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Reactions of Fluoronitrobenzenes with TBD in Acetonitrile in the Presence of Water Molecules*

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Products of the reaction between three fluorinated nitrobenzenes (2,3,4,6-tetrafluoronitrobenzene, mNF4; 2,3,4,5-tetrafluoronitrobenzene, oNF4; pentafluoronitro-benzene, NF5) and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) in the presence of the water molecules in acetonitrile were isolated and identified by analytical and spectroscopic methods. The reaction products included *ortho* and *para* substituted nitro-compounds. The kinetics of these reactions is independent of the substrates studied. The rate-determining step of these reactions is the hydrolysis of one ring of the TBD molecule after the fast formation of the Meisenheimer complex. The mechanism of these reactions and the structures of the products are discussed.

Key words: fluorinated compounds, fluorinated nitrobenzene, TBD, NMR studies, kinetics

The base of guanidine-like character 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) [1] belongs to a group of very strong N-bases ($pK_a = 24.97$) with small nucleophilicity [2–5]. Amidines and guanidines are very important agents in the deprotonation reactions of weak O–H [6–10] , N–H [11–13] and C–H [14–16] acids, whereas after protonation all of them, except for MTBD (7-methy-1,5,7-triazabicyclo[4.4.0]dec-5-ene), can form homoconjugated complexes [17]. Furthermore, in our previous works we have demonstrated that TBD with phenols, 2,2′-biphenols and N-H acids can form hydrogen-bonded chains of complicated structures, both in solutions and in solid state [18–20].

Recently, we have also demonstrated that the reaction between tetramethylguanidine and fluorinated nitrobenzenes yielded *ortho* and *para* substituted products *via* Meisenheimer complexes, whereas the TBD molecule reacts with chloropentafluorobenzene yielding a derivative of benzimidazole after the hydrolysis of the N-base with formation of amine, known as hard nucleophile [21,22]. Furthermore, in the reaction of MTBD and fluorinated benzoic acid a decarboxylation was observed leading to fluorinated benzene [23].

In this work we report results of spectroscopic and kinetic study of reactions of three fluorinated nitrobenzenes (Scheme 1) with TBD in acetonitrile. We isolated all the reaction products and identified them by spectroscopic methods (Scheme 2).

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* Dedicated to Prof. M. Szafran on the occasion of his 70th birthday.

