2-Polyfluoroalkylchromones
9.* Synthesis and structures of 5-(2-hydroxyaryl)-7-polyfluoroalkyl-1,4,8-triazabicyclo[5.3.0]dec-4-enes

V. Ya. Sosnovskikh,[a]★ I. I. Vorontsov,[b] and V. A. Kutsenko[a]

[a]*A. M. Gorky Ural State University,*
51 prosp. Lenina, 620083 Ekaterinburg, Russian Federation.
Fax: 007 (343 2) 61 5978. E-mail: Vyacheslav.Sosnovskikh@usu.ru
[b]*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,*
28 ul. Vavilova, 119991 Moscow, Russian Federation.
Fax: 007 (095) 135 5085. E-mail: ivorontsov@xray.ineos.ac.ru

2-Polyfluoroalkylchromones reacted with diethylenetriamine at ~20 °C to form the corresponding 1,4,8-triazabicyclo[5.3.0]dec-4-ene derivatives. The crystal structures of 5-(2-hydroxyphenyl)-7-trifluoromethyl-1,4,8-triazabicyclo[5.3.0]dec-4-ene and 1-(2-aminoethyl)-7-(2-hydroxy-5-methoxyphenyl)-5-(1,1,2,2-tetrafluoroethyl)-2,3-dihydro-1*H*-1,4-diazepine were established by X-ray diffraction analysis.

Key words: 2-polyfluoroalkylchromones, diethylenetriamine, derivatives of 1,4,8-triazabicyclo[5.3.0]dec-4-ene, X-ray diffraction analysis.

Recently,[2] we have described the reactions of aromatic β-amino-β-polyfluoroalkylvinyl ketones with diethylenetriamine (DETA). Under conditions of kinetic control (~20 °C, 4—7 days), these reactions afforded 5-aryl-7-polyfluoroalkyl-1,4,8-triazabicyclo[5.3.0]dec-4-enes, which represent the cyclic form of 2,3-dihydro-1*H*-1,4-diazepines containing the 2-aminoethyl group at the nitrogen atom adjacent to the fluorinated substituent.

In the present study, we examined the reactions of 2-polyfluoroalkylchromones **1a—r** with DETA with the aim of preparing 5-(2-hydroxyaryl)-7-polyfluoroalkyl-1,4,8-triazabicyclo[5.3.0]dec-4-enes.

Results and Discussion

We found that the reactions of 2-polyfluoroalkylchromones **1a—r** with DETA proceeded in ethanolic solutions or without a solvent at ~20 °C for 24 h to form 2-hydroxyaryl-containing 1,4,8-triazabicyclo[5.3.0]dec-4-ene derivatives **2a—r** in 35—91% yields (for a preliminary communication, see Ref. 3). A rise in the temperature is unfavorable for the reaction. In the latter case, the reactions gave rise to mixtures of products, which were difficult to identify.

The first stage of the reactions of 2-polyfluoroalkylchromones **1** with DETA involved the nucleophilic addition of the primary amino group at the C(2) atom of the pyrone ring accompanied by the cleavage of chromones **1** to give *N*-substituted aminoenones. At the subsequent stage, the latter compounds underwent cyclization to form triazabicycles **2** involving both electrophilic centers with elimination of the water molecule (Scheme 1).

Unlike fluorine-containing aminoenones, which can be involved in reactions only if $R^F = CF_3$ or $(CF_2)_2H$,[2] 2-polyfluoroalkylchromones containing various fluorinated groups can enter into reactions with DETA. These reactions proceeded readily with both 2-difluoromethyl- and 2-perfluorobutylchromones (**1k,q**). The nature and the position of the substituent in the benzene ring have only a slight effect on the course of the reaction. Apparently, considerable synthetic possibilities of the conversion **1** → **2** are associated with the presence of the hydroxy group at position 2 of the benzene ring, which forms a strong intramolecular hydrogen bond with the imine nitrogen atom (δ 15.6—16.4; the X-ray diffraction data are given below) resulting in stabilization of the triazabicyclic structure.

It should be noted that compounds **2** were also formed from 3-amino-1-(2-hydroxyaryl)-3-polyfluoroalkylprop-2-en-1-ones **3**, which, in turn, can be prepared by condensation of 2-hydroxyacetophenones with R^FCN [4] or by pyrone ring opening of chromones **1** under the action of ammonia.[5] Thus, compounds **2a,b,k,m** were synthesized from aminoenones **3a,b,k,m**. It is best to perform the latter reactions without a solvent in a DETA medium. Naphthalene derivatives **1r,3r** [6] also entered into these reactions to yield bicycle **2r** (Scheme 2).

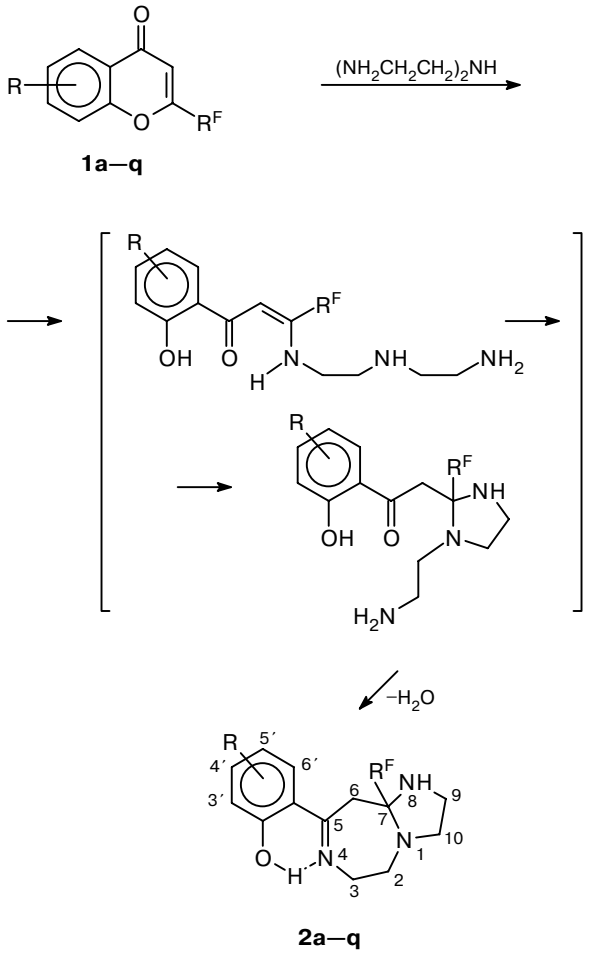
It should be emphasized that the above-described conversion is typical only of β-amino-β-polyfluoroalkylvinyl ketones and 2-polyfluoroalkylchromones and did not proceed in the case of nonfluorinated analogs of these compounds. We found that flavone did not react with DETA under the above-mentioned reaction conditions. The reaction of chromone afforded a mixture of resinous products, which were difficult to identify, whereas the reaction of 2-methylchromone performed

* For Part 8, see Ref. 1.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 8, pp. 1360—1368, August, 2001.

