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1,3,2-Dioxaborines as potential components in advanced materials—a theoretical study on electron affinity

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ABSTRACT: 1,3,2-Dioxaborines with fluorine and other substituents at boron were calculated by first-principles methods based on density functional theory (DFT: B3-LYP) or many-body perturbation theory at the second order [MBPT(2): MP2]. 1,3,2-Dioxaborines are derivatives of 1,3-dicarbonyl compounds also known as 1,3-diketoborates. According to quantum chemical calculations, 2,2-difluoro-1,3,2-dioxaborines are of puckered structure with a low barrier to inversion. The calculated charge distribution does not reflect well the traditional formula description. The boron atom carries a positive rather than a negative charge. Some compounds have a pronounced zwitterionic character accompanied by relatively high dipole moments. The calculated positive electron affinities (*EA*s) classify 1,3,2-dioxaborines as organic electron-acceptor compounds. Depending on the type of substitution, the *EA*s vary between about 0.5 and 3.5 eV (DFT calculations). The *EA*s of various substituted 1,3,2-dioxaborines are of the same order of magnitude as those of quinones and close to electron affinities of strong organic acceptor compounds such as tetracyanoethylene (TCNE). Numerical predictions are verified by comparison with *EA*s of a series of well-known medium-sized organic compounds studied experimentally and theoretically at the same level of theory. In good agreement with results reported for other series of compounds, the average absolute error between theoretical and experimental *EA*s was 0.19 eV. Because of the ability of 3,5-diaryl-2,2-difluoro-1,3,2-dioxaboranes to fluoresce efficiently and to accept electrons easily, these compounds are potential candidates for future applications.

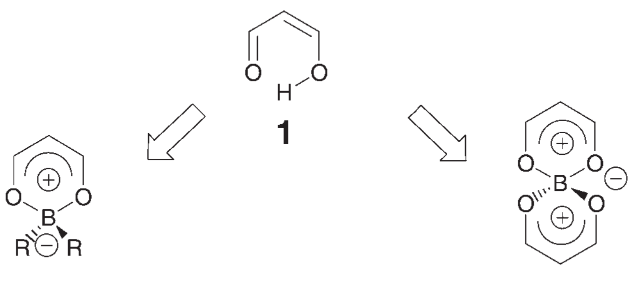
Additional material for this paper is available in Wiley Interscience

KEYWORDS: boron–organic compounds; molecular structure; electron distribution; electron affinity; vertical electron attachment and detachment energy; density functional theory

INTRODUCTION

1,3-Diketoboronates (1,3-diketoborates, boryl acyl ketones) have been known for more than 90 years.[1] The compounds are chelate complexes (**2**) formed from enolizable 1,3-dicarbonyl compounds (**1**). A large variety of these compounds with various substituents at the carbon atoms are readily available. As is well established by structural analysis, the compounds have the cyclic 1,3,2-dioxaborine structure **2**.

2,2-Difluoro-1,3,2-dioxaborines (**2**, R = F) are prepared by reaction of **1** with boron trifluoride[2] and 2,2-dialkyl- and 2,2-diaryl-1,3,2-dioxaborines (**2**, R = alkyl, aryl) from **A** with trialkyl- and triarylboranes, respectively.[3] The compounds are substituted at the carbons. Cationic spirocyclic 1,3,2-dioxaborines of the general formula **3** are synthesized from **1** and boron trichloride[4] or trialkylborates in the presence of strong mineral acids or water-binding reagents.[5]



1

2

3

In contrast to the 1,3-dicarbonyl precursors **1**,[6] 1,3,2-dioxaborines **2** generally exhibit strong fluorescence in solution at room temperature[7] and, in some cases, in the solid state.[8] They are used as laser dyes[9] and as active components in solar collectors.[10] Some 1,3,2-dioxaborines with specific heterocyclic substituents in the 4- and 6-positions are reported as red emitters in organic light-emitting diodes.[11] 2,2-Difluoro-1,3,2-dioxaborines can

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be used as photosensitizers in electrophotographic materials[12] and photoreactants with alkenes[13] and aromatic compounds.[14] Moreover, 1,3,2-dioxaborines are chromogenic building blocks in the synthesis of deeply colored compounds, such as donor-substituted styryl compounds[15] and natural curcumines.[16] 1,3,2-Dioxaborine-containing polymethine dyes with extremely long-wavelength absorptions in the NIR region[17] and pronounced non-linear optical properties[18] are also known. Anions containing the 1,3,2-dioxaborines ring twice[19] have recently been discussed in terms of mixed-valence systems.[20]

Less is known about the capability of 1,3,2-dioxaborines to accept electrons. As is well known, 1,3,2-dioxaborines form ground-state donor–acceptor complexes or exciplexes with organic donors.[20] The donor–acceptor complexes display long-wavelength intermolecular charge-transfer (CT) absorption bands. Moreover, 1,3,2-dioxaborines are easily reduced under ambient conditions.[21] By one-electron transfer they form relatively stable anion radicals which have been characterized by ESR techniques.[22] 1,3,2-Dioxaborines are, therefore, promising candidates for producing electron-transport materials.[23]

Molecular electron affinities (*EA*s) of 1,3,2-dioxaborines as specific measures of electron acceptor strength, however, are not yet known. The development of new emitter and charge transport materials for organic light-emitting diodes (OLEDs) and other optoelectronic applications requires a better knowledge about the electron acceptor properties of the title compounds. From a practical point of view, fluorescent 1,3,2-dioxaborines with large *EA*s deserve particular interest.

This study is mainly directed to the molecular structure and electronic properties of 1,3,2-dioxaborines of the series **2** and **3** and the tendency of these compounds to form radical anions.

