$ -difluorostyrenes react with solid carbon dioxide or *N*-formylpiperidine and DMF to give the *E*- $\alpha,\beta$ -difluorocinnamic acid or *E*- $\alpha,\beta$ -difluorocinnamaldehyde derivatives, respectively [41,50].



These are general methods for the synthesis of *E*- $\alpha,\beta$ -difluorosubstituted cinnamic acids and cinnamaldehydes with various substituents.

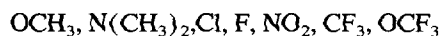
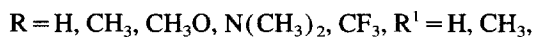
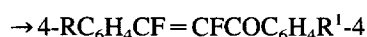
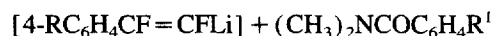
*Z*- $\alpha,\beta$ -Difluorocinnamic acid was first obtained by hydrolysis of its nitrile. The latter was separated by GLC from the mixture of *E*- and *Z*-isomer formed in the reaction of sodium cyanide with  $\alpha,\beta,\beta$ -trifluorostyrene. Hydrolysis of each of the nitriles was carried out by heating in 10% aqueous potassium hydroxide [51].



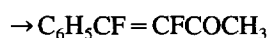
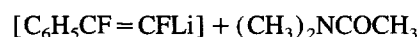
Nitration of *E*- $\alpha,\beta$ -difluorocinnamic acid with nitric acid gives a mixture of 3- and 4-nitro derivatives of *E*- $\alpha,\beta$ -difluorocinnamic acid in 14% and 66% yields, respectively. Thus, the  $\text{CF}=\text{CFCOOH}$  group is an *ortho-para*-directing substituent [52].

Silver salts of *E*- $\alpha,\beta$ -difluorocinnamic acid and its 4-nitro- and 4-dimethylamino derivatives were converted into  $\beta$ -iodo- $\alpha,\beta$ -difluorostyrene derivatives in 50–75% yield by the Hunsdiecker reaction [52]. These compounds were used in the synthesis of asymmetrical 1,4-diarylperfluoro-1,3-butadienes [35].

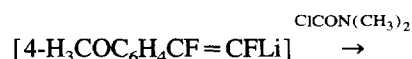
$\alpha,\beta$ -Difluorostyryllithium derivatives reacted with 4-substituted *N,N*-dimethylbenzamides to give  $\alpha,\beta$ -difluoroacrylate derivatives in 35–45% yield [53].



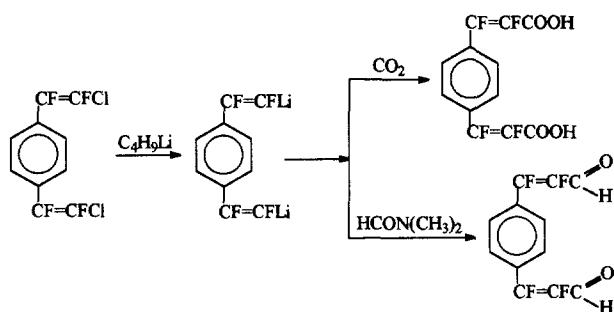
Aliphatic dimethylamides also react by this scheme [53].



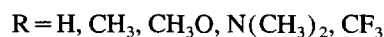
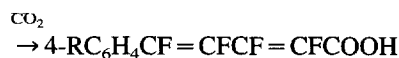
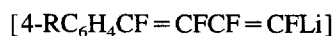
Symmetrical bis( $\alpha,\beta$ -difluorostyryl)ketone was obtained by the interaction of 4-methoxy- $\alpha,\beta$ -difluorostyryllithium with dimethylaminocarbamic acid chloride [53].



The metalation of 4-phenylene-bis( $\beta$ -chloro- $\alpha,\beta$ -difluoropropene) (a 4:1 mixture of *Z,Z*- and *E,E*-isomers) with butyllithium in a mixture of THF, ether and hexane at the temperature of  $-65$  to  $-93^\circ\text{C}$ , was found to involve two chlorine atoms in this molecule [54]. The reaction of the dilithium derivative with carbon dioxide gave *E,E*-4-phenylene-bis( $\alpha,\beta$ -difluoroacrylic) acid in 46% yield. A similar reaction with DMF furnishes *E,E*-4-phenylene-bis( $\alpha,\beta$ -difluoropropenal) in 13% yield [54].



The reaction of 1-aryl-4-lithio-perfluoro-1,3-butadiene derivatives with carbon dioxide at  $-98^\circ\text{C}$  produced a series of 5-arylpentafluoro-2,4-pentadiene acids [8,45].



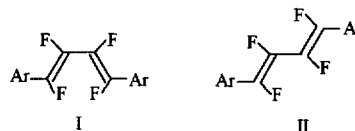
## 5. Structures of $\alpha,\omega$ -diarylperfluoropolyenes

All the diarylperfluoropolyenes known, except  $\alpha,\beta$ -difluorocinnamaldehyde and 4-phenylene-bis-( $\alpha,\beta$ -difluoropropenal) are crystalline solids.

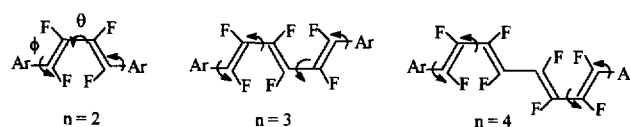
$\alpha,\beta$ -Difluorostilbene obtained by Dixon's method [34] is the pure *E*-isomer. Attempts to prepare the *Z*-isomer were unsuccessful. It has been shown, that *E*- $\alpha,\beta$ -difluorostilbene could be converted to the *Z*-isomer by UV-irradiation [55].

The  $\alpha,\beta$ -difluorostilbene molecule is non planar and the torsional angle ( $\phi$ ) between the benzene rings relative to the double bond planes is  $25\text{--}26^\circ$  [56,57].

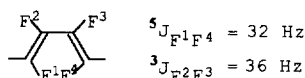
All other members of the conjugated  $\alpha,\omega$ -diarylperfluoropolyenes showed all-*trans* configurations of fluorine atoms [8,38,43,45,47]. The structure of these compounds depends not only on the positions of fluorine atoms relative to the double bonds, but also on the relative positions of the double bonds themselves, i.e., cisoid (I) or transoid (II).



X-ray diffraction analysis of  $\alpha,\omega$ -diarylperfluoropolyenes  $\text{Ar}(\text{CF}=\text{CF})_n\text{Ar}$ , where  $n=2\text{--}4$ , has shown that these compounds exist in twist nonplanar cisoid conformations with the rotation angles  $\phi$  from  $0$  to  $23^\circ$ . Torsional angles  $\theta$  of the double bond planes relative to each other are from  $47$  to  $49^\circ$  [58,59]. The conformation of these molecules appears not to depend on substituents in the benzene rings.

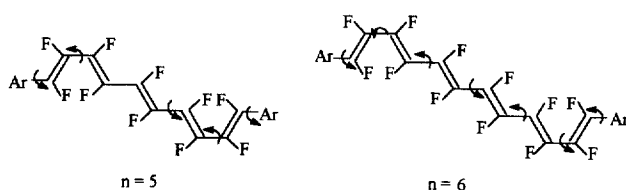


$^{19}\text{F}$  NMR spectra of  $\text{Ar}(\text{CF}=\text{CF})_n\text{Ar}$  ( $n=2\text{--}6$ ) with various substituents in benzene rings have different chemical shift values, but the spin-spin coupling constants ( $^nJ$ ) are similar for these compounds. Investigation of symmetrical and asymmetrical 1,4-diarylperfluoro-1,3-butadienes by  $^{19}\text{F}$  NMR spectroscopy and comparison with the reference compounds which have proved *S*-cisoid structure gives the following spin-spin coupling constants for the cisoid perfluoro-1,3-butadiene fragment [60]:



The presence of such constants in the  $^{19}\text{F}$  NMR spectra of other novel synthesized molecules with perfluoro-1,3-butadiene fragment makes it possible to affirm that the perfluoro-1,3-butadiene moiety in these molecules has a *S*-cisoid structure.

