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REGULAR ARTICLE

A systematic density functional and wavefunction-based study on dicarboxyl dianions $^{-}O_2C–R–CO_2^{-}$ with R = C_2, C_2X_2, C_2X_4, and C_6X_4 (X = H, F)

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Abstract The possible existence of the gas phase *cis*- and *trans*-maleate, i.e. completely deprotonated maleic acid $(O_2C–CH=CH–CO_2)^{2-}$, is investigated by density functional (B3LYP) and ab-initio quantum chemical methods (MP2, CCSD(T)) using large basis sets. The calculations reveal that only the *trans*-isomer is Coulomb stable with respect to electron loss. The results are compared to other previously investigated dicarboxylate dianions of the general form $^{-}O_2C–R–CO_2^{-}$ with R = C_2, C_2X_2, C_2X_4, and C_6X_4 (X = H, F). Fluorine substitution on the carbon framework helps to stabilize these doubly charged systems, and we predict that all of the aromatic fluorine substituted dicarboxylate dianions are Coulomb stable in the gas phase. Only the highest levels of theory reveal the slight stabilization of both the succinate dianion and the *ortho*-isomer of the phthalic acid dianion in unprecedented agreement with experiments.

Keywords Dicarboxylate dianions · Density functional theory · Wavefunction-based theory · Coulomb repulsion · Charge conjugation

Dedicated to the memory of Professor Jean-Pierre Daudey and published as part of the Daudey Memorial Issue.

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1 Introduction

Atomic (A^{2-}) or diatomic dianions (AB^{2-}) do not exist if they are not confined [1, 2]. These systems represent unstable resonance states, and ions like O^{2-} or $C_2{}^{2-}$ only describe formal oxidation states as useful concepts in chemistry [3–5]. Some small inorganic species like $CO_3{}^{2-}$, $PO_4{}^{3-}$, or the recently proposed [6, 7] aromatic molecule $Al_4{}^{2-}$ [8], are also unstable with respect to electron loss [9–11]. The reason is that a dynamic system consisting of an electron and a negatively charged atom or molecule has to overcome a large Coulomb barrier of several electron volts before they end up in a bound state [12], and it is currently not clear from simple electronic arguments whether or not a stable minimum (stable with respect to electron loss by tunneling) beyond the repulsive Coulomb barrier exists for these multiple-charged anions [13, 14]. Moreover, it is currently not feasible to correctly model the dynamic interaction between an electron and the negatively charged molecule in order to determine the Coulomb barrier and the stable (or metastable) multiple-charged state [15]. Finite basis set calculations missing important plane wave solutions artificially stabilize such multiple-charged anions, and in quantum chemical calculations one should always compare the total electronic energies of both anions, A^{n-} and $A^{(n-1)-}$, to ensure that an additional electron can indeed be accommodated within the molecular system. The situation is somewhat similar for the repulsive Coulomb wall between positively charged atomic or molecular fragments, i.e. $A^{q+} + B^{(n-q)+}$ [16–19], although at a different time scale as larger masses are involved. Recent examples, where multiple-charged diatomic cations AB^{n+} were found to be stable with respect to Coulomb explosion include $PbHe^{2+}$ [20], MHe^{2+} [21] (M = first row transition element), $HeAr^{2+}$ [22], or even UF^{3+} [23] and YHe^{3+}

[24]. In the solid state such multiple-charged ions are well known, but often require the counter-ions for stabilizing such systems, e.g. the recently published work by Yoldi et al. on the bonding in the π-[terthiophene]$_2^{2+}$ dimer [25].

The smallest stable dianions predicted by theory are the metal fluorides MX_3^{2-} (M = Li, Na, X = F or Cl) [26]. Cederbaum et al. [27, 28] also predicted MX_4^{2-} (M = Be, Mg, Ca, X = F or Cl) to be stable with respect to electron loss, which has been confirmed by mass spectroscopy by Middleton and Klein [29]. Multiple-charged anionic species of larger molecules have better chances to be Coulomb stable [13, 30–34]. However, Sommerfeld showed that even dianions of well-known aromatic compounds, such as cyclooctatetraene and cyclobutadiene are unstable with respect to electron loss [35].

Concerning organic compounds one might ask when successive deprotonation yields multiple-charged anions, which are stable with respect to electron loss or fragmentation [36, 37], especially for molecules containing functional groups with large electron-affinities. In a recent paper we investigated α,ω-dialkoxide species (deprotonated terminal diols) in the gas phase applying both density functional and wavefunction-based methods [38]. We found that terminal aliphatic dialkoxides $^{-}O–(CH_2)_n–O^{-}$ in the gas phase are all unstable with respect to electron loss up to very high chain lengths n separating the two charges by up to 30 Å ($n = 22$). It was noted that charge conjugation through an alkene or alkyne chain is required to accommodate two negative charges, with $^{-}O–(C_2H_2)_m–O^{-}$ ($m \geq 10$) and $^{-}O–(C{\equiv}C)_k–O^{-}$ ($k \geq 6$) are predicted to become Coulomb stable with respect to electron loss. This strongly suggests that delocalization of the two negative charges helps to stabilize such multiple-charged anions as has also been pointed out by Feuerbacher and Cederbaum [39].

