A Simple Route to 4-Aryl and 4-Hetaryl substituted 6-Methyl-2,2-difluoro-1,3,2-(2*H*)-dioxaborines

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Dedicated to Prof. Dr. H.-D. Martin on the Occasion of his 60th Birthday

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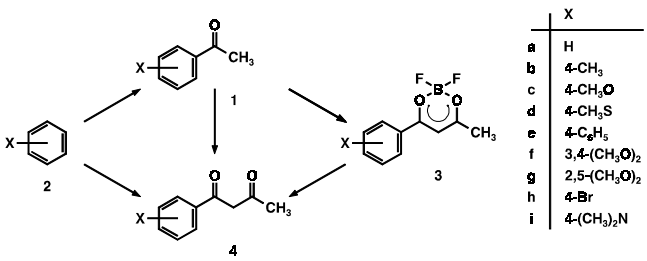
Abstract. 4-(Het)aryl-2,2-difluoro-6-methyl-1,3,2-(2*H*)-dioxaborines **3a**–**3i**, **6a**–**6c**, **8** were prepared in a one-pot reaction from donor substituted arenes and hetarenes **2a**–**2i**, **5a**–**5c**, **7**, resp., by a boron trifluoride mediated acetoacetylation. With resorcinol dimethylether (**11**), diphenyl ether (**13a**), and 1,3-phenoxy-propane (**13b**) this acetoacetylation gives rise to the formation of bis-1,3,2-(2*H*)-dioxaborines **12**, **14a**, and **14b**, respectively. From triphenylamine (**9**) a tris-1,3,2-(2*H*)-dioxaborine **10** has been obtained. Phloroglucinol trimethylether (**15a**) is demethylated as well as acetylated and acetoacetylated at once to give a bis-1,3,2-(2*H*)-dioxaborine derivative **17**.

Similar to other 1,3-diketones, aroylacetones **4** are versatile synthones, *e.g.*, for the preparation of different types of heterocyclic compounds, such as pyrylium and benzopyrylium salts [1a, 1b], 4*H*-pyran-4-ones [1c], hetero-condensed pyrimidinium salts [1d], 1,2-dithiolium salts [1e], pyrazoles [1f], isoxazoles [1g], and others. Therefore, simple routes for the synthesis of **4** are of common interest.

The usual methods for the synthesis of aroylacetones **4** starts from acetophenones **1** which are condensed with alkyl acetates in presence of alkali alkoxides (Claisen condensation [2]). An alternative synthetic route starts from the same educts **1** but uses acetic anhydride and boron trifluoride as reagents (Meerwein condensation [3]). This reaction runs *via* on intermediate 4-aryl-2,2-difluoro-6-methyl-1,3,2-(2*H*)-dioxaborines **3** [4] which can be isolated, if desired, from the reaction mixture.

Because the 4-aryl-2,2-difluoro-6-methyl-1,3,2-(2*H*)-dioxaborines **3** can be also used, as demonstrated recently [5], instead of the corresponding aroylacetones **4** as synthones for preparing several types of heterocyclic compounds, their boron trifluoride mediated synthesis is of considerable preparative interest also. Its application became more attractive since the formation of 2,4-diaryl-6-methyl-pyrylium tetrafluoroborates as side-products [6] during the preparation of the 1,3,2-dioxaborines **3** has been significantly diminished by applying optimized reaction conditions [7].

Moreover, 4-aryl-2,2-difluoro-6-methyl-1,3,2-(2*H*)-di-oxaborines **3** have been used as educts for preparing several types of organic dyes, such as laser dyes [8], NLO-active dyes [9], or NIR absorbing dyes [10].



Scheme 1

A further improvement of the synthetic applications of aroylacetones **4** and 4-aryl-2,2-difluoro-6-methyl-1,3,2-(2*H*)-dioxaborines **3** should be possible if the transformation of the acetophenones **1** into the products **3** or **4** is combined with their synthesis from suited precursors. Because acetophenones **1** can be prepared, *inter alia*, by a boron trifluoride-catalysed acetylation of aromatic hydrocarbons **2** [3, 11], this reaction should be