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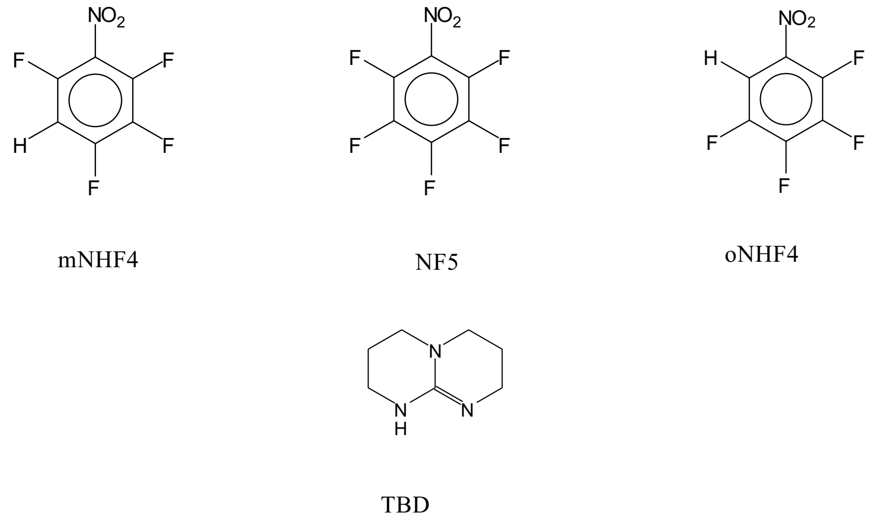
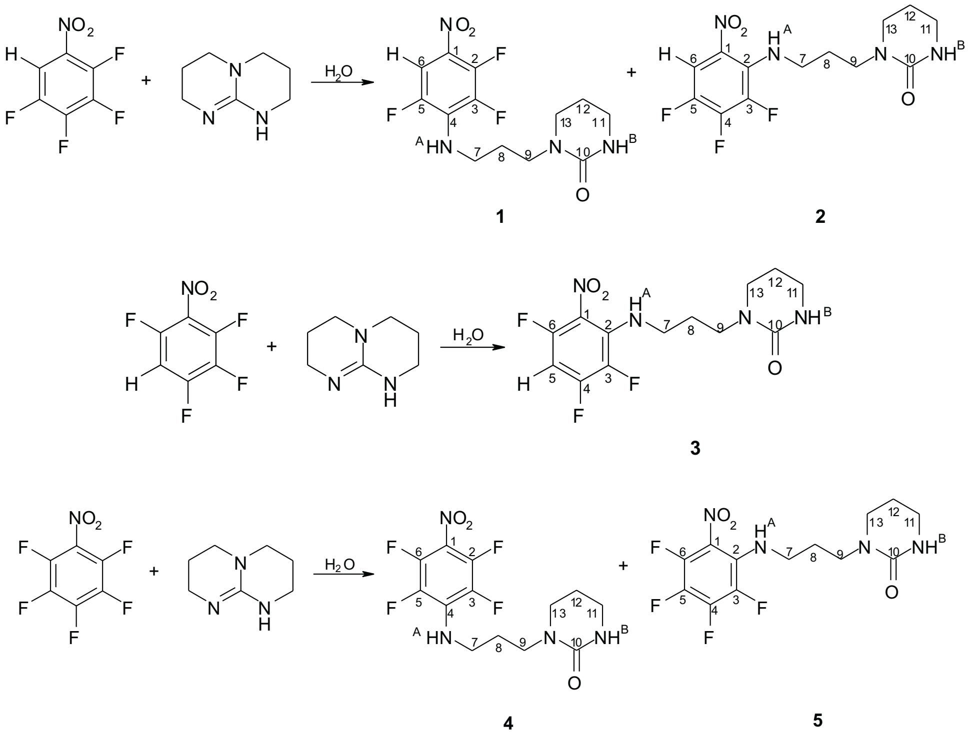
Scheme 1



Scheme 2



RESULTS AND DISCUSSION

The reaction between TBD and fluorinated nitrobenzenes in the presence of water yielded *ortho* and *para* substituted novel compounds **1–5**. In all cases the bicycled structure of the TBD base was eliminated as shown in Scheme 2. This scheme also gives the numbering of the atoms. The isolation and determination of the products (compounds **1–5**) was necessary to carry out a correct discussion of the spectroscopic data and kinetics of the reactions investigated. The structures of compounds **1–5** were determined by ^{1}H, ^{17}F NMR and spectroscopic methods. The UV-VIS data are collected in Table 1. The *ortho* and *para* isomers, formed in the reaction between TBD and NF5 or oNF4, cannot be separated. Therefore, the NMR spectra and the respective physicochemical properties are measured for their mixtures.

The ^{1}H, and ^{19}F spectroscopic data are given in Tables 2–3.

Table 1. Melting points and UV-VIS data for compounds **1–5**.

Compound	UV-VIS data		Yield	Melting point
	λ_{max} [nm]	ε [$1\times mol^{-1}\times cm^{-1}$]		
1	378	3.91×10^5	15%	
2	375	3.85×10^5	62%	132–138°C
3	362	3.39×10^5	78%	162–163°C
4	380	2.90×10^5	40%	
5	398	3.04×10^5	32%	174–184°C

The ^{1}H NMR spectra of compounds **1–5** are very complex because of the presence of fluorine atoms and their additional couplings with hydrogen nucleus. An additional complication is observed in the spectra of the mixtures of isomers **1** and **2** as well as **4** and **5** because the signals are strongly overlapped. Due to this reason, the exact chemical shifts of the aliphatic protons in the spectra cannot be determined. In the ^{1}H NMR spectrum of product **3**, which is a pure *ortho*-isomer, typical multiplets of two $A_2B_2C_2$ systems are observed. The H7 protons are additionally coupled with NH(A) proton and F3 atom. The H11 proton signal is split because of H11 coupling with the NH(B) hydrogen atom. The signals of both NH protons are so broadened that no couplings or multiplicity in then are found. The hydrogen atom at the benzene ring couples with all fluorine atoms at this ring and their coupling constants decrease going from J^3_{HF} to J^5_{HF} (Table 2).