To evaluate the acceptor strength of 1,3,2-dioxaborines, the *EA*s of the compounds of series **2** and **3** were calculated by quantum chemical methods and compared with those of a series of well-known organic acceptor compounds.

The *EA* of a neutral molecule measures the ability of the molecule to gain an electron, as described by the reaction $X + e^- \rightarrow X^-$.[24] The *EA* is traditionally defined as the negative of the energy of the following reaction:

$$EA = -[E(X^-) - E(X)] \qquad (1)$$

If the anion is more stable than the neutral compound *EA* is positive and if the anion is less stable *EA* is negative. This definition in sign is at variance with the thermodynamic convention.

The calculated *EA*s refer to free molecules and should correspond to experimental values obtained by electron transmission spectroscopy (ETS),[25–27] (anion) photoelectron spectroscopy (PES),[27] threshold photodetachment[27] and various other methods carried out in gas-phase experiments.[27,28]

COMPUTATIONAL

Satisfactory results of *EA* calculations have been reported both for the state-oriented *ab initio* approaches such as post-Hartree–Fock and multiconfiguration methods[29] and the transition-oriented approaches such as OVGF (outer-valence Green's function) or propagator methods.[30] However, *ab initio* quantum chemical calculations performed at any high level of theory are time consuming and become prohibitively expensive when applied to polyatomic molecules. To avoid large amounts of computer time and/or disk storage, the Hohenberg–Kohn–Sham density functional theory (DFT)[31] was used in this study.

To obtain the first *EA*s according to Eqn (1) the energies of the molecular species X and X^- were calculated. Geometry optimization of both the neutral compound and the anion provides the 'adiabatic electron affinity' or *EA*. If the optimized ground-state geometry is used in the calculation of the anion, the 'vertical electron attachment energy' (VAE) is obtained. On the other hand, the vertical ionization energy of the anion corresponds to the 'vertical electron detachment energy' (VDE). Although the *EA*s calculated by DFT are generally less accurate than those of high-level *ab initio* levels, such as GaussianX ($X = 2, 3$),[32] the results of DFT calculations reproduce experimental *EA*s reasonably well. The calculations allow the derivation of general features and trends. The average absolute error in the calculation of the *EA*s of a series of small inorganic compounds[32,33] and of some medium-sized organic compounds[27,33–36] was found to be about 0.2 eV or slightly lower. The error in calculating *EA*s is of the same order of magnitude as UV–visible excitation energies when calculated by time-dependent density functional response theory.[37]

DFT calculations were performed with the hybrid Hartree–Fock/density functional using the exchange functional defined by Becke's three-parameter equation and the correlation functional proposed by Lee, Yang and Parr (B3-LYP).[38] DFT B3-LYP is a valuable alternative to MO methods considering correlation effects and has found wide acceptance in computational chemistry.[31] The good performance of B3-LYP in calculating *EA*s of small inorganic and organic compounds was shown in previous studies.[33–36] Split valence double-zeta and triple-zeta basis sets plus polarization functions with or without diffuse functions were generally used. For the calculation in this study, we mostly employed the 6–31 + G(d,p) (= 6–31 + G**) basis set. This basis set was replaced, in some cases, by the more extended valence triple-zeta basis sets 611 + G(2df,p).

The spin-unrestricted UB3-LYP method was used to calculate the open-shell radicals The wavefunctions of the unrestricted DFT calculations suffer less than UHF from spin contaminations. The calculated the expectation value $\langle S \rangle^2$ of the radicals are close to the theoretical value of the pure doublet state (0.75). This approach is also known to provide good geometries and relative energies for organic radical ions.[39]

For the sake of comparison, (U)MP2(fc) calculations were also performed, where fc stands for the frozen core. UMP2 energies used in the calculation of *EA* are those after spin projection (PUMP2). G2(MP2) and G3(MP2) energies are additionally corrected with respect to the basis set error and the error in the correlation energy.[40]

Molecular geometries were fully optimized. Total charges were defined by the traditional Mulliken population analysis (MPA) and by the natural population analysis (NPA) of Reed *et al.*[41] The quantum chemical calculations were carried out using the 1998 release of the Gaussian suite of programs (Revision A7).[42]

RESULTS AND DISCUSSION

Molecular and electronic structure of the diflouro-1,3,2-dioxaborine parent compound

To reveal essential features of ring structure of **1**, the unsubstituted compound **1a** ('parent compound') was first studied in more detail. The heterocyclic ring of the neutral compound is not fully planar. The molecule is puckered with boron placed out of the plane. The out-of-plane displacement depends sensitively on the theoretical model used and is larger for MP2 (32°) than for DFT (less than 12°). The calculations were performed with the same basis set (cf. Table 2). The MP2 structure is shown in Fig. 1.

The barrier to inversion of the puckered 2,2-difluoro-1,3,2-dioxaborine, however, is very low. It amounts at the G3(MP2) to $\Delta H^{\neq} = 0.26\,\mathrm{kcal\,mol^{-1}}$ ($\mathrm{kcal} = 4.184\,\mathrm{kJ}$). The very low barrier height may account for the loss of the puckered structure in the crystal. Crystal forces obviously override the weak intramolecular forces that are responsible for the non-planarity. In general, the bond lengths of **2a** predicted by DFT and MP2 are closely similar (Table 1).