Dicarboxylate dianions are promising candidates for stabilizing two negative charges, and have, therefore, been studied in the past by theoretical [13, 40], as well as by experimental methods [13, 40]. Both experiment and theory confirm that acetylene dicarboxylate $(O_2C–C{\equiv}C–CO_2)^{2-}$ is adiabatically stable with respect to electron loss. The situation is not so clear for the succinate dianion $(O_2C–CH_2–CH_2–CO_2)^{2-}$. Whereas previous theoretical investigations suggested that it is only stable against vertical electron detachment [40, 41], there are hints from a collisionally-induced ion-pair formation study [42] and photoelectron spectroscopy [40] that it might be formed in small amounts. For the aromatic dicarboxylate dianions derived from phthalic acids, $(O_2C–C_6H_4–CO_2)^{2-}$, there are only two studies available: Wang et al. used MP2 calculations with 6–311+G(2df) basis sets to investigate the three isomers, *o*-, *m*- and *p*-$(O_2C–C_6H_4–CO_2)^{2-}$ [13]. They found the *para* compound to be the most stable and the *ortho* the least, in agreement with the spatial charge separation. Their results are also in accordance with electron binding energies obtained from photoelectron spectroscopy [13]. Enlow and Ortiz used MP2 calculations and outer-valence Greens function techniques for the calculation of electron detachment energies for hydrogen and fluorine substituted aromatic dianions and obtained results similar to Wang et al. [43].

In this paper we use density functional theory and wavefunction-based theories together with Dunning's series of augmented correlation consistent basis sets for a systematic comparison of dicarboxyl dianions of the general form $^{-}O_2C–R–CO_2^{-}$ with R = C_2, C_2X_2, C_2X_4, and C_6X_4 (X = H, F). Structures of aliphatic species are shown in Figs. 1 and 2 (hydrogen substituted (**1**) to (**4-H**) and perfluorinated species (**2-F**) to (**4-F**)) and for the aromatic compounds in Figs. 3 and 4 ((**5-X**) to (**7-X**) for X = H, F

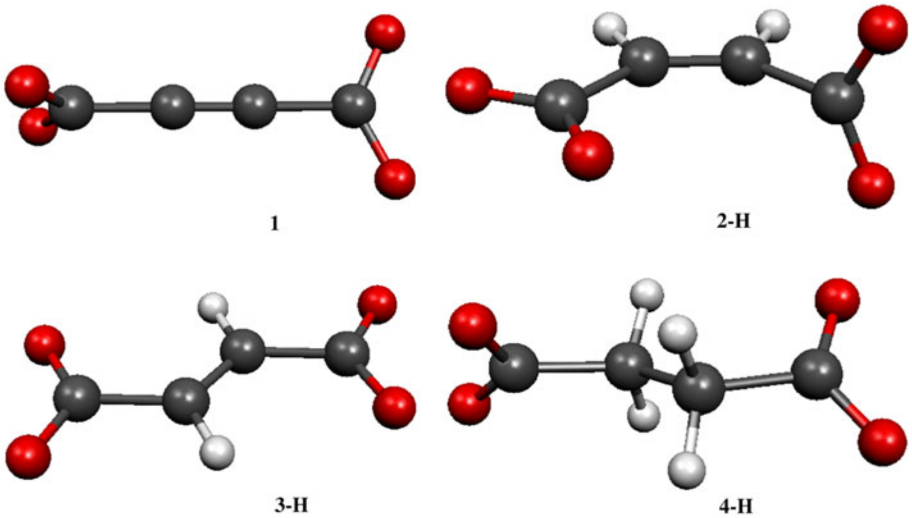


Fig. 1 Optimized geometries (B3-TZ) for the aliphatic dianionic species $^{-}O_2C–C_2–CO_2^{-}$ (**1**), *cis*-$^{-}O_2C–C_2H_2–CO_2^{-}$ (**2-H**), *trans*-$^{-}O_2C–C_2H_2–CO_2^{-}$ (**3-H**), and $^{-}O_2C–C_2H_4–CO_2^{-}$ (**4-H**). Color code: C(*black*), O(*red*), H(*white*)

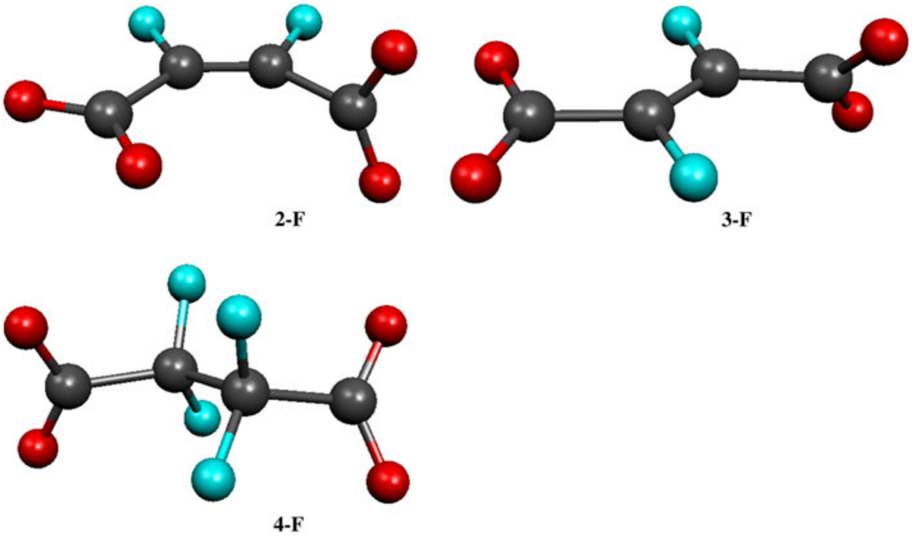

2-F
3-F
4-F

Fig. 2 Optimized geometries (B3-TZ) for the perfluorinated aliphatic dianionic species *cis*-$^{-}O_2C–C_2F_2–CO_2^{-}$ (**2-F**), *trans*-$^{-}O_2C–C_2F_2–CO_2^{-}$ (**3-F**), and $^{-}O_2C–C_2F_4–CO_2^{-}$ (**4-F**). Color code: C(*black*), O(*red*), F(*cyan*)