The ^{19}F NMR spectra of compounds **1–5** are also very complex because of the fluorine – fluorine couplings (Table 3) but the spectral features are different for *ortho* and *para* isomers. Therefore, these spectra are very informative in respect of the identification of the isomers. For instance, for compound **4** because of its structural symmetry the simplest ^{19}F NMR spectrum showing only two doublets is observed, typical of AA'BB' spin system. For compound **5**, *ortho* isomer of compound **4**, which contains the ABCD spin system, the respective spectrum is much more complicated.

Table 2. ^{1}H NMR chemical shifts (ppm) and J_{CF} coupling constants (Hz) for compounds **1–5** [a].

Compound	Chemical shift and coupling constants									
	H5	H6	H7	H8	H9	H11	H12	H13	NH(A)[b]	NH(B)[b]
1	–	6.93 ddd $^3J_{HF} = 12.9$ $^4J_{HF} = 7.2$ $^5J_{HF} = 1.9$	3.6 m	1.7 m	3.40 m	3.30 m	1.9 m	3.30 m	7.26 bt	5.56 bs
2	–	7.97 ddd $^3J_{HF} = 11.0$ $^4J_{HF} = 8.4$ $^5J_{HF} = 2.2$	3.6 m	1.7 m	3.40 m	3.30 m	1.9 m	3.30 m	8.22 bs	5.74 bs
3	6.29 td $^3J_{HF} = {}^{3'}J_{HF} = 10.6$ $^4J_{HF} = 6.1$	–	3.48 dtd $^3J_{HH} = 3.6$ $^3J_{HH} = 6.1$ $^5J_{HF} = 6.3$	1.78 q $^3J_{HH} = 6.1$	3.43 t $^3J_{HH} = 6.1$	3.34 td $^3J_{HH} = 2.5$ $^3J_{HH} = 5.8$	1.94 q $^3J_{HH} = 5.8$	3.26 t $^3J_{HH} = 5.8$	7.25 bs	5.67 bs
4	–	–	3.34 m	1.75 m	3.26 m	3.42 m	1.96 m	3.50 m	6.97 bt	4.87 bs
5	–	–	3.34 m	1.75 m	3.26 m	3.42 m	1.96 m	3.50 m	6.85 bs	4.78 bs

[a] b, broad; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet

[b] chemical shifts strongly depend on concentration, temperature and water presence

Table 3. ^{19}F chemical shift (ppm) and J_{FF} coupling constants (Hz) for compounds **1–5**[a].

Compound	Chemical shift and coupling constants				
	F2	F3	F4	F5	F6
1	–146.0 dt $^3J_{FF} = 18.5$ $^4J_{HF} = 7.2$	–156.0 dd $^3J_{FF} = 18.5$ $^4J_{FF} = 14.0$	–	–134.5 m	–
2	–	–148.5 bd $^3J_{FF} = \sim 20$	–149.2 ddd $^3J_{FF} = 22.1$ $^3J_{FF} = 20.3$ $^4J_{HF} = 8.4$	–151.5 dtd $^3J_{FF} = 22.1$ $^3J_{HF} = 11.0$ $^4J_{FF} = 2.3$	–
3	–	–158.8 dddt $^4J_{HF} = 6.1$ $^4J_{HF} = 6.3$ $^3J_{FF} = 18.8$ $^5J_{FF} = 10.6$	–126.9 ddd $^3J_{HF} = 10.6$ $^3J_{FF} = 18.8$ $^4J_{FF} = 7.6$	–	–119.7 td $^3J_{HF} = {}^5J_{FF} = 10.6$ $^4J_{FF} = 7.6$
4	–147.5 d $^3J_{FF} = 17.2$	–161.3 d $^3J_{FF} = 17.2$	–	–161.3 d $^3J_{FF} = 17.2$	–147.5 d $^3J_{FF} = 17.2$
5	–	–156.3 ddd $^3J_{FF} = 20.0$ $^4J_{FF} = 6.7$ $^5J_{FF} = 5.0$	–148.4 td $^3J_{FF} = {}^{3'}J_{FF} = 20.0$ $^4J_{FF} = 7.0$	–172.1 td $^3J_{FF} = {}^{3'}J_{FF} = 20.0$ $^4J_{FF} = 6.7$	–145.3 ddd $^3J_{FF} = 20.0$ $^4J_{FF} = 7.0$ $^5J_{FF} = 5.0$

