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Interaction of polyfluoroaromatic imidoyl chloride derivatives with compounds containing nitrogen–carbon multiple bonds in the presence of $AlCl_3$

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Abstract

Interactions of polyfluoroaromatic imidoyl chloride derivatives with compounds containing nitrogen–carbon multiple bond in the presence of $AlCl_3$ proceed as a cycloaddition type process and lead to five- or six-membered N-containing ring systems. *N*-(*p*-R–tetrafluorophenyl)carbonimidoyl dichlorides ($R = F, CH_3$) react with *N*-pentafluorophenyltrichloroacetimidoyl chloride and $AlCl_3$ to give in good yields 1-(*p*-R–tetrafluorophenyl)-3-pentafluorophenyl-4,4,5,5-tetrachloro-2-imidazolidones. *N*-Pentafluorophenyltrichloroacetimidoyl chloride "dimerizes" by heating with $AlCl_3$ to 1,3-bis(pentafluorophenyl)-4,5-dichloro-2-imidazolone. This compound was also obtained from 1,3-bis(pentafluorophenyl)-4,4,5,5-tetrachloro-2-imidazolidone under the action of $AlCl_3$. Heating of 1,3-bis(pentafluorophenyl)-4,4,5,5-tetrachloro-2-imidazolidone with $AlCl_3$ in toluene leads to 1,3-bis(pentafluorophenyl)-4,5-dichloro-2-imidazolone and its 5-tolyl derivatives as a result of a reaction with toluene. Interaction of *N*-pentafluorophenylcarbonimidoyl dichloride with benzonitrile and $AlCl_3$ leads to 1-pentafluorophenyl-4,6-diphenyl-1,3,5-triazine-2-one along with *N*-pentafluorophenyl-*N*′-benzoylurea and an *N*-pentafluorophenylurea complex with benzamide. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Polyfluoroaromatic imidoyl chloride derivatives; 2-Imidazolidones; 2-Imidazolones; 1-Pentafluorophenyl-4,6-diphenyl-1,3,5-triazine-2-one; $AlCl_3$

1. Introduction

It is known that aromatic imidoyl chlorides react with Lewis acids to give nitrilium salts which can further interact with starting imidoyl chloride to give heterocyclic derivatives [1]. The transformation of perfluoroazapropene to the cyclic trimer — 1,3,5-tris(trifluoromethyl)hexafluorohexahydrotriazine [2] or 3,5-bis(trifluoromethyl)-4,4-difluorohexahydrotriazine-4,6-dione [3] under the action of SbF_5 has been shown. Nitrilium salts forming from *N*-arylimidoyl chloride derivatives by $AlCl_3$ react with aliphatic or aromatic nitriles to give new nitrilium salts which transform to quinazoline derivatives if at least one *ortho*-position in the *N*-aromatic ring of the starting imidoyl chloride derivative is unoccupied [4].

We have previously shown that polyfluoroarylimidoyl chlorides in the presence of $AlCl_3$ can act as efficient electrophilic reagents towards electron-donating substrates, for example, aromatic amines [5] or benzene and alkylbenzenes [6]. This work describes the ability of such electrophilic reagents to undergo cycloaddition reactions with compounds containing a nitrogen–carbon multiple bond (preliminary communication [7]).

2. Results and discussion

N-Pentafluorophenylcarbonimidoyl dichloride **1** did not change during heating with 1–3 mol of $AlCl_3$ at 110°C. At the same time *N*-pentafluorophenyltrichloroacetimidoyl chloride **2** under similar conditions turns into 1,3-bis(pentafluorophenyl)-4,5-dichloro-2-imidazolone **3** (Scheme 1).

Imidazolone **3** is probably formed as a result of a cyclic "dimerization" of **2** with subsequent hydrolysis of the product formed. This assumption is in agreement with the ability of **2** to undergo cycloaddition type reactions with imidoyl chlorides **1** and **4** in the presence of $AlCl_3$. Thus, the

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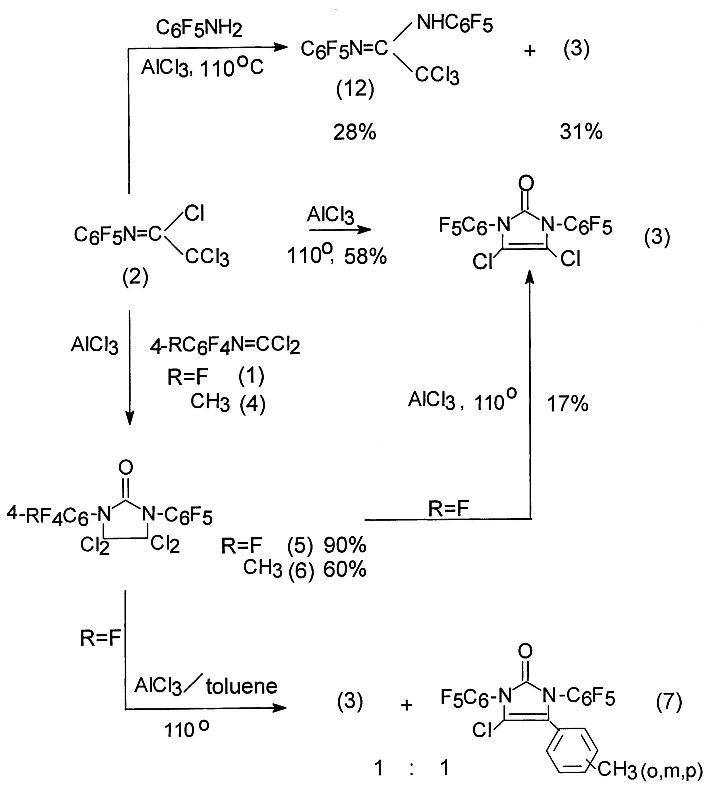


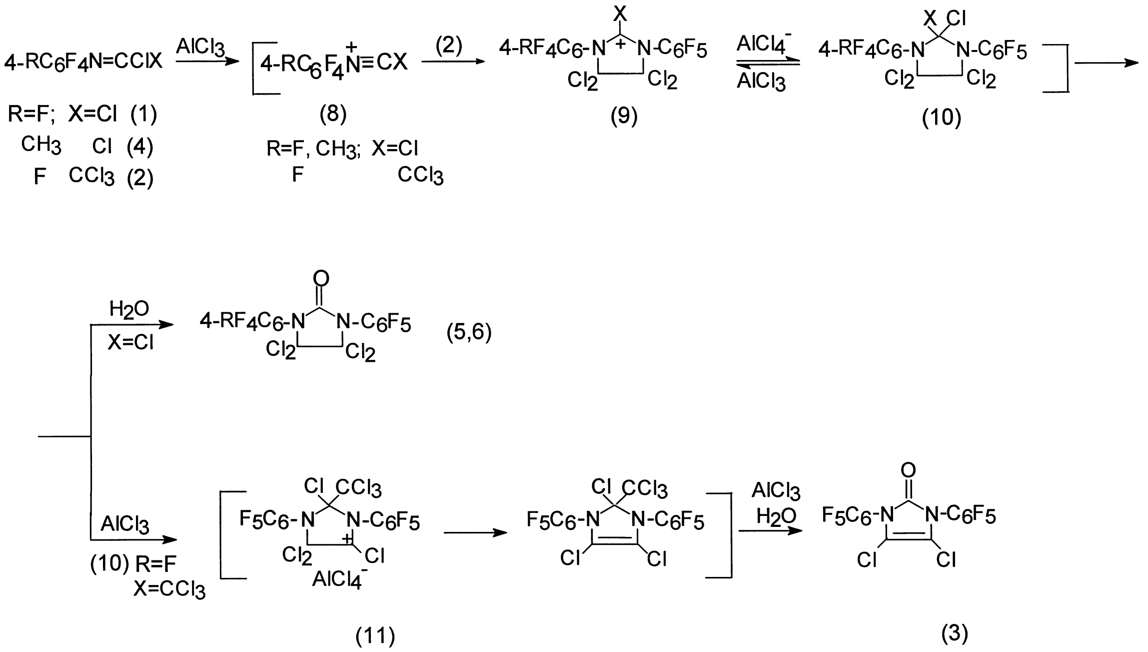
Scheme 1.