Thus, the above data of X-ray diffraction analysis for the conjugated compounds  $\text{Ar}(\text{CF}=\text{CF})_n\text{Ar}$  ( $n=2,3,4$ ) and  $^{19}\text{F}$  NMR data for all-*E*-1,10-diarylperfluoro-1,3,5,7,9-decapentaenes ( $n=5$ ) and all-*E*-1,12-diarylperfluoro-1,3,5,7,9,11-dodecahexaenes ( $n=6$ ) allowed us to propose for the higher conjugated  $\alpha,\omega$ -diarylperfluoropolyenes ( $n=5,6$ ) the following structures [61]:



The torsion angles  $\phi$  and  $\theta$  appear practically similar to the  $\alpha,\omega$ -diarylperfluoropolyenes with  $n=2,3,4$ .

The values of  $\lambda_{\text{max}}$  in UV spectra of  $4\text{-RC}_6\text{H}_4\text{-(CF=CF)}_n\text{C}_6\text{H}_4\text{-R}$  were found to be as follows:  $R=\text{CH}_3$ ,  $n=2$  (305 nm),  $n=3$  (318 nm),  $n=4$  (330 nm),  $n=5$  (340 nm),  $n=6$  (342 nm);  $R=\text{CH}_3\text{O}$ ,  $n=2$  (315 nm),  $n=3$  (330 nm),  $n=4$  (340 nm),  $n=5$  (350 nm),  $n=6$  (352 nm) [37,38,43,61].

Comparison of the UV spectra for the  $\alpha,\omega$ -diarylperfluoropolyenes shows a shift of the absorption maximum towards longer wave length of 10–15 nm for each  $(\text{CF}=\text{CF})$  link but the shift for the six on difluorovinylene link is only 2 nm. Such a behaviour of the absorption maximum may be explained by the elongation and conversion of conformation in the conjugated perfluoropolyene system in 1,12-diarylperfluorododecahexaenes. One can suppose that absorption maxima of the following members of  $\alpha,\omega$ -diarylperfluoropolyenes will be similar to maxima of 1,12-diarylperfluoro-1,3,5,7,9,11-dodecahexaenes.

The replacement of hydrogen by fluorine at carbon atom generally leads to compression of the charge density around the carbon and hence to the shortening of  $\text{C}=\text{C}$  bond length from 1.344 Å in butadiene-1,3 to  $1.336 \pm 0.018$  Å in perfluoro-1,3-butadiene [14] and  $1.327 \pm 0.006$  Å in diarylperfluoropolyenes [58,59].

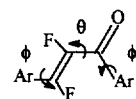
The spatial structures of the conjugated  $\alpha,\omega$ -diarylperfluoropolyenes molecules proved to be substantially different from the corresponding hydrogen analogues. The conjugated polyene system of the latter has a planar *S-trans* conformation that easily converts into the *S-cis* form [62]. Fluorinated *E*-polyenes exist in a twist *S-cis* conformation with the angles  $\phi=0\text{--}23^\circ$  and  $\theta=47\text{--}49^\circ$  as demonstrated by X-ray diffrac-

tion analysis [58,59]. The major structural element of the conjugated perfluoropolyene system is the 1,2,3,4-tetrafluoro-1,3-butadiene moiety. Atoms  $\text{F}^1$ ,  $\text{C}^1$ ,  $\text{C}^2$ ,  $\text{C}^3$ ,  $\text{C}^4$  and  $\text{F}^4$  in the 1,4-diarylperfluoro-1,3-butadiene compounds are located along the spiral coil, which can be directed either to the left or to the right. Hence, the derivatives of this diene exhibit atropoisomerism and are a racemic mixture of two enantiomers.

The stable cisoid conformation of  $\alpha,\omega$ -diarylperfluoropolyenes can be explained by the nonbonded p–p interaction of fluorine atoms in the 1- and 4-positions of the perfluoro-1,3-butadiene fragment [63].

$\alpha,\beta$ -Difluorocinnamic acid and its derivatives, 5-aryltetrafluoro-2,4-pentadienecarboxylic acids, derivatives of  $\alpha,\beta$ -difluorocinnamaldehyde and  $\alpha,\beta$ -difluorochalcone are *E*-isomers as determined by  $^{19}\text{F}$  NMR [41,44,50]. 5-Aryltetrafluoro-2,4-pentadienecarboxylic acids exist in the cisoid conformation [44].

Judging by IR and X-ray diffraction analysis data,  $\alpha,\beta$ -difluorochalcone derivatives exist in nonplanar *S-trans* conformations with angles  $\phi=9^\circ$ ,  $\phi^1=20^\circ$  and  $\theta=40^\circ$ .



## 6. Transmission of electronic influences via conjugated perfluoropolyene systems

The substitution of hydrogen atoms with fluorine in conjugated polyene systems, especially in  $\alpha,\omega$ -diarylperfluoropolyenes, changes the molecular structures and increases their nonplanarity. Data in the literature deny the possibility for transmission of electronic influences to occur via the difluorovinylene link. Authors of report [64] have investigated the conjugation of the benzene ring and the double bond in  $\alpha,\beta$ -trifluorostyrene by dipole moment determinations. They came to the conclusion that the presence of fluorine atom in the  $\alpha$ -position breaks down the coplanarity of olefin group and benzene ring, so that the parts of the molecule do not interact. However, this conclusion turned out to be erroneous. We have proven that the transmission of electronic effects via perfluoropolyene systems does occur [36,45,65,66].

The investigations of electronic influence transmission via the  $\alpha,\beta$ -difluorovinylene link were carried out by the determination of  $pK_a$  for *E*- $\alpha,\beta$ -difluorocinnamic acid and its derivatives —  $4\text{-XC}_6\text{H}_4\text{CF}=\text{CFCOOH}$ ,  $X(pK_a)$ :  $\text{Me}_2\text{N}$  (4.20),  $\text{CH}_3\text{O}$  (3.87),  $\text{H}$  (3.70),  $\text{CF}_3\text{CONH}$  (3.63),  $\text{I}$  (3.59),  $\text{CF}_3$  (3.63),  $\text{NO}_2$  (3.21) [65] and *E*,*E*-5-arylperfluoro-2,4-pentadienecarboxylic acids  $4\text{-RC}_6\text{H}_4\text{CF}=\text{CFCF}=\text{CFCOOH}$ ,  $R(pK_a)$ :  $\text{Me}_2\text{N}$  (3.35),  $\text{CH}_3\text{O}$  (3.02),  $\text{CH}_3$  (2.96),  $\text{H}$  (2.91),  $\text{CF}_3$  (2.73) [45]. All the  $pK_a$  values of  $\alpha,\beta$ -difluorocinnamic acid and 5-arylperfluoro-2,4-pentadi-



carboxylic acid derivatives give reasonable correlation with substituent  $\sigma_p$ -constants. The correlation equations are  $pK_a = 3.70 - 0.64\sigma_p$ ,  $r = 0.998$ ; for  $\alpha,\beta$ -difluorocinnamic acid and its derivatives and  $pK_a = 2.93 - 0.45\sigma_p$ ,  $r = 0.980$ ; for *E,E*-5-arylperfluoro-2,4-pentadienecarboxylic acids. The reaction constant  $\rho$  characterizing the susceptibility of the reaction centre M in a X–M–Y system to the effect of the substituent X allows quantitative estimation of the electronic conductivity of bridge group M that bonds structural fragments X and Y.