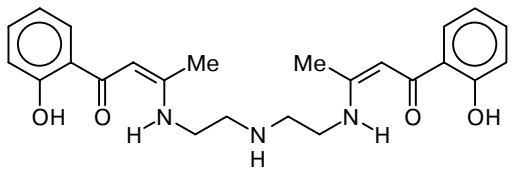
1066-5285/01/5008-1430 $25.00

Scheme 1



	R^F	R (**1**)	R (**2**)		R^F	R (**1**)	R (**2**)
a	CF_3	H	H	**j**	$(CF_2)_2H$	6-Cl	5′-Cl
b	CF_3	6-Me	5′-Me	**k**	CF_2H	H	H
c	CF_3	6-MeO	5′-MeO	**l**	CF_2H	6-Me	5′-Me
d	CF_3	7-MeO	4′-MeO	**m**	CF_2H	6-MeO	5′-MeO
e	CF_3	6-Cl	5′-Cl	**n**	CF_2H	7-MeO	4′-MeO
f	$(CF_2)_2H$	H	H	**o**	CF_2H	6-Cl	5′-Cl
g	$(CF_2)_2H$	6-Me	5′-Me	**p**	$(CF_2)_2OCF_3$	H	H
h	$(CF_2)_2H$	6-MeO	5′-MeO	**q**	$(CF_2)_3CF_3$	H	H
i	$(CF_2)_2H$	7-MeO	4′-MeO				

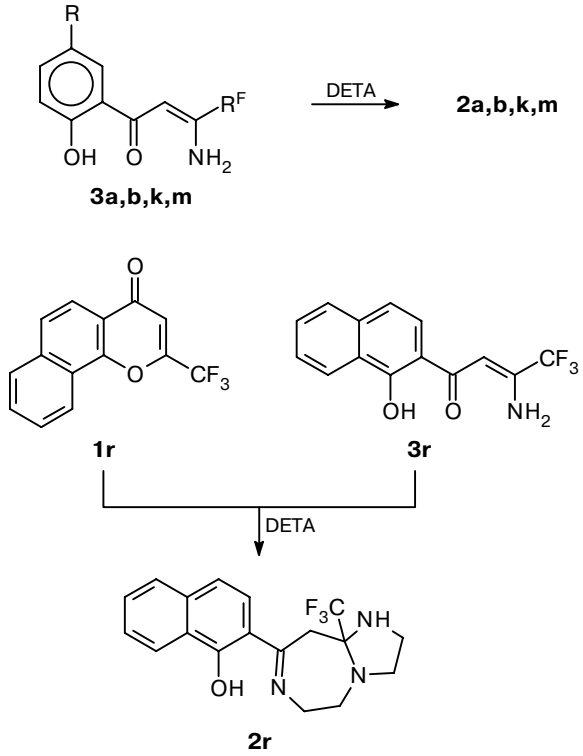
under the conditions of the synthesis of bicycles **2** gave rise to 1,13-di(2′-hydroxyphenyl)-3,11-dimethyl-4,7,10-triazatrideca-2,11-diene-1,13-dione (**4**).



4

Previously,[7] compound **4** has been synthesized (but has not been characterized) by the reaction of DETA with *o*-acetoacetylphenol and has been used for the preparation of complexes with Ni^{II} and Cu^{II} salts. It was believed[8] that the reaction of 2-ethoxycarbonyl-5,6,7,8-tetrafluorochromone with DETA afforded a 1,4,8-triazabicyclo[4.4.0]decane derivative (**5**) existing in the dienol form (Scheme 3).

Scheme 2



The structures of compounds **2a—r** agree well with the data from elemental analysis (Table 1) and with the results of IR and ^1H NMR spectroscopy (Table 2). The ^1H NMR spectra of analogs of compounds **2**, which did not contain the *ortho*-hydroxy group, have been discussed previously.[2] It should be noted that compounds **2a—r**, like analogs described earlier, were cleaved in an acidic medium to form dihydrodiazepinium cations **6** containing the 2-aminoethyl group at the nitrogen atom adjacent to the R^F group. This conclusion is evident from the ^1H NMR spectra of bicycles **2g,l,n,p,q** measured after the addition of CD_3CO_2D to solutions of these compounds in $CDCl_3$. These spectra have a singlet for the vinyl proton at δ 5.80—6.22. In addition, these spectra show two triplets of the A_2X_2 system of the 2-aminoethyl substituent and two broadened singlets of the methylene groups of the ring, which correspond to the signals of dications **6g,l,n,p,q** (Scheme 4, Table 2), instead of complex multiplets of four methylene groups and the AB spectrum of the $C(6)H_2$ group.

Therefore, the reactions of 2-polyfluoroalkylchromones with diethylenetriamine provide a new approach to the synthesis of the 1,4,8-triazabicyclo[5.3.0]dec-4-

Table 1. Physicochemical characteristics of compounds **2d,e,g,i,j,l—r**

Compound	Yield* (%)	M.p./°C	Found / Calculated (%)			Molecular formula
			C	H	N	
2d	50	116—117	54.78 54.71	5.27 5.51	12.76 12.76	$C_{15}H_{18}F_3N_3O_2$
2e	48	123—124	50.32 50.38	4.59 4.53	12.61 12.59	$C_{14}H_{15}ClF_3N_3O$
2g	65	184—185	55.55 55.65	5.56 5.55	12.32 12.17	$C_{16}H_{19}F_4N_3O$
2i	89	125—126	53.12 53.18	5.28 5.30	11.60 11.63	$C_{16}H_{19}F_4N_3O_2$
2j	53	162—163	49.33 49.26	4.52 4.41	11.49 11.49	$C_{15}H_{16}ClF_4N_3O$
2l	50	112—113	61.18 61.00	6.41 6.48	14.27 14.23	$C_{15}H_{19}F_2N_3O$
2m	35 (43)	82—83	57.98 57.87	6.05 6.15	13.36 13.50	$C_{15}H_{19}F_2N_3O_2$
2n	75	94—95	61.86 61.70	6.42 6.33	12.01 11.99	$C_{15}H_{19}F_2N_3O_2 \cdot 0.5C_6H_6$
2o	70	105—106	52.98 53.26	5.39 5.11	13.56 13.31	$C_{14}H_{16}ClF_2N_3O$
2p	80	103—104	46.36 46.27	3.96 3.88	10.05 10.12	$C_{16}H_{16}F_7N_3O_2$
2q	41	94—95	45.50 45.44	3.75 3.59	9.40 9.35	$C_{17}H_{16}F_9N_3O$
2r	91 (74)	195—196	61.88 61.89	5.06 5.19	12.34 12.03	$C_{18}H_{18}F_3N_3O$

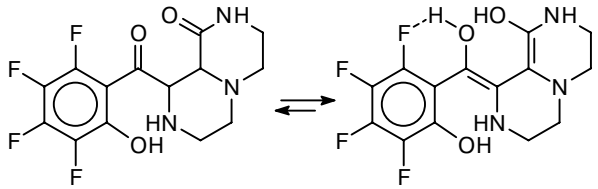
* The yields of the products prepared according to procedure *B* are given in parentheses.

ene system due to which 2-hydroxyaryl derivatives **2** became accessible.

With the aim of unambiguously establishing the structures of compounds **2**, which, like 5-aryl-7-polyfluoroalkyl-1,4,8-triazabicyclo[5.3.0]dec-4-enes,[2] can be considered as the cyclic forms of the corresponding 2,3-dihydro-1*H*-1,4-diazepines containing the 2-aminoethyl group at the N(1) atom, we carried out X-ray diffraction study of the crystals of bicycle **2a**. The overall view of molecule **2a** and the atomic numbering scheme are shown in Fig. 1.

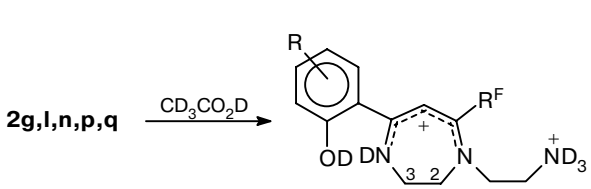
The seven-membered heterocycle of **2a** is nonplanar. The deviations of the N(4), C(5), C(6), and C(7) atoms from the plane passing through the N(1), C(2), and C(3) atoms are −0.932(1), −0.656(2), +0.698(2), and +0.906(1) Å, respectively. The ring has a conformation intermediate between a twist-boat and a boat. Calculations using the RICON program demonstrated that the contributions of these forms were 62% and 33%, respectively.[9] The five-membered heterocycle also adopts a nearly twist conformation. The N(1) and C(7) atoms deviate from the N(8)—C(9)—N(10) plane by −0.263(1) and +0.214(1) Å, respectively. The molecule as a whole consists of two flattened fragments. One of these fragments of molecule **2a** includes the phenyl ring and the C(3), N(4), C(5), and C(6) atoms (the average deviation of these atoms from the mean plane is 0.043 Å). In another fragment consisting of the remaining atoms (except for the CF_3 group), the average deviation of the atoms from the mean plane is 0.18 Å. The dihedral angle between the mean planes of the two fragments is 99.92(1)°. Therefore, molecule **2a** is folded along the C(3)...C(6) line.