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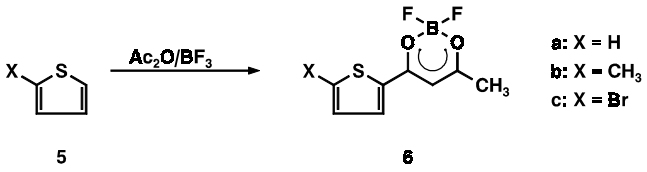
suited to be combine with the transformation of the acetophenones **1** into their corresponding 4-aryl-2,2-difluoro-6-methyl-1,3,2-(2*H*)-dioxaborines **3** or aroylacetones **4**. However, apart from one example in the 2,2-difluoro-6-methyl-1,3,2-(2*H*)-dioxaborine series **3** [12] and few ones in the aroylacetone series **4** [13], this synthetic route has not been demonstrated in the literature until now.

For elaborating a simple one-pot method for preparing4-aryl-2,2-difluoro-6-methyl-1,3,2-(2*H*)-dioxaborines **3** from corresponding arene or hetarene precursors a variety of such compounds have been allowed to react with acetic anhydride in presence of $BF_3(CH_3COOH)_2$.

Results and Discussion

For obtaining noticeable yields on 4-aryl-2,2-difluoro-6-methyl-1,3,2-(2*H*)-dioxaborines **3** from simple aromatic or heteroaromatic hydrocarbons **2**, special substituted derivatives of these compounds have to be used as starting compounds, however. Thus, with anisole **2c**, thioanisole **2d**, biphenyle **2e**, as well as with 1,2- and 1,4-bismethoxy-benzene **2f** and **2g** the corresponding 2,2-difluoro-6-methyl-1,3,2-(2*H*)-dioxaborines **3c**– **3g**, resp., could be obtained in satisfactory yields (see table 1) provided the products crystallize from the reaction mixture, as was the case for most of the alkoxy-substituted compounds.



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Scheme 2

In contrast, no 2,2-difluoro-1,3,2-(2*H*)-dioxaborines have been obtained by starting with benzene **2a** or with the simple bromo-substituted benzene **2h**. This is in a marked contrast to the behaviour of analogously substituted thiophenes **5a** and **5c** which were transformed as well as compound **5b** into their corresponding 2,2-difluoro-1,3,2-(2*H*)-dioxaborine derivatives **6a**–**6c** by the same procedure. In these cases, the yields are comparable or better than those ones received by a two step route starting with the Friedel-Crafts acetylation of the parent thiophenes **5** [11] and subsequent Meerwein acetylation of the resulting 5-acetylthiophenes with acetic anhydride in presence of boron trifluoride [14].

In this context it is worth mentioning that *N,N*-dimethylaniline **2i**, although belonging to the class of electron-rich aromatic compounds which are highly reactive against electrophilic reagents, does not give the corresponding 4(4-dimethylaminophenyl)-substituted 6-methyl-1,3,2-(2*H*)-dioxaborine **3i** or, at least, its 4-

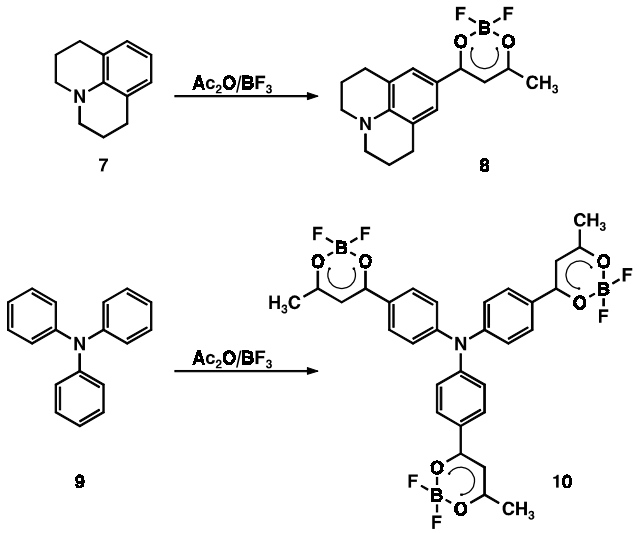
Table 1 Characteristic data of 2,2-difluoro-1,3,2-(2*H*)-dioxaborines prepared