reaction of **2** with **1** in the presence of $AlCl_3$ at 110°C (7 h) gave 1,3-bis(pentafluorophenyl)-4,4,5,5-tetrachloro-2-imidazolidone **5** (~90% yield). Compound **2** reacts with *N*-(4-methyl-2,3,5,6-tetrafluorophenyl)carbonimidoyl dichloride **4** under similar conditions to give 1-pentafluorophenyl-3-(4′-methyl-2′,3′,5′,6′-tetrafluorophenyl)-4,4,5,5-tetrachloro-2-imidazolidone **6** (~60% yield). Formation of **5** from **1** and **2** is observed at 60°C to give 15–20% of **5** (GLC data). At a higher temperature (80°C), the yield of **5** may run to 90%. At the same time the imidoyl chloride **2** changes to a small extent at 80°C in the presence of $AlCl_3$. A reaction mixture containing only ~4% of **3** (GLC) was formed. The transformation of **2** under the action of $AlCl_3$ took place at a higher temperature (110°C).

It should be noted that the reaction of **2** with compounds **1** or **4** and $AlCl_3$ leads mainly to the corresponding imidazolidones **5** and **6**, but not the derivatives of imidazolone. The reaction mixture after interaction of the compounds **2** and **1** contained no or ~2% of imidazolone **3**. Compound **5** was partially transformed into imidazolone **3** when pure **5** was heated with $AlCl_3$ at 110°C. The reaction did not take place without $AlCl_3$. The attempt to increase the conversion of **5** into **3** by use of toluene as a solvent and potential chlorine acceptor led to the mixture of compound **3** and the products of interaction with toluene in the ratio ~1:1 (^{19}F NMR and GC–MS). These products **7** have the structure of 5-tolyl derivatives of 1,3-bis(pentafluorophenyl)-4-chloro-2-imidazolone with different positions of CH_3-groups in the aromatic ring. By GC–MS-analysis three isomers were monitored (38, 6 and 1%). The *p*-CH_3 isomer probably predominates. These isomers have identical ^{19}F NMR spectra. The reaction in toluene did not take place in the absence of $AlCl_3$. One of the possible schemes for the transformation is presented in Scheme 2.

According to this scheme a cationic intermediate having in the limit the structure of a nitrilium ion of type **8** is formed at the first stage of the reaction. The formation of such a type of a cationic intermediate from the compound **1** and $AlCl_3$ was previously proposed by us and supported by reactions with aromatic amines or benzene and alkylbenzenes [5,6]. This intermediate interacts with a molecule of **2** to give cyclic intermediate cation **9** stabilized by resonance participation of the nitrogen lone pairs. Intermediate **9** reacts with water to give compounds **5** and **6**. Intermediate **10** with $X = CCl_3$ with $AlCl_3$ could be transformed into a cationic intermediate **11**. In this intermediate spatial nonvalent “1,3-interaction” of the bulky CCl_3-group and a chlorine atom of the CCl_2-group may be hypothesized which should favor the rupture (for example, the heterolysis) of the C–Cl bond and the formation of the fragment with a double bond. Futher reactions with $AlCl_3$ and water could result in compound **3**.

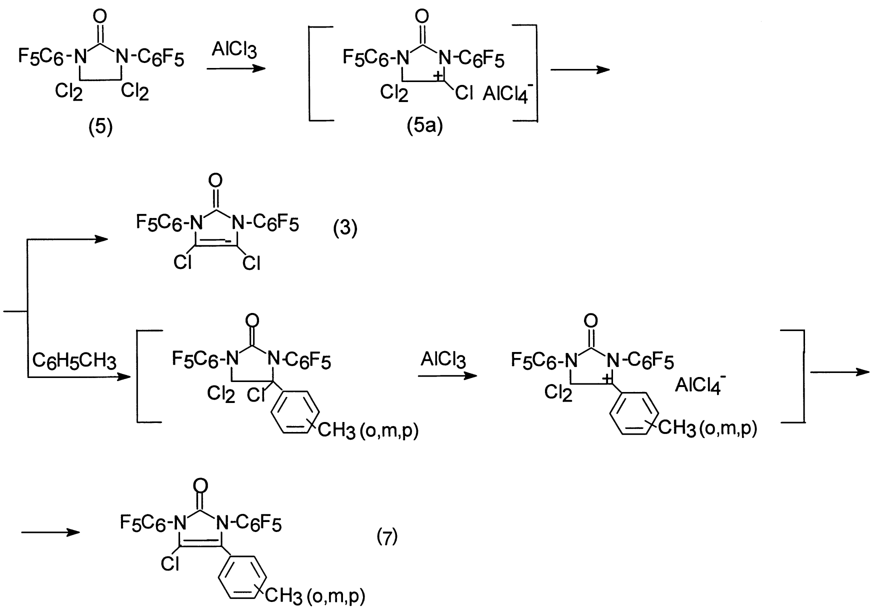
Reactions of compounds **1** or **4** with **2** proceed more readily than “dimerization” of **2** (lower temperature of the reactions and the higher yields of the end products). This could be explained by the ease of the formation of cationic intermediate **8** when X = Cl owing to increased stability of the former in comparison with $X = CCl_3$ as well as greater stability of **9** when X = Cl in comparison with $X = CCl_3$.



Scheme 2.

There is also the possibility of the formation of allylic type cationic intermediates [$C_6F_5N = CCl{-}CCl_2^+ \cdot AlCl_4^-$] from compound **2** and $AlCl_3$. The interaction of such an intermediate with **2** should also result in compound **3** but this possibility is less probable from the literature and our data about the reactivity of a trichloroacetimidoyl chloride group. According to Ref. [8], only the chlorine atom and C=N bond participate in a reaction, for example, with nucleophiles, CCl_3-group remains unchanged. According to our data, compound **2** reacts with pentafluoroaniline and $AlCl_3$ to give imidazolone **3** and *N*,*N*′-bis(pentafluorophenyl)trichloroacetamidine **12** (Scheme 1). The structure of compound **12** is supported by analytical and spectral data. The stability of this compound towards the action of a base on heating agrees with this structure.