[a] b, broad; d, doublet; t, triplet

The kinetic data for the reactions of TBD with fluorinated nitrobenzenes are collected in Tables 4–6. A comparison of the rate constants and thermodynamic data for these reactions demonstrates that all these values are independent of the substituted nitrobenzenes. Thus, the rate-determining steps of all the reactions are similar and independent of the *ortho* and *para* substitution at the fluorinated benzene ring. The question arises what is this reaction. In the previous work, we observed that the TBD base reacts with water molecule yielding 1,3,7-triaza-2-oxo-decane, which further condenses with chloropentafluorobenzene yielding benzimidazole derivative. In this work we have obtained different compounds, *i.e.* derivative of N-aminopropyl-2-piperimidone. This result already suggests a different pathway of the reactions studied than that of the reaction observed between TBD and chloropentafluorobenzene [22]. The vanishing of the Bohlmann bands [24–26], observed in the FT-IR spectrum of TBD, in the spectra of the mixtures of fluorinated benzenes with TBD without water molecules indicates the formation of the Meisenheimer complexes. For NF5 the respective complexes are formed quantitatively on the spectroscopic scale, whereas for the mixtures of tetrafluorinated nitrobenzenes an equilibrium shown in Scheme 3 is realized. Thus, the rate determining step is the hydrolysis of one ring of TBD molecule within the Meisenheimer complex, as shown in Scheme 4, and it is understandable that the kinetics and thermodynamic data of such reactions are similar.

Table 4. Kinetic parameters (± standard deviation) for reaction of TBD with mNHF4 in acetonitrile/water solution.

Temp. °C	k_{obs} [s^{-1}] for the base concentration			k [M^{-1} s^{-1}]	int [s^{-1}]	$\Delta H^{\#}$ [kJ mol^{-1}]	$-\Delta S^{\#}$ [J mol^{-1} deg^{-1}]	$\Delta G^{\#}$ [kJ mol^{-1}]
	0.0050 [M]	0.0100 [M]	0.0150 [M]					
5	0.0054±0.0003	0.0108±0.0001	0.0155±0.0001	1.01±0.04	0.0005±0.0001	40.7±1.6	99±5	70.4±1.6
10	0.0059±0.0001	0.0124±0.0002	0.0180±0.0003	1.21±0.05	0.0005±0.0001			
15	0.0080±0.0003	0.0155±0.0002	0.0229±0.0004	1.49±0.01	0.0005±0.0001			
20	0.0109±0.0005	0.0211±0.0003	0.0320±0.0004	2.11±0.04	0.0002±0.0001			
25	0.0137±0.0007	0.0267±0.0003	0.0399±0.0005	2.62±0.01	0.0004±0.0001			
30	0.0187±0.0007	0.0360±0.0005	0.0548±0.0005	3.61±0.09	0.0004±0.0001			
35	0.0265±0.0007	0.0534±0.0005	0.0790±0.0006	5.25±0.07	0.0004±0.0001			
40	0.0367±0.0007	0.0725±0.0006	0.1070±0.0005	7.03±0.08	0.0017±0.0008			
45	0.0486±0.0008	0.0971±0.008	0.1451±0.0007	9.65±0.03	0.0004±0.0003			
50	0.0651±0.0011	0.1302±0.0009	0.1875±0.0009	12.24±0.05	0.0052±0.0011			

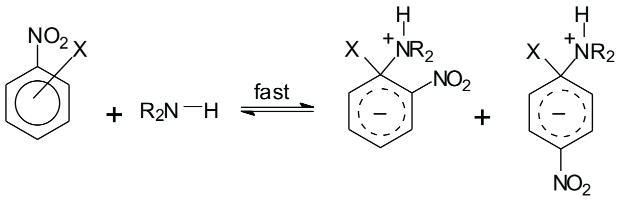
Table 5. Kinetic parameters (± standard deviation) for reaction of TBD with oNHF4 in acetonitrile/water solution.