A comparison of the reaction constant  $\rho = 0.64$  ( $\alpha,\beta$ -difluorostyryl group) with the value of  $\rho = 0.73$  (styryl group) has demonstrated that a *E*- $\alpha,\beta$ -difluorovinylene link was conjugated with a benzene ring and transmitted electronic influences of substituents to the reaction centre a little less than the *E*-vinylene link and similarly to the ethyne link. Comparison between the transmission factors  $\gamma_M$  has confirmed this conclusion. The transmission factors depend slightly on the type of reaction and the nature of the reaction centre. They are defined as  $\gamma_M = \rho_M / \rho_{(\text{phenylene})}$  (for the benzoic acid  $\gamma_M$  was 1.35). The values of  $\gamma_M$  for styryl, phenylacetylenyl and  $\alpha,\beta$ -difluorostyryl groups were 0.54, 0.51 and 0.47, respectively [65]. Elongation of fluorine-containing conjugated system by a single  $\alpha,\beta$ -difluorovinylene link leads to values of  $\rho[\text{C}_6\text{H}_4(\text{CF}=\text{CF})_2] = 0.45$  and  $\gamma[\text{C}_6\text{H}_4(\text{CF}=\text{CF})_2] = 0.33$ . They are 1.5 times smaller than the values of  $\rho$  and  $\gamma_M$  for the  $\text{C}_6\text{H}_5\text{CF}=\text{CF}$ -bridge. Thus, elongation of the conjugated perfluoropolyene system produces an approximately 1.5-fold decrease in efficiency of the electronic influence transmission [45].

A comparison of these data has demonstrated that the strongest alteration of electronic transmission of bridge groups  $\text{M} = \text{C}_6\text{H}_4(\text{CF}=\text{CF})_n$  ( $n = 0, 1, 2, 3, \dots$ ) is observed in going from the 4-phenylene to the  $\alpha,\beta$ -difluorostyryl system. Probably, the difference in the conductivity of homologous series  $\Delta\gamma_M = \gamma^n - \gamma^{n-1}$  will decrease with successive elongation of the perfluoropolyene chain.

Investigation of compounds having the  $\alpha,\beta$ -difluorovinylene group conjugated with the benzene ring by  $^{19}\text{F}$  NMR spectroscopy leads to similar conclusions. The use of  $^1\text{H}$  chemical shifts is difficult for the calculation of correlative dependences because they show a low sensitivity to the influence of substituents in the benzene ring. Chemical shifts of the fluorine atoms in  $\alpha$ -arylperfluoropolyene systems are more sensitive to alteration of substituents in the benzene ring and allowed us to correlate  $\delta^{19}\text{F}$  and  $\sigma_p$ -constants of substituents by means of  $^{19}\text{F}$  NMR spectroscopy. Such correlative dependences were found for the derivatives of *E*- $\alpha,\beta$ -difluorocinnamic acid and *E*- and *Z*- $\beta$ -chloro- $\alpha,\beta$ -difluorostyrenes [65].

It has been found that the difference of chemical shift values of fluorine atoms near the  $\text{C}^2$ -atom  $\Delta\delta\text{F}^2 = (\delta\text{F}_X - \delta\text{F}_H)$  in the substituted and unsubstituted compounds  $4\text{-XC}_6\text{H}_4\text{CF}^\beta=\text{CF}^\alpha\text{COOH}$  ( $\text{F}^2=\text{F}^\alpha$ ) and  $4\text{-XC}_6\text{H}_4\text{CF}^\alpha=\text{CF}^\beta\text{Cl}$  ( $\text{F}^2=\text{F}^\beta$ ) structures correlated well with  $\sigma_p$  constants of the X substituents in the benzene ring [65].

The equation for the derivatives of  $\alpha,\beta$ -difluorocinnamic acid is  $\Delta\delta\text{F}^\alpha = 0.16 - 6.58\sigma_p$ ,  $r = 0.989$ . The absolute value of constant  $\rho = 6.58$  in this equation indicates that the electronic influences of X substituents are effectively transmitted towards the fluorine atom ( $\text{F}^2$ ). However the transmission of electronic influences to the  $\alpha$ -atom of fluorine in the corresponding derivatives of  $\alpha,\beta$ -difluorocinnamic acid is about three times less in comparison with 4-substituted fluorobenzene. A similar decrease in the transmission of electronic influences was observed in the series of 4-substituted *E*- and *Z*- $\beta$ -chloro- $\alpha,\beta$ -difluorostyrenes. This effect is more noticeable in *Z*- $\beta$ -chloro- $\alpha,\beta$ -difluorostyrene and its derivatives due to the influence of steric hindrances.

The transmission influence of substituent X on the fluorine atoms  $\text{F}^2$  and  $\text{F}^4$  in *E,E*-5-arylperfluoropenta-2,4-dienecarboxylic acids ( $4\text{-XC}_6\text{H}_4\text{CF}=\text{CF}^4\text{CF}=\text{CF}^2\text{COOH}$ ) was quantitatively estimated by  $^{19}\text{F}$  NMR. It is  $\Delta\delta\text{F}^2 = -0.17 - 3.86\sigma_p$  for the atom  $\text{F}^2$  and is  $\Delta\delta\text{F}^4 = -0.28 - 10.86\sigma_p$  for the  $\text{F}^4$  atom [45]. The influence of substituents on atom  $\text{F}^2$  is approximately three times weaker than on the atom  $\text{F}^4$ . A comparison between the transmission to atom  $\text{F}^4$  ( $\rho = 10.86$ ) in the arylperfluoropentadiene acids and to the structurally equivalent atom  $\text{F}^\alpha$  ( $\rho = 6.58$ ) in *E*- $\alpha,\beta$ -difluorocinnamic acids has shown, that the sensitivity of atom  $\text{F}^4$  in the tetrafluorobutadiene system to changes in electronic density induced by substituents X, is stronger than on the atom  $\text{F}^\alpha$  ( $10.86 > 6.58$ ). That is probably due to the strong influence of the electron-accepting carboxylic group in the conjugated chain. As a result the influence of electron-accepting substituents on the benzene ring on the atom  $\text{F}^\alpha$  in the  $\alpha,\beta$ -difluorocinnamic acid derivatives decreases as the carboxylic group shifts electronic density in the opposite direction to the electron-accepting substituents. The reverse occurred in the case of electron donating substituents. The shift of electronic density become stronger if the groups X and COOH act in the same direction.

Thus, it was found that both the *E*-difluorovinylene group conjugated with the benzene ring and the nonplanar cisoid *E,E*-1,2,3,4-tetrafluoro-1,3-butadiene system transmit the electronic influence of the substituent to the corresponding reaction centre—the carboxylic group or fluorine atom. However, the transmission over a  $-\text{CF}=\text{CF}^\alpha\text{CF}=\text{CF}-$  fragment is weaker than for the  $-\text{CF}=\text{CF}-$  group due to the nonplanar structure of the perfluorobutadiene system.