It is reasonable to suppose the formation of cationic intermediates **11** in Scheme 2 taking into account data obtained in experiments with compound **5** and $AlCl_3$ in toluene. These can be explained by the proposal (Scheme 3) that imidazolone **5** reacts with $AlCl_3$ to give cationic inter-



Scheme 3.

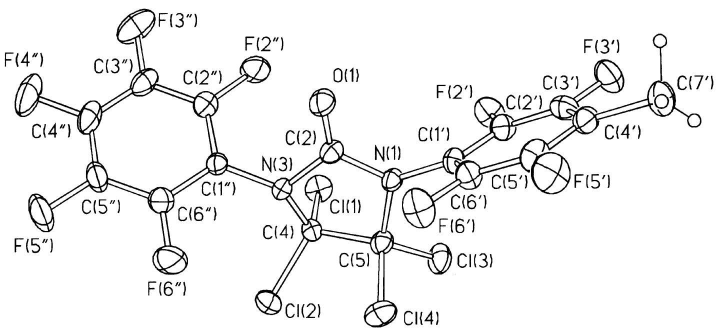


Fig. 1. X-ray crystal structure of 1-pentafluorophenyl-3-(4′-methyl-2′,3′,5′,6′-tetrafluorophenyl)-4.4.5,5-tetrachloro-2-imidazolidone **6**.

mediate **5a**, similarly **11** is transformed to **3** in the absence of toluene and to 5-tolyl derivatives **7** in the presence of toluene. Eclipsed interaction of the tolyl-group and chlorine atom should favor the rupture of the C–Cl bond and the formation of a double bond.

The structures of compounds **3**, **5**, **7** and **12** were established on the basis of their analytical and spectroscopic data and by comparison with analogues. The structure of compound **6** was determined by X-ray structural analysis (Fig. 1).

The results obtained by us in the study of interaction of carbonimidoyl dichloride **1** with nitriles are shown in Scheme 4.

Compound **1** did not react with acetonitrile on boiling in the presence of $AlCl_3$. The 1:1 reaction of **1** and $AlCl_3$ in benzonitrile at 150°C gave 1-pentafluorophenyl-4,6-diphenyl-1,3,5-triazine-2-one **13** although unreacted starting material **1** remained in the mixture (ratio of **1** and **13** was ~3:1 according to ^{19}F NMR data). A temperature rise to 175°C, increased the amount of $AlCl_3$ and further heating favored the formation of **13** although unreacted starting compound **1** also remained in the mixture. The reaction is complicated due to the formation of *N*-pentafluorophenyl-*N*′-benzoylurea **14** and of *N*-pentafluorophenylurea **15** which was isolated as a complex with benzamide **16**. Amide **16** could result from a side reaction. The suggested reaction Scheme 5 can explain the formation of observed products.

It can be supposed that a cationic intermediate formed from compound **1** and $AlCl_3$ reacts with benzonitrile to give a new intermediate. This reacting with another molecule of benzonitrile could be transformed to heterocycle **13** or hydrolyzed to ureas **14** and **15**. The compounds **15** and **16** formed gave a complex **17**.

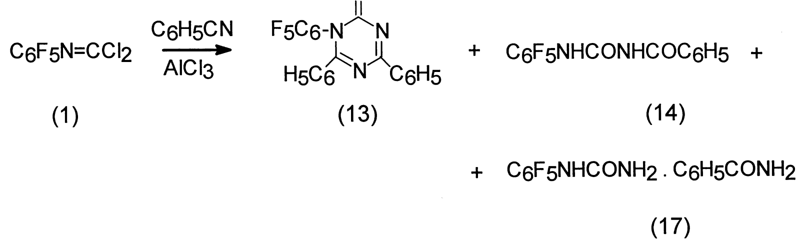
The structure of **13** was determined by X-ray structural analysis (Fig. 2).

The structure of **17** is based on X-ray structural analysis data (Fig. 3) and spectroscopic characteristics.

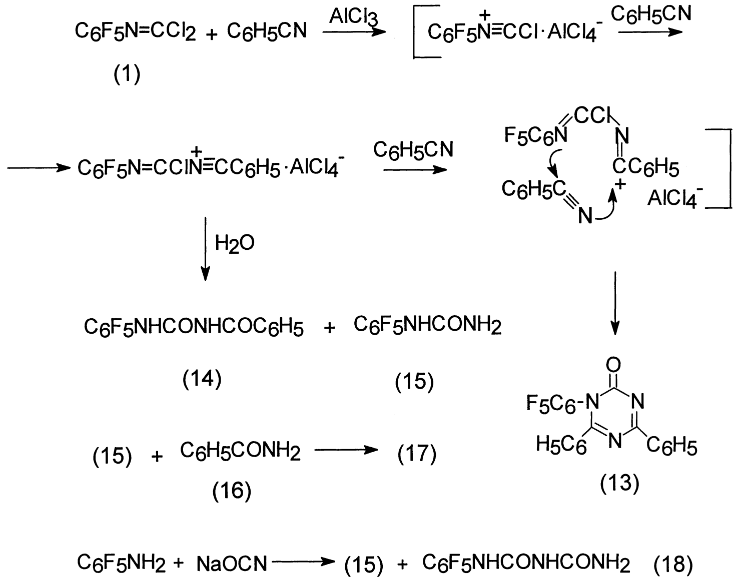
The ^{19}F NMR data for **17** are very similar to those for compound **15** obtained by us in the reaction of pentafluoroaniline with NaOCN (cf. [9]). 1-Pentafluorophenyl biuret **18** was also isolated from the reaction mixture along with **15**. Its ^{19}F NMR spectra is similar to that of compound **14**. This, together with PMR, IR and MS data confirms the structure of **14**.

3. Experimental

^{19}F and ^{1}H spectra were recorded on a Bruker WP-200SY instrument, internal standards were hexafluorobenzene (+162.9 ppm from CCl_3F) and hexamethyldisiloxane (0.04 ppm). IR spectra were measured on a Specord M-80 instrument for a 5% CCl_4 solution. GLC analyses were carried out on an LHM-7a instrument with a thermal conductivity detector and a linear temperature program of 10°C min, using internal normalization (180–270°C, a $4000 \times 4\ mm^2$ column packed with methylsilicon E-30, fluorosilicon QF-1/Chromosorb W, silicon SKTFT-50 and SKTFV-803/Celite, 5:100 and 15:100 with He carrier at 60 ml min^{-1}). Column chromatography was carried out on silica gel 140–315 mesh. GC–MS analyses of the reaction mixtures were performed with a Hewlett-Packard apparatus 5890 (70 eV) using a 30 m capillary column coated with



Scheme 4.



Scheme 5.

HP5 oil. Molecular weights and molecular formulae were determined mass spectrometrically on a Finnigan-MAT-8200 instrument. The nominal energy of the ionizing electrons was 70 eV. The starting compounds **1** and **2** were obtained by described procedures [10,11].

3.1. *Heating of compound **1** with $AlCl_3$*

A mixture of carbonimidoyl dichloride **1** (0.26 g) and $AlCl_3$ (0.4 g) was vigorously stirred for 7 h at 110°C. After cooling the mixture was poured into water and extracted with ether. The ether layer was washed with water, dried over $CaCl_2$, the solvent distilled off and the residue (0.15 g) was analyzed by ^{19}F NMR spectroscopy and GLC. The residue contained only starting compound **1**.