Temp. °C	k_{obs} [s^{-1}] for the base concentration			k [M^{-1} s^{-1}]	int [s^{-1}]	$\Delta H^{\#}$ [kJ mol^{-1}]	$-\Delta S^{\#}$ [J mol^{-1} deg^{-1}]	$\Delta G^{\#}$ [kJ mol^{-1}]
	0.0050 [M]	0.0100 [M]	0.0150 [M]					
5	0.0049±0.0003	0.0100±0.0001	0.0153±0.0001	1.04±0.01	0.0006±0.0001	40.1±2.6	102±9	70.6±2.6
10	0.0051±0.0002	0.0115±0.0002	0.0168±0.0003	1.11±0.06	0.0004±0.0006			
15	0.0065±0.0003	0.0128±0.0002	0.0187±0.0005	1.22±0.02	0.0005±0.0002			
20	0.0091±0.0004	0.0175±0.0004	0.0287±0.0005	1.96±0.16	0.0000±0.0001			
25	0.0125±0.00009	0.0260±0.0004	0.0379±0.0004	2.54±0.09	0.0001±0.0001			
30	0.0165±0.0007	0.0322±0.0003	0.0499±0.0006	3.34±0.11	0.0001±0.0001			
35	0.0198±0.0006	0.0400±0.0006	0.0589±0.0007	3.91±0.07	0.0004±0.0001			
40	0.0323±0.0006	0.0635±0.0006	0.0961±0.0004	6.38±0.08	0.0017±0.0008			
45	0.0444±0.0009	0.0875±0.005	0.1341±0.0007	8.97±0.20	0.0004±0.0003			
50	0.0581±0.0012	0.1100±0.0010	0.1766±0.0011	11.85±0.24	0.0000±0.0010			

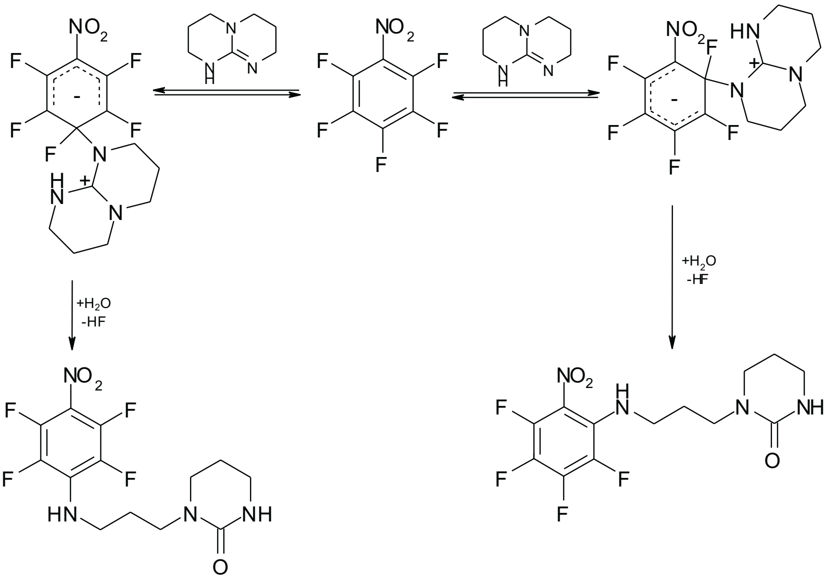
Table 6. Kinetic parameters (± standard deviation) for reaction of TBD with NF5 in acetonitrile/water solution.

