Electronic Supporting Information (ESI) for "Solvent-mediated folding in dicarboxylate dianions: aliphatic chain length dependence and origin of the IR intensity quenching"

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MD Simulations on the Succinate Dianion

MD's were performed at three different temperatures (195, 210, and 240 K). Experiments suggest folding to occur around n=9. Hence, structures were prepared for n=4, 6, 8, 10, and 12. Structures

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for n=0 and 2 were constructed manually. For n=4 and 6, the linear configuration ($D \approx 3.80$ Å) was predominant at all temperatures. For n=8, the linear configuration was prevalent, but folded structures ($D \approx 3.45$ Å) were obtained, as well. For n=10, the linear configuration was predominant at 240 K, the folded one at 195 K, and at 210 K, a mixture of both was obtained. Also strongly folded structures ($D \approx 3.10$ Å) were found. For n=12, the folded configuration was predominant.

For n=8, 10, and 12, a soft constraint for the separation between the carboxylate groups was set to obtain separate ensembles of linear and folded structures. For n=8, the temperature was set to 210 K. In order to obtain the strongly folded configuration, the temperature was lowered to 190 K and a harder constraint was used. For n=10 (12), 210 (195) K were chosen, respectively, and a hard constraint was used to sample the linear configuration.

After the final evaluation of energies, the folded configurations were found more stable than the strongly folded ones.

MD Simulations on the Adipate Dianion

In the case of the adipic acid once again 195 K, 210 K, and 240 K were chosen.

As the experiment suggests folding to occur for n=13, structures were prepared with n=4, 6, 8, 10, 12, and 14 waters (manual construction for n=0 and 2). For n=4, 6, 8, and 10, the linear configuration was predominant. For n=12 and n=14, also folded structures ($D \approx 4.10$ Å) were obtained and constraints were set to obtain separate samples of linear and folded configurations. Temperatures of 195–210 K were used (210 K for the linear ensemble).



Figure S-1: Experimental IRPD spectra of microsolvated succinate (upper left), adipate (upper right), and sebacate (lower) dianions. Shown is the region of the symmetric and antisymmetric C=O stretching bands.



Figure S-2: Experimental and theoretical spectra of microsolvated adipic acid dianions.



Figure S-2: (continued).



Figure S-3: Experimental and theoretical spectra of microsolvated succinic acid dianions.



Figure S-3: (continued).

Table S-1: Adipate dianion isomers: Energies (kcal/mol), carboxylic stretch frequencies (cm^{-1}) and intensities.^{*a*}