Nr.	Yield (%)	*m.p.* (°C)	formula (m.w.)	C	H	others	
				calcd/found			
3c	65	164–165 [a)]	$C_{11}H_{11}BF_2O_3$	55.05	4.62		
			(240.02)	55.20	4.38		
3d	77	177–179	$C_{11}H_{11}BF_2O_2S$	51.59	4.33	S: 12.52	
			(256.07)	51.56	4.10	12.51	
3e	15	196–197 [a)]	$C_{16}H_{13}BF_2O_2$	67.17	4.58		
			(286.10)	67.52	4.23		
3f	68	156–158 [a)]	$C_{12}H_{13}BF_2O_4$	53.37	4.85		
			(270.04)	53.30	4.52		
3g	57	143–144 [a)]	$C_{12}H_{13}BF_2O_4$	53.37	4.85		
			(270.04)	53.39	4.57		
6a	24	170–172 [a)]	$C_8H_7BF_2O_2S$	44.48	3.27	S: 14.84	
		(174–175[14])	(216.02)	44.34	2.98	14.62	
6b	12	190–192 [b)]	$C_9H_9BF_2O_2S$	46.99	3.94	S: 13.94	
			(230.04)	47.04	3.76	13.92	
6c	60	214–215 [a)]	$C_8H_6BBrF_2O_2S$	32.58	2.05	S: 10.87	Br: 27.10
			(294.88)	32.54	1.99	10.67	27.38
8	4	174 dec. [c)]	$C_{16}H_{18}BF_2NO_2$	62.98	5.95	N: 4.59	
			(305.14)	62.70	6.08	4.41	
10	37	305–307 [a/d)]	$C_{30}H_{24}B_3F_6O_6N$	56.22	3.77	N: 2.19	
			(640.66)	56.21	4.14	2.20	
12	10	315–318 [d)]	$C_{16}H_{16}B_2F_4O_6$	47.82	4.01		
			(401.92)	48.10	4.12		
14a	47	265–168 [d)]	$C_{20}H_{16}B_2F_4O_5$	55.36	3.72		
			(433.97)	55.31	3.24		
14b	71	239–240 [d)]	$C_{23}H_{23}B_2F_4O_6$	56.15	4.51		
			(492.05)	56.06	4.56		
17	70	217–219 [b/d)]	$C_{14}H_{14}B_2F_4O_6$	44.74	3.75		
			(375.88)	44.70	3.89		

recrystallized from [a)] acetic acid, [b)] toluene, [c)] ethyl acetate [d)] nitromethane

dimethylamino-acetophenone precursor **1i**, by reaction with the acetic anhydride/boron trifluoride reagent. Obviously, the acylation of **2i** is prevented due to the formation of a complex between the Lewis acid BF_3 and the amino group of the educt. Surprisingly therefore, starting from julolidine **7** which can be regarded as a bridged dialkylaniline derivate the corresponding 4-(9-julolidinyl)-substituted 6-methyl-1,3,2-(2*H*)-dioxaborine derivative **8** could be isolated in noticeable yields.

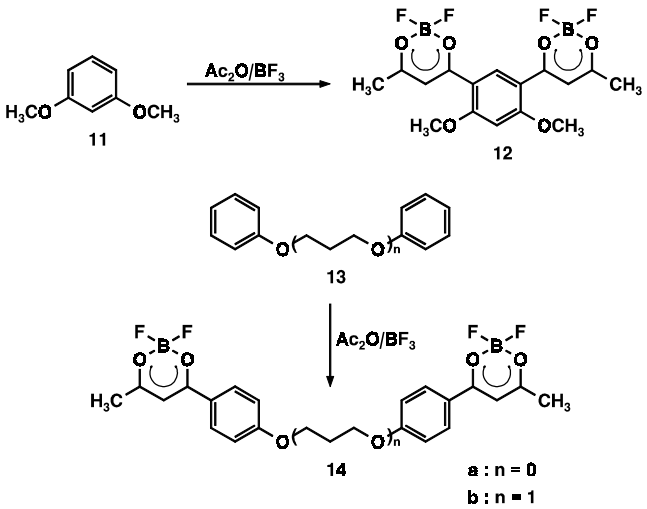
Triphenylamine **9**, however, yielded the *tris*-dioxaborine derivative **10** in 37% even. Here, due to the steric demand of the propeller-shaped geometry, complex formation is unfavourable. Very remarkably, as result of this one-pot domino reaction [15] twelve (!) new bonds are formed at once.