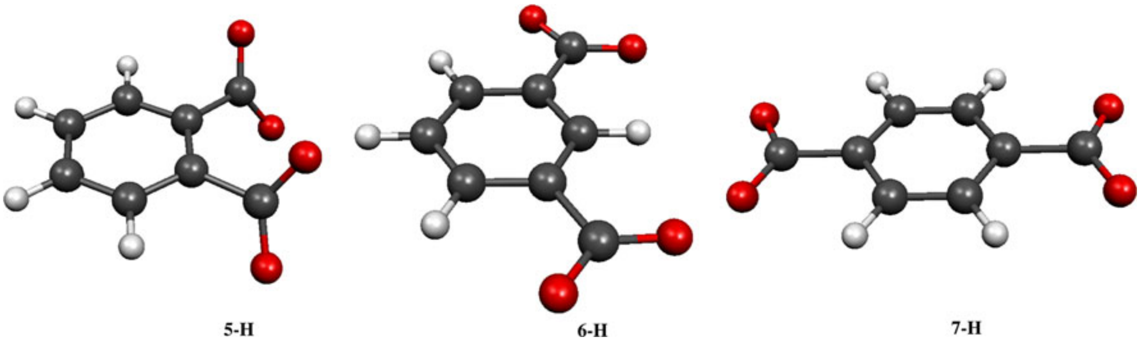

5-H
6-H
7-H

Fig. 3 Optimized geometries (B3-TZ) for the aromatic dianionic species *o*-$^{-}O_2C–C_6H_4–CO_2^{-}$ (**5-H**), *m*-$^{-}O_2C–C_6H_4–CO_2^{-}$ (**6-H**), *p*-$^{-}O_2C–C_6H_4–CO_2^{-}$ (**7-H**). Color code: C(*black*), O(*red*), H(*white*)

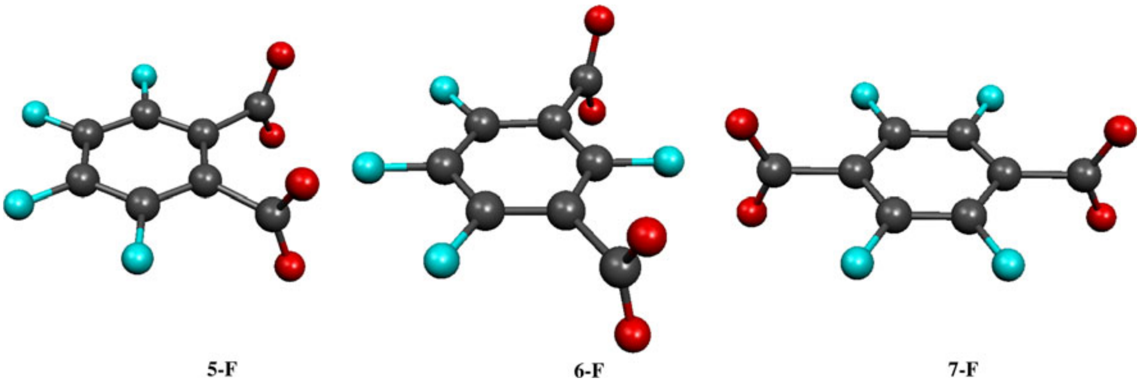

5-F
6-F
7-F

Fig. 4 Optimized geometries (B3-TZ) for the perfluorinated aromatic dianionic species *o*-$^{-}O_2C–C_6F_4–CO_2^{-}$ (**5-F**), *m*-$^{-}O_2C–C_6F_4–CO_2^{-}$ (**6-F**), *p*-$^{-}O_2C–C_6F_4–CO_2^{-}$ (**7-F**). Color code: C(*black*), O(*red*), F(*cyan*)

respectively). The aim of this study is to determine their structures and corresponding adiabatic and vertical electron detachment energies. We note that the two isomers of maleate (the dianions of the deprotonated form of *cis*- and *trans*-maleic acid) have not yet been investigated.

2 Computational details

Geometry optimizations were carried out for the dicarboxyl anions and dianions at the density functional level applying the widely used B3LYP functional [44, 45] together with

Dunning's correlation consistent aug-cc-pVDZ (DZ) and aug-cc-pVTZ basis sets (TZ) [46, 47] abbreviated here as B3-DZ and B3-TZ. Improved total electronic energies were derived from single-point calculations using aug-cc-pVQZ (B3-QZ) basis sets at the optimized B3-TZ geometries. These basis sets are found to be sufficient to describe bound states for these doubly negatively charged species, i.e. calculations for the smallest molecules using aug-cc-pV5Z basis sets gave very similar results compared to aug-cc-pVQZ and addition of further diffuse functions did not significantly alter the results either. Further geometry optimizations were carried out at the second-order Møller-Plesset level of theory (MP2) keeping the orbital space fully active and applying the aug-cc-pVDZ basis sets (MP2-DZ). Based on this geometry, improved energies were derived with the aug-cc-pVTZ (MP2-TZ) and aug-cc-pVQZ (MP2-QZ) basis sets. Coupled cluster (CCSD(T)) energies with the aug-cc-pVDZ (CC-DZ) and aug-cc-pVTZ (CC-TZ) basis sets were derived at the MP2-DZ geometries for the aliphatic hydrogen substituted species. These calculations were already at the limit of our computational resources. Following the initial geometry optimization without symmetry constraints, symmetry was used in subsequent single-point calculations if possible. All open-shell species were calculated within unrestricted Kohn–Sham and Hartree-Fock theory [49]. The character of the stationary points was confirmed by calculating the Hessian matrix analytically at the B3-DZ and MP2-DZ levels of theory for all optimized species. Correction terms for zero-point vibrational energy have been taken from these calculations as well. Vertical electron detachment energies (VEDE) have been calculated as the energy difference between the total energies of the monoanion (as single-point calculation on the optimized dianionic structure) and the dianion. Adiabatic electron detachment energies (AEDE) employed the total energy of the optimized anion instead. Atomic partial charges have been calculated with the natural population analysis (NPA) method of Reed and Weinhold [48, 49]. All calculations have been carried out with the program package Gaussian03 [49]. For the plots of molecular structures and molecular orbitals shown in Figs. 1, 2, 3, 4 and 5 the program Molekel was used [50].