Temp. °C	k_{obs} [s^{-1}] for the base concentration			k [M^{-1} s^{-1}]	int [s^{-1}]	$\Delta H^{\#}$ [kJ mol^{-1}]	$-\Delta S^{\#}$ [J mol^{-1} deg^{-1}]	$\Delta G^{\#}$ [kJ mol^{-1}]
	0.005 [M]	0.01 [M]	0.015 [M]					
5	0.0050±0.0004	0.0102±0.0006	0.0150±0.0007	1.00±0.02	0.0000±0.0000	40.3±2.4	101±8	70.5±2.4
10	0.0054±0.0004	0.0120±0.0003	0.0172±0.0004	1.18±0.02	0.0003±0.0001			
15	0.0070±0.0002	0.0140±0.0004	0.0202±0.0003	1.32±0.05	0.0005±0.0001			
20	0.0100±0.0006	0.0195±0.0003	0.0297±0.0006	1.97±0.03	0.0000±0.0000			
25	0.0131±0.0007	0.0266±0.0002	0.0409±0.0007	2.78±0.02	0.0009±0.0002			
30	0.0177±0.0002	0.0342±0.0002	0.0512±0.0006	3.35±0.08	0.0009±0.0001			
35	0.0225±0.0004	0.0453±0.0003	0.0615±0.0007	3.90±0.05	0.0041±0.0001			
40	0.0341±0.0002	0.0690±0.0002	0.1013±0.0002	6.72±0.08	0.0009±0.0001			
45	0.0460±0.0003	0.0925±0.0004	0.1395±0.0003	9.35±0.02	0.0008±0.0002			
50	0.0605±0.0003	0.1154±0.0006	0.1829±0.0007	12.24±0.05	0.0028±0.0001			

Scheme 3



Scheme 4



EXPERIMENTAL

2,3,4,6-Tetrafluoronitrobenzene, 2,3,4,5-tetrafluoronitrobenzene, pentafluoronitrobenzene and TBD (Scheme 1) were purchased from Aldrich and were used without any purification.

Synthesis: To the solution of fluorinated-nitrobenzene (0.01 mol) in acetonitrile (50 cm^3), containing water (0.012 mol), TBD was added (0.01 mol). The mixture was heated under reflux for 6 h and then the solvent was evaporated. The semisolid residue was dissolved in diethyl ether and the solution was dried over $MgSO_4$. After the solvent removal the product was purified by column chromatography on SiO_2, using hexane-acetone 1:1 mixture as an eluent. The combined fractions were evaporated to dryness under reduced pressure. The melting points and the UV-VIS data are given in Table 1.

NMR measurements: ^{1}H, and ^{19}F NMR spectra were recorded on Varian-Gemini 300 spectrophotometer at 300.075, 75.461 and 282.352 MHz respectively in 0.1 M [^{2}H]$_6$-acetone solutions in 5 mm tubes. The chemical shifts were measured to an internal standard (TMS for ^{1}H and $CFCl_3$ for ^{19}F NMR spectra; $\delta = 0.000$ ppm). For ^{1}H NMR spectra 60° pulse widths, 4500 Hz spectral widths; 2 s acquisition time; 32 k FT-size.

The ^{19}F NMR spectra were measured with spectral width 128 k, 60° pulse widths and 0.64 s acquisition time.

Kinetic measurements: The kinetic runs were carried out using a diode-array spectrophotometer (Agilent 8452) with the cellblock thermostated to +/–0.1°C. The kinetic runs were completed under pseudo-first-order conditions with the base concentration in large excess. The observed rate constants were calculated from the traces of absorbance *vs.* time. The kinetic curves in all cases are exponential.

The observed rate constant k_{obs} depends on the base concentration and is given by the equation: $k_{obs} = k[B] + k_{-}$, where k is the rate constant for the forward reactions for *ortho* and *para* products, k_{-} (int) is the rate constant for the reverse reactions, [B] is the initial base concentration. The int values are almost zero, *i.e.*, the studied reactions are irreversible. The exponential character of the kinetic curves indicates that the rate constants of the *ortho* and *para* products formation are almost similar. Rate constants of the forward (k) reaction were calculated by the linear least-squares fit of the variation of k_{obs} *vs.* base concentration. The activation parameters were calculated by the linear least-squares fit of ln k *vs.* 1/T.