Investigations of dipole moments, UV and  $^{19}\text{F}$  NMR spectra of derivatives of *E*- $\alpha,\beta$ -difluorostilbene and *E,E*-1,4-diphenyl-1,3-tetrafluorobutadiene have shown that in spite of their nonplanarity, transmission of the conjugation effect occurred [35,36].

Correlation of  $\sigma_p$  constants with absorption frequencies for carbonyl groups in IR spectra of *E*- $\alpha,\beta$ -difluoro-chalcone derivatives also confirms the transmission of electronic effects through a  $-\text{CF}=\text{CF}-$  link [53].

The shifts of absorption maxima in UV spectra to longer wavelength in  $4\text{-XC}_6\text{H}_4(\text{CR}=\text{CR})_n\text{C}_6\text{H}_4\text{Y}-4$  [ $n = 1, 2$ ,  $\text{X} = \text{NO}_2$ ,  $\text{Y} = \text{N}(\text{CH}_3)_2$ ] are more than 100 nm both with

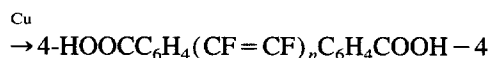
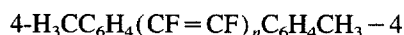
$R=H$  and  $R=F$  as compared with the compounds ( $X=Y=H$ ) unsubstituted in the benzene ring [35].

A formula for quantitative characterization of electronic transmission  $d^Z$  in the conjugated system of an 4- $XC_6H_4ZC_6H_4Y$ -4 structure was proposed by Skulski on the basis of their UV spectra data [67];  $d^Z$  characterizes the efficacy of the interaction of different substituents  $X$  and  $Y$  with the bridge  $Z$ .

The values of  $d^Z$  for stilbene, 1,4-diphenyl-1,3-butadiene derivatives and their fluorinated analogues were calculated [37]. They are: for stilbene  $d^{CH=CH} = 1.63$ , for  $\alpha,\beta$ -difluorostilbene  $d^{CF=CF} = 1.51$ , for the derivatives of 1,4-diphenyl-1,3-butadiene  $d^{CH=CHCH=CH} = 1.56$  and  $d^{CF=CFCF=CF} = 1.38$ . From these data it is seen that elongation of the polyene chain makes transmission of electronic influences worse ( $d^{CR=CR} > d^{CR=CRCR=CR}$ ). These effects are stronger for the fluorinated compounds than for nonfluorinated systems. Substitution of hydrogen for fluorine atoms in the polyene chain brings about attenuation of the transmission:  $d^{CH=CH} > d^{CF=CF} > d^{CH=CHCH=CH} > d^{CF=CFCF=CF}$ . Such a decrease is likely to suggest that the introduction of fluorine atoms into the polyene system modifies the molecular structure. Thus, the benzene ring turns in  $\alpha,\beta$ -difluorostilbene by  $26^\circ$  relative to the double bond. The planar transoid system in 1,4-diphenyl-1,3-butadiene converts into the nonplanar cisoid fragment for the 1,4-diphenyl-1,3-perfluoro-1,3-butadiene. However, steric hindrances do not totally prevent the transmission of electronic influences in the perfluorinated conjugated system.

## 7. Chemical properties of $\alpha,\omega$ -diarylperfluoropolyenes

$\alpha,\omega$ -Diarylperfluoropolyenes, as other unsaturated compounds, undergo chlorination and bromination at the double bonds. Chlorine adds to exocyclic double bonds in  $E$ -1,2-di(4-tolyl)-1,2-difluoroethene,  $E,E$ -1,4-di(4-tolyl)perfluoro-1,3-butadiene and  $E,E,E$ -1,6-di(4-tolyl)perfluoro-1,3,5-hexatriene.

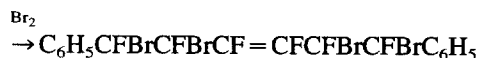
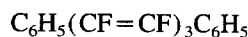


$$n = 1-3$$

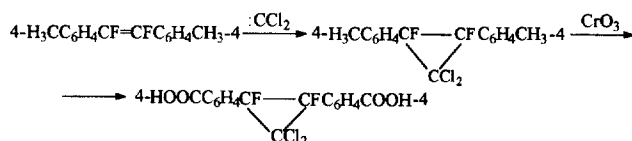
Methyl groups in the addition products are oxidized to carboxylic groups. Carboxyl-containing compounds are dechlorinated with copper powder in pyridine to  $\alpha,\omega$ -di(4-carboxyphenyl)per-fluoropolyenes [37].

$E,E$ -1,4-Diphenylperfluoro-1,3-butadiene adds bromine in tetrachloromethane only to the 1,2-position. Bromination of

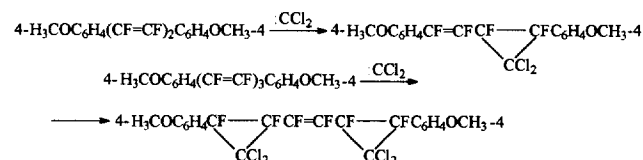
$E,E,E$ -1,6-diphenylperfluoro-1,3,5-hexatriene occurs exclusively at the terminal double bonds, as the  $CFBr-CFBr$  groups appear to shield the central  $C=C$  bond and inhibit the addition of bromine [36].



Similarly to bromine atoms dichlorocarbene adds selectively to difluorovinylene links of the perfluoropolyene chain [68]. The addition of dichlorocarbene is sensitive to the nucleophilicity of the double bond. Dichlorocarbene adds only to  $\alpha,\omega$ -diarylperfluoropolyenes having an electron-donating group, such as methyl- or methoxy- in position 4 of the benzene ring.  $E$ -4,4'-Dimethyl- $\alpha,\beta$ -difluorostilbene reacts with dichlorocarbene generated by the reaction of trichloromethane with aqueous sodium hydroxide in the presence of benzyltriethylammonium chloride to give  $E$ -1,2-bis(4-tolyl)-1,2-difluoro-3,3-dichlorocyclopropane in high yield. Oxidation of the methyl groups produces the corresponding dicarboxyl-containing compounds [68].

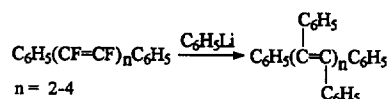


$E,E$ -1,4-Di(4-methoxyphenyl)perfluoro-1,3-butadiene and  $E,E,E$ -1,6-di(4-methoxyphenyl)-perfluoro-1,3,5-hexatriene add dichlorocarbene to one and two double bonds, respectively in contrast to conjugated  $\alpha,\omega$ -diphenylpolyenes that add dichlorocarbene to all double bonds [69].

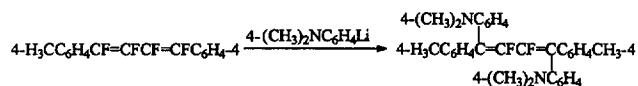


The interaction of dichlorocarbene with  $E,E,E$ -1,6-di(4-methylphenyl)perfluoro-1,3,5-hexatriene occurs similarly to the 4,4'-dimethoxyderivative, but the reaction product is a mixture of the meso and racemate of 1,2-bis[1-(4-methylphenyl)-3,3-dichloro-1,2-difluoro-cyclopropyl]- $E$ -1,2-difluoroethene [68].

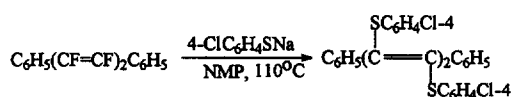
Some nucleophilic reactions of conjugated  $\alpha,\omega$ -diarylperfluoropolyenes have been investigated [70]. A new type of hydrocarbons—perphenylpolyenes were obtained by reaction of diphenylperfluoropolyenes with excess of phenyllithium in diethyl ether under reflux.