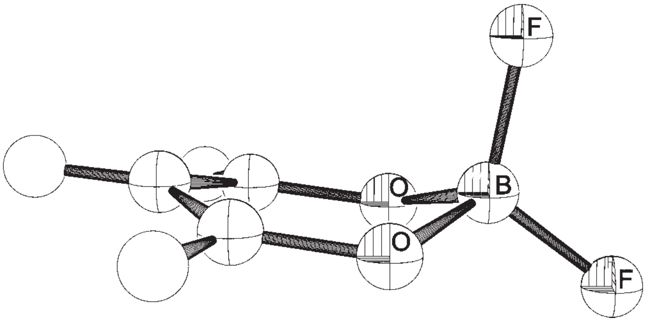

Figure 1. Structure of 2,2-difluoro-1,3,2-dioxaborine (MP2 calculation)

The calculated bond lengths fit well with standard bond lengths. The calculated C—F bonds are slightly elongated with respect to the C—F bond length of 1.365 Å reported for the tetrafluoroborates.[43] The CC bond lengths of the ring calculated at about 1.4 Å reflect a trimethine substructures.[44] This outcome is in good harmony with the model of a delocalized CC bond as displayed in formula **2**. Moreover, the parent compound exhibits an almost planar OCCCO trimethine fragment that is forced by BF_2 into a cyclic *cis* structure. Experimental knowledge of the structure of 1,3,2-dioxaborine is restricted to results of x-ray studies of derivatives.[45] Table 1 contains data on the theoretical and experimental structure of the 4-methyl-6-phenyl-1,3,2-dioxaborine (**2k**). Except for the B—O bonds the predicted and measured bond lengths agree reasonably well. Close agreement between theory and experiment is not to be expected. The calculated bond lengths refer to the free molecule whereas the experimental data are more or less affected by crystal forces.

Whereas the DFT ring structure of the anion of **2a** is puckered like the neutral compound, the cation is planar. Some bond lengths vary considerably in passing from the

Table 1. Selected bond lengths of the two 2,2-difluoro-1,3,2-dioxaborines **2a** and **2k** and angle of folding calculated by (U)DFT and (U)MP2

Compound	Symmetry	Method	C—C (Å)	C—O (Å)	B—O (Å)	B—F (Å)	Angle(°)[a]
2a	C_s	DFT	1.393	1.283	1.529	1.369, 1.362	12
		MP2	1.391	1.289	1.530	1.379, 1.364	32
2a$^-$	C_s	UDFT	1.392	1.348	1.485	1.422, 1.405	28
		UMP2	1.382	1.351	1.489	1.426, 1.408	36
2a$^+$	C_{2v}	UDFT	1.449	1.251	1.600	1.326, 1.325	0
	C_s	UMP2	1.465	1.242	1.600	1.345, 1.325	32
2k							
Calc.	C_1[b]	DFT	1.392	1.292	1.519	1.731	18
Exp.[b,c]		X-ray	1.372	1.290	1.475	1.363	~0

[a] The OCCCO trimethine fragment of the ring is almost planar. The angle defines the out-of-plane deviation of the BF_2 fragment relative to this plane. The angle is lower with extended basis sets such as 6–311 + G(2df,p) (7°) and cc-VTZ (3°).

[b] Average bond lengths of corresponding bonds.

[c] For experimental bond lengths, see Ref. 45.

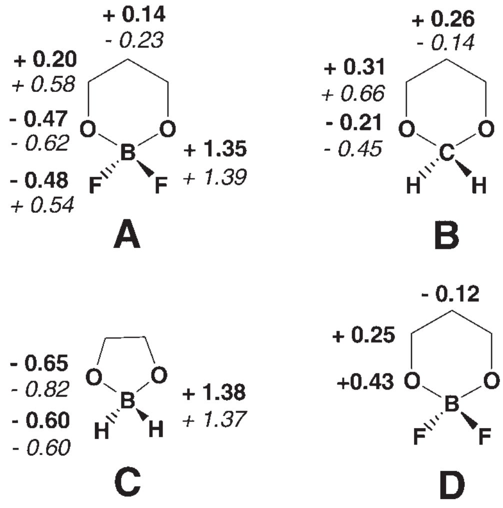

Figure 2. MPA and NPA total charges (NPA charges in italics) of **2a** are given in **A** and those of the related *O*,*O*-methylene bridged trimethine cation and the *O*,*O*-ethylene bridged borate in **B** and **C**, respectively. The charge of hydrogen was added to the charge of the carbon atom for each bond. **D** contains charges of the π-system of the nearly planar fragment of **2a**

neutral **2a** to the ion radicals. The results of DFT and MP2 calculations are similar (cf. Table 1).

The CHCHCH trimethine fragment of **2a** defines a 6π-system that is essentially localized. The absence of a significant cyclic delocalization is supported by the NICS (nucleus independent chemical shift) criterion. NICS is defined as the negative isotropic shielding at the center of the ring[46] [GIAO B3-LYP/6–31 + G(d) calculation. If NICS is lower than about -3 ppm the ring systems may classed as aromatic and larger than about $+3$ ppm as antiaromatic (H. Jiao, Universität Erlangen-Nürnberg, personal communication, 1997)]. The calculated NICS values of **2a** of $+2.3$ ppm (NICS-1 + 0.59 ppm) are in favor with an essentially localized rather than a delocalized structure. Thus, the contribution of the CF$_2$ group to the cyclic delocalization is low.

According to Mulliken population analysis (MPA), the CH groups in 4-, 5- and 6-positions of **2a** carry positive net charges whereas the oxygen atoms are negative (cf. **A**, Fig. 2). The outcome of the natural population analysis (NPA) is similar except for position 4 with a negative natural charge. The electron distributions at the trimethine fragments of **A** and the carbocation **B** are very similar (cf. Fig. 2).