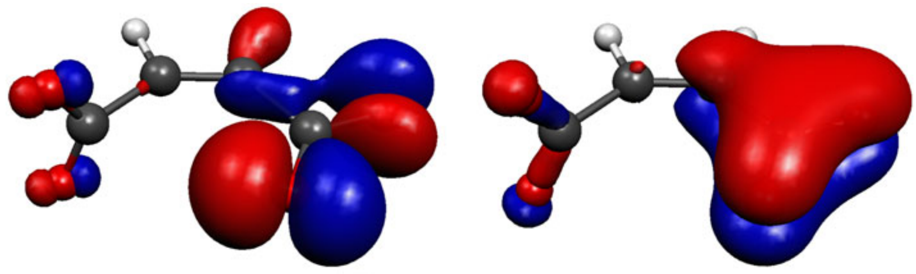
3 Results and discussion

The optimized structural parameters are shown in Tables 1, 2 and 3 using the labeling of atoms as shown in Scheme 1.

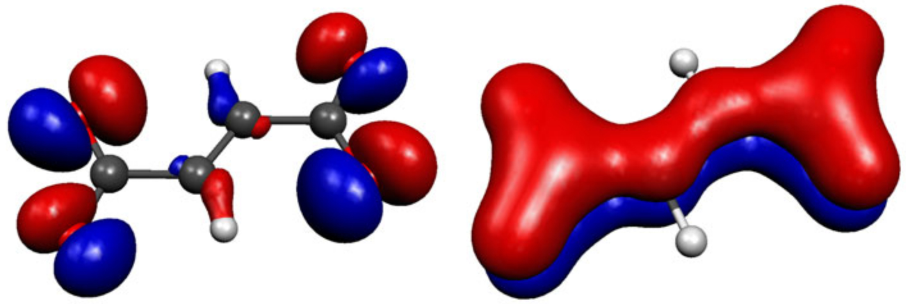
Improving the basis set from DZ to TZ leads in general to shorter bond distances for the B3LYP structures while the bond and torsion angles remain almost unchanged. There is also good agreement between the B3-DZ and MP2-DZ structures, although the deviations between the two methods are somewhat larger for the singly charged systems compared to the doubly charged ones. Nevertheless, we believe that the B3-TZ structures are accurate enough for the calculation of electron detachment energies.

Concerning the overall structures (**1**) to (**4-H**) shown in Fig. 1 we note that for the acetylene dicarboxylate (dianion (**1**)) the D_{2d} structure is adopted with the CO_2 groups

Fig. 5 Molecular orbital plot (B3-TZ) for *cis*- and *trans*-maleate showing both the highest occupied orbital (HOMO) and the total bonding HOMO-*n* π-orbital being the *n*th lowest lying HOMO. Color code: C(*black*), O(*red*), F(*cyan*))



HOMO *cis*-maleate (**2-H**) HOMO-9 *cis*-maleate (**2-H**)



HOMO *trans*-maleate (**3-H**) HOMO-10 *trans*-maleate (**3-H**)

Table 1 Important geometrical parameters (in Å and degrees) for the B3-DZ and B3-TZ structures (**1**)–(**7-H**) of $(O_2C–R–CO_2)^q$ (charge $q = -2, -1$)