3.2. *1,3-Bis(pentafluorophenyl)-4,5-dichloro-2-imidazolone **3***

1. To 0.09 g of $AlCl_3$ was added 0.3 g of compound **2**, 0.5 ml of hexafluorobenzene and the mixture was vigorously stirred for 7 h at 110°C. The treatment of

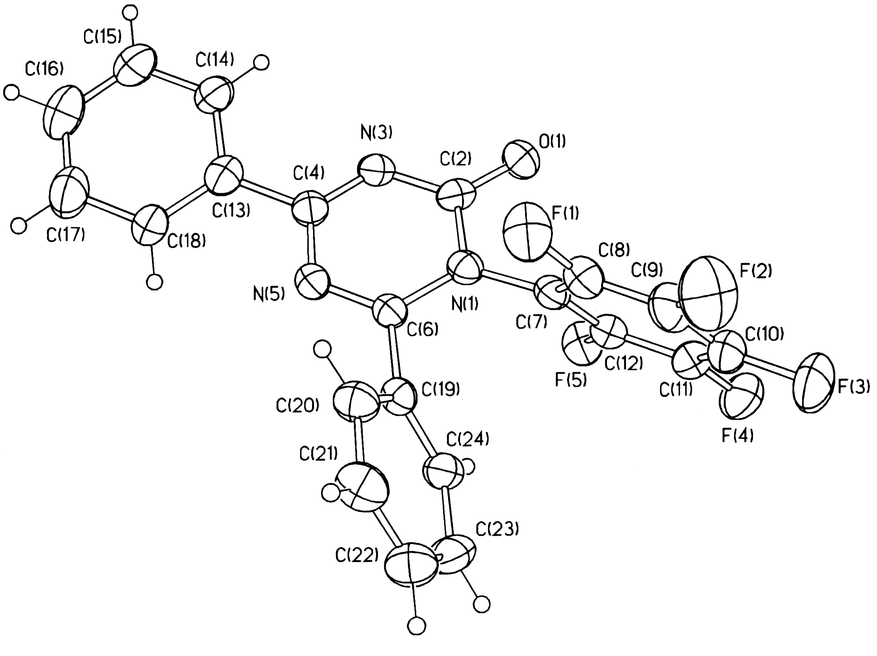


Fig. 2. X-ray crystal structure of 1-pentafluorophenyl-4,6-diphenyl-1,3,5-triazine-2-one **13**.

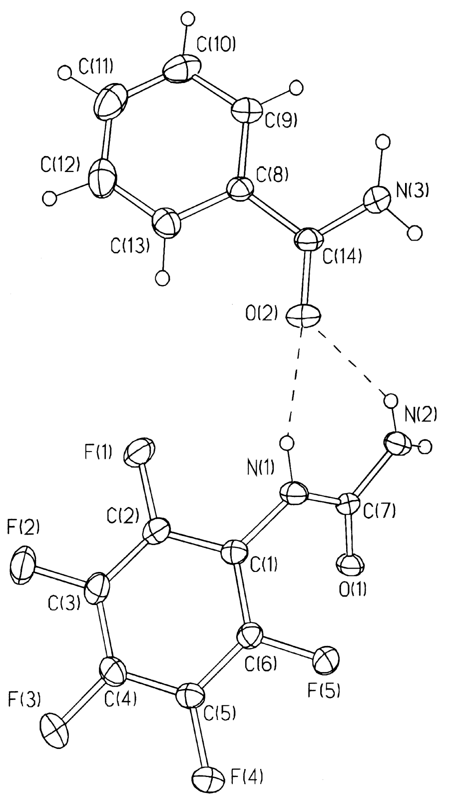


Fig. 3. X-ray crystal structure of complex **17**.

the reaction mixture was similar to that described above. The residue (0.28 g) was washed with a small amount of petroleum ether (70–100°C), sublimed at 90°C/5 mm Hg and then recrystallized from hexane to give 0.08 g of compound **3**. m.p. 95.5–97°C. ^{19}F NMR (ether): $\delta = 19.43$ ($4F_o$), 12.62 ($2F_p$), 1.76 ($4F_m$). IR: $\nu = 1005$vs, 1140m, 1300m, 1530vs, 1765vs, 1800w. *Anal.* Calc. for $C_{15}Cl_2F_{10}N_2O$: C, 37.11; Cl, 14.64; F, 39.18; N, 5.77%; M, 483.9228. Found: C, 37.68; Cl, 14.93; F, 38.68; N, 5.53%; M, 483.9278.

The reaction mixture obtained after stirring 0.3 g of compound **2**, 0.22 g of $AlCl_3$ and 5 ml of hexafluorobenzene at 80°C for 7 h contained starting compound **2** and 4% of compound **3** by GLC data.

2. A mixture of compound **5** (0.05 g) and $AlCl_3$ (0.04 g) was heated in a sealed glass ampoule for 7 h at 110°C. After reaction, the mixture was poured into water, the precipitate was filtered off, washed with water, and air-dried to give 0.04 g of the mixture of starting compound **5** and imidazolone **3** in a ratio 4:1 (^{19}F NMR and GLC data).
3. A mixture of compound **5** (0.2 g) and $AlCl_3$ (0.14 g) in 2 ml of anhydrous toluene was stirred for 7 h at 110°C. Subsequent treatment was similar to that described in step 1. The residue contained imidazolone **3** and tolyl derivatives **7**. This residue was subjected to column chromatography on silica gel into 0.06 g of compound **3** and 0.21 g of the mixture of **3** (19%) and **7** (15%) and unidentified unfluorinated compound (66%) (GC–MS and ^{19}F NMR data). The eluents were hexane and CCl_4.

1,3-Bis(pentafluorophenyl)-4-chloro-5-tolyl-2-imidazolones 7. ^{19}F NMR (CCl_4): $\delta = 18.48$ ($4F_o$), 11.49 (F_p), 11.03 (F_p), 1.34 ($4F_m$). *Anal.* Calc. for $C_{22}H_7ClF_{10}N_2O$: M, 540.00871. Found: M, 540.00745.

*3.3. 1,3-Bis(pentafluorophenyl)-4,4,5,5-tetrachloro-2-imidazolidone **5***

1. A mixture of trichloroacetimidoyl chloride **2** (0.35 g), carbonimidoyl dichloride **1** (0.26 g), $AlCl_3$ (0.4 g) and hexafluorobenzene (0.5 ml) was stirred vigorously for 7 h at 110°C. After reaction, the mixture was poured into water and extracted with ether. The ether layer was washed with water, dried over $CaCl_2$, the solvent distilled off and solid residue (0.59 g) was sublimed at 105–110°C/7 mm Hg to afford 0.48 g of compound **5**, m.p. 114–115°C. ^{19}F NMR ($CHCl_3$): $\delta = 24.17$ ($4F_o$), 14.42 ($2F_p$), 2.22 ($4F_m$). *Anal.* Calc. for $C_{15}Cl_4F_{10}N_2O$: C, 32.37; Cl, 25.54; F, 34.17; N, 5.04%; M, 553.86050. Found: C, 32.56; Cl, 25.16; F, 33.73; N, 4.99%; M, 553.86108.
2. Analogously, the reaction of trichloroacetimidoyl chloride **2** (0.35 g) with **1** (0.26 g) and $AlCl_3$ (0.4 g) in hexafluorobenzene (0.5 ml) at 80°C (10 h) afforded a residue containing compounds **1** and **5** in the ratio 2:19 (^{19}F NMR). The reaction of trichloroacetimidoyl chloride **2** (0.7 g) with **1** (0.52 g) and $AlCl_3$ (0.8 g) in hexafluorobenzene (1.5 ml) at 80°C (10 h) afforded 1.1 g of **5** which was purified by sublimation at 105–110°C/7 mm Hg.
3. Analogously, the reaction of trichloroacetimidoyl chloride **2** (0.35 g), carbonimidoyl dichloride **1** (0.26 g) and $AlCl_3$ (0.4 g) in chloroform (2 ml) at 60°C (10 h) afforded a residue containing compounds **1**, **2** and **5** in the ratio 1:1:0.5 (^{19}F NMR).