Scheme 3



5

Scheme 4



6g,l,n,p,q

Table 2. Spectral characteristics of compounds **2d,e,g,i,j,l—r** and **6g,l,n,p,q**

Compound	^{1}H NMR ($CDCl_3$, δ, *J*/Hz)	IR, ν/cm^{-1}
2d	2.13 (br.s, 1 H, NH); 2.95—3.15 (m, 4 H, $C(9)H_2$, $C(10)H_2$); 3.16—3.27 (m, 1 H, C(2)HH); 3.33 (s, 2 H, $C(6)H_2$); 3.43—3.56 (m, 1 H, C(2)HH); 3.80 (s, 3 H, MeO); 3.89 (ddd, 1 H, C(3)HH, ^2J = 15.2, ^3J = 6.7, 5.7); 4.02 (td, 1 H, C(3)HH, ^2J = 15.2, ^3J = 6.3); 6.30 (dd, 1 H, H(5′), J_o = 9.0, J_m = 2.2); 6.37 (d, 1 H, H(3′), J_m = 2.2), 7.35 (d, 1 H, H(6′), J_o = 9.0); 16.58 (br.s, 1 H, OH)	3340, 1605, 1535
2e	2.13 (br.s, 1 H, NH); 3.00—3.26 (m, 5 H, $C(9)H_2$, $C(10)H_2$, C(2)HH); 3.31 (AB system, Δδ 0.06, 2 H, CH_2(6), J_{AB} = 15.2); 3.43—3.51 (m, 1 H, C(2)HH); 3.96 (ddd, 1 H, C(3)HH, ^2J = 15.4, ^3J = 6.7, 4.9); 4.17 (dt, 1 H, C(3)HH, ^2J = 15.4, ^3J = 5.5); 6.88 (d, 1 H, H(3′), J_o = 8.3); 7.24 (dd, 1 H, H(4′), J_o = 8.3, J_m = 2.4); 7.45 (d, 1 H, H(6′), J_m = 2.4), 15.98 (br.s, 1 H, OH)	3350, 1610, 1570
2g	2.12 (br.s, 1 H, NH); 2.30 (s, 3 H, Me); 2.86—3.22 (m, 5 H, $C(9)H_2$, $C(10)H_2$, C(2)HH); 3.37 (AB system, Δδ 0.12, 2 H, $C(6)H_2$, J_{AB} = 15.3); 3.42—3.55 (m, 1 H, C(2)HH); 3.93 (ddd, 1 H, C(3)HH, ^2J = 14.9, ^3J = 6.9, 4.9); 4.13 (dt, 1 H, C(3)HH, ^2J = 14.9, ^3J = 6.0); 6.12 (tdd, 1 H, CF_2CF_2H, $^2J_{H,F}$ = 53.5, $^3J_{H,F}$ = 8.0, 4.6); 6.86 (d, 1 H, H(3′), J_o = 8.5); 7.13 (dd, 1 H, H(4′), J_o = 8.5, J_m = 1.7); 7.30 (d, 1 H, H(6′), J_m = 1.7); 15.64 (br.s, 1 H, OH)	3400, 1620, 1585, 1500
6g	2.24 (s, 3 H, Me); 3.31 (t, 2 H, CH_2—N^+D_3, J = 7.0); 3.68 (br.s, 2 H, $C(2)H_2$); 3.79 (t, 2 H, CH_2—N(1), J = 7.0); 3.95 (br.s, 2 H, $C(3)H_2$); 5.95 (s, 1 H, =CH); 6.16 (t.t, 1 H, CF_2CF_2H, $^2J_{H,F}$ = 52.6, $^3J_{H,F}$ = 3.6); 6.91 (d, 1 H, H(3′), J_o = 8.0); 7.13 (dd, 1 H, H(4′), J_o = 8.0, J_m = 1.9); 7.18 (br.s, 1 H, H(6′))	
2i*	2.12 (t, 1 H, NH, J = 6.1); 2.90—3.22 (m, 5 H, $C(9)H_2$, $C(10)H_2$, C(2)HH); 3.34 (AB system, Δδ 0.13, 2 H, $C(6)H_2$, J_{AB} = 15.0); 3.46—3.52 (m, 1 H, C(2)HH); 3.80 (s, 1 H, MeO); 3.87 (ddd, 1 H, C(3)HH, ^2J = 14.9, ^3J = 7.1, 5.4); 4.00 (dt, 1 H, C(3)HH, ^2J = 14.9, ^3J = 6.0); 6.12 (tdd, 1 H, CF_2CF_2H, $^2J_{H,F}$ = 53.6, $^3J_{H,F}$ = 8.2, 4.4); 6.29 (dd, 1 H, H(5′), J_o = 9.1, J_m = 2.6); 6.35 (d, 1 H, H(3′), J_m = 2.6); 7.35 (d, 1 H, H(6′), J_o = 9.1); 16.63 (br.s, 1 H, OH)	3300, 1605, 1540
2j	2.12 (br.s, 1 H, NH); 2.90—3.23 (m, 5 H, $C(9)H_2$, $C(10)H_2$, C(2)HH); 3.32 (AB system, Δδ 0.15, 2 H, $C(6)H_2$, J_{AB} = 15.2); 3.42—3.51 (m, 1 H, C(2)HH); 3.91 (ddd, 1 H, C(3)HH, ^2J = 14.9, ^3J = 6.6, 4.6); 4.14 (dt, 1 H, C(3)HH, ^2J = 14.9, ^3J = 5.5); 6.12 (tdd, 1 H, CF_2CF_2H, $^2J_{H,F}$ = 53.4, $^3J_{H,F}$ = 8.3, 4.3); 6.88 (d, 1 H, H(3′), J_o = 8.8); 7.24 (dd, 1 H, H(4′), J_o = 8.8, J_m = 2.4); 7.49 (d, 1 H, H(6′), J_m = 2.4); 16.01 (br.s, 1 H, OH)	3405, 1615, 1540
2l	2.04 (br.s, 1 H, NH); 2.28 (s, 3 H, Me); 2.96—3.25 (m, 5 H, $C(9)H_2$, $C(10)H_2$, C(2)HH); 3.29 (AB system, Δδ 0.15, 2 H, $C(6)H_2$, J_{AB} = 15.4); 3.38—3.48 (m, 1 H, C(2)HH); 3.94 (ddd, 1 H, CHH(3), ^2J = 15.6, ^3J = 6.8, 4.2); 4.14 (ddd, 1 H, C(3)HH, ^2J = 15.6, ^3J = 7.3, 4.7); 5.51 (t, 1 H, CHF_2, $J_{H,F}$ = 56.2); 6.85 (d, 1 H, H(3′), J_o = 8.5); 7.12 (dd, 1 H, H(4′), J_o = 8.5, J_m = 2.0); 7.32 (br.s, 1 H, H(6′)); 15.78 (br.s, 1 H, OH)	3390, 1625, 1570, 1510
6l	2.22 (s, 3 H, Me); 3.29 (br.s, 2 H, CH_2—N^+D_3); 3.76 (br.s, 2 H, CH_2—N(1)); 3.91 (br.s, 4 H, $C(2)H_2$, $C(3)H_2$); 5.80 (s, 1 H, =CH); 6.62 (t, 1 H, CHF_2, $J_{H,F}$ = 53.0); 6.90 (d, 1 H, H(3′), J_o = 8.6); 7.11 (dd, 1 H, H(4′), J_o = 8.6, J_m = 1.6); 7.23 (br.s, 1 H, H(6′))	
2m	2.10 (br.s, 1 H, NH); 2.93—3.23 (m, 5 H, $C(9)H_2$, $C(10)H_2$, C(2)HH); 3.26 (AB system, Δδ 0.17, 2 H, $C(6)H_2$, J_{AB} = 15.4); 3.36—3.48 (m, 1 H, C(2)HH); 3.78 (s, 3 H, MeO); 3.94 (ddd, 1 H, C(3)HH, ^2J = 15.4, ^3J = 6.5, 4.0); 4.15 (ddd, 1 H, C(3)HH, ^2J = 15.4, ^3J = 7.6, 4.0); 5.51 (t, 1 H, CHF_2, $J_{H,F}$ = 56.1); 6.88 (d, 1 H, H(3′), J_o = 8.9); 6.95 (dd, 1 H, H(4′), J_o = 8.9, J_m = 2.8); 7.08 (d, 1 H, H(6′), J_m = 2.8); 15.33 (br.s, 1 H, OH)	3320, 1620, 1585
2n*	2.07 (br.s, 1 H, NH); 2.96—3.24 (m, 5 H, $C(9)H_2$, $C(10)H_2$, C(2)HH); 3.26 (AB system, Δδ 0.16, 2 H, $C(6)H_2$, J_{AB} = 15.4); 3.41—3.47 (m, 1 H, C(2)HH); 3.80 (s, 3 H, MeO); 3.86 (ddd, 1 H, C(3)HH, ^2J = 15.4, ^3J = 6.4, 4.3); 4.03 (ddd, 1 H, C(3)HH, ^2J = 15.4, ^3J = 7.5, 4.7); 5.52 (t, 1 H, CHF_2, $J_{H,F}$ = 56.1); 6.27 (dd, 1 H, H(5′), J_o = 9.2, J_m = 2.6); 6.35 (d, 1 H, H(3′), J_m = 2.6); 7.36 (s, 3 H, 0.5 C_6H_6); 7.38 (d, 1 H, H(6′), J_o = 9.2); 16.78 (br.s, 1 H, OH)	3310, 1600, 1535, 1510
6n*	3.28 (t, 2 H, CH_2—N^+D_3, ^3J = 7.1); 3.73 (br.s, 2 H, $C(2)H_2$); 3.80 (s, 3 H, MeO); 3.87 (t, 2 H, CH_2—N(1), ^3J = 7.1); 3.93 (br.s, 2 H, $C(3)H_2$); 5.81 (s, 1 H, =CH); 6.33 (dd, 1 H, H(5′), J_o = 9.2, J_m = 2.6); 6.51 (t, 1 H, CHF_2, $J_{H,F}$ = 53.2); 6.52 (d, 1 H, H(3′), J_m = 2.6); 7.35 (s, 3 H, 0.5 C_6H_6); 7.45 (d, 1 H, H(6′), J_o = 9.2)	
2o	2.10 (br.s, 1 H, NH); 2.95—3.23 (m, 5 H, $C(9)H_2$, $C(10)H_2$, C(2)HH); 3.26 (AB system, Δδ 0.13, 2 H, $C(6)H_2$, J_{AB} = 15.6); 3.38—3.51 (m, 1 H, C(2)HH); 3.94 (ddd, 1 H, C(3)HH, ^2J = 15.6, ^3J = 6.4, 4.2); 4.16 (ddd, 1 H, C(3)HH, ^2J = 15.6, ^3J = 7.7, 4.3); 5.51 (t, 1 H, CHF_2, $J_{H,F}$ = 56.2); 6.88 (d, 1 H, H(3′), J_o = 8.9); 7.24 (dd, 1 H, H(4′), J_o = 8.9, J_m = 2.4); 7.51 (d, 1 H, H(6′), J_m = 2.4); 16.08 (br.s, 1 H, OH)	3350, 1605, 1545