Scheme 3

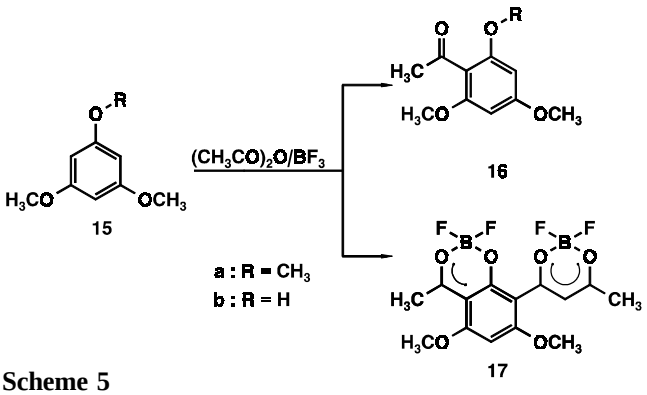
A repeated domino acylation was found also by starting with several phenol ethers. Thus, by allowing to react resorcinol dimethylether **11**, diphenylether **13a**, or 1,4-*bis*-phenoxybutane **13b** with acetic anhydride and boron trifluoride/acetic acid the corresponding *bis*-1,3,2-(2*H*)-dioxaborine derivatives **12**, **14a**, and **14b**, resp., have been obtained in satisfactory yields.

A remarkable result has also been obtained by allowing to react phloroglucinol trimethyl ether **15a** with acetic anhydride and the acetic acid/boron trifluoride reagent. Instead of 2,4,6-tris-methoxy-acetophenone **16a** or its corresponding 1,3,2-(2*H*)-dioxaborine derivative the 5,7-*bis*-methoxy-2,2-difluoro-4-methyl-8-(6-methyl-1,3,2-dioxaborin-4-yl)-benzo-1,3,2-(2*H*)-dioxaborine **17** was obtained. Obviously, in course of the formation of **17** demethylation occurs. It is probably initiated by the boron trifluoride reagent and gives rise to the intermediate formation of phloroglucinol dimethylether **15b** which is able, as demonstrated in the literature [16], to react with the boron trifluoride reagent to give 3,5-bis-methoxy-2-hydroxy-acetophenone **16b**.



Scheme 4

The structures of all the 1,3,2-dioxaborines prepared have been elucidated unambiguously by their elemental analytic and NMR spectroscopic data. Thus, all 2,2-di-fluoro-1,3,2-(2*H*)-dioxaborines exhibit in their ^{1}H NMR spectra characteristic signals at about 6.80 ppm and 2.50 ppm as depicted in table 2. These signals can be unambiguously attributed to the protons at C(5) and at the methyl groups at C(6), resp., of their appropriate 1,3,2-(2*H*)-dioxaborine moieties.



Scheme 5

Furthermore, all 1,3,2-dioxaborines exhibit characteristic ^{13}C NMR signals at about 180 and 200 ppm. These signals can be attributed to the C(4) and C(6) atoms, resp., in their 1,3,2-(2*H*)-dioxaborine moieties (see table 3).

For the 1,3,2-(2*H*)-dioxaborines **10** and **17**, an additional structural proof was derived from their X-ray data. From figure 1 in which the crystal structure of compound **17** is depicted not only the chemical constitution follows but also several details of this compound. Thus,

Table 2 ^{1}H NMR data (δ-values in CD_3NO_2) of 2,2-difluoro-1,3,2-(*2H*)-dioxaborines prepared