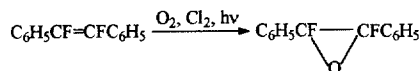
The substitution of fluorine atoms in the polyene chain of diarylperfluoropolyenes by aromatic radicals depends on the nature of substituents in the aromatic rings. The reaction of 1,4-di(4-methylphenyl)perfluoro-1,3-butadiene with excess of 4-(dimethylamino)phenyl lithium gives solely the product of 1,4-substitution. The other two fluorine atoms were not substituted due to the introduction of electron-donating 4-dimethylaminophenyl groups to the fluorinated diene system decreasing its electrophilicity.



Sodium 4-chlorothiophenolate substitutes all the fluorine atoms in 1,4-diphenylperfluoro-1,3-butadiene on heating in *N*-methylpyrrolidone (NMP) [70].

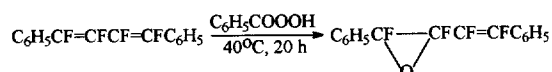


Oxidation of *E*- $\alpha,\beta$ -difluorostilbene in a mixture of oxygen/chlorine (3:1 wt/wt) at UV irradiation in benzene gives 1,2-diphenyl-1,2-difluoro-1,2-epoxyethane in 60% yield [71].



Oxidation of *E*- $\alpha,\beta$ -difluorostilbene with perbenzoic acid in dichloromethane at room temperature raises the yield of this epoxide to 82%.

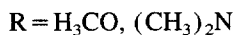
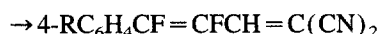
Oxidation of *E,E*-1,4-diphenylperfluoro-1,3-butadiene with perbenzoic acid in dichloromethane at room temperature did not occur even over 48 h. 1,4-Diphenyl-1,2,3,4-tetrafluoro-1,2-epoxy-3-butene was formed in 30% yield only at 40°C.



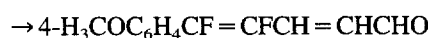
In contrast, the oxidation of 1,4-diphenyl-1,3-butadiene gave the di-epoxide [72].

Investigation of the chemical properties of the *E*- $\alpha,\beta$ -difluorocinnamic aldehyde derivatives has shown that nucleophilic reagents attack both the carbonyl group and the  $\beta$ -carbon atom of these compounds [50]. The interaction of *E*-4-methoxy- and *E*-4-dimethylamino- $\alpha,\beta$ -difluorocinnamic aldehydes with malononitrile in the presence of pyri-

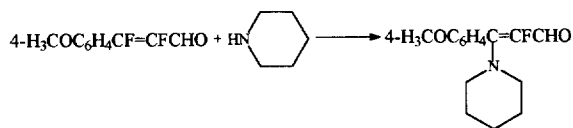
dine gave 4-(4-methoxyphenyl)- or 4-(4-dimethylamino-phenyl)-3,4-difluoro-1,1-dicyanobutadiene, respectively, in 90% yield.



*E*-4-Methoxy- $\alpha,\beta$ -difluorocinnamaldehyde with formylmethyltriphenylphosphorane in benzene forms *E,E*-5-(4-methoxyphenyl)-4,5-difluoro-2,4-pentadienal in 25% yield.



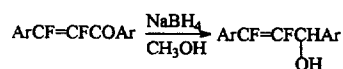
The reaction of *E*-4-methoxy- $\alpha,\beta$ -difluorocinnamaldehyde with excess of piperidine gives only the product of the  $\beta$ -fluorine atom substitution.



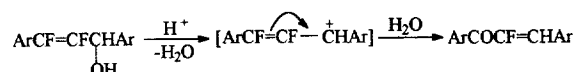
Similarly *E,E*-phenylene-bis( $\alpha,\beta$ -difluoropropenal) reacted with malononitrile to give a 4-phenylene-bis(3,4-difluoro-1,1-dicyano-1,3-butadiene) in 40% yield [54].



The carbonyl group in *E*- $\alpha,\beta$ -difluoroaldehydes was reduced with sodium borohydride to the corresponding carbinols. Fluorine atoms in the vinylic fragment are not involved in this reaction [53].



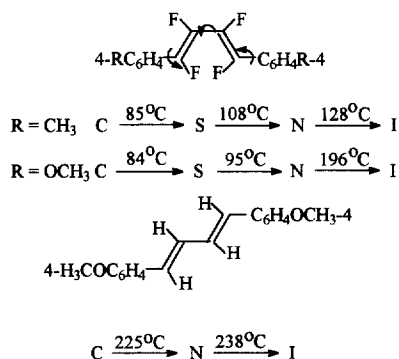
These carbinols are unstable compounds. They are readily converted into  $\alpha$ -fluoroaldehydes either on heating or by sulphuric acid.



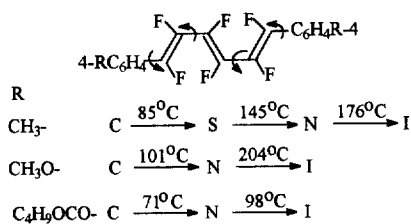
## 8. Liquid crystal properties of aryl- and diarylperfluoropolyenes

4,4'-Dimethyl- and 4,4'-dimethoxyderivatives of 1,4-diphenylperfluoro-1,3-butadiene are liquid crystals of the smectic and nematic type with a wide phase temperature

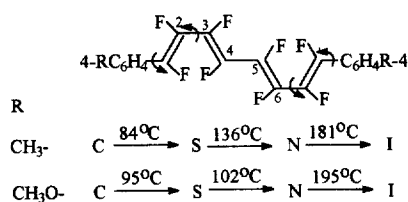
range and high thermal stability [73]. Their hydrogen analogue, 1,4-di(4-methoxyphenyl)-1,3-butadiene, forms a high-melting nematic phase with the range of 13°C [74].



X-ray diffraction data of 4,4'-dimethyl- and 4,4'-dimethoxyderivatives of 1,6-diphenylperfluoro-1,3,5-hexatriene shows two perfluorobutadiene moieties of the perfluoropolyene chain with the common double bond turned in the opposite directions [58,59]. Therefore, these compounds are mesoforms. The 4,4'-dimethyl derivative of 1,6-diphenylperfluoro-1,3,5-hexatriene, similar to 1,4-diarylperfluoro-1,3-butadiene also forms smectic and nematic phases, being however thermally much more stable, while its dimethoxy derivative is only nematic [58]. The compound containing butoxycarbonyl groups is also a liquid crystal of the nematic type, but its phase is narrow and of low thermal stability. The mesophase appearance in this substance with two electron-withdrawing end groups may be explained by the appreciable weakening of the electronic interaction transmission via the nonplanar perfluorohexatriene system [45].

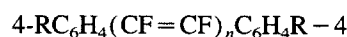


With the further elongation of the perfluoropolyene chain—the transition to the substituted compounds of 1,8-diphenylperfluoro-1,3,5,7-octatetraene—the same regularity was observed, that is the smectogenic character of the di(4-methylphenyl) derivative and tendency of the corresponding dimethoxy derivative to form nematics.



X-ray diffraction shows that the conjugated perfluorotetraene system in this group of compounds is symmetric and consists of two isolated perfluorobutadiene cisoid-structure moieties turned in opposite directions being in a transoid conformation relative to the central single bond. At the same time the C<sup>3</sup>–C<sup>4</sup>–C<sup>5</sup>–C<sup>6</sup> system is almost planar. The structural features of 1,8-diarylperfluoro-1,3,5,7-octatetraenes suggest that the compounds of this series, similar to 1,6-diarylperfluoro-1,3,5-hexatrienes, are mesomorphic.