In contrast to the traditional formula presentation, the boron atom is positively charged. This result is qualitatively the same in the MPA and NPA calculations. According to the calculations the expected negative charge is shifted to the adjacent more electronegative atoms. This outcome is the same for other organic borates, such as **C** (cf. Fig. 2), or inorganic borates, such as BF$_4^-$. Thus, the commonly used formulas of borate structures are misleading. To give a more realistic charge distribution with a positive charge at boron, additional resonance structures have to be invoked.

The parent compound **2a** has a significant charge separation. The electric dipole moment of 6.49 D is remarkably large. The experimental value of the parent compound is unknown but substituted compounds have actually dipole moments in the same order of magnitude as calculated (~7 D[47]).

To define formal charges of the conjugated OCCCO fragment, the π-type population of **2a** was analyzed. The π-charges are defined by the population of the p$_\pi$-orbitals and core charges of 1 (for carbon) and 2 (for oxygen) as defined within the Pariser–Parr–Pople approach. In agreement with formula **2a**, the oxygen and the carbon atoms adjacent to oxygen have positive charges. The π-charges of the nearly planar OCCCO fragment of **2a** are shown in **D** in Fig. 2).

Choice of compounds

Some more general considerations are helpful in searching for proper compounds with higher *EA*s. The zwitterionic character of **2a** visualized in formula **2** with the positive charge of the trimethine fragment and negative charge of boron-containing fragment encouraged us to replace the fragment by other suitable charged fragments. A more trivial case is replacement of the trimethine fragment by substituted trimethine fragments as shown in the series **2b–2w** (Table 2).

Alternatively, carbocylic cations may replace the chain-type trimethine fragment. This substitution pattern is exemplified by **9–11** later.

The proper choice of the substituents of 1,3,2-dioxaborine (**2a**) is assisted by simple MO theoretical considerations. 1,3,2-Dioxaborines of enhanced *EA* relative to the parent compound should exhibit the LUMO at lower energies. This is realized by suitable substitution by acceptor substituents. Since the LUMO of the 1,3,2-dioxaborine parent compound **2a** is mainly localized at the trimethine fragment, the inspection of the π-type characteristics of the polymethine MOs is informative. The Hückel MOs of polymethines are known in closed form.[48] The solutions for the 6π-system imply that the LUMO is antisymmetric to the plane that is perpendicular to the plane of the π-system. The squared coefficients of the LUMO are large at the carbons adjacent to the terminal heteroatom groups. This conclusion is the same when the Hartree–Fock (*ab initio*) and Kohn–Sham (DFT) LUMOs are considered. The shape of the LUMO is illustrated in Fig. 3 (B3-LYP functionals).

Because of the nodal property of the pi-type LUMO (and SOMO of radical anion) of 2a replacement of the BF2 group in 2-position or substitution in 5-position should be less effective on the electron affinity than substitution in the 4- and 6-positions. The majority of the selected compounds of the series **2** therefore contain substituents in the favored 4- or (and) 6-position.

Table 2. Choice of compounds

Compound[a]	R	R^1	R^2	R^3
2a	F	H	H	H
2b	F	CN	H	H
2c	F	H	CN	H
2d	F	NO_2	H	H
2e	F	H	NO_2	H
2f	F	F	H	F
2g	F	CF_3	H	CF_3
2h	F	CN	H	CN
2i	F	NO_2	H	NO_2
2j	F	CH_3	H	CH_3
2k	F	CH_3	H	C_6H_5
2l	F	C_6H_5	H	C_6H_5
2m	F	4-$CF_3C_6H_4$	H	4-$CF_3C_6H_4$
2n	F	4-$CH_3COC_6H_4$	H	4-$CH_3COC_6H_4$
2o	F	4-NCC_6H_4	H	4-NCC_6H_4
2p	F	3-NCC_6H_4	H	3-NCC_6H_4
2q	F	2-NCC_6H_4	H	2-NCC_6H_4
2r	F	3,5-$(NC)_2C_6H_3$	H	3,5-$(NC)_2C_6H_3$
2s	F	2,4-$(NC)_2C_6H_3$	H	2,4-$(NC)_2C_6H_3$
2t	F	4-$NO_2C_6H_4$	H	4-$NO_2C_6H_4$
2u	F	2,4-$(NO_2)_2C_6H_3$	H	2,4-$(NO_2)_2C_6H_3$
2v	F	2,4,6-$(NO_2)_3C_6H_2$	H	2,4,6-$(NO_2)_3C_6H_2$
2w	F	$NH_2C_6H_4$	H	NH_2-C_6H_4
2x	F	4-Pyridyl	H	4-Pyridyl
2y	F	2-Triazinyl	H	2-Triazinyl
2z	Cl	CH_3	H	CH_3
2α	OCH_3	CH_3	H	CH_3
2ß	CH_3	CH_3	H	CH_3
2γ[a]	C_6H_5	CH_3	H	CH_3
3a	—	H	H	H
3b	—	CH_3	H	CH_3

[a] For compounds **2δ** and **2ε**, see footnote of Table 4.

The same type of MO consideration was applied to the substituents attached to 1,3,2-dioxaborines. In the case of phenyl substitution there is an efficient overlap between the LUMOs at the carbon atoms in 4- and 6-positions of the ring and at the carbon atom in the 4-position (*para*-position) of acceptor-substituted phenyl groups.