Nr.	6-CH_3	5-CH	4-Ar (assignment)	coupling constants (Hz)	additional signals (assignment)
3c	2.36	6.72	8.09 (d, 2H, H2', H6') 7.08 (d, 2H, H3', H5')	$J_{2'3'} = J_{5'6'} = 9.10$	3.91 (s, 3H, OCH_3)
3d	2.38	6.77	8.00 (d, 2H, H2', H6') 7.39 (d, 2H, H3', H5')	$J_{2'3'} = J_{5'6'} = 8.61$	2.55 (s, 3H, SCH_3)
3e	2.44 (3H)	6.89 (1H)	8.20 (d, 2H, H2', H6') 7.87 (d, 2H, H3', H5')	$J_{2'3'} = J_{5'6'} = 8.55$	7.75 (d, 2H, *o*-PhH, $J = 7.11$ 7.42–7.53 (*m*, 3H, *m*,*p*-PhH)
3f	2.36 (3H)	6.75 (1H)	7.60 (s, 1H, H2') 7.09 (s, 1H, H5') 7.80 (s, 1H, H6')	$J_{5'6'} = 8.56$ $J_{2'6'} = 2.02$	3.93 (s, 3H, OCH_3) 3.90 (s, 3H, OCH_3)
3g	2.39 (3H)	7.23 (1H)	7.12 (s, 1H, H3') 7.24 (dd, 1H, H4') 7.57 (d, 1H, H6')	$J_{3'4'} = 9.16$ $J_{4'6'} = 2.84$	3.81 (s, 3H, OCH_3) 3.94 (s, 3H, OCH_3)
6a	2.40 (3H)	6.71 (1H)	8.15 (d, 1H, H2') 7.36 (t, 1H, H3') 8.10 (d, 1H, H4')	$J_{2'3'} = 3.84$ $J_{3'4'} = 4.80$	
6b	2.33 (3H)	6.56 (1H)	7.97 (d, 1H, H2') 7.04 (d, 1H, H3')	$J_{2'3'} = 3.65$	2.61 (s, 3H, 4-thienyl-CH_3)
6c	2.37 (3H)	6.64 (1H)	7.90 (d, 1H, H2') 7.35 (d, 1H, H3')	$J_{2'3'} = 3.83$	
8	2.19 (3H)	6.43 (1H)	7.53 (s, 2H, H2', H6')		3.39 (t, 4H, NCH_2), $J = 5.75$ 2.72 (t, 4H, CH_2-Ph), $J = 6.17$ 1.92 (q, 4H, CH_2)
10	2.41 (9H)	6.82 (3H)	8.12 (d, 6H, H2', H6') 7.37 (d, 6H, H3', H5')	$J_{2'3'} = J_{5'6'} = 8.79$	
12	2.391 (6H)	7.16 (2H)	8.90 (s, 1H, H2') 6.85 (s, 1H, H5')		4.17 (s, 3H, OCH_3)
14a	2.53 (6H)	7.30 (2H)	8.31 (d, 4H, H2', H6') 7.39 (d, 4H, H3', H5')	$J_{2'3'} = J_{5'6'} = 8.87$	
14b	2.38 (6H)	7.14 (2H)	8.16 (d, 4H, H2', H6') 7.19 (d, 4H, H3', H5')	$J_{2'3'} = J_{5'6'} = 8.73$	2.26 (q, 2H, CH_2) 4.31 (t, 4H, OCH_2)

Table 3 ^{13}C NMR data (δ-values in CD_3NO_2) of 2,2-difluoro-1,3,2-(2*H*)-dioxaborines prepared

Nr.	C1'	C2'	C3'	C4'	C5'	C6'	C4	C5	C6	6-CH_3	others
3c	124.8	133.1	116.2	167.7	116.2	133.1	183.3	98.0	193.1	24.7	56.8 (OCH_3)
3e	131.5	131.0	128.6	149.3	128.6	131.0	183.5	99.2	195.4	25.0	140.4 (*ipso*), 130.6 (*o*), 129.0 (*m*), 130.4 (*p*)
3f	124.8	112.8	151.1	157.7	112.3	126.6	183.3	98.2	192.9	24.7	56.8 (OCH_3) 57.0 (OCH_3)
3g	121.6	157.4	115.4	125.0	155.1	115.5	181.5	103.8	195.3	25.1	56.7 (OCH_3) 57.3 (OCH_3)
6a	n.d.	137.7	131.3	139.9	–	–	177.7	98.3	193.5	24.6	
6b	134.8	138.5	130.6	157.9	–	–	177.4	97.7	191.9	24.4	16.5 (thienyl-CH_3)
6c	n.d.	137.7	134.8	127.6	–	–	176.2	98.0	n.d.	24.8	
8	116.2	130.5	122.9	151.7	122.9	130.5	180.7	95.9	184.9	23.9	28.7 (Ar–CH_2-) 22.1 (CH_2–CH_2–CH_2) 51.5 (N–CH_2-)
12	n.d.	137.6	n.d.	169.2	102.8	169.2	187.2	98.2	n.d.	25.1	58.0 (OCH_3)
14a	126.7	132.1	119.9	161.4	119.9	132.1	180.3	98.1	193.9	24.5	
14b	122.9	132.0	115.7	165.0	115.7	132.0	180.7	97.2	191.7	24.3	65.3 (O–CH_2–CH_2) 28.4 (O–CH_2–CH_2-)
10	128.6	132.3	126.3	153.3	126.3	132.3	182.3	98.8	194.7	24.9	
17	n.d.	165.0	n.d.	173.0	107.0	170.6	183.3	91.2	195.3	25.6	201.0 (CO–CH_3) 30.1 (CO–CH_3) 59.1 (OCH_3) 59.2 (OCH_3)