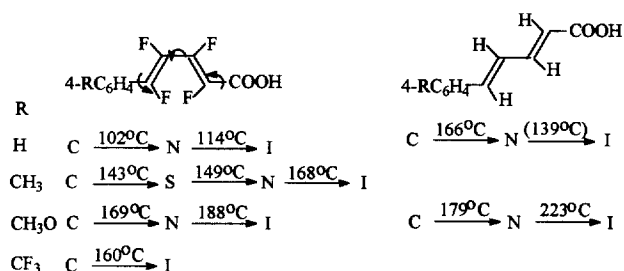
The substituted structures of diphenylperfluorodecapentaene and dodecahexaene also exhibit mesomorphism but only of the nematic type with wide and thermally stable phases [47].



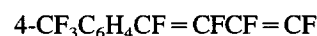
R	n	Phase Transitions
CH <sub>3</sub>	5	C → N → I (74°C, 174°C)
		C → N → I (103°C, 207°C)
CH <sub>3</sub> O	5	C → N → I (87°C, 207°C)
		C → N → I (82°C, 176°C)

Liquid-crystal properties are also exhibited by some aryl-fluorocarboxylic acids and their aryl esters containing a perfluoropolyene conjugated system [75].

*E,E*-5-Phenylperfluoro-2,4-pentadienecarboxylic acid and its 4-methyl- and 4-methoxy-substituted compounds display mainly nematogenic character, the acid itself, in contrast to its monotropic hydrogen analogue, being enantiotropic nematic. The case of the 4-trifluoromethyl derivative supports the regularity observed previously in the series of 4-perfluoroalkylbenzoic acids, i.e., that introduction of an electron-withdrawing substituent into the aromatic ring of a mesogen with a conjugated system, prevents the appearance of liquid-crystalline properties.



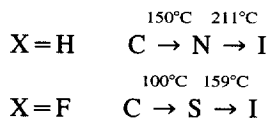
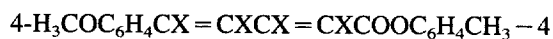
5-(4-Trifluoromethylphenyl)perfluoro-2,4-pentadienecarboxylic acid esters form a nematic phase [75].



76°C 101°C  
C → N → I

Unexpectedly, 4-tolyl-[5-(4-methoxyphenyl)perfluoro-2,4-

pentadiene]carboxylate proved to be smectic, in contrast to the hydrogen analogue which is nematic.

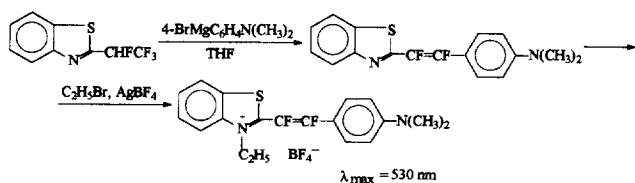


The nematogenic effect observed in the perfluoropolyene mesogens series is conditioned by their past history—the character of the crystal packing of the molecules. The type of phase is also connected with weakening of the lateral and intramolecular interactions, that favour the formation of the layer molecular arrangement of mesogens in smectics.

### 9. Dyestuffs with fluorinated polymethine chains

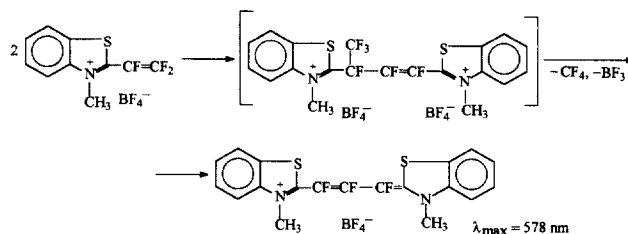
The establishment of electronic effect transmission in the fluorinated polyene chains stimulated the synthesis of dyes with  $-\text{CF}=\text{CF}-$  and  $-\text{CF}=\text{CF}-\text{CF}=\text{CF}-$  links, i.e., styryl and thiocarbocyanine, respectively. These dyes are stable.

The styryl-dye with an  $\alpha,\beta$ -difluorovinylene group [76–78] shows the same absorption maximum as the nonfluorinated analogue (530 nm).



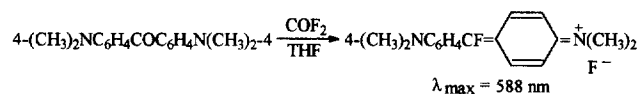
Fluorine atoms in the polymethine chain act as strong electron donating substituents due to their resonance effect. The latter alters the dye absorption maximum more strongly than does the inductive effect. A fluorine atom in the  $\alpha$ -position of the polymethine chain, like other electron-donating substituents, shifts the absorption maximum towards longer wavelengths. A fluorine atom in the  $\beta$ -position of polymethine chain shifts the absorption maximum to shorter wavelengths. Thus, fluorine atoms in  $\alpha$ - and  $\beta$ -positions of polymethine chains of the styryl-dyes counterbalance their mutual influence and the absorption maxima of the dyes with vinylene and  $\alpha,\beta$ -difluorovinylene groups are identical.

It was of interest to elucidate the reason for the formation of systems with conjugated polyfluoromethine bonds observed by dimerization of a 2-trifluorovinylbenzothiazole quaternary salt in the presence of diethylaniline. The reaction occurs under mild conditions at ambient temperature and results in breaking the strong C–C bond with elimination of carbon tetrafluoride and boron trifluoride [79].

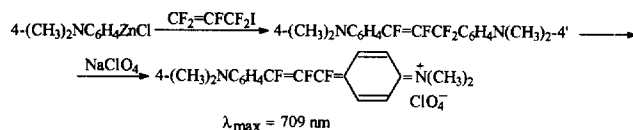


The thiocarbocyanine dye with a completely fluorinated trimethine chain turned out to be a stable, deeper coloured compound with a shift about 20 nm but shows the same absorption intensity as the dye with a unsubstituted chain.

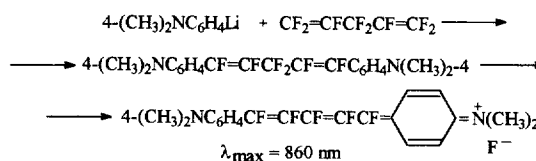
The simplest bis(dimethylaminophenyl)polyfluoromethine dye with the  $[4\text{-(CH}_3)_2\text{NC}_6\text{H}_4(\text{CF}=\text{CF})_n\text{-CFC}_6\text{H}_4\text{N(CH}_3)_2\text{-4}']$  structure ( $n=0$ ) was synthesized by heating bis(4-dimethylaminophenyl) ketone with carbonyl fluoride in THF in an autoclave at  $70^\circ\text{C}$  [80].



The second member of bis(dimethylaminophenyl)polyfluoromethine dyes ( $n=1$ ) was obtained by the reaction of 4-dimethylaminophenylzinc chloride with 1-iodoperfluoroprop-2-ene in THF at room temperature. The activated fluorine atom in the  $\text{CF}_2$ -group is substituted for  $\text{ClO}_4^-$  [81].



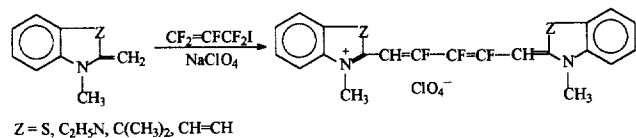
The polyfluoromethine dye containing two  $\alpha,\beta$ -difluorovinylene groups ( $n=2$ ) was prepared from 1,5-bis(4-dimethylaminophenyl)perfluoropenta-1,4-diene by the reaction of perfluoropenta-1,4-diene with 4-dimethylaminophenyllithium [81].