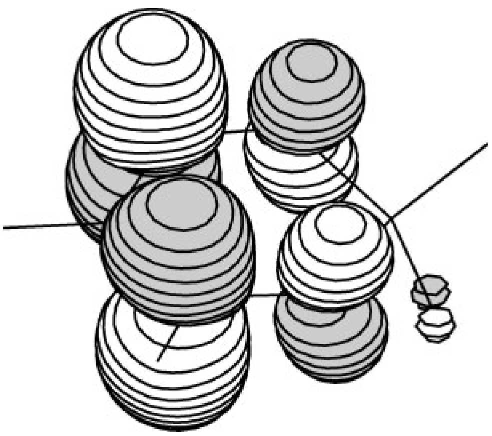

Figure 3. Shape of the lowest energy empty Kohn–Sham orbital of **2a**

Electron affinities and electron attachment energies of 2,2-difluoro-1,3,2-dioxaborine and electron detachment energies of its anion

To understand better the sensitivity of the theoretical model, the differently defined electron affinities of the parent compound **2a** was calculated first. The results in Table 3 show that *EA*s of **2a** calculated by different theoretical models have a positive sign in all cases. In other words, the open-shell radical anion of **2a** resulting from the capture of one electron is more stable than the neutral closed-shell compound. The *EA* amounts to about 1 eV, which indicates a weak electron acceptor strength. As is to be expected, the VAE is smaller than the adiabatic *EA*. On the other hand, the VDE of the anion is larger than the adiabatic *EA*. Independent of the theoretical model, the energy increases on passing from the VAEs to the VDEs by 0.7 eV. The *EA*s are approximately the mean values of the two vertical energies. Both the zero-point vibrational energy and thermal corrections did not much effect the adiabatic *EA* (cf. footnote a of Table 3).

The *EA* of **2a** calculated by DFT is 0.2 eV higher than the value calculated by MP2. However, the difference in

Table 3. Calculated lowest energy vertical electron detachment energies (VAE) and adiabatic electron affinities (*EA*)[a,b] of the neutral **2a** and of vertical electron detachment energies (VDE) of the anion of **2a** in eV calculated by DFT, MP2 and GaussianX(MP2) (X = 2, 3)

	B3-LYP			MP2		
Parameter	6–31 + G(d,p)	6–311 + G(2df,p)	aug-cc-pVTZ	MP2(fc)	G2(MP2)[a]	G3(MP2)[a]
VAE	0.97	0.92	0.94	0.70	—	—
EA	1.31	1.28	1.28	1.07	1.27	1.39
VDE	1.66	1.65	1.65	1.86	—	—

[a] EAs calculated by G2(MP2) and G3(MP2) without consideration of zero-point vibrational energies (corrections of ~0.10 eV). Change of enthalpy (ΔH) at 298 K, including the ZPVE correction): $\Delta H = 1.26$ eV with G2(MP2) and $\Delta H = 1.38 =$ eV with G3(MP2).

[b] The VAE of **2a** increases from about 1 to 3 eV on passing from the free molecule to a molecule in a polar environment with a dielectric constant of 78.39 (water). This model-type calculation indicates a considerable increase in the reduction potential that may occur in condensed phases in practical applications. The self-consistent reaction field calculation on **2a** was performed using the polarizable dielectric model (PCM) at the DFT B3-LYP level of theory using the 6–311 + G(2df,p) basis set.

the *EA* values between the DFT calculation and the *ab initio* calculation is reduced on passing from MP2 to the more elaborate G2(MP2) and G3(MP2) calculations. The results in Table 3 encouraged the use of the DFT approach using the economical 6–31 + G(d,p) basis set.

It should be mentioned that the formation of the anion from the neutral compound is strongly favored in polar media. As a consequence, the *EA* is increased. Under the conditions defined in Table 3 (see footnotes), the self-consistent reaction field (SCRF)[49] calculation predicts an increase in the electron attachment energy by about 2 eV. The parent compound **2a** now appears as a strong electron acceptor.

Electron attachment energies of substituted 2,2-difluoro-1,3,2-dioxaborines

Since the vertical electron attachment energies are only slightly higher than adiabatic *EA*s, the following calculations on various 2,2-difluoro-1,3,2-dioxaborines were restricted to VAEs. The calculated energies of the series **2a**–**2y** with different substituents at carbon and boron are given in Table 4. According to the calculations, the VAE values extend from 0.5 to 3.5 eV. Whereas twofold substitution of hydrogen by methyl or fluorine in 4- and 6-positions lowers the energy relative to **2a**, electron-withdrawing substituents such as CF_3, CN and NO_2 increase the VAEs significantly. In qualitative agreement with the Hammett substituent constants (both σ_{para} and σ_{meta}[50]), the electron acceptor strength increases in the order $CF_3 < CN < NO_2$. In the case of the 4,6-dinitro derivative (**2i**, $R^1 = R^3 = NO_2$), the *EA* is more than three times as large as that of the parent compound (**2a**). Compounds with acceptor substituents at the ring are not yet known.

A more practical starting material for application is the well-known 4,6-diphenyl-1,3,2-dioxaborine (**2l**). According to the DFT calculation, the *EA* of **2l** is 2.11 eV. Hence the *EA* is about twice as large as that of the parent compound **2a**. In general, acceptor substitution in 4- and 4′-positions of the phenyls is less effective direct substitution at the ring. Again, the effect of acceptor substitution increases in the order $CF_3 < CN < NO_2$ (cf. Table 4). The phenyl groups of **2l** and of the 4,4′-phenyl-substituted compounds **2m**, **2o** and **2t** are slightly distorted out-of-plane (OCCC dihedral angles of 15 ± 1°, with OC at the ring and CC at phenyl). The VAE value of 2,2′,4,4′-tetranitro-2,2-difluoro-1,3,2-dioxaborine (**2u**) (3.06 eV) is not much larger than that of the 4,4′-dinitro-substituted compound (**2t**) (2.98 eV). The small increase is obviously due to fact that the phenyl groups are twisted relative to the ring by about 60° because of steric hindrance of the NO_2 groups in an *ortho*-position to phenyl and adjacent to the nucleus. Steric strain is additionally released by distortion of the two NO_2 groups that are adjacent to the ring (27°). The phenyl groups of the 2,2′,4,4′,6,6′-hexanitro-substituted 1,3,2-dioxaborine (**2v**) are situated nearly orthogonal to the plane of the nucleus (OCCC dihedral angles of about 89°). Despite the strong twisting, the electron attachment energy of **2v** is additionally enhanced.