	structure	E(CEPA/1)	ZPVE	$E_{\rm tot}$	$v_{\rm S}$	VA	Is	IA	$I_{\rm S}/(I_{\rm S}+I_{\rm A})$
n = 0	linear-1	-334541.2	81.7	-334459.5	1334	1604	496	1128	0.31
n = 1	linear-1	-382422.9	96.8	-382326.0	1345	1595	594	955	0.38
n = 2	linear-1	-430304.2	112.1	-430192.1	1355	1583	682	782	0.47
<i>n</i> = 4	linear-1	-526057.5	143.3	-525914.1	1367	1584	699	834	0.46
	linear-2	-526056.5	142.5	0.1	1373	1591	773	1112	0.41
<i>n</i> = 6	linear-1	-621810.1	174.4	-621635.7	1376	1579	755	889	0.46
	linear-2	-621808.4	174.4	1.7	1376	1581	638	1000	0.39
n = 8	linear-1	-717560.0	206.4	-717353.6	1380	1565	732	911	0.45
	linear-2	-717559.4	206.3	0.5	1381	1562	806	720	0.53
n = 10	linear-1	-813308.8	237.7	-813071.1	1380	1566	823	887	0.48
	linear-2	-813307.9	237.1	0.3	1381	1605	851	802	0.51
	linear-3	-813308.5	237.7	0.3	1380	1568	822	784	0.51
	linear-4	-813307.4	237.1	0.8	1383	1566	841	906	0.48
n = 12	linear-1	-909057.3	268.7	-908788.6	1348	1527	888	879	0.50
	folded-1	-909061.0	270.6	-1.8	1404	1582	312	1370	0.19
	folded-2	-909060.9	270.6	-1.6	1399	1578	315	1366	0.19
	folded-3	-909060.3	270.3	-1.4	1399	1566	291	1334	0.18
	folded-4	-909060.2	270.3	-1.3	1361	1533	287	1271	0.18
	folded-5	-909060.4	270.7	-1.1	1396	1574	297	1250	0.19
	folded-6	-909059.8	270.2	-1.0	1402	1577	307	1535	0.17
	folded-7	-909060.1	270.6	-0.9	1398	1577	326	1312	0.20
	folded-8	-909060.3	270.8	-0.8	1397	1573	289	1266	0.19
	folded-9	-909060.3	270.8	-0.8	1362	1534	297	1250	0.19
<i>n</i> = 14	folded-1	-1004808.3	301.1	-1004507.2	1403	1570	311	1436	0.18
	folded-2	-1004807.9	301.5	0.8	1404	1566	309	1298	0.19
	linear-1	-1004801.1	299.2	5.2	1390	1562	777	886	0.47
	linear-2	-1004801.4	299.7	5.5	1392	1568	751	869	0.46
	linear-3	-1004800.9	299.3	5.5	1388	1574	729	799	0.48
	linear-4	-1004801.1	299.6	5.6	1386	1574	783	873	0.47
	linear-5	-1004800.7	299.3	5.7	1378	1568	782	874	0.47

^{*a*}Energies from CEPA/1 calculations using the aug-cc-pVDZ basis set; zero point vibrational energies (ZPVE) from PBE/aug-cc-pVDZ. The sum of the two (E_{tot}) is given as an absolute value for the reference geometry of each cluster; relative energies are provided for alternative isomers.



Figure S-4: Typical mass spectra of succinate (upper) and adipate (lower) dianions, as produced in a commercial Z-spray source from a solution of succinic/adipic acid (1 mM) and NaOH (2 mM) in a water/acetonitrile mixture (20/80). The source parameters have been tuned to optimize the formation of hydrated dianions with n = 20.

Table S-2: Adipate dianion isomer energies (kcal/mol).^a

	structure	E(CEPA/1)	ZPVE	$E_{\rm tot}^{DZ/PBE_b}$	E _{tot}
n = 0	linear-1	-334813.6	84.2	-334459.5	-334729.4
n = 1	linear-1	-382736.6	99.8	-382326.0	-382636.7
n = 2	linear-1	-430659.1	115.6	-430192.1	-430543.5
<i>n</i> = 4	linear-1	-526494.6	147.6	-525914.1	-526347.0
	linear-2	-526493.9	146.9	0.1	0.1
<i>n</i> = 6	linear-1	-622329.6	180.1	-621635.7	-622149.5
	linear-2	-622327.4	179.5	1.7	1.6

^{*a*}CEPA/1 energies calculated with the larger aug-cc-pVTZ basis set; ZPVE from B3LYP/aug-cc-pVDZ. The sum of the two (E_{tot}) is given as an absolute value for the reference geometry of each cluster; relative energies are provided for alternative isomers. ^{*b*} E_{tot} from Table S-3 is given for comparison.