*3.4. 1-Pentafluorophenyl-3-(4′-methyl-2′,3′,5′,6′-tetrafluorophenyl)-4,4,5,5,-tetrachloro-2-imidazolidone **6***

A mixture of trichloroacetimidoyl chloride **2** (0.35 g), carbonimidoyl dichloride **4** (0.26 g) and $AlCl_3$ (0.4 g) in hexafluorobenzene (1.5 ml) was stirred vigorously for 9 h at 80°C. Treatment of reaction mixture was similar to that described above. A solid residue was recrystallized from hexane, 0.32 g of imidazolidone **6** was obtained which was further purified by sublimation at 140°C/12 mm Hg. m.p. 146.5–148°C. ^{1}H NMR ($CDCl_3$): $\delta = 2.41$ (CH_3). ^{19}F NMR ($CDCl_3$): $\delta = 24.29$ ($2F_o$), 14.09 (F_p), 2.03 ($2F_m$), 21.19 (2F), 20.45 (2F). IR ($CHCl_3$): $\nu = 1000$vs, 1140s, 1160s, 1300vs, 1360m, 1520vs, 1785vs. *Anal.* Calc. for $C_{16}H_3Cl_4F_9N_2O$: C, 34.78; H, 0.54; Cl, 25.72; F, 30.98;

N, 5.07%; M, 549.8856. Found: C, 34.98; H, 0.57; Cl, 26.02; F, 31.46; N, 5.26%; M, 549.8822.

*3.5. Bis(pentafluorophenyl)trichloroacetamidine **12***

To a suspension of trichloroacetimidoyl chloride **2** (1.5 g) and $AlCl_3$ (0.66 g) was added pentafluoroaniline (0.3 g). The mixture was stirred vigorously for 7 h at 110°C. Subsequent work-up was similar to that described above. A residue (1.5 g) contained starting material **2**, imidazolone **3** and amidine **12** in the ratio 1:3.25:2.75 (^{19}F NMR). This residue was subjected to column chromatography on silica gel into 1.4 g of the mixture of compound **3** and **12** (eluent hexane/benzene (20:1 by vol.)). Then this procedure was repeated to yield compound **3** (0.24 g) and amidine **12** (0.66 g) along with a mixture of compounds **3** and **12** (0.18 g) (eluent hexane/benzene (1:1 by vol.)). Amidine **12** was purified by recrystallization from hexane, m.p. 76–78°C. ^{19}F NMR (CCl_4): $\delta = 17.7$ (2F), 13.3 (2F), 8.2 (F), 0.5 (2F), -0.2 (F), -1.6 (2F). IR: $v = 1005$vs, 1050s, 1530vs, 1700s, 3400m, 3430m. MS (*m/z*, formula): 492 (M^+, 3Cl), 473 (M–F), 457 (M–Cl), 375 ($M–CCl_3$), 310 ($M–NHC_6F_5$). *Anal.* Calc. for $C_{14}HCl_3F_{10}N_2$: C, 34.04; H, 0.20; Cl, 21.58; F, 38.50; N, 5.67%; M, 491.9045. Found: C, 33.99; H, 0; Cl, 21.64; F, 38.60; N, 5.36%; M, 491.9057.

*3.6. Heating of **12** with a base*

To a vigorously stirred suspension of freshly prepared anhydrous K_2CO_3 (0.04 g) in anhydrous benzene (3 ml) was added amidine **12** (0.15 g) and this mixture was refluxed for 11 h. The precipitate was filtered off and solvent was distilled off from the filtrate. The residue contained only starting amidine **12** (^{19}F NMR data).

*3.7. Interaction of carbonimidoyldichloride **1** with benzonitrile in the presence of $AlCl_3$*

A mixture of compound **1** (0.26 g) and $AlCl_3$ in benzonitrile (1.5 ml) was stirred vigorously at the temperature indicated in Table 1. After reaction, the mixture was poured into cold water and extracted with ether. The ether layer was dried over $CaCl_2$, the ether distilled off and the residue analyzed by ^{19}F NMR spectroscopy, GLC and GC–MS. The results are shown in Table 1. The solid precipitate filtered off and analyzed. In experiment 1 (see Table 1), solid compound **13** was obtained when benzonitrile was removed under vacuum from residue and purified by recrystallization from acetone. A mixture of compounds **14** and **17** was treated with the solution of 25% aq. NH_3. The insoluble precipitate of **14** was filtered off, washed with water and recrystallized from acetone and ethanol. After evaporation

Table 1
Interaction of compound **1** with benzonitrile in the presence of $AlCl_3$

Experiment	$AlCl_3$, g (mmol)	Reaction temperature, °C (time, h)	Reaction products		
			Compound	Ratio by ^{19}F NMR (g)	
				Residue after reaction	Precipitate
1	0.14 (1)	150 (7.5)	**1**	3	
			13	1 (0.06)	
2	0.14 (1)	150 (19.5)	**1**	6	
			13	3.8	
			14	1	1
			15	1	1.7 (0.06)
3	0.27 (2)	150 (6.5)	**1**	9.6	
			13	3.6	
			14	1	1
			15	1.4	4.5 (0.02)
4	0.4 (3)	150 (15)	**1**	6.5[a]	
			13	13	1
			14	2	1.7 (0.06)
			15	1	2
5	0.14 (1)	175 (6)	**1**	3.5	
			13	7.5	
			14	2	1
			15	1	1 (0.09)
6	0.14 (1)	175 (9.5)	**1**	2[a]	
			13	7	2
			14	2	5 (0.15)
			15	1	4
7	0.27 (2)	175 (7)	**1**	1	
			13	12.5	1
			14	9	2.5 (0.06)
			15	4	1.25

[a] Ratio of the products in filtrate.

of aq. NH_3 the residue of **17** was recrystallized (petroleum ether (70–100°C) and acetone (1:1 by vol.)).

1-Pentafluorophenyl-4,6-diphenyl-1,3,5-triazine-2-one ***13***. m.p. 227–231°C (in sealed capillary). ^1H NMR (d-acetone): $\delta = 7.49–7.75$ ($2C_6H_5$). ^{19}F NMR (d-acetone): $\delta = 20.22$ ($2F_o$), 11.99 (F_p), 1.73 ($2F_m$). IR (KBr): $v = 990$vs, 1360vs, 1436m, 1480m, 1525vs, 1590m, 1710vs, 3050w. *Anal.* Calc. for $C_{21}H_{10}F_5N_3O$: M, 415.07439. Found: M, 415.07458.