(*to be continued*)

Table 2 (*continue*)

Compound	^{1}H NMR ($CDCl_3$, δ, *J*/Hz)	IR, ν/cm^{-1}
2p	2.16 (br.s, 1 H, NH); 2.90—3.24 (m, 5 H, $C(9)H_2$, $C(10)H_2$, C(2)HH); 3.42 (AB system, Δδ 0.07, 2 H, $C(6)H_2$, J_{AB} = 14.5); 3.48—3.58 (m, 1 H, C(2)HH); 3.95 (ddd, 1 H, C(3)HH, ^2J = 14.9, ^3J = 6.8, 5.2); 4.15 (dt, 1 H, C(3)HH, ^2J = 14.9, ^3J = 6.1); 6.81 (ddd, 1 H, H(5′), $J_{H(5'),H(6')}$ = 8.2, $J_{H(5'),H(4')}$ = 7.1, $J_{H(5'),H(3')}$ = 1.2); 6.95 (dd, 1 H, H(3′), $J_{H(3'),H(4')}$ = 8.4, $J_{H(3'),H(5')}$ = 1.2); 7.31 (ddd, 1 H, H(4′), $J_{H(4'),H(3')}$ = 8.4, $J_{H(4'),H(5')}$ = 7.2, $J_{H(4'),H(6')}$ = 1.4); 7.50 (dd, 1 H, H(6′), $J_{H(6'),H(5')}$ = 8.2, $J_{H(6'),H(4')}$ = 1.4); 15.92 (br.s, 1 H, OH)	3400, 1620, 1580, 1505
6p	3.29 (t, 2 H, CH_2—N^+D_3, ^3J = 7.3); 3.55 (br.s, 2 H, $C(2)H_2$); 3.65 (t, 2 H, CH_2—N(1), ^3J = 7.3); 4.04 (br.s, 2 H, $C(3)H_2$); 6.22 (s, 1 H, =CH); 6.80 (ddd, 1 H, H(5′), $J_{H(5'),H(6')}$ = 8.2, $J_{H(5'),H(4')}$ = 7.2, $J_{H(5'),H(3')}$ = 1.0); 6.98 (dd, 1 H, H(3′), $J_{H(3'),H(4')}$ = 8.4, $J_{H(3'),H(5')}$ = 1.0); 7.32 (ddd, 1 H, H(4′), $J_{H(4'),H(3')}$ = 8.4, $J_{H(4'),H(5')}$ = 7.2, $J_{H(4'),H(6')}$ = 1.5); 7.48 (dd, 1 H, H(6′), $J_{H(6'),H(5')}$ = 8.2, $J_{H(6'),H(4')}$ = 1.5)	
2q	2.16 (br.s, 1 H, NH); 2.89—3.27 (m, 5 H, $C(9)H_2$, $C(10)H_2$, C(2)HH); 3.44 (s, 2 H, $C(6)H_2$); 3.52—3.63 (m, 1 H, C(2)HH); 3.97 (dt, 1 H, C(3)HH, ^2J = 14.9, ^3J = 7.1); 4.15 (dt, 1 H, C(3)HH, ^2J = 14.9, ^3J = 6.0); 6.81 (t, 1 H, H(5′), J_o = 7.6); 6.96 (d, 1 H, H(3′), J_o = 8.3); 7.32 (t, 1 H, H(4′), J_o = 7.8); 7.49 (d, 1 H, H(6′), J_o = 8.4); 15.91 (br.s, 1 H, OH)	3410, 1615, 1580, 1510
6q	3.30 (t, 2 H, CH_2—N^+D_3, ^3J = 7.0); 3.56 (br.s, 2 H, $C(2)H_2$); 3.65 (t, 2 H, CH_2—N(1), ^3J = 7.0); 4.05 (br.s, 2 H, $C(3)H_2$); 6.22 (s, 1 H, =CH); 6.81 (t, 1 H, H(5′), J_o = 7.5); 6.99 (d, 1 H, H(3′), J_o = 8.1); 7.33 (t, 1 H, H(4′), J_o = 7.8); 7.48 (d, 1 H, H(6′), J_o = 8.1)	
2r	2.20 (br.s, 1 H, NH); 2.96—3.30 (m, 5 H, $C(9)H_2$, $C(10)H_2$, C(2)HH); 3.41 (AB system, Δδ 0.10, 2 H, $C(6)H_2$, J_{AB} = 14.8); 3.85—3.93 (m, 2 H, $C(3)H_2$); 6.81 (d, 1 H, H(4′), J_o = 9.4); 7.25 (d, 1 H, H(3′), J_o = 9.4); 7.42 (ddd, 1 H, H(7′), $J_{H(7'),H(8')}$ = 8.2, $J_{H(7'),H(6')}$ = 6.3, $J_{H(7'),H(5')}$ = 1.8); 7.50—7.60 (m, 2 H, H(5′), H(6′)); 8.49 (d, 1 H, H(8′), J_o = 8.2); 15.90 (br.s, 1 H, OH)	3330, 1600, 1545, 1525

* The ^{1}H NMR spectra were recorded on a Bruker-DRX-400 spectrometer in $CDCl_3$ operating at 400 MHz with Me_4Si as the internal standard.