Compound	Symmetry	Basis set	d(C–O1)	d(C–O2)	d(C1–C2′)	d(C–C_{CO_2})	<(OCO)	<(CO_2/plane)[a]	
$q = -2$									
(**1**)	D_{2d}	DZ	1.265	1.265	1.228	1.493	127.7	0.0	90.0
		TZ	1.259	1.259	1.215	1.489	127.7	0.0	90.0
(**2-H**)	C_s	DZ	1.281/1.264	1.257/1.264	1.352	1.531/1.529	127.7/126.9	0.0	94.1
		TZ	1.274/1.257	1.251/1.257	1.342	1.529/1.527	127.8/127.0	0.0	94.1
(**3-H**)	C_{2h}	DZ	1.274	1.266	1.345	1.531	126.4	0.0	0.0
		TZ	1.267	1.259	1.335	1.529	126.5	0.0	0.0
(**4-H**)	C_2	DZ	1.272	1.266	1.536	1.560	126.2	40.2	−40.2
		TZ	1.265	1.259	1.531	1.559	126.4	40.7	−40.7
(**5-H**)[b]	C_2	DZ	1.266	1.257	1.420	1.547	128.4	55.3	53.7
		TZ	1.259	1.250	1.412	1.546	128.5	55.6	53.9
(**6-H**)[c]	C_{2v}	DZ	1.268	1.260	1.408	1.551	127.3	0.0	0.0
		TZ	1.262	1.254	1.400	1.550	127.5	0.0	0.0
(**7-H**)[d]	D_{2h}	DZ	1.265	1.265	1.405	1.547	127.2	0.0	0.0
		TZ	1.258	1.258	1.397	1.545	127.3	0.0	0.0
$q = -1$									
(**1**)	D_{2h}	DZ	1.254	1.253	1.233	1.466	126.9	0.0	0.0
		TZ	1.247	1.247	1.219	1.461	126.9	0.0	0.0
(**2-H**)	C_2	DZ	1.270	1.236	1.356	1.512	129.7	74.1	74.1
		TZ	1.264	1.228	1.345	1.513	130.4	75.7	75.7
(**3-H**)	C_i	DZ	1.268	1.251	1.358	1.493	125.2	49.1	48.4
		TZ	1.267	1.227	1.347	1.514	130.4	76.3	−76.3
(**4-H**)	C_i	DZ	1.234	1.246	1.489	1.659	134.6	58.3	58.3
		TZ	1.232	1.226	1.474	1.696	136.1	71.4	71.4
(**5-H**)[e]	C_{2v}	DZ	1.246	1.282	1.413	1.526	122.1	0.0	0.0
		TZ	1.276	1.239	1.405	1.524	122.3	0.0	0.0
(**6-H**)[f]	C_{2v}	DZ	1.262	1.265	1.403	1.509	120.7	0.0	0.0
		TZ	1.264	1.252	1.392	1.506	121.0	0.0	0.0
(**7-H**)[g]	D_2	DZ	1.260	1.260	1.410	1.503	124.0	38.1	−38.1
		TZ	1.253	1.253	1.402	1.500	124.3	40.3	−40.3

[a] Smallest dihedral angles between CO_2 units and the molecular plane of the carbon framework. See text for sign convention

[b] DZ: d(C2–C3) = 1.410, d(C3–C4) = 1.398, d(C4–C5) = 1.401; TZ: d(C2–C3) = 1.402, d(C3–C4) = 1.390, d(C4–C5) = 1.393

[c] DZ: d(C2–C3) = 1.408, d(C3–C4) = 1.405, d(C4–C5) = 1.400; TZ: d(C2–C3) = 1.400, d(C3–C4) = 1.397, d(C4–C5) = 1.392

[d] DZ: d(C2–C3) = 1.401; TZ: d(C2–C3) = 1.391

[e] DZ: d(C2–C3) = 1.407, d(C3–C4) = 1.393, d(C4–C5) = 1.400; TZ: d(C2–C3) = 1.400, d(C3–C4) = 1.385, d(C4–C5) = 1.392

[f] DZ: d(C2–C3) = 1.403, d(C3–C4) = 1.403, d(C4–C5) = 1.398; TZ: d(C2–C3) = 1.392, d(C3–C4) = 1.394, d(C4–C5) = 1.390

[g] DZ: d(C2–C3) = 1.391; TZ: d(C2–C3) = 1.382

perpendicular to each other (Fig. 1), whereas for the monoanion we calculate a non-linear (planar) C_{2h} structure at MP2-DZ level with the CO_2 groups in the same plane. This is in agreement with the results obtained earlier by Skurski et al. [40]. However, geometry optimization with B3LYP results in a linear D_{2h} structure for the monoanion.

The change from C_{2h} to D_{2d} upon adding an extra electron to the monoanion is also evident from the rotational barriers listed in Table 4. It is clear that both forms can resonate with the triple bonds and corresponding molecular orbital plots are given in [40]. The sign for a dihedral angle in Tables 1, 2 and 3 is negative if the two CO_2 groups are disrotatory with respect to the molecular plane. The Coulomb repulsion between the two carboxylate groups in *cis*-maleate **2-H** is obviously so large that one of the carboxylate groups rotates out of the plane by 90° and becomes off-resonance with the double bond, which is clearly seen in the molecular orbital (MO) picture of the totally bonding MO shown in Fig. 5. This is not the case for *trans*-maleate **3-H** as shown in Fig. 5 as well. Going

Table 2 Important geometrical parameters (in Å and degrees) for the MP2-DZ structures (**1**)–(**7-H**) of $(O_2C\text{–}R\text{–}CO_2)^q$ (charge $q = -2, -1$)

Compound	Symmetry	*d*(C–O1)	*d*(C–O2)	*d*(C1–C2′)	*d*(C–C_{CO_2})	<(OCO)	<(CO_2/plane)[a]	
$q = -2$								
(**1**)	D_{2d}	1.273	1.273	1.246	1.501	127.8	0.0	90.0
(**2-H**)	C_s	1.273/1.265	1.273/1.290	1.363	1.529/1.527	128.0/127.3	0.0	93.9
(**3-H**)	C_{2h}	1.283	1.274	1.358	1.529	126.6	0.0	0.0
(**4-H**)	C_2	1.281	1.275	1.536	1.554	126.5	45.7	−45.7
(**5-H**)[b]	C_2	1.276	1.266	1.423	1.541	128.9	52.7	52.1
(**6-H**)[c]	C_{2v}	1.277	1.269	1.415	1.549	127.7	0.0	0.0
(**7-H**)[d]	D_{2h}	1.274	1.274	1.413	1.543	127.6	0.0	0.0
$q = -1$								
(**1**)	C_{2h}	1.301	1.237	1.249	1.459	129.3	0.0	0.0
(**2-H**)	C_2	1.287	1.239	1.366	1.510	131.8	87.6	−87.6
(**3-H**)	C_2	1.294	1.238	1.359	1.505	130.5	85.4	−85.4
(**4-H**)	C_{2h}	1.249	1.249	1.486	1.660	135.7	90.1	90.1
(**5-H**)[e]	C_{2v}	1.293	1.253	1.417	1.522	122.8	0.0	0.0
(**6-H**)[f]	C_{2v}	1.257	1.254	1.406	1.594	133.9	0.0	0.0
(**7-H**)[g]	D_{2h}	1.275	1.275	1.413	1.494	121.2	0.0	0.0