N-Pentafluorophenyl-N′-benzoylurea ***14***. m.p. 189–194°C. ^1H NMR (acetone): $\delta = 10.48$ (NH), 10.44 (NH), 8.10 ($2H_{Ar}$), 7.74–7.54 m ($3H_{Ar}$) ^{19}F NMR (acetone): $\delta = 17.83$ ($2F_o$), 4.70 (F_p), -1.15 ($2F_m$). IR (KBr): $v =$ 1025s, 1270vs, 1325m, 1450–1475vs, 1525vs, 1670s, 1700–1715vs, 3175m, 3250m. *Anal.* Calc. for $C_{14}H_7F_5N_2O_2$: M, 330.04276. Found: M, 330.04175.

Complex ***17*** *of N-pentafluorophenylurea* ***15*** *and benzamide* ***16***. m.p. 127–130°C. ^{19}F NMR (acetone): $\delta = 16.40$ ($2F_o$), 2.10 (F_p), -1.95 ($2F_m$).

3.8. N-Pentafluorophenylurea **15** and N-pentafluorophenylbiuret **18**

A solution of 0.33 g NaNCO in 3 ml water was added to a solution of 0.91 g pentafluoroaniline in 3 ml of acetic acid and stirred for 2 h at 50–60°C, then cooled to room temperature. The reaction mixture contained (^{19}F NMR) unreacted pentafluoroaniline together with **15** and **18** and an unidentified product having a C_6F_5-group (ratio was 9.8:1.9:2.6:1). A precipitate (0.08 g) from the reaction mixture was filtered off, washed with water and a small amount of hexane to give compound **18** (m.p. 194–196°C) after recrystallization from aq. ethanol. ^1H NMR (acetone): $\delta = 9.86$ (NH), 8.86 (NH), 6.54 (NH_2). ^{19}F NMR (acetone): $\delta = 17.28$ ($2F_o$), 4.05 (F_p), -1.35 ($2F_m$). IR (KBr): $v =$ 1000–1010s, 1240m, 1250m, 1325m, 1460m, 1500–1525vs, 1610s, 1700vs, 1705s, 3000m, 3200s, 3480vs. *Anal.* Calc. for $C_8H_4F_5N_3O_2$: M, 269.02236. Found: M, 269. 02292. The filtrate was diluted with water and the precipitate formed (0.12 g) was filtered off, washed with water and recrystallized from aq. ethanol. It contained **15** and **18** and the above unidentified product (^{19}F NMR (acetone): $\delta = 17.59$ ($2F_o$), 4.62 (F_p), -1.14 ($2F_m$)) in the ratio 2.5:1.4:1 (^{19}F NMR).

N-Pentafluorophenylurea ***15***. ^{19}F NMR (acetone): $\delta =$ 16.40 ($2F_o$), 2.56 (F_p), -1.72 ($2F_m$). *Anal.* Calc. for $C_7H_3F_5N_2O$: M, 226.01655. Found:M, 226.01753.

3.9. X-ray structural analysis of compounds **6**, **13** and complex **17**

Molecular structures of compounds **6**, **13** and **17** are illustrated in Figs. 1–3. X-ray data were measured on a Syntex P2$_1$ diffractometer with graphite monochromated Cu Kα radiation using $\theta/2\theta$ scans with $2\theta < 130°$ for **6** and $2\theta < 140°$ for **13** and **17**. Numerical corrections for absorption were applied. The structures were solved using direct methods (SHELXS-86) [12] and refined in the anisotropic–

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($A^2 \times 10^3$) for compound **6**

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(eq)[a]
O(1)	6289(2)	13136(5)	812(2)	50(1)
N(1)	6345(2)	10200(6)	913(2)	34(1)
C(2)	6054(3)	11808(7)	955(2)	37(1)
N(3)	5413(2)	11597(6)	1192(2)	35(1)
C(4)	5233(3)	9828(7)	1212(2)	38(1)
C(5)	5995(3)	8987(7)	1219(2)	39(1)
C(1′)	7060(3)	10034(7)	775(2)	36(1)
C(2′)	7211(3)	9227(8)	318(2)	44(1)
C(3′)	7903(3)	9080(9)	185(2)	50(2)
C(4′)	8472(3)	9647(8)	481(2)	48(2)
C(5′)	8307(3)	10431(8)	935(2)	50(2)
C(6′)	7621(3)	10642(8)	1076(2)	44(1)
C(7′)	9222(4)	9397(15)	328(4)	69(2)
C(1″)	4904(3)	12924(7)	1180(2)	35(1)
C(2″)	4608(3)	13562(8)	724(2)	43(1)
C(3″)	4112(3)	14813(9)	716(3)	54(2)
C(4″)	3895(3)	15487(9)	1171(3)	65(2)
C(5″)	4186(4)	14900(9)	1630(3)	67(2)
C(6″)	4690(4)	13642(8)	1634(2)	54(2)
F(2″)	6687(2)	8666(5)	2(1)	62(1)
F(3′)	8029(2)	8278(5)	−266(1)	72(1)
F(5′)	8836(2)	11049(6)	1251(2)	76(1)
F(6′)	7504(2)	11486(5)	1509(1)	66(1)
F(2″)	4820(2)	12966(5)	278(1)	63(1)
F(3″)	3848(2)	15442(6)	269(2)	88(1)
F(4″)	3402(2)	16715(5)	1159(2)	103(2)
F(5″)	3986(3)	15583(6)	2066(2)	118(2)
F(6″)	4987(3)	13107(5)	2080(1)	87(1)
Cl(1)	4716(1)	9193(2)	652(1)	52(1)
Cl(2)	4749(1)	9290(2)	1747(1)	57(1)
Cl(3)	6007(1)	6908(2)	979(1)	59(1)
Cl(4)	6373(1)	8931(2)	1858(1)	63(1)
O(1A)	422(2)	8234(5)	1269(2)	54(1)
N(1A)	321(2)	5323(6)	1398(2)	44(1)
C(2A)	628(3)	6899(7)	1453(2)	39(1)
N(3A)	1239(2)	6700(6)	1773(2)	42(1)
C(4A)	1395(3)	4920(8)	1832(2)	48(2)
C(5A)	632(3)	4148(8)	1771(2)	47(2)
C(1′A)	−334(3)	5098(7)	1116(2)	40(1)
C(2′A)	−348(3)	4275(8)	646(2)	45(1)
C(3′A)	−961(3)	4078(8)	355(2)	50(2)
C(4′A)	−1601(3)	4663(8)	512(2)	46(2)
C(5′A)	−1586(3)	5517(9)	972(2)	49(2)
C(6′A)	−971(3)	5720(8)	1273(2)	44(1)
C(7′A)	−2282(5)	4405(14)	194(4)	65(2)
C(1″A)	1751(3)	8014(7)	1841(2)	40(1)
C(2″A)	2111(3)	8660(8)	1427(2)	42(1)
C(3″A)	2615(3)	9909(8)	1507(2)	49(2)
C(4″A)	2778(3)	10515(8)	1984(2)	50(2)
C(5″A)	2421(3)	9920(8)	2394(2)	49(2)
C(6″A)	1920(3)	8684(8)	2319(2)	44(1)
F(2″A)	1952(2)	8086(5)	953(1)	62(1)
F(3″A)	2954(2)	10518(5)	1105(1)	72(1)
F(4″A)	3281(2)	11732(5)	2058(2)	77(1)
F(5″A)	2580(2)	10539(6)	2863(1)	78(1)
F(6″A)	1558(2)	8173(5)	2722(1)	59(1)
F(6′A)	−983(2)	6576(5)	1716(1)	65(1)
F(5′A)	−2185(2)	6178(6)	1145(1)	72(1)
F(3′A)	−944(2)	3249(5)	−101(1)	71(1)
F(2′A)	255(2)	3663(5)	469(1)	62(1)
Cl(1A)	1923(1)	4176(2)	1324(1)	62(1)
Cl(2A)	1849(1)	4401(2)	2412(1)	63(1)