n.d.: not detectable

the dimethoxy-substituted benzdioxaborine moiety is nearly planar, while the methylaryldioxaborine moiety is envelope-shaped with a tilt angle of 13° between the planes through the B(1)–O(1)–O(2) and C(2)–C(3)–C(4)–O(2)–O(1) planes. B(1) is located 20.6 pm above the latter plane. The benzo[*d*]-1,3,2-(2*H*)-dioxaborine and 6-methyl-1,3,2-(2*H*)-dioxaborine moiety are distorted along their bond at 49°. Due to the planarity of the benzo[*d*]-1,3,2-(2*H*)-dioxaborine its aromatic CH moiety is shielded by two methoxy groups, and a further electrophilic substitution of the benzene ring is prevented.

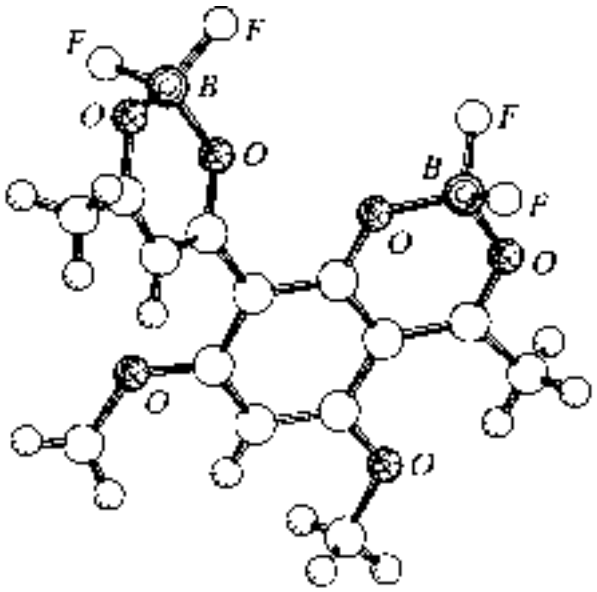


Fig. 1 X-ray structure of 2,2-difluoro-5,5-*bis*-methoxy-4-methyl-8-(2,2-difluoro-6-methyl-1,3,2-(2H)-dioxaborin-4-yl)-ben-zo[d]-1,3,2-(2*H*)-dioxaborine **17**

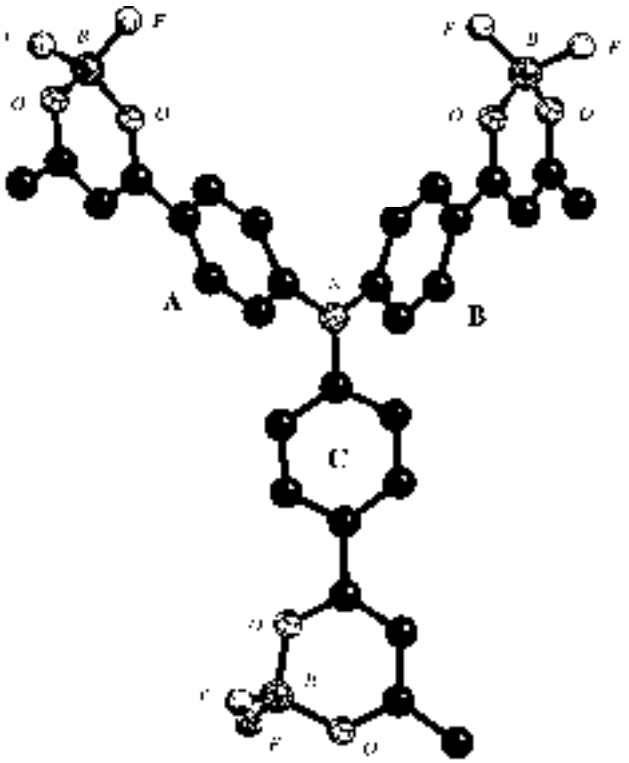


Fig. 2 X-ray structure of *tris*-[4-(2,2-difluoro-6-methyl-1,3,2-(2*H*)-dioxaborin-4-yl)-phenyl]-amine **10**