[a] Smallest dihedral angles between CO_2 units and the molecular plane of the carbon framework. See text for sign convention

[b] *d*(C2–C3) = 1.416, *d*(C3–C4) = 1.407, *d*(C4–C5) = 1.409

[c] *d*(C2–C3) = 1.415, *d*(C3–C4) = 1.412, *d*(C4-C5) = 1.408

[d] *d*(C2–C3) = 1.408

[e] *d*(C2–C3) = 1.414, *d*(C3–C4) = 1.401, *d*(C4–C5) = 1.409

[f] *d*(C2–C3) = 1.406, *d*(C3–C4) = 1.411, *d*(C4–C5) = 1.409

[g] *d*(C2–C3) = 1.403

Table 3 Important geometrical parameters (in Å and degrees) for the B3-TZ structures (**2-F**)–(**7-F**) of perfluorated $(O_2C\text{–}R\text{–}CO_2)^q$ (charge $q = -2, -1$)

Compound	Symmetry	*d*(C–O1)	*d*(C–O2)	*d*(C1–C2′)	*d*(C–C_{CO_2})	<(OCO)	<(CO_2/plane)[a]	
$q = -2$								
(**2-F**)	C_s	1.248/1.251	1.259/1.251	1.336	1.528/1.542	128.9	0.0	93.4
(**3-F**)	C_1	1.256	1.254/1.252	1.339	1.537/1.544	128.3/128.7	5.8	−60.6
(**4-F**)	C_2	1.247	1.246	1.559	1.597	130.4	69.9	−69.9
(**5-F**)[b]	C_{2v}	1.247	1.247	1.413	1.563	130.4	88.4	−88.4
(**6-F**)[c]	C_{2v}	1.247	1.247	1.393	1.561	130.4	89.5	−89.5
(**7-F**)[d]	D_{2h}	1.247	1.247	1.386	1.561	130.4	90.0	90.0
$q = -1$								
(**2-F**)	C_{2v}	1.280	1.231	1.337	1.502	124.3	0.0	0.0
(**3-F**)	C_1	1.258	1.226	1.365	1.519	132.0	80.0	−80.1
(**4-F**)	C_{2h}	1.215	1.215	1.523	1.779	141.2	87.7	−87.7
(**5-F**)[e]	C_s	1.278	1.230	1.405	1.526	124.3	38.3	−38.3
(**6-F**)[f]	C_{2v}	1.246	1.246	1.399	1.520	125.7	90.0	90.0
(**7-F**)[g]	D_{2h}	1.243	1.243	1.398	1.514	127.9	90.0	90.0

[a] Smallest dihedral angles between CO_2 units and the molecular plane of the carbon framework. See text for sign convention

[b] *d*(C2–C3) = 1.388, *d*(C3–C4) = 1.385, *d*(C4–C5) = 1.382

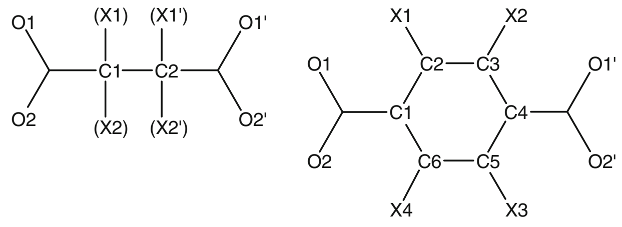
[c] *d*(C2–C3) = 1.393, *d*(C3–C4) = 1.384, *d*(C4–C5) = 1.385

[d] *d*(C2–C3) = 1.388

[e] *d*(C2–C3) = 1.392, *d*(C3–C4) = 1.386, *d*(C4–C5) = 1.382

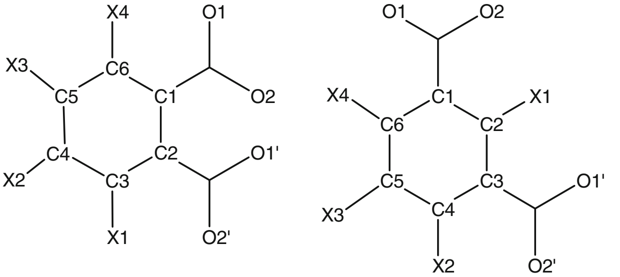
[f] *d*(C2–C3) = 1.399, *d*(C3–C4) = 1.382, *d*(C4–C5) = 1.388

[g] *d*(C2–C3) = 1.377



aliphatic species

para-substituted aromatic species



ortho-substituted aromatic species

meta-substituted aromatic species

Scheme 1 Labeling of atoms in investigated compounds

from the anion to the dianion, therefore, decreases the bond length of the C=C double bond and substantially elongates the C–CO_2 bonds as shown in Tables 1 and 2.

Our results for succinate (**4-H**) are in good agreement with a previous study [40], although we find a distorted C_2-structure instead of the C_{2h} structure given in [40]. In this structure which is ca. 0.3 kcal/mol more stable than the C_{2h} structure, the CO_2^- groups are aligned such that the negatively charged oxygen atom can weakly interact with the neighboring H-atoms from the C_2H_4 framework (with O–H non-bonding distances between 2.4 and 2.8 Å), the hydrogen atoms thereby carrying a positive charge of 0.17e and 0.20e as confirmed by our NPA (Table 5).