Table 2 (*Continued*)

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(eq)[a]
Cl(3A)	596(1)	2016(2)	1568(1)	61(1)
Cl(4A)	200(1)	4286(2)	2364(1)	66(1)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

isotropic approximation using SHELXL-93 [13] program package. The positions of hydrogen atoms were located from different Fourier synthesis **6**, **17** or given geometrically **13**.

Compound **6** (Fig. 1) is monoclinic, space group P2$_1$/c, $a = 18.894(6)$, $b = 7.834(2)$, $c = 26.070(9)$ Å, $\beta = 93.01(3)°$ $V = 5853(2)$ Å^3, $C_{16}H_3Cl_4F_9N_2O$, $M = 552.00$, $Z = 8$, $D_c = 1.903$ g cm^{-3}, $\mu = 6.546$ mm^{-1}, F(0 0 0) = 2160, crystal size 0.10 × 0.17 × 0.90 mm^3, 6340 independent reflections (transmission 0.20–0.64), w$R_2 = 0.1480$, $S = 0.983$ for all reflections ($R = 0.0596$ for 3547 $F > 4\sigma$) (see Tables 2 and 3).

Compound **13** (Fig. 2) is orthorhombic, space group P2$_1$2$_1$2$_1$, $a = 7.766(3)$, $b = 9.349(3)$, $c = 25.180(10)$ Å, $V = 1828(1)$ Å^3, $C_{21}H_{10}F_5N_3O$, $M = 415.32$, $Z = 4$, $D_c = 1.509$ g cm^{-3}, $\mu = 1.139$ mm^{-1}, F(0 0 0) = 840, crystal size 0.04 × 0.70 × 0.85 mm^3, 1767 independent reflections (transmission 0.56–0.96), w$R_2 = 0.1930$, $S = 1.016$, for all reflections ($R = 0.0619$ for 1180 $F > 4\sigma$). Delocalized π-system of s-triazine is broken in compound **13** (Fig. 2) and a new one is formed on atoms N(1), C(2), N(3), C(4), C(13), C(14), C(15), C(16), C(17), C(18). This conclusion was drawn on the basis of bond lengths. Bonds N(1)–C(2) (1.441(8) Å) and C(4)–N(5) (1.384(7) Å) are

Table 4
Atomic coordinates (×10^4) and equivalent isotropic displacement parameters ($A^2 \times 10^3$) for compound **13**

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(eq)[a]
N(1)	278(6)	6067(5)	5223(2)	50(1)
C(2)	−12(8)	7237(7)	4860(2)	55(2)
N(3)	376(6)	7002(6)	4349(2)	55(1)
C(4)	978(8)	5763(7)	4203(2)	53(1)
N(5)	1354(6)	4642(5)	4543(2)	53(1)
C(6)	1043(7)	4832(6)	5037(2)	47(1)
C(7)	−289(7)	6194(6)	5756(2)	51(1)
C(8)	−1681(8)	5381(7)	5937(3)	63(2)
C(9)	−2169(10)	5434(9)	6449(3)	79(2)
C(10)	−1333(11)	6293(9)	6817(3)	80(2)
C(11)	3(9)	7155(8)	6634(2)	66(2)
C(12)	484(8)	7067(6)	6116(2)	52(1)
C(13)	1239(8)	5444(8)	3640(2)	60(2)
C(14)	528(9)	6326(8)	3251(2)	68(2)
C(15)	767(11)	6011(10)	2725(3)	86(2)
C(16)	1730(13)	4880(10)	2572(3)	98(3)
C(17)	2432(13)	3990(10)	2946(3)	96(3)
C(18)	2212(10)	4291(8)	3478(2)	76(2)
C(19)	1472(7)	3682(6)	5422(2)	47(1)
C(20)	783(9)	2357(6)	5340(3)	64(2)
C(21)	1145(10)	1259(8)	5683(3)	76(2)
C(22)	2215(11)	1472(8)	6107(3)	78(2)
C(23)	2956(10)	2809(8)	6189(3)	78(2)
C(24)	2594(9)	3919(7)	5842(2)	61(2)
F(1)	−2516(6)	4545(5)	5594(2)	89(1)
F(2)	−3501(7)	4636(6)	6623(2)	124(2)
F(3)	−1802(8)	6326(6)	7320(2)	115(2)
F(4)	793(7)	8019(5)	6976(2)	97(2)
F(5)	1825(5)	7891(4)	5961(2)	71(1)
O(1)	−703(6)	8317(4)	5036(2)	67(1)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 3
Bond lengths (Å) and selected torsional angles (°) for compound **6**

O(1)–C(2)	1.198(6)	O(1A)–C(2A)	1.206(6)
N(1)–C(2)	1.381(7)	N(1A)–C(2A)	1.369(7)
N(1)–C(1′)	1.422(6)	N(1A)–C(1′)	1.417(6)
N(1)–C(5)	1.425(7)	N(1A)–C(5A)	1.441(7)
C(2)–N(3)	1.398(7)	C(2A)–N(3A)	1.398(6)
N(3)–C(1″)	1.414(6)	N(3A)–C(1″A)	1.417(7)
N(3)–C(4)	1.428(7)	N(3A)–C(4A)	1.432(7)
C(4)–C(5)	1.583(7)	C(4A)–C(5A)	1.564(8)
C(4)–Cl(2)	1.759(5)	C(4A)–Cl(2A)	1.746(6)
C(4)–Cl(1)	1.785(5)	C(4A)–Cl(1A)	1.798(6)
C(5)–Cl(3)	1.745(6)	C(5A)–Cl(3A)	1.752(6)
C(5)–Cl(4)	1.780(5)	C(5A)–Cl(4A)	1.790(6)
C(5)–N(1)–C(2)–N(3)	−13.2(6)	C(5A)–N(1A)–C(2A)–N(3A)	13.3(6)
C(1′)–N(1)–C(2)–N(3)	−168.3(6)	C(1′A)–N(1A)–C(2A)–N(3A)	176.5(6)
C(6′)–C(1′)–N(1)–C(5)	−88.4(6)	C(6′A)–C(1′A)–N(1A)–C(5A)	92.7(6)
N(1)–C(2)–N(3)–C(4)	−11.0(6)	N(1A)–C(2A)–N(3A)–C(4A)	12.0(7)
O(1)–C(2)–N(3)–C(4)	168.0(6)	O(1A)–C(2A)–N(3A)–C(4A)	−168.3(7)
C(2)–N(3)–C(4)–C(5)	27.4(5)	C(2A)–N(3A)–C(4A)–C(5A)	−29.5(6)
N(3)–C(4)–C(5)–N(1)	−32.5(5)	N(3A)–C(4A)–C(5A)–N(1A)	34.6(5)
C(4)–C(5)–N(1)–C(2)	28.7(5)	C(4A)–C(5A)–N(1A)–C(2A)	−30.1(6)
C(1″)–N(3)–C(2)–N(1)	−164.8(6)	C(1″A)–N(3A)–C(2A)–N(1A)	168.8(6)
C(6″)–C(1″)–N(3)–C(2)	−119.8(6)	C(6″A)–C(1″A)–N(3A)–C(2A)	120.6(6)