In the solid state the compound **10** has, other than expected, instead of a C_3 a C_1 symmetry (see figure 2). The unit cell belongs to a centrosymmetrical point group. The central nitrogen in compound **10** is almost planar (sum of bond angles is 359.5°) and located 5.7 pm above the plane through C(1)–C(11)–C(21). Two of the phenyl rings are turned only moderately from coplanarity with the central nitrogen (26° and 31° resp., for ring A and B) while the larger rotation of the third ring C (58°) compares well with the distortion angles reported for other substituted triphenylamines [17]. Push-pull interaction between the nitrogen donor and the electron-accepting dioxaborine groups is more pronounced in the former case, because the C–N bond lengths emanating from ring A and B amount to 140.4 pm and are shorter then those usually found in neutral triphenylamines [18]. They compare well with those found in a triphenylammonium radical cation [19]. The dioxaborine moieties are nearly planar, but are slightly twisted with respect to the phenyl residue (A, 14°; B, 15°, C; 6°).

The low symmetry of compound **10** in the solid state as well as the centrosymmetric unit cell of its crystals prevent, contrary to oriented layers of push-pull substituted 1,3,2-(2*H*)-dioxaborines [9], the use of solid **10** as an non-linear optical (NLO) active crystalline material [20].

An other field of applications for the 1,3,2-(2*H*)-dioxaborines described results, however, from their ability to fluoresce in the solid state. Detailed informations on this phenomenon have been recently published by us elsewhere [21].

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Experimental

Melting points: Boëtius hot-stage microscope, corrected. – IR: Philips FTIR spectrometer PU 9624 (in potassium bromide pellets). – NMR: Varian 300 MHz spectrometer Gemini 300 or JEOL 200 MHz spectrometer JNM FX 200. – Elemental analytic data: LECO analyser CHNS 932. – MS: AMO spectrometer 402 (70 eV, EI).

Preparation of 4-Aryl- or 4-Hetaryl-substituted 2,2-Difluoro-6-methyl-1,3,2-(2*H*)-dioxaborines (General Procedure)

To a mixture of boron trifluoride/acetic acid complex (18.79 g, 0.1 mol) and acetic anhydride (30.63 g, 0.3 mol) the appropriate aromatic or heteroaromatic compound (0.05 mol) was added neat and dropwise at 45 °C during 6 to 8 h. Solid educts were added dissolved or suspended in acetic anhydride. After the addition, the mixture was stirred for further 3 h. If the products did not precipitate on cooling, the reacting mixture was diluted with some methanol under cooling. The precipitated prod- ucts were isolated by suction and successively washed with acetic acid, ethyl acetate, and diethyl ether. After drying the 1,3,2-(2*H*)-dioxaborines were recrystallized from the solvent listed in table 1. Their yields, melting points, and analytical data are compiled in Tables 1–3.

For the following products some modification of the general procedure were performed:

Compound **8**: As starting material julolidine hydrobromide **7·HBr** was used. This salt (0.1 mol, 25.4 g) was, after mixing with acetic anhydride (0.3 mol, 30.63 g) and boron trifluoride/acetic acid complex (0.3 mol, 56.37 g), warmed at 45 °C under stirring for 8 h. Then, the reaction mixture was diluted by addition of methanol (100 ml), and the product crystallized was purified, after filtration, by chromatography on silica using dichloromethane as eluent.

Compounds **12**, **14a**, *and* **14b**: For the corresponding educt **11** and **13**, resp., (0.1 mol) boron trifluoride/acetic acid complex (0.2 mol, 37.58 g) and acetic anhydride (0.6 mol, 61.25 g) were used.

Compound **10** and **17**: For the corresponding educt (0.1 mol) boron trifluoride/acetic acid complex (0.3 mol, 56.37 g) and acetic anhydride (0.9 mol, 91.88 g) were used. For isolation of compound **10** the reaction mixture was diluted with methanol (100 ml) and subsequently evaporated. The residue obtained was isolated by filtration over silica and recystallized from nitromethane.

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