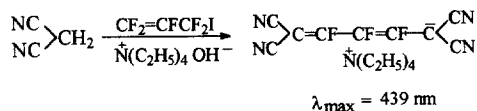
These polyfluoromethine dyes are unstable and readily hydrolyzed. The first member of the polymethine dye series has its absorption maximum shifted towards shorter wavelengths relative to the hydrogen analogue probably because of steric hindrance. The second and third members exhibit longer wavelength absorption due to the longer distance between the benzene rings. The shift in the absorption maximum corresponding to a difluorovinylene group in the polyfluoromethine dye series was ca. 1.5-times greater than that

of the hydrogen analogue being 120–150 nm. Based on quantum-chemical calculations, it has been shown that the shift corresponding to  $\alpha,\beta$ -difluorovinylene in polymethine dyes exceeds that of the vinylene group [82].

The interaction of heterocycle methylene bases with 1-iodoperfluoroprop-2-ene in acetonitrile results in the formation of  $\beta,\gamma,\delta$ -trifluorodicyanines [83,84].



The reaction is general and proceeds not only with methylene bases but also with other nucleophiles that are able to delocalize the negative charge. Thus, the reaction of malondinitrile with 1-iodoperfluoroprop-2-ene leads to the formation of an anionic dye with a completely fluorinated chain.



## 10. Abbreviations

Ar	Aryl
C	Crystal
DMF	<i>N,N</i> -Dimethylformamide
GLC	Gas–liquid chromatography
I	Isotropic liquid
IR	Infrared
N	Nematic phase
NMP	<i>N</i> -Methylpyrrolidone
S	Smectic phase
THF	Tetrahydrofuran
UV	Ultraviolet

## References

- [1] L.M. Yagupolskii, M.M. Kremlev, *Ukr. Khim. Zh.* 55 (1989) 943.
- [2] U.S. Patent 2668182 (1954), *Chem. Abstr.*, 49 (1955) 2478.
- [3] U.S. Patent 2777004 (1957), *Chem. Abstr.*, 51 (1957) 11370.
- [4] W.T. Miller, P.L. Ditton, R.L. Ehrenfeld, *Ind. Eng. Chem.* 39 (1947) 333.
- [5] A.L. Henne, Wm.J. Postelnek, *J. Am. Chem. Soc.* 77 (1955) 2334.
- [6] U.S. Patent 3046304 (1962), *Chem. Abstr.*, 58 (1963) 11217.
- [7] U.S. Patent 2745885 (1956), *Chem. Abstr.*, 51 (1957) 1242.
- [8] M.M. Kremlev, L.I. Moklyachuk, Yu.A. Fialkov, L.M. Yagupolskii, *Zh. Org. Khim.* 20 (1984) 1162.
- [9] M.M. Kremlev, P.G. Cherednichenko, L.I. Moklyachuk, L.M. Yagupolskii, *Zh. Org. Khim.* 25 (1989) 2582.

- [10] V.P. Sass, T.A. Nadervel, D.S. Rondarev, L.S. Bresler, S.V. Sokolov, *Zh. Org. Khim.* 9 (1973) 225.
- [11] R.N. Haszeldine, *J. Chem. Soc.* (1954) 4026.
- [12] C.R. Brundle, M.B. Robin, *J. Am. Chem. Soc.* 92 (1970) 5550.
- [13] J.C. Albright, J.R. Nielsen, *J. Chem. Phys.* 26 (1957) 370.
- [14] C.H. Chang, A.L. Andreasen, S.H. Bauer, *J. Org. Chem.* 36 (1971) 924.
- [15] U.S. Patent 2705228 (1955), *Chem. Abstr.*, 50 (1956) 2446.
- [16] V. Dedek, Z. Chvatal, *J. Fluor. Chem.* 31 (1986) 363.
- [17] V. Dedek, I. Linhart, M. Kovac, *Collect. Czech. Commun.* 50 (1985) 1714.
- [18] N. Jing, D.M. Lemal, *J. Org. Chem.* 59 (1994) 1844.
- [19] I.L. Knunyants, B.L. Dyatkin, L.S. German, *Dokl. Akad. Nauk SSSR* 124 (1959) 1065.
- [20] V. Dedek, M. Kovac, *Collect. Czech. Commun.* 44 (1979) 2660.
- [21] Wm.T. Miller, W. Frass, R.F. Resnick, *J. Am. Chem. Soc.* 83 (1961) 1767.
- [22] I.L. Knunyants, A.V. Fokin, Yu.M. Kosyrev, I.N. Sorokin, *Izv. Akad. Nauk SSSR, Ser. Khim.* N 10 (1963) 1772.
- [23] U.S. Patent 2729613 (1956), *Chem. Abstr.*, 50 (1956) 11365.
- [24] I.L. Karle, J. Karle, T.B. Owen, R.W. Brode, A.H. Fox, J.L. Hoard, *J. Am. Chem. Soc.* 86 (1964) 2353.
- [25] I.L. Knunyants, V.R. Polishchuk, *Uspekhi Khimii.* 44 (1975) 685.
- [26] R.E. Banks, M.G. Barlow, R.N. Haszeldine, *J. Chem. Soc.* (1965) 6149.
- [27] A.V. Fokin, A.T. Uzun, O.V. Dement'eva, *Zh. Obshch. Khim.* 37 (1967) 834.
- [28] N.V. Kazmina, I.L. Knunyants, E.I. Mysov, *Izv. Akad. Nauk SSSR, Ser. Khim.* N 10 (1975) 2379.
- [29] N.V. Kazmina, V.D. Lavrukhin, M.Yu. Antipin, A.I. Akhmedov, Yu.T. Struchkov, *Izv. Akad. Nauk SSSR, Ser. Khim.* N 4 (1981) 851.
- [30] N.V. Kazmina, L.S. Kurbakova, B.A. Leytes, B.A. Kvasov, E.I. Mysov, *Zh. Org. Khim.* 22 (1986) 1668.
- [31] A.L. Klebanskii, O.A. Timofeev, *Zh. Prikladn. Khim.* 32 (1959) 2064.
- [32] V. Dedek, R. Hrabal, P. Dedek, Presented at XIIth International Symposium of Fluorine Chemistry, Santa-Cruz, CA, USA, Abstract, 1988, p. 129.
- [33] R. Hrabal, Z. Chvatal, V. Dedek, *J. Fluor. Chem.* 63 (1993) 185.
- [34] S. Dixon, *J. Org. Chem.* 21 (1956) 400.
- [35] Yu.A. Fialkov, A.P. Sevastyan, V.A. Khranovskii, L.M. Yagupolskii, *Zh. Org. Khim.* 4 (1978) 1005.
- [36] L.M. Yagupolskii, A.P. Sevastyan, V.F. Bystrov, A.E. Lutskii, G.P. Syrova, E.M. Obukhova, V.M. Volchenok, *Zh. Obshch. Khim.* 38 (1968) 671.
- [37] L.M. Yagupolskii, A.P. Sevastyan, *Zh. Obsch. Khim.* 38 (1968) 1500.
- [38] L.M. Yagupolskii, M.M. Kremlev, Yu.A. Fialkov, V.A. Khranovskii, V.M. Yurchenko, *Zh. Org. Khim.* 12 (1976) 1589.
- [39] E.M. Panov, L.F. Rybakova, K.A. Kocheshkov, *Dokl. Akad. Nauk SSSR* 190 (1970) 122.
- [40] J.F. Normant, J.P. Foulon, D. Masure, J. Villieras, *Synthesis* N 2 (1975) 122.
- [41] L.M. Yagupolskii, M.M. Kremlev, V.A. Khranovskii, Yu.A. Fialkov, *Zh. Org. Khim.* 12 (1976) 1372.
- [42] M.M. Kremlev, P.G. Cherednichenko, L.M. Yagupolskii, *Zh. Org. Khim.* 23 (1987) 279.
- [43] L.M. Yagupolskii, M.M. Kremlev, Yu.A. Fialkov, V.A. Khranovskii, V.M. Yurchenko, *Zh. Org. Khim.* 13 (1977) 1561.
- [44] M.M. Kremlev, L.I. Moklyachuk, *Ukr. Khim. Zh.* 48 (1982) 64.
- [45] M.M. Kremlev, L.I. Moklyachuk, Yu.A. Fialkov, N.V. Ignatiev, L.M. Yagupolskii, *Zh. Org. Khim.* 21 (1985) 769.
- [46] L.M. Yagupolskii, P.G. Cherednichenko, M.M. Kremlev, *Zh. Org. Khim.* 23 (1987) 445.
- [47] L.M. Yagupolskii, M.M. Kremlev, L.I. Moklyachuk, Yu.A. Fialkov, *Zh. Org. Khim.* 21 (1985) 654.
- [48] L.M. Yagupolskii, A.S. Shtepanek, *Zh. Obshch. Khim.* 29 (1959) 3086.