	structure	E(CEPA/1)	ZPVE	$E_{\rm tot}$	$v_{\rm S}$	$v_{\rm A}$	Is	$I_{\rm A}$	$I_{\rm S}/(I_{\rm S}+I_{\rm A})$
n = 0	linear-1	-285326.6	47.7	-285278.9	1335	1574	412	1161	0.26
n = 1	linear-1	-333210.3	62.8	-333147.5	1348	1572	540	963	0.36
	bridged-1	-333210.2	63.8	1.2	1339	1583	337	1355	0.20
n = 2	linear-1	-381093.3	77.9	-381015.4	1357	1562	666	780	0.46
	bridged-1	-381092.3	79.0	2.1	1351	1581	442	1178	0.27
n = 3	bridged-1	-428973.7	94.1	-428879.6	1360	1571	521	1015	0.34
	linear-1	-428970.6	93.0	1.9	1365	1565	739	963	0.43
n = 4	bridged-1	-476850.0	109.1	-476741.0	1361	1578	591	1125	0.34
	linear-1	-476847.6	108.0	1.3	1373	1569	792	1128	0.41
<i>n</i> = 6	linear-1	-572602.4	140.6	-572461.8	1377	1564	856	906	0.49
	bridged-1	-572602.7	140.3	-0.7	1369	1577	668	1173	0.36
	bridged-2	-572601.5	140.0	0.2	1363	1595	614	1307	0.32
n = 8	bridged-1	-668354.8	172.8	-668182.1	1380	1567	539	1169	0.32
	linear-1	-668353.5	171.9	0.5	1381	1549	836	934	0.47
	folded-1	-668356.3	173.0	-1.2	1380	1572	322	1107	0.23
	folded-2	-668355.3	172.6	-0.6	1383	1570	324	1107	0.23
	folded-3	-668355.1	172.5	-0.6	1384	1572	302	1217	0.20
	folded-4	-668354.9	172.6	-0.3	1387	1571	299	1089	0.22
	folded-5	-668354.4	172.1	-0.2	1382	1569	337	1201	0.22
n = 10	folded-1	-764107.9	204.2	-763903.8	1390	1574	264	1458	0.15
	folded-2	-764107.2	204.0	0.6	1384	1575	332	897	0.27
	folded-3	-764107.2	204.0	0.6	1383	1571	347	779	0.31
	folded-4	-764107.0	203.9	0.6	1391	1579	302	1211	0.20
	linear-1	-764102.0	202.6	4.4	1372	1590	1055	824	0.56
	linear-2	-764103.1	203.2	3.9	1374	1554	890	893	0.50
	bridged-1	-764103.0	203.0	3.8	1385	1560	586	1017	0.37
	bridged-2	-764103.5	202.9	3.2	1382	1564	663	1028	0.39
	bridged-3	-764103.9	204.1	4.0	1382	1569	471	1139	0.29
	bridged-4	-764103.4	203.6	4.0	1381	1567	449	1169	0.28
	bridged-5	-764103.4	203.7	4.1	1366	1576	611	1171	0.34
n = 12	folded-1	-859855.6	234.6	-859621.0	1390	1574	269	1385	0.16
	folded-2	-859856.2	235.3	0.1	1381	1581	320	1221	0.21
	folded-3	-859855.8	235.1	0.4	1392	1571	256	1543	0.14
	folded-4	-859855.4	234.9	0.5	1392	1568	270	1008	0.21
	folded-5	-859856.2	235.9	0.7	1399	1579	286	1630	0.15
	folded-6	-859856.1	235.9	0.8	1384	1575	341	1287	0.21
	linear-1	-859851.5	234.6	4.1	1381	1554	898	895	0.50
	bridged-1	-859854.7	236.1	2.3	1366	1582	525	1009	0.34
	bridged-2	-859852.9	235.1	3.2	1368	1571	534	1090	0.33

Table S-3: Succinate dianion isomers: Energies (kcal/mol), carboxylic stretch frequencies (cm^{-1}) and intensities.^{*a*}

^{*a*}Energies from CEPA/1 calculations using the aug-cc-pVDZ basis set; ZPVE from PBE/aug-cc-pVDZ. The sum of the two (E_{tot}) is given as an absolute value for the reference geometry of each cluster; relative energies are provided for alternative isomers.