Regarding the perfluorinated compounds shown in Fig. 2 we note that except for compound (**2-F**) all CO_2^- groups are rotated out of the carbon framework plane. For (**2-F**) one CO_2^- group lies in the plane for the dianion, and the anion shows C_{2v} symmetry with both carboxyl groups in the plane. This is most likely due to the additional Coulomb repulsion between the CO_2^- groups and the negatively charged fluorine atoms, which is obviously larger than the resonance stabilization. Indeed, the NBO charges in Table 5 show charge concentration at the oxygen and fluorine atoms. We note that the calculated range of C–F distances at the B3-TZ level of theory is 1.332 to 1.389 Å.

For the aromatic compounds (structures (**5-H**) to (**7-H**) shown in Fig. 3) we obtain the same general structures compared to Wang et al. [13], i.e. all structures are planar except for the *ortho*-isomer of the benzene dicarboxylate dianion and the anion of (**7-H**), which we find to be non-planar at the B3LYP level, but planar with MP2-DZ. The main structural features have already been explained in detail by Wang et al. [13] and will not be repeated here. For (**7-H**) we list rotational barriers in Table 4. B3LYP and MP2 agree well that there are relatively large barriers for rotation in the dianions underlining the resonance stabilization in these compounds. We do not list C–H bond distances in Tables 1 and 2 as they all are in the range of 1.087–1.102 at the B3-DZ level of theory (1.080–1.094 for B3-TZ and 1.089–1.104 for MP2-DZ).

For the perfluorinated aromatic compounds (structures (**5-F**) to (**7-F**) shown in Fig. 4), there is rotation of the CO_2^--groups analogous to the aliphatic structures. Other parameters are similar to the H-substituted analogs as well.

The adiabatic and vertical detachment energies of the various dianions are listed in Table 6. It is well known that

Table 4 Estimates for rotational barriers for $(O_2C–C{\equiv}C–CO_2)^{-2}$ (**1**) and $(p\text{-}O_2C–C_6H_4–CO_2)^{-2}$ (**7-H**) at the B3-DZ, B3-TZ and MP2-DZ level of theory. Relative energies are given in eV

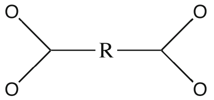
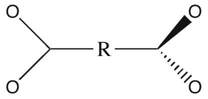
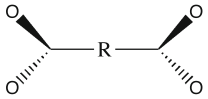
Compound			
(**1**)			
B3-DZ	0.0	−0.10	
B3-TZ	0.0	−0.10	
MP2-DZ	0.0	−0.04	
(**7-H**)			
B3-DZ	0.0	+0.18	+0.40
B3-TZ	0.0	+0.17	+0.38
MP2-DZ	0.0	+0.19	+0.40

Table 5 Atomic partial charges (NBO, B3-TZ, in e) for the dicarboxyl dianions with structures (**1**)–(**7-X**)

	X	C1	O1	O2	C_{CO_2}	X1	X2
(**1**)	–	−0.15	−0.77	−0.77	0.69	–	–
(**2-X**)[a]	H	−0.33/−0.24	−0.83/−0.78	−0.76/−0.78	0.70/0.73	0.15	–
	F	0.17/0.27	−0.79/−0.76	−0.75/−0.76	0.68/0.71	−0.39	–
(**3-X**)	H	−0.28	−0.81	−0.80	0.70	0.18	–
	F	0.18/0.26	−0.77	−0.78/−0.76	0.68/0.69	−0.35/−0.37	–
(**4-X**)	H	−0.48	−0.81	−0.83	0.75	0.17	0.20
	F	0.58	−0.76	−0.76	0.69	−0.38	−0.38
(**5-X**)	H	−0.08	−0.79	−0.75	0.75	0.16	0.19
	F	−0.12	−0.74	−0.74	0.75	−0.35	−0.35
(**6-X**)	H	−0.14	−0.80	−0.77	0.73	0.24	0.21
	F	−0.21	−0.75	−0.75	0.76	−0.35	−0.35
(**7-X**)	H	−0.14	−0.80	−0.80	0.76	0.20	–
	F	−0.16	−0.75	−0.75	0.75	−0.35	–

[a] Second set of values for C2 and substituents

density functionals often can over-stabilize negative charges [51], but the B3LYP functional usually gives accurate results within 0.1–0.2 eV [52]. Nevertheless, in comparison to our coupled cluster results we see that the B3LYP values tend to underestimate electron detachment energies by about 0.4–0.5 eV. MP2 on the other hand shows rather good agreement at least for the adiabatic detachment energies. Nevertheless, the B3LYP values for such systems can be seen as a lower bound.

We also note that the VEDEs are slightly more sensitive to basis set effects than the AEDEs. This can be understood as the former entities are more difficult to calculate since they result from an electron density calculation on a non-optimized geometry. Regarding the basis set effects for the different methods, the B3-DZ values are somewhat surprisingly already converged for the vast majority of the species. Regarding the MP2 results for AEDE we note a change by about 0.05–0.10 eV upon going from DZ to TZ basis set and about the same amount on increasing the basis set to QZ quality while the VEDEs show somewhat larger deviations. This is in line with the well-known slower basis set convergence of ab-initio methods. The basis set effect on the coupled cluster values is very similar to the MP2 method.