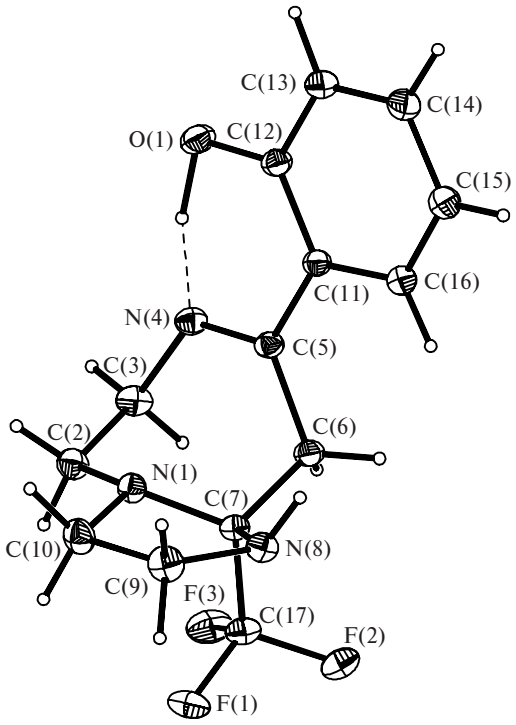


Fig. 1. Overall view of molecule **2a**.

The H(O(1)) atom is involved in the O(1)—H(O(1))...N(4) intramolecular hydrogen bond characterized by the following parameters:

Bond	*d*/Å	Angle	ω/deg
O(1)—H(O(1))	1.11(2)	O(1)—H(O(1))...N(4)	160(2)
O(1)...N(4)	2.481(1)		
H(O(1))...N(4)	1.41(2)		

Apparently, this bond is responsible for the planar structure of the first fragment. The six-membered H(O(1))—O(1)—C(12)≃C(11)—C(5)=N(4) ring is planar (the average deviation from the plane is 0.021(1) Å). The C(12)—C(11) and C(5)—N(4) bond lengths (1.4286(6) and 1.2964(6) Å, respectively) are larger than the standard values (1.380(13) and 1.279(8) Å for the C_{ar}≃C_{ar} and C_{sp2}=N bonds, respectively), whereas the O(1)—C(12) and C(11)—C(5) bond lengths (1.3307(6) and 1.4683(6) Å, respectively) are smaller than the standard values (1.362(15) and 1.485(13) Å for the O—C_{ar} and C_{ar}—C_{sp2} bonds, respectively).[10] Therefore, in spite of the localization of the hydrogen atom, it can be assumed that the contribution of the keto-enamine form is rather essential, the more so as the H(O(1))...N(4) distance is also rather short (1.41(2) Å).

With the aim of comparing the distribution of the bond lengths in the imino-enol fragments of other

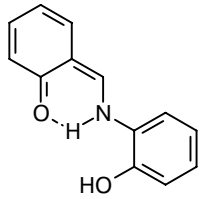
compounds available in the Cambridge Structural Database (CSD, April 2000), we searched for the structures analogous to compound **2a** containing the imino-enol fragment. In the search, the H...N distance was limited by 2.2 Å and the C(3) and C(13) atoms were specified. A total of 145 fragments were found in 110 structures. The ranges of the reference distances and the bond angles are as follows:

Distance	d (d_{aver})/Å	Bond	d (d_{aver})/Å
O(1)...N(4)	2.471—2.668 (2.586)	C(12)—C(11)	1.371—1.435 (1.405)
H(O(1))...N(4)	1.354—2.090 (1.732)	C(11)—C(5)	1.424—1.484 (1.453)
O(1)...C(12)	1.320—1.375 (1.349)	C(5)—N(4)	1.246—1.311 (1.282)

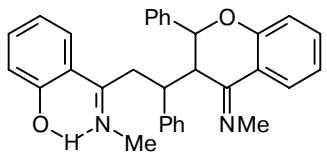
The bond lengths and the distances typical of compound **2a** fall within the above-mentioned ranges. In addition, the CSD includes the only keto-enamine structure (*N*-salicylidene-2-hydroxyaniline (**7**))[11] containing the *ortho*-quinoid analog of the corresponding fragment of compound **2a** (Tables 3 and 4).

It should be noted that the intramolecular hydrogen bond in compound **2a** is one of the shortest bonds. Among the structures under consideration, three compounds possess the O...N intramolecular distances, which are smaller or close to that observed in compound **2a**. These are 2-[3-(4-methylimino-2-phenyl-2,3-dihydro-4*H*-1-benzopyran-3-yl)-1-methylimino-3-phenylpropyl]phenol (**8**),[12] 2,2′-[2,2-dimethyl-1,3-propanediylbis(nitrilopropylidine)]diphenol (**9**),[13] and 3,5-di-*tert*-butyl-2-[(3,5-di-*tert*-butyl-2-hydroxyphenyl){(*Z*)-methylimino}-methyl]cyclopent-2-en-1-one (**10**).[14]

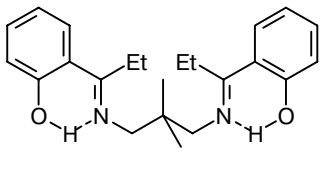
The parameters of the shortest intramolecular hydrogen bonds and selected bond lengths and bond angles in the structures of **7—10** are compared with the corresponding values for compound **2a** in Tables 3 and 4. It can be seen that the N(4)—C(5) and C(11)—C(12) bond lengths in the six-membered rings are not distinctive, whereas the bond lengths corresponding to the



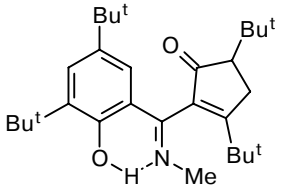
7



8

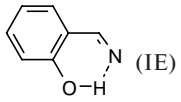


9

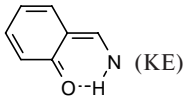


10

Table 3. Selected bond lengths and distances (d) in the imino-enol (IE) and keto-enamine (KE) fragments of compounds **2a** and **7—10**



(IE)



(KE)

Bond (distance)	d/Å				
	IE				KE
	2a	**8**	**9**	**10**	**7**
O(1)—H(O(1))	1.11(2)	1.08	0.84	1.01	—
H(O(1))...N(4)	1.41(2)	1.46	1.73	2.09	—
H(N(4))...O(1)	—	—	—	—	1.82
O(1)...N(4)	2.481(1)	2.471	2.476	2.481	2.598
O(1)—C(12)	1.3307(6)	1.337	1.341	1.356	1.301
C(11)—C(12)	1.4286(6)	1.424	1.415	1.417	1.431
C(5)—C(11)	1.4683(6)	1.474	1.481	1.483	1.410
N(4)—C(5)	1.2964(6)	1.293	1.287	1.283	1.303
C(12)—C(13)	1.4104(7)	1.394	1.398	1.379	1.420
C(11)—C(16)	1.4079(6)	1.376	1.402	1.388	1.419

Note. The bond lengths and distances were determined at the following temperatures: 100 (**2a**), 120 (**7** and **9**), 123 (**8**), and 295 K (**10**).