UV-VIS measurements: The UV-VIS spectra were recorded in CH_3CN on an Agilent 8453 spectrometer using a 1 cm cell thick and the samples of the concentration 5×10^{-4} mol dm^{-3}. The characteristic data obtained from these spectra are collected in Table 1.

REFERENCES

1. Schwesinger R., Willaredt J., Schlemper H., Keller M., Schmitt D. and Fritz H., *Chem. Ber.*, **127**, 2435 (1994).
2. Schwesinger R., *Nachr. Chem. Tech. Lab.*, **38**, 1214 (1990).
3. Pietzonka T. and Seebach D., *Chem. Ber.*, **124**, 1837 (1990).
4. Gais H.-J., Vollhardt J. and Kürger C., *Angew. Chem.*, **100**, 108 (1988).
5. Fletschinger M., Zipperer B., Fritz H. and Prinzbach H., *Tetrahedron Lett.*, **28**, 2517 (1987).
6. Brzezinski B., Schroeder G., Grech E., Malarski Z., Rospenk M. and Sobczyk L., *J. Chem. Res. (S)*, 151 (1997); *J. Chem. Res. (M)*, 1021 (1997).
7. Brzezinski B., Radziejewski P. and Zundel G., *J. Chem. Soc. Farad. Trans*., **91**, 3141 (1995).
8. Brzezinski B. and Zundel G., *J. Mol. Struct.*, **380**, 195 (1996).
9. Wojciechowski G., Schroeder G., Zundel G. and Brzezinski B., *J. Phys. Chem. A*, **104**, 7469 (2000).
10. Brzezinski B., Wojciechowski G., Bartl F. and Zundel G., *J. Mol. Struct.*, **554**, 245 (2000).
11. Brzezinski B., Wojciechowski G., Zundel G., Sobczyk L. and Grech E., *J. Mol. Struct*., **508**, 175 (1999).
12. Brzezinski B. and Zundel G., *J. Mol. Struct.*, **446**, 199 (1998).
13. Brzezinski B., Bauer R. and Zundel G., *J. Mol. Struct.*, **436–437**, 297 (1997).
14. Schroeder G., Łeska B., Bartl F., Różalski B. and Brzezinski B., *J. Mol. Struct.*, **478**, 255 (1999).
15. Schroeder G., Łęska B., Gierczyk B., Rózalski B. and Brzezinski B., *J. Mol. Struct*., **476**, 173 (1999).
16. Schroeder G., Brzezinski B., Jarczewski A., Grech E. and Nowicka-Scheibe J., *J. Mol. Struct.*, **344**, 89 (1995).
17. Gałęzowski W., Jarczewski A., Stańczyk M., Brzezinski B., Bartl F. and Zundel G., *J. Chem. Soc. Farad. Trans.*, **93**, 2515 (1997).
18. Wojciechowski G., Brzezinski B., Naumov P., Chantrapromma S. Ibrahim A.R., Fun H.-K. and Ng S.W., *J. Mol. Struct.*, **598**, 153 (2001).
19. Ng S.W., Naumov P., Chantrapromma S., Raj S.S.S., Fun H.-K., Ibrahim A.R., Wojciechowski G. and Brzezinski B., *J. Mol. Struct.*, **569**, 139 (2001).
20. Ng S.W., Chantrapromma S., Raj S.S.S., Fun H.-K., Ibrahim A.R.,Wojciechowski G. and Brzezinski B., *J. Mol. Struct.*, **562**, 185 (2001).
21. Schroeder G., Eitner K., Gierczyk B., Różalski B. and Brzezinski B., *J. Mol. Struct.*, **478**, 243 (1999).
22. Gierczyk B., Schroeder G. and Brzezinski B., *J. Org. Chem*., **68**, 3139 (2003).
23. Gierczyk B., Wojciechowski G., Brzezinski B., Grech E. and Schroeder G., *J. Phys. Org. Chem.*, **14**, 1 (2001).
24. Bohlmann F., *Angew. Chem.*, **69**, 64 (1957).
25. Bohlmann F., *Chem. Ber.*, **91**, 2157 (1958).
26. Konarski J., *J. Mol. Struct.*, **7**, 337 (1971).