The selection of compounds was stimulated by the nodal properties of the LUMO. The question may be asked whether *EA* values are actually lower with acceptor substitution introduced in unfavored positions. As expected, the *EA* is relatively low with substitution in the 4-position compared with substitution in the 3-position of 1,3,2-dioxaborine (cf. Table 4). This is supported with the cyano- and nitro-substituted **2c** and **2e**, respectively. However, in spite of the unfavored 4-position, these compounds display higher *EA*s than the parent compound **2a**. Hence the results of the numerical calculations show some limitations of the simple MO model. It should be mentioned that the bonds of the substituents at the 4-position of the ring are shorter and the total energies of the 4-substituted compound are lower than those of the isomer with substitution in the 3-position.

As expected, the *EA* is larger for 4,4′-cyanophenyl than for 3,3′-cyanophenyl substitution of **2a**. Because of the molecular structure, the *EA* of the 2,2′-isomer is low. The cyanophenyl groups of **2q** are twisted out of plane twice

Table 4. Electron attachment energies of 2,2-disubstituted 1,3,2-dioxaborines (**2**) and of the related compounds **3** in eV calculated by DFT B3-LYP

Compound	R	R^3	R^4	R^5	VAE
2a	F	H	H	H	0.97[a]
2b	F	CN	H	H	2.17
2c	F	H	CN	H	1.81
2d	F	NO_2	H	H	2.51
2e	F	H	NO_2	H	1.80
2f	F	F	H	F	0.73
2g	F	CF_3	H	CF_3	2.34
2h	F	CN	H	CN	3.37
2i	F	NO_2	H	NO_2	3.52
2j	F	CH_3	H	CH_3	0.63
2k	F	CH_3	H	C_6H_5	2.31
2l	F	C_6H_5	H	C_6H_5	2.11
2m	F	4-$CF_3C_6H_4$	H	4-$CF_3C_6H_4$	2.31
2n	F	4-$CH_3COC_6H_4$	H	4-$CH_3COC_6H_4$	2.35
2o	F	4-CNC_6H_4	H	4-CNC_6H_4	2.63
2p	F	3-CNC_6H_4	H	3-CNC_6H_4	2.39
2q	F	2-CNC_6H_4	H	2-CNC_6H_4	2.23
2r	F	3,5-Di-CNC_6H_3	H	3,5-Di-CNC_6H_3	3.06
2s	F	2,4-Di-CNC_6H_3	H	2,4-Di-CNC_6H_3	3.10
2t	F	4-$NO_2C_6H_4$	H	4-$NO_2C_6H_4$	2.98
2u	F	2,4-Di-$NO_2C_6H_3$	H	2,4-Di-$NO_2C_6H_3$	3.06
2v	F	2,4,6-Tri-$NO_2C_6H_2$	H	2,4,6-Tri-$NO_2C_6H_2$	3.20
2w	F	4-$NH_2C_6H_4$	H	4-$NH_2C_6H_4$	1.10
2x	F	4-Pyridyl	H	4-Pyridyl	2.28
2y	F	2-Triazinyl	H	2-Triazinyl	2.68
2z	Cl	CH_3	H	CH_3	1.04
2α	OCH_3	CH_3	H	CH_3	0.39
2β	CH_3	CH_3	H	CH_3	0.22
2γ	C_6H_5	CH_3	H	CH_3	0.69
3a	—	H	H	H	5.62
3b	—	CH_3	H	CH_3	4.66

[a] Replacement of boron of **2a** by aluminum to give **2δ** resulted in an increase in VAE from 0.97 to 1.06 eV, and replacement of two oxygen atoms of **2a** by two sulfur atoms to give **2ε** in an increase from 0.97 to 1.70 eV.

as much as in **2p** and **2o** and the CN groups become slightly bent with valence angles of about 173° rather than 180°. This indicates the repulsive force between CN and the nucleus. There is also a surprisingly small difference in the *EA*s between the 3,5- and 2,4-substituted compounds **2r** and **2s**. 2,4-Substitution is again less effective because of molecular distortion. In contrast to acceptor-substituted compounds, the *EA* of the 4,6-bis(2-aminophenyl) donor-substituted **2w** is essentially unchanged with respect to **2l**.

A remarkable increase in the *EA* is calculated when the phenyl groups of **2l** are replaced by 4-pyridyl or 1,3,5-trazinyl groups (**2x** and **2y**, respectively). The increases are 2.11 to 2.68 eV on passing from the 4,6-diphenyl- (**2l**) to the 4,6-bis(2-triazinyl)-2,2-difluoro-1,3,2-dioxaborine (**2y**). The heterocylic derivative is predicted to be planar.

In agreement with the node property of the LUMO of **2a**, the *EA* is less affected by structural changes in the 2-position, such as replacement of boron by aluminum (**2**δ, cf. footnote a of Table 4), or replacement of fluorine by chlorine (**2z**). However, a marked increase in the *EA* is found on passing from **2a** to compounds substituted by alkyl or aryl groups rather than by fluorine at boron (**2**β and **2**γ, respectively). Replacement of two oxygen atoms of **2a** by two sulfur atoms to give 2,2-difluoro-1,3,2-dithiaborine (**2ε**) results in a heteroanalogous compound with a higher *EA* than that of **2a** (cf. footnote a of Table 4).