Table 4. Selected bond angles (ω) in the imino-enol (IE) and keto-enamine (KE) fragments of compounds **2a** and **7—10**

Angle	ω/deg				
	IE				KE
	2a	**8**	**9**	**10**	**7**
O(1)—H(O(1))...N(4)	160(2)	154	147	101	—
N(4)—H(N(4))...O(1)	—	—	—	—	140
C(16)—C(11)—C(12)	118.51(4)	117.5	118.0	119.2	120.4
C(13)—C(12)—C(11)	119.22(4)	119.5	119.7	119.0	116.7
O(1)—C(12)—C(11)	122.30(4)	121.5	122.2	118.4	121.5
C(12)—C(11)—C(5)	119.37(4)	120.2	120.0	120.2	120.8
N(4)—C(5)—C(11)	117.38(4)	116.1	116.1	119.4	123.1

Note. The bond angles were determined at the following temperatures: 100 (**2a**), 120 (**7** and **9**), 123 (**8**), and 295 K (**10**).

bonds C(5)—C(11) and O(1)—C(12) of compound **2a** in the imino-enol and keto-enamine fragments, respectively, are substantially different and, are, apparently, characteristic. Evidently, the bond angles corresponding to the C(16)—C(11)—C(12), C(11)—C(12)—C(13), and N(4)—C(5)—C(11) angles in compound **2a** are also characteristic. In spite of the fact that the experimental data were obtained at different temperatures, all bond lengths analogous to O(1)—C(12) (the average value is 1.341 Å), C(11)—C(12) (1.421 Å), and N(4)—C(5) (1.290 Å) in all these structures have values intermediate between the corresponding double and single bond lengths. This tendency is also typical for compounds possessing homoatomic O—H...O[15,16] or heteroatomic N—H...O[17,18] intramolecular hydrogen bonds in which

such redistribution of the bond lengths is accounted for by the electron density delocalization. Therefore, the geometric parameters of compound **2a** correspond, most likely, to the imino-enol tautomer with the electron density delocalization in the O—C=C—C=N fragment rather than to a superposition of two tautomeric forms.

Yet another characteristic structural feature of molecule **2a** is the short intramolecular H...H distance in C(16)—H(C(16))...H_A(C(6))—C(6) (2.00 Å; the C(16)...C(6) distance is 3.023(1) Å), which is substantially smaller than the sum of the van der Waals radii of the hydrogen atoms. However, analysis of 38 Ph—C(=N—C)—C—C fragments, which are analogous to the fragment in compound **2a** but do not contain the OH group (consequently, which do not possess an intramolecular hydrogen bond), available in the CSD demonstrated that the distribution of the H...H contacts has a pronounced maximum in the region of 1.888—2.270 Å with the average value of 2.056 Å. This fact indicates that the above-mentioned short distances are, presumably, normal intramolecular H...H contacts.

In the crystal of **2a**, the molecules are packed in layers parallel to the *ac* plane. No intermolecular hydrogen bonds and shortened contacts were found in the crystal structure of **2a**.

Apparently, the absence of intermolecular hydrogen bonds in the crystal structure of **2a** is associated with the high strength of the intramolecular O—H...N hydrogen bond. At the same time, the OH group can be involved in formation of strong intermolecular hydrogen bonds. Recently,[19] we have reported isomerization of bicycle **2h**. Based on the X-ray diffraction data, the structure of 1-(2-aminoethyl)-7-(2-hydroxy-5-methoxyphenyl)-5-(1,1,2,2-tetrafluoroethyl)-2,3-dihydro-1*H*-1,4-diazepine (**11**) (Scheme 5) has been assigned to the resulting compound.

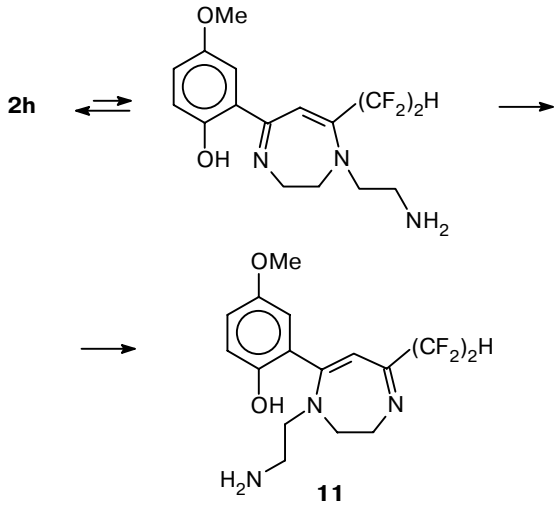
In the crystal of compound **11**, the molecules are packed in bulky layers parallel to the crystallographic plane (001) through the system of weak intermolecular hydrogen bonds between the oxygen atoms and the hydrogen atoms of the amino groups (the O(1)...H_A(N(3))—N(3) and O(2)...H_B(N(3))—N(3) distances are 2.32(6) and 2.49(5) Å, respectively; the corresponding N...O distances are 3.095(5) and 3.167(5) Å). In addition, these structures have systems of strong hydrogen bonds between the nitrogen atoms and the hydrogen atoms of the hydroxy groups, which are favorable for layered structures. The bond parameters are as follows:

Distance (bond)	*d*/Å	Angle	ω/deg
H(O(2))...N(3)	1.85(6)	O(2)—H(O(2))...N(3)	170(5)
O(2)—H(O(2))	0.86		
O(2)...N(3)	2.684(4)		

The layers are linked through the shortened intermolecular F(1)...F(2), F(1)...F(4A), and F(2)...F(1) contacts (2.810(9), 2.621(13), and 2.695(14) Å, respectively).[20]

Interestingly, the N(3)H_2 amino group serves the dual function in the system of intermolecular hydrogen bonds. On the one hand, it acts as a donor (in the N—H...O bonds). On the other hand, this group serves as a strong acceptor and is involved in intermolecular N...H—O hydrogen bonds through which molecules **11** are linked in centrosymmetric dimers (Fig. 2).

Scheme 5



With the aim of analyzing the acceptor role of the NH_2 groups, we searched for organic structures containing intermolecular hydrogen bonds of the C—(H_2)N...H—O—C type (CSD, April 1999). In the search, we did not take into account structures, which were established with the *R* factor >10%, structures in which the hydrogen atoms of the amino and hydroxy groups were not revealed, and structures in which these groups are disordered. Structures in which the hydroxy group is involved in the COOH fragment were also rejected.

We found 62 examples (52 structures) of this intermolecular hydrogen bond with the N...O distances < 3 Å; these bonds are characterized by the following parameters:

Distance	*d*	d_{aver}	Angle	ω	ω_{aver}
	Å			deg	
N...O	2.600—2.985	2.778	N...H—O	147.1—178.8	168.8
N...H	1.641—2.143	1.881			

We found only five structures[21—25] in which the N...O distances are smaller or close to that observed in compound **11** (2.600—2.696 Å). In these structures, the intermolecular hydrogen bonds are formed between the major molecule and the less bulky molecule of solvation or they link the molecules in chains, unlike the structure of **11** in which the molecules are linked in dimers. The dimers were found only in two structures, *viz.*, in 3-amino-4-butoxy-1-(5,5-dimethyl-1,3-dioxan-2-yl)-1,2-butanediol and 2-amino-5-(4-bromophenoxy)cyclopentan-1-ol.[26,27] However, the hydrogen bonds in these compounds are substantially weaker (the N...O distances are 2.752 and 2.787 Å, the N...H distances are 1.942 and