	structure	E(CEPA/1)	ZPVE	$E_{\rm tot}^{DZ/PBE_b}$	E _{tot}
n = 0	linear-1	-285555.3	49.2	-285278.9	-285506.0
n = 1	linear-1	-333480.3	64.9	-333147.5	-333415.4
	bridged-1	-333479.8	65.9	1.2	1.5
n = 2	linear-1	-381404.5	80.5	-381015.4	-381324.1
	bridged-1	-381403.2	81.5	2.1	2.3
n = 3	bridged-1	-429325.9	97.1	-428879.6	-429228.8
	linear-1	-429323.1	96.1	1.9	1.7
n = 4	bridged-1	-477243.4	112.5	-476741.0	-477130.9
	linear-1	-477241.4	111.6	1.3	1.1
<i>n</i> = 6	linear-1	-573078.1	144.8	-572461.8	-572933.3
	bridged-1	-573078.2	144.6	-0.7	-0.2
	bridged-2	-573077.1	144.3	0.2	0.6
n = 8	bridged-1	-668911.9	178.0	-668182.1	-668734.0
	linear-1	-668910.5	177.2	0.5	0.6
	folded-1	-668912.9	178.2	-1.2	-0.7
n = 10	folded-1	-764745.4	210.2	-763903.8	-764535.3
	linear-1	-764741.3	208.4	4.4	2.5
	linear-2	-764741.8	209.5	3.9	2.9
	bridged-1	-764741.9	208.9	3.8	2.3
	bridged-2	-764742.3	209.5	3.2	2.4
	bridged-3	-764742.7	210.0	4.0	2.5
	bridged-4	-764742.0	209.7	4.0	3.0
	bridged-5	-764742.2	210.1	4.1	3.1

Table S-4: Succinate dianion isomer energies (kcal/mol).^a

^{*a*}CEPA/1 energies calculated with the larger aug-cc-pVTZ basis set; ZPVE from B3LYP/aug-cc-pVDZ. The sum of the two (E_{tot}) is given as an absolute value for the reference geometry of each cluster; relative energies are provided for alternative isomers. ^{*b*} E_{tot} from Table S-3 is given for comparison.

Table S-5: Relative energies of different CHOO⁻·(H₂O)₇ cluster isomers (kcal/mol).^a

cluster	$E_{\text{CCSD}(T)}$	PBE	$MP2^{b}$	$CEPA/1^b$	CCSD^b
min2002	0.80	-0.69	0.33	-0.20	-0.27
min2003	1.23	-1.07	0.36	0.01	-0.15
min2004	1.09	-0.97	0.30	-0.14	-0.20
min2006	0.87	-0.75	0.31	-0.17	-0.26

^{*a*}Energies of CHOO⁻·(H₂O)_{*n*} cluster isomers with n = 7, relative to the average of the energies of the n = 6 and n = 8 lowest-energy clusters. CCSD(T) results and the deviation of various methods from CCSD(T) are shown. The aug-cc-pVDZ basis set and MP2/TZVP-optimized geometries were used throughout. ^{*b*}Data from Wende et al., Angew. Chem. Int. Ed., 2011, **50**, 3807.

Table S-6: Relative energies of different CHOO⁻·(H₂O)₅ cluster isomers (kcal/mol).^a

cluster	$E_{\text{CCSD}(T)}$	PBE	MP2	CEPA/1	CCSD	BSE^b
1	0.00	0.00	0.00	0.00	0.00	0.00
2	0.40	-0.50	-0.14	0.11	0.22	-0.18
3	1.30	-1.44	-0.35	0.14	0.18	-0.11
4	1.70	0.63	0.15	-0.16	-0.28	-0.01
5	2.24	-2.54	-0.52	0.04	0.10	-0.06
6	2.57	0.24	0.09	-0.15	-0.15	0.06

^aEnergies of different cluster isomers, relative to lowest-energy isomer. CCSD(T) results and the deviation of various methods from CCSD(T) are shown. The aug-cc-pVDZ basis set and PBE-optimized geometries were used throughout. ^bDifference between MP2/aug-cc-pVDZ and MP2/aug-cc-pV5Z relative energies.