markedly lengthened by comparison with analogues 1.412(4) and 1.351(4) Å in 4,6-dimethoxy-3-methyl-1,3,5-triazine-2(3H)-one [14] and 1.382(4) and 1.353(4) Å in 4,6-dimethoxy-1,3,5-triazine-2(1H)-one [15]. Bond C(5)=N(6) (1.279(6) Å) is the same as the literature double bond C_{Ar}–C=N–C# 1.279(8) Å [16] (see Tables 4 and 5).

Molecular complex **17** (Fig. 3) is triclinic, space group P1, $a = 6.837(1)$, $b = 7.120(1)$, $c = 15.283(2)$ Å, $\alpha = 91.09(1)$, $\beta = 96.16(1)$, $\gamma = 97.79(1)^\circ$, $V = 732.4(2)$ Å^3, $C_{14}H_{10}F_5N_3O_2$, $M = 347.25$, $Z = 2$, $D_c = 1.575$ g cm^{-3}, $\mu = 1.333$ mm^{-1}, F(0 0 0) = 352, crystal size 0.08 × 0.35 × 0.8 mm^3, 2717 independent reflections (transmission 0.49–0.90), $wR_2 = 0.1132$, $S = 1.048$ for all reflections ($R = 0.0394$ for 2064 $F > 4\sigma$) (see Tables 6 and 7).

The molecular complex is formed by hydrogen bonds N(1)–H···O(2) (N–H 0.85(2), O···H 2.06(2) Å, N–H···O 157(2)°) and N(2)–H(2A)···O(2) (N–H 0.82(2), O···H 2.28(2) Å, N–H···O 147(2)°).

Atomic coordinates, bond lengths and angles have been deposited at the Cambridge Crystallographic Data Center.

Table 5
Bond lengths (Å) and selected torsional angles (°) for compound **13**

N(1)–C(6)	1.380(7)
N(1)–C(7)	1.418(7)
N(1)–C(2)	1.441(8)
C(2)–O(1)	1.226(7)
C(2)–N(3)	1.342(7)
N(3)–C(4)	1.301(8)
C(4)–N(5)	1.384(7)
C(4)–C(13)	1.463(8)
N(5)–C(6)	1.279(6)
C(6)–C(19)	1.485(8)
C(7)–C(12)	1.360(8)
C(7)–C(8)	1.398(8)
C(8)–F(1)	1.333(7)
C(8)–C(9)	1.345(9)
C(9)–F(2)	1.348(9)
C(9)–C(10)	1.386(11)
C(10)–F(3)	1.320(7)
C(10)–C(11)	1.392(10)
C(11)–F(4)	1.332(7)
C(11)–C(12)	1.357(8)
C(12)–F(5)	1.353(7)
C(13)–C(18)	1.378(10)
C(13)–C(14)	1.395(9)
C(14)–C(15)	1.369(9)
C(15)–C(16)	1.352(11)
C(16)–C(17)	1.370(11)
C(17)–C(18)	1.380(9)
C(19)–C(20)	1.365(8)
C(19)–C(24)	1.388(8)
C(20)–C(21)	1.369(9)
C(21)–C(22)	1.369(10)
C(22)–C(23)	1.391(10)
C(23)–C(24)	1.386(9)
C(2)–N(1)–C(7)–C(8)	−71.7(2)
N(1)–C(6)–C(19)–C(24)	−60.1(2)
N(3)–C(4)–C(13)–C(14)	−13.2(3)

Table 6
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($A^2 \times 10^3$) for molecular complex **17**

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(eq)[a]
C(1)	−2566(3)	2353(2)	2850(1)	43(1)
C(2)	−3177(3)	2360(3)	1956(1)	49(1)
C(3)	−1884(3)	2912(3)	1354(1)	55(1)
C(4)	77(3)	3521(3)	1630(1)	52(1)
C(5)	739(3)	3525(3)	2511(1)	48(1)
C(6)	−559(3)	2906(3)	3104(1)	44(1)
C(7)	−4167(2)	2998(3)	4135(1)	42(1)
C(8)	−10581(3)	−1951(2)	2516(1)	46(1)
C(9)	−12603(3)	−2556(3)	2509(2)	58(1)
C(10)	−13814(4)	−2745(4)	1717(2)	78(1)
C(11)	−13036(5)	−2351(4)	938(2)	89(1)
C(12)	−11055(5)	−1752(4)	943(2)	81(1)
C(13)	−9825(4)	−1539(3)	1723(2)	60(1)
C(14)	−9160(3)	−1750(3)	3335(1)	53(1)
N(1)	−3897(2)	1790(2)	3462(1)	48(1)
N(2)	−5540(3)	2319(3)	4651(1)	55(1)
N(3)	−9714(3)	−2685(3)	4033(1)	72(1)
O(1)	−3161(2)	4560(2)	4271(1)	55(1)
O(2)	−7547(2)	−755(2)	3359(1)	80(1)
F(1)	−5101(2)	1805(2)	1669(1)	71(1)
F(2)	−2531(2)	2888(2)	494(1)	83(1)
F(3)	1345(2)	4107(2)	1051(1)	76(1)
F(4)	2649(2)	4131(2)	2787(1)	67(1)
F(5)	152(2)	2826(2)	3954(1)	60(1)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 7
Bond lengths (Å) and selected torsional angles (°) for molecular complex **17**

C(1)–C(2)	1.386(3)
C(1)–C(6)	1.386(2)
C(1)–N(1)	1.400(2)
C(2)–F(1)	1.344(2)
C(2)–C(3)	1.370(3)
C(3)–F(2)	1.340(2)
C(3)–C(4)	1.370(3)
C(4)–F(3)	1.339(2)
C(4)–C(5)	1.373(3)
C(5)–F(4)	1.339(2)
C(5)–C(6)	1.373(3)
C(6)–F(5)	1.343(2)
C(7)–O(1)	1.228(2)
C(7)–N(2)	1.337(2)
C(7)–N(1)	1.371(2)
C(8)–C(13)	1.388(3)
C(8)–C(9)	1.390(3)
C(8)–C(14)	1.492(3)
C(9)–C(10)	1.386(3)
C(10)–C(11)	1.373(4)
C(11)–C(12)	1.362(4)
C(12)–C(13)	1.377(4)
C(14)–O(2)	1.224(2)
C(14)–N(3)	1.331(3)
C(6)–C(1)–N(1)–C(7)	59.9(7)

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