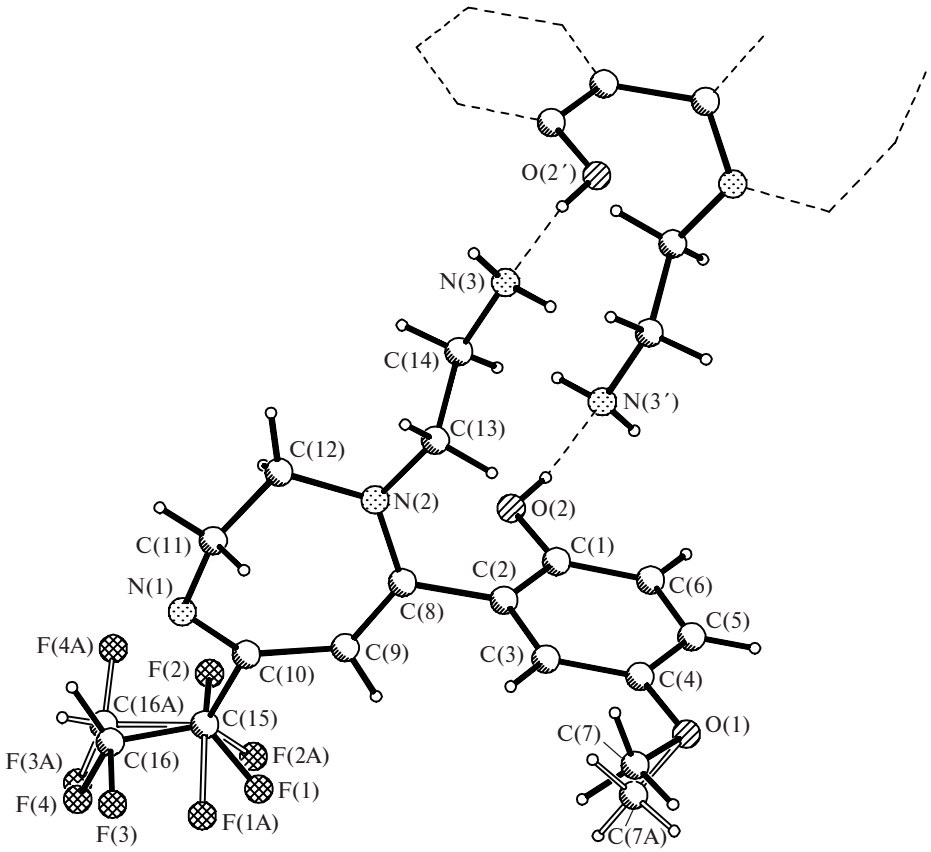


Fig. 2. Overall view of molecule **11** and the atomic numbering scheme. The second positions of the disordered Me and CF_2—CF_2H groups are labelled by A. In the crystal, the molecules are linked in centrosymmetric dimers through O—H...N hydrogen bonds. The O(2′) and N(3′) atoms belong to the second molecule of the dimer.

1.942 Å, and the N...H—O angles are 172.2° and 170.9°, respectively).

Therefore, dihydrodiazepine **11** provides a rather rare example of the formation of an intermolecular dimer possessing one of the strongest intermolecular $N(H_2)$...H—O hydrogen bonds.

Experimental

Crystals of compound **2a** ($C_{14}H_{16}F_3N_3O$) are triclinic. At 100 K, a = 8.37680(10) Å, b = 8.6199(2) Å, c = 10.3608(2) Å, α = 101.333(1)°, β = 109.230(1)°, γ = 104.624(1)°, V = 650.69(2) Å^3, d_{calc} = 1.528 g cm^{-3}, the absorption coefficient μ = 0.128 mm^{-1}, space group P-1, Z = 2. The intensities of 11037 independent reflections (R_{int} = 0.05) were measured on a Bruker SMART 1K CCD diffractometer (Mo-Kα radiation, λ = 0.71073 Å, graphite monochromator, ω scanning technique, $2\theta_{max}$ = 100°). The intensities of all measured reflections were corrected for the Lorentz and polarization factors.[28,29] Absorption was ignored.

The structure was solved by the direct method using the SHELXTL PLUS 5.0 program package.[30] The nonhydrogen atoms were refined anisotropically by the full-matrix least-squares method (based on F^2). The positions of the hydrogen atoms were revealed from the difference Fourier synthesis and refined isotropically. The final R factors were as follows: R_1 = 0.0466 (based on F for 7337 reflections with $I > 2\sigma(I)$), wR_2 = 0.1404 (calculated based on F^2 for all 10987 reflections used at the final stage of the refinement); the number of the parameters in the refinement was 255, GOOF = 0.953.

Crystals of compound **11** ($C_{16}H_{19}F_4N_3O_2$) are monoclinic. At 300 K, a = 7.821(6) Å, b = 9.394(6) Å, c = 23.785(16) Å, β = 80.64(6)°, V = 1724(2) Å^3, d_{calc} = 1.392 g cm^{-3}, the absorption coefficient μ = 0.12 mm^{-1}, space group $P2_1/n$, Z = 4. The intensities of 3720 independent reflections (R_{int} = 0.06) were measured on a four-circle automated Siemens P3/PC diffractometer (Mo-Kα radiation, λ = 0.71093 Å, graphite monochromator, $\theta/2\theta$ scanning technique, $2\theta_{max}$ = 55°).

The structure was solved by the direct method using the SHELXTL PLUS 5.0 program package.[30] The nonhydrogen atoms were refined anisotropically by the full-matrix least-squares method (based on F^2). The atoms of the MeO and $(CF_2)_2H$ groups are disordered over two positions with the equally probable occupancies. In the course of the refinement, the ranges of variations in the O(1)—C(7A), O(1)—C(7B), and C—F bond lengths were limited by 0.02 Å. The hydrogen atoms bound to the carbon atoms were placed in calculated positions and refined using the riding model with fixed C—H distances (0.97 Å) and isotropic displacement parameters $U_{iso} = 1.5U_{eq}$ for the methyl groups and $U_{iso} = 1.2U_{eq}$ for the remaining groups (U_{eq} are equivalent isotropic displacement parameters of the corresponding C atoms). The positions of the hydrogen atoms of the amino and hydroxy groups were located from the difference Fourier synthesis and refined isotropically. The final R factors were as follows: R_1 = 0.074, wR_2 = 0.19, GOOF = 1.172 using 2486 reflections with $I > 2\sigma(I)$.

The IR spectra were recorded on an IKS-29 instrument in Nujol mulls. The ^{1}H NMR spectra were measured on a Bruker WM-250 spectrometer in $CDCl_3$ operating at 250 MHz with Me_4Si as the internal standard.

Diethylenetriamine was purchased from Lancaster. Chromones **1a—q** were prepared according to a known procedure.[31]

Compounds **2a—c,f,h,k** were synthesized according to procedures described previously.[3,19]

5-(2′-Hydroxy-4′-methoxyphenyl)-7-trifluoromethyl-1,4,8-triazabicyclo[5.3.0]dec-4-ene (2d). ***A.*** Chromone **1d** (200 mg, 0.86 mmol) and diethylenetriamine (200 μL, 191 mg, 1.86 mmol) were dissolved upon heating in EtOH (3 mL). The reaction mixture was kept at ~20 °C for 24 h and the crystals of bicycle **2d** that formed were washed with H_2O and recrystallized from EtOH. The yield was 140 mg (50%). Compounds **2e,g,i,j,l—r** were prepared analogously.

7-Difluoromethyl-5-(2′-hydroxy-5′-methoxyphenyl)-1,4,8-triazabicyclo[5.3.0]dec-4-ene (2m). ***B.*** Aminoenone **3m** (200 mg, 0.82 mmol) was dissolved in diethylenetriamine (200 μL, 191 mg, 1.86 mmol) and the reaction mixture was kept at ~20 °C for 24 h. The crystals of bicycle **2m** that formed were washed with H_2O and recrystallized from EtOH. The yield was 110 mg (43%).

The physicochemical and spectral characteristics of compounds **2d,e,g,i,j,l—r** are given in Tables 1 and 2, respectively.