- [49] A.B. Shtarev, M.M. Kremlev, Z. Chvatal, *J. Org. Chem.* 62 (1997) 3040.
- [50] L.M. Yagupolskii, P.G. Cherednichenko, S.V. Pazenok, M.M. Kremlev, *Zh. Org. Khim.* 24 (1988) 612.
- [51] A.P. Sevastyan, V.A. Khranovskii, Yu.A. Fialkov, L.M. Yagupolskii, *Zh. Org. Khim.* 10 (1974) 413.
- [52] A.P. Sevastyan, Yu.A. Fialkov, V.A. Khranovskii, L.M. Yagupolskii, *Zh. Org. Khim.* 14 (1978) 204.
- [53] S.N. Yarmolenko, Yu.A. Fialkov, M.M. Kremlev, L.M. Yagupolskii, *Zh. Org. Khim.* 24 (1988) 2584.
- [54] M.M. Kremlev, P.G. Cherednichenko, L.M. Yagupolskii, *Zh. Org. Khim.* 25 (1989) 1451.
- [55] V.N. Vasil'eva, K.A. Kocheshkov, *Dokl. Akad. Nauk SSSR* 153 (1963) 1325.
- [56] Yu.P. Egorov, V.A. Khranovskii, V.V. Rossikhin, N.F. Kovalenko, L.M. Yagupolskii, *Teoret. Eksp. Khim.* 6 (1970) 743.
- [57] S. Kashino, K. Ito, M. Haisa, *Bull. Soc. Chem. Jpn.* 52 (1974) 365.
- [58] V.M. Yurchenko, M.Yu. Antipin, Yu.T. Struchkov, L.M. Yagupolskii, *Cryst. Struct. Commun.* 7 (1978) 77.
- [59] V.M. Yurchenko, M.Yu. Antipin, Yu.T. Struchkov, L.M. Yagupolskii, *Cryst. Struct. Commun.* 7 (1978) 81.
- [60] V.M. Yurchenko, M.M. Kremlev, Yu.A. Fialkov, Yu.P. Egorov, V.P. Sass, L.M. Yagupolskii, *Teoret. Eksp. Khim.* 18 (1982) 745.
- [61] M.M. Kremlev, *Author's Abstr. Doc. Chem. Sci. Dis.*, Institute of Organic Chemistry, Kiev, 1993.
- [62] A. Parczewski, *Tetrahedron* 26 (1970) 3539.
- [63] N.D. Epiotis, *J. Am. Chem. Soc.* 95 (1973) 3087.
- [64] V.N. Vasil'eva, K.A. Kocheshkov, T.V. Talalaeva, L.F. Rybakova, *Dokl. Akad. Nauk SSSR* 143 (1962) 844.
- [65] L.M. Yagupolskii, A.P. Sevastyan, M.M. Kremlev, V.A. Khranovskii, Yu.A. Fialkov, *Zh. Org. Khim.* 12 (1976) 1967.
- [66] E.A. Lutskii, E.M. Obukhova, S.A. Volchenok, Yu.A. Fialkov, L.M. Yagupolskii, *Teoret. Eksp. Khim.* 3 (1967) 160.
- [67] L. Skulskii, *Bull. Acad. Polski, Ser. Khim.* 10 (1962) 201.
- [68] M.M. Kremlev, Yu.A. Fialkov, L.M. Yagupolskii, *Zh. Org. Khim.* 17 (1981) 332.
- [69] E.A. Drygailova, R.R. Kostikov, K.A. Ogloblin, *Zh. Org. Khim.* 14 (1978) 2008.
- [70] M.M. Kremlev, Yu.A. Fialkov, V.A. Khranovskii, L.M. Yagupolskii, *Zh. Org. Khim.* 15 (1979) 2066.
- [71] M.M. Kremlev, I.S. Mazny, Yu.L. Yagupolskii, *Zh. Org. Khim.* 28 (1992) 982.
- [72] J.L. Everett, A.R. Kon, *J. Chem. Soc.* (1950) 3131.
- [73] V.M. Yurchenko, Yu.P. Egorov, V.A. Khranovskii, M.M. Kremlev, Yu.A. Fialkov, A.P. Sevastyan, L.M. Yagupolskii, *Ukr. Fiz. Zh.* 23 (1978) 337.
- [74] D. Demus, H. Zschke, *Flussige Kristalle in Tabellen*. VEB Deutscher Verlag für Grundstoffindustrie, Leipzig, 1974, p. 52.
- [75] L.I. Moklyachuk, M.Yu. Kornilov, Yu.A. Fialkov, M.M. Kremlev, L.M. Yagupolskii, *Zh. Org. Khim.* 26 (1990) 1533.
- [76] B.E. Gruz, L.I. Katerinenko, L.M. Yagupolskii, *Zh. Obshch. Khim.* 37 (1967) 2029.
- [77] L.M. Yagupolskii, B.E. Gruz, *Zh. Obshch. Khim.* 37 (1967) 2470.
- [78] L.M. Yagupolskii, A.Ya. Ilchenko, L.Z. Gandelsman, *Uspekhi Khimii* 52 (1983) 1732.
- [79] L.M. Yagupolskii, M.M. Kulchitskii, A.Ya. Ilchenko, *Zh. Org. Khim.* 8 (1972) 2447.
- [80] A.Ya. Ilchenko, R.E. Kovalchuk, L.M. Yagupolskii, *Zh. Org. Khim.* 9 (1973) 1744.
- [81] L.M. Yagupolskii, M.M. Kremlev, *J. Fluor. Chem.* 67 (1994) 241.
- [82] G.G. Dyadusha, M.N. Ushomirskii, *Zh. Strukt. Khim.* N 1 (1987) 17.
- [83] S.V. Pazenok, I.P. Kovtyukh, L.M. Yagupolskii, *Tetrahedron Lett.* 32 (1991) 4595.
- [84] L.M. Yagupolskii, S.V. Pazenok, A.Ya. Zapevalov, *Zh. Org. Khim.* 29 (1993) 2438.