The heterocyles **4** and **5** with two adjacent dioxaborine rings exhibit higher vertical electron attachment energies than the parent compound **2a**, but the calculated *EA*s do not exceed 3 eV (cf. Fig. 4). The *EA* decreases on passing from **5** to **6** or the isomeric **7**. The compound **8** is no longer planar.

With regard to the electron attachment energy, compounds of the series **3** take an exceptional position. These compounds are cations and the capability for an electron capture is therefore strongly enhanced. The calculated VAEs of the spiro compounds **3a** and **3b** are much larger than the *EA* of **2a** and its derivatives (see Table 4).

Related carbocyclic borate compounds

The more complex boron compounds **9–11** with carbocation fragments have higher *EA*s than **2a** (cf. Fig. 5). The electron attachment energy increases on passing from **9** to **11** such as found for a series of carbocations of analogous topology (**9a–11a**). Surprisingly, the structures

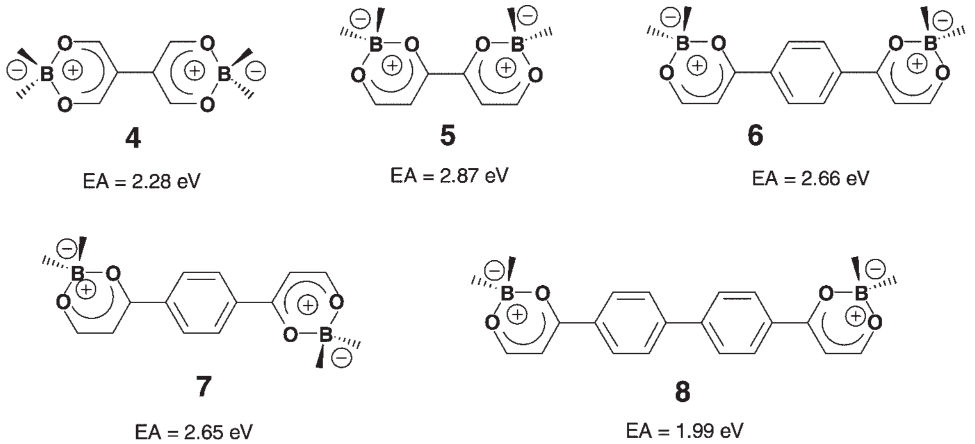

Figure 4. Vertical electron affinities of dimers and phenylene bridged dimers of 1.3.2-oxaborines calculated by DFT. To achieve convergence in calculating **8**, the set of diffuse orbitals was neglected for both the neutral compound and the anion

of **10** and **10a** display reduced molecular symmetries, probably owing to a quasi-Jahn–Teller distortion. The CC bonds alternate along the perimeter between about 1.35 and 1.45 Å. The symmetric structure of C_{2v} symmetry is a transition structure (one imaginary frequency) that is considerably higher in energy than the bond alternating structure of C_s symmetry. It should be mentioned that **9–11** are distinguished from **2a** by higher electric dipole moments. The dipole moments increase in this series from 9.33 (**9**) through 9.67 (**10**) to 10.17 D (**11**). Hence these organic compounds are strongly polar compounds.

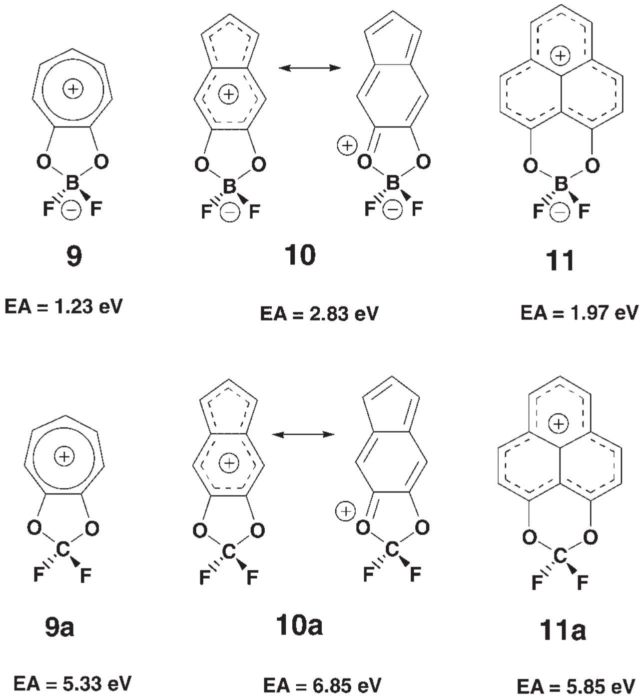

Figure 5. Vertical *EA*s of carbocyclic anionic borate compounds and related carbocations with BF_2 replaced by CH_2 [DFT B3-LYP/6–31 + G(d,p)]

Accuracy of the electron affinity calculations on conjugated organic compounds

The question should be raised of how the calculated *EA*s of 1,3,2-dioxaborines are classified among the experimentally known *EA* values and how large the error in the prediction might be. To estimate the error, a series of organic compounds with experimentally known *EA*s were selected and studied. The calculations on these reference compounds were performed with the same theoretical model as used in the study of 1,3,2-dioxaborines. The results are assembled in Table 5.