1,13-Di(2′-hydroxyphenyl)-3,11-dimethyl-4,7,10-triazatrideca-2,11-diene-1,13-dione (4)* was prepared from 2-methylchromone and DETA analogously to the syntheses of compounds **2a—r**. The yield was 38%, m.p. 155—156 °C. Found (%): C, 66.81; H, 7.00; N, 9.79. $C_{24}H_{29}N_3O_4 \cdot 0.5\ H_2O$. Calculated (%): C, 66.65; H, 6.99; N, 9.72. IR, ν/cm^{-1}: 3210 (NH), 1610, 1575, 1565, 1545, 1515 (C=O, C=C, NH, benzene ring). ^{1}H NMR, δ: 2.12 (s, 6 H, 2 Me); 2.95 (t, 4 H, 2 CH_2N, J = 6.0 Hz); 3.48 (q, 4 H, 2 CH_2NC=, J = 6.0 Hz); 5.66 (s, 2 H, 2 =CH); 6.76 (ddd, 2 H, 2 H(5), $J_{H(5),H(6)}$ = 8.0 Hz, $J_{H(5),H(4)}$ = 7.0 Hz, $J_{H(5),H(3)}$ = 1.2 Hz); 6.89 (dd, 2 H, 2 H(3), $J_{H(3),H(4)}$ = 8.2 Hz, $J_{H(3),H(5)}$ = 1.2 Hz); 7.29 (ddd, 2 H, 2 H(4), $J_{H(4),H(3)}$ = 8.2 Hz, $J_{H(4),H(5)}$ = 7.0 Hz, $J_{H(4),H(6)}$ = 1.5 Hz); 7.57 (dd, 2 H, 2 H(6), $J_{H(6),H(5)}$ = 8.0 Hz, $J_{H(6),H(4)}$ = 1.5 Hz); 11.04 (br.s, 2 H, 2 NH...O); 13.54 (br.s, 2 H, 2 OH); NH is not manifested.

This work was financially supported by the Russian Foundation for Basic Research (Project Nos. 99-03-32960, 00-15-97359, 99-07-90133, and 00-03-32807) and partially by the US Civilian Research and Development Foundation (Grant REC-005).

References

1. V. Ya. Sosnovskikh and B. I. Usachev, *Izv. Akad. Nauk, Ser. Khim.*, 2001, 1357 [*Russ. Chem. Bull., Int. Ed.*, 2001, **50**, 1426].
2. V. Ya. Sosnovskikh, V. A. Kutsenko, and Yu. G. Yatluk, *Izv. Akad. Nauk, Ser. Khim.*, 2000, 1432 [*Russ. Chem. Bull., Int. Ed.*, 2000, **49**, 1426].
3. V. Ya. Sosnovskikh, Yu. G. Yatluk, and V. A. Kutsenko, *Izv. Akad. Nauk, Ser. Khim.*, 1999, 1825 [*Russ. Chem. Bull.*, 1999, **48**, 1800 (Engl. Transl.)].
4. V. Ya. Sosnovskikh and I. S. Ovsyannikov, *Zh. Org. Khim.*, 1993, **29**, 89 [*Russ. J. Org. Chem.*, 1993, **29**, 74 (Engl. Transl.)].
5. V. Ya. Sosnovskikh, V. A. Kutsenko, and D. S. Yachevskii, *Mendeleev Commun.*, 1999, 204.
6. V. Ya. Sosnovskikh, *Mendeleev Commun.*, 1996, 189.
7. U. Casellato, D. Fregona, S. Sitran, S. Tamburini, P. A. Vigato, and P. Zanello, *Inorg. Chim. Acta*, 1984, 279.
8. V. I. Saloutin, I. T. Bazyl′, Z. E. Skryabina, M. I. Kodess, and O. N. Chupakhin, *Zh. Org. Khim.*, 1995, **31**, 1432 [*Russ. J. Org. Chem.*, 1995, **31** (Engl. Transl.)].
9. N. S. Zefirov, V. A. Palyulin, and E. E. Dashevskaya, *J. Phys. Org. Chem.*, 1990, **3**, 147.
10. F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1987, S1.
11. S. V. Lindeman, M. Yu. Antipin, and Yu. T. Struchkov, *Kristallografiya*, 1988, **33**, 365 [*Sov. Phys.-Crystallogr.*, 1988, **33** (Engl. Transl.)].
12. C. J. Adams, L. Main, and B. K. Nicholson, *Acta Crystallogr.*, 1990, **C46**, 2424.
13. J. P. Corden, W. Errington, P. Moore, P. R. Phillips, and M. G. H. Wallbridge, *Acta Crystallogr.*, 1996, **C52**, 3199.
14. H.-D. Becker, B. W. Skelton, and A. H. White, *Aust. J. Chem.*, 1983, **36**, 2073.
15. G. Gilli, F. Bellucci, V. Ferretti, and V. Bertolasi, *J. Am. Chem. Soc.*, 1989, **111**, 1023.
16. V. Bertolasi, P. Gilli, V. Ferretti, and G. Gilli, *J. Am. Chem. Soc.*, 1991, **113**, 4917.
17. V. Bertolasi, P. Gilli, V. Ferretti, and G. Gilli, *Acta Crystallogr.*, 1994, **B50**, 617.
18. P. Gilli, V. Ferretti, and V. Bertolasi, *19-th European Crystallogr. Meeting, Abstrs. (Nancy, France, 25—31 August, 2000),* Université Henri Poincaré, Bialec, Nancy, 2000, 308.
19. V. Ya. Sosnovskikh, I. I. Vorontsov, V. A. Kutsenko, and Y. G. Yatluk, *Mendeleev Commun.*, 2000, 56.
20. Yu. V. Zefirov and P. M. Zorkii, *Usp. Khim.*, 1995, **64**, 446 [*Russ. Chem. Rev.*, 1995, **64** (Engl. Transl.)].
21. E. Weber, N. Dorpinghaus, and I. Goldberg, *J. Chem. Soc., Chem. Commun.*, 1988, 1566.
22. G. Ferguson, C. Glidewell, R. M. Gregson, and P. R. Meehan, *Acta Crystallogr.*, 1998, **B54**, 330.
23. M. R. Caira, A. Horne, L. R. Nassimbeni, K. Okuda, and F. Toda, *J. Chem. Soc., Perkin Trans. 2*, 1995, 1063.
24. F. H. Cano, C. Foces-Foces, A. Alemany, M. Bernabe, M. L. Jimeno, and M. Martin-Lomas, *Carbohydr. Res.*, 1985, **139**, 65.
25. K. Hegetschweiler, R. D. Hancock, M. Ghisletta, T. Kradolfer, V. Gramlich, and H. W. Schmalle, *Inorg. Chem.*, 1993, **32**, 5273.
26. V. Jager, I. Muller, and E. F. Paulus, *Tetrahedron Lett.*, 1985, **26**, 2997.
27. J. R. McCarthy, P. E. Wiedeman, A. J. Schuster, J. P. Whitten, R. J. Barbuch, and J. C. Huffman, *J. Org. Chem*, 1985, **50**, 3095.
28. *SMART and SAINT*, *Area Detector Control and Integration Software*. Bruker AXS, Analitical X-Ray Instruments, Release 5.0, Madison, Wisconsin, USA, 1998.
29. G. M. Sheldrick, *SADABS: A Program for Exploiting the Redundancy of Area-Detector X-Ray Data*, University of Göttingen, Germany, 1999.
30. G. M. Sheldrick, *SHELXTL-Plus,* Release 5.0, Siemens Analytical Instruments Inc., Madison, Wisconsin, USA, 1994.
31. V. Ya. Sosnovskikh and B. I. Usachev, *Izv. Akad. Nauk, Ser. Khim.*, 2001, 434 [*Russ. Chem. Bull., Int. Ed.*, 2001, **50**, 453].

* V. A. Anufriev (the Department of Organic Chemistry of the A. M. Gorky Ural State University) took part in the synthesis of bisaminoenone **4**.

Received December 15, 2000;
in revised form April 10, 2001