The results in Table 6 clearly show that (**3-H**) is stable with respect to electron loss, by 0.26 eV at the CC-TZ level of theory whereby the (**2-H**) isomer is not. We expect that increasing the basis set to QZ quality will bring this value up to about 0.33 eV. This estimate is based on the rather constant basis set effect on the AEDEs with the MP2 method which increase by 0.07 eV on average in going from MP2-TZ to MP2-QZ. On first sight, the only other stable aliphatic compound is acetylene dicarboxylate. In agreement with [40] we find with all MP2 calculations that (**4-H**) is stable against vertical but not adiabatic electron detachment. But a closer look at the CC-TZ results reveals that the dianion is only marginally unstable at this level of theory. Applying the above mentioned basis set correction (0.07 eV in going from TZ to QZ) we find a slight stabilization of the dianion (0.06 eV) which would be in excellent agreement with the spurious detection of this dianion in previous experiments as mentioned earlier. This finding underlines the need for large basis sets and high-level correlation methods in ab-initio calculations of VEDEs and AEDEs. Hence, concerning the adiabatic electron detachment for the different dianions we have the following series in stability based on CC-TZ values: $(O_2C\text{–}C{\equiv}C\text{–}CO_2)^{2-} >$ *trans*-$(O_2C\text{–}CH{=}CH\text{–}CO_2)^{2-} > (O_2C\text{–}CH_2\text{–}CH_2\text{–}CO_2)^{2-} >$ *cis*-$(O_2C\text{–}CH{=}CH\text{–}CO_2)^{2-}$. Regarding the aromatic dianions we find in accordance with previous investigations [13] that *meta*- and *para*-benzo-dicarboxylates are stable with respect to electron loss. But our much larger basis sets in the MP2-QZ calculations suggest, that even the *ortho*-isomer could be slightly stable which is in agreement with the experimental results of the same publication which employed only DZ quality basis sets in the theoretical part [13].

The perfluoro compounds all show larger stabilities with respect to electron loss (see Table 6). Interestingly, (**2-F**) and (**3-F**) are the only species unstable with respect to electron loss. But since B3-TZ is most likely a lower bound for electron detachment energies, these species are promising for future search for stable dianions. Even the aliphatic $(O_2C\text{–}CF_2\text{–}CF_2\text{–}CO_2)^{2-}$ compound seems to be Coulomb stable.

Table 6 Electron detachment energies (in eV) for the dicarboxyl dianions (**1**)–(**7-X**) at the B3LYP, MP2 and CCSD(T) level of theory employing aug-cc-pV*n*Z basis sets

Compound	X = H										X = F
	B3LYP				MP2				CCSD(T)		B3LYP
	DZ	DZ[a]	TZ	QZ	DZ	DZ[a]	TZ	QZ[b]	DZ	TZ	TZ
(**1**)											
VEDE	0.49		0.50	0.50	1.29		1.48	1.57	0.76	0.91	–
AEDE	−0.02	−0.09	−0.01	−0.01	0.52	0.71	0.60	0.67	0.41	0.50	–
(**2-X**)											
VEDE	−0.10		−0.11	−0.02	0.81		1.15	1.22	0.26	0.33	0.35
AEDE	−0.55	−0.60	−0.56	−0.57	−0.21	−0.15	−0.13	−0.07	−0.24	−0.16	−0.43
(**3-X**)											
VEDE	0.10		0.12	0.10	0.48		0.63	0.70	0.54	0.67	0.41
AEDE	−0.16	−0.24	−0.20	−0.20	0.24	0.29	0.31	0.37	0.18	0.26	−0.06
(**4-X**)											
VEDE	−0.13		−0.14	−0.14	0.42		0.58	0.65	0.37	0.50	0.68
AEDE	−0.41	−0.45	−0.46	−0.47	−0.29	−0.20	−0.22	−0.17	−0.07	−0.01	0.23
(**5-X**)											
VEDE	−0.05		−0.05	−0.04	1.59		1.76	1.80	–		0.58
AEDE	−0.63	−0.59	−0.61	−0.61	−0.15	0.03	−0.08	0.03	–		0.27
(**6-X**)											
VEDE	1.04		1.04	1.04	1.09		1.24	1.30	–		1.02
AEDE	0.43	0.39	0.44	0.45	0.55	0.70	0.62	0.66	–		1.01
(**7-X**)											
VEDE	0.74		0.75	0.75	0.96		1.11	1.16	–		1.00
AEDE	0.51	0.45	0.51	0.51	0.77	0.94	0.86	0.94	–		0.88

[a] ZPE corrected values

[b] MP2 has been used together with the frozen core approximation for **5-H**, **6-H** and **7-H**

4 Conclusions

We presented a systematic comparison of aliphatic and aromatic dicarboxylate dianions. The main findings of concern in the search for further stable dianions are that the *trans*-isomer of the maleate dianion is Coulomb stable with respect to electron loss while the *cis*-isomer is not and that fluorine substitution helps to stabilize all dianions. From a methodological point of view it is noteworthy that while DFT results are converged with a basis set of augmented double zeta quality, MP2 and CCSD(T) need basis sets of at least augmented quadruple zeta quality. Only on the highest levels of theory applied in this paper we achieve agreement with experimental observations regarding the slight stabilization of the succinate dianion and the *ortho*-isomer of the phthalic acid dianion in contrast to all previous theoretical work. It would be very useful to perform experimental studies on both the *cis* and *trans* form of $(O_2C–CH=CH–CO_2)^{2-}$ and $(O_2C–CF=CF–CO_2)^{2-}$ to verify the results presented in this paper.

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