Since experimental *EA*s are either adiabatic or vertical, or not assigned at all, adiabatic *EA*s and vertical attachment and detachment energies were calculated. If the assignment of the experimental energies was disregarded and the statistics were performed including all experimental data irrespective of the origin, the mean absolute deviation amounted to 0.19 eV. If the compared energies were restricted to those of the same origin, the deviation was not lowered but rather became higher. The numerical calculations are obviously not accurate enough to reproduce differences in energy as large as vibrational energies. The mean absolute deviation of 0.19 eV corresponds to the error reported in former B3-LYP studies of medium-sized molecules (0.22 eV).[36]

The *EA* of TCNE (experimental, 3.17 eV[51]) was also overestimated in a previous DFT study and is underestimated by MP2 calculations[36] (cf. footnote i of Table 5). The adiabatic *EA* calculated by G3(MP2), however, reproduces the experimental value fairly well. It should be mentioned that the error of the experimental *EA* of TCNE is larger than those for other compounds (± 0.2 eV).[51] Since the experimental value of TCNQ is not considered to be reliable,[52] (electron binding energies calculated by OVGF, however, were in good agreement with the experimental data[53]) the calculated energies are not compared with the experimental value. According to

Table 5. Adiabatic *EA*s, VEAs and VDEs of some reference acceptor compounds in eV calculated by DFT

	Theory				Deviation (theor. − exp.)[a]	
Compound	VAE	EA	VDE	Experiment	D1	D2
Ethylene	−1.74	−1.61	−1.46	−1.78 VAE[b]	+0.17	+0.04
Butadiene	−0.81	−0.59	−0.35	−0.62 VAE[b]	−0.03	−0.19
Benzene	−1.48	−1.37	−1.37	−1.15 VAE[b]	−0.22	−0.33
Benzonitrile	−0.06	−0.11	−0.29	0.26[c]	−0.37	—
Anthracene	0.46	0.55	−0.64	0.53[d]	+0.02	—
Azulene	0.54	0.64	0.88	0.79[e]	−0.15	—
Nitrobenzene	0.90	1.21	1.51	1.00 EA[f]	−0.30	+0.30
p-Benzoquinone	1.90	2.16	2.44	1.86 EA[g]	+0.23	+0.23
TCNE	3.33	3.48[b]	3.67	3.17 EA[h,i]	+ 0.31	+ 0.31
TCNQ	3.60	3.73	3.86	(2.8)[j]	—	—
Tropylium	5.80	5.94	6.08	– 6.24 EA[k]	−0.30	−0.30
Absolute average deviation					0.19	

[a] The deviations D1 are the differences between the calculated *EA* and the experimental value in eV disregarding the different origin of the experimental *EA* as given in the literature. The deviations D2 consider the origin of the values.
[b] ETS: VAE, Ref. 25.
[c] ECD, Ref. 55.
[d] PES, Ref. 56.
[e] PES, Ref. 57.
[f] PES: *EA* Ref. 58.
[g] PES: *EA*, Ref. 54.
[h] Gas-phase electron-transfer equilibria: *EA*, Ref. 57.
[i] Relatively large *EA* values of were also calculated at the DFT level using more extended basis sets such as 6–311-G(2df,p) (3.48 eV, this study) or using a non-Gaussian double-zeta basis set with polarization and diffuse functions. (3.51 eV, see Ref. 36). In contrast, the MP2/6–31 + G(d,p) calculation underestimates the *EA* of TCNE whereas the G3(MP2) provided a good result (2.49 and 3.24 eV, respectively).
[j] Magnetron method, Ref. 59, value not reliable, cf. Ref. 52.
[k] PES: *EA*, Ref. 60.

the calculation, the *EA* of TCNQ is significantly larger than that of TCNE (3.73 vs 3.48 eV).

The comparison of the calculated electron attachment energies of 2,2-difluoro-1,3,2-dioxaborines with the data in Table 4 shows that the energies of the diphenyl-substituted derivative **2l** (2.11 eV) is approximately the same as the experimental *EA* of *p*-benzoquinone (1.86 eV[54]). The VAE values of the acceptor-substituted 1,3,2-dioxaborines calculated up to 3.20 eV in this study are in the same range as the experimental *EA*s of *p*-benzoquinone derivatives measured up to 2.78 eV.[35] Finally, the highest VAE values of the acceptor-substituted 1,3,2-dioxaborines are close to the experimental *EA* of TCNE.

CONCLUSIONS

To evaluate the acceptor strength, a series of 2,2-difluoro-1,3,2-dioxaborines derived from **2a** were studied. Vertical electron attachment energies of these compounds were calculated by DFT B3-LYP calculations with split valence basis sets including polarization and diffuse functions. The predicted values were verified by test calculations with known organic compounds of comparable size.

According to the calculations, the parent compound **2a** is a weak acceptor molecule ($EA \approx 1$ eV), but 4,6-diphenyl-1,3,2-dioxaborine (**2l**) and acceptor-substituted derivatives have *EA*s larger than 2 eV, comparable to those of quinones (2.2 ± 0.6 eV). Acceptor substituents increase the *EA* efficiently when introduced in 4- and (or) 6-positions of the boron heterocycle or in the 4,4′-position of phenyl residues of 4,6-diphenyl-1,3,2-dioxaborines. Less efficient are structural modifications of 1- and 4-positions of the ring where the LUMO has a node. With substitution in the *ortho*-position of the phenyl groups of 4,6-diphenyl-1,3,2-dioxaborines, stronger distortions about the inter-ring bonds occur because of steric hindrance. Then the *EA* is lower than expected.

This study has shown that 1,3,2-dioxaborines are distinguished from many other organic compounds not only by the capability to fluoresce but also by the enhanced acceptor strength. This is of interest for the ongoing research work on practical applications of these compounds.

Supporting information

Molecular structures of the calculated 2–11, including *x,y, z*-coordinates in ångstroms, are available in Wiley Interscience.

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