Electronic Supplementary Material for Organic & Biomolecular Chemistry


**Acidity of *ortho*-substituted benzoic acids: an infrared and theoretical study of the intramolecular hydrogen bonds**

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# Supplementary information

**Table S1** Experimental vibrational frequencies of 2-hydroxybenzoic a **1** ($cm^{-1}$)

| Solvent | $CCl_4$ | $CCl_4$ | $CCl_4$ | KBr |
|---|---|---|---|---|
| *c* mol $l^{-1}$ | $1.10^{-5}$ | $1.10^{-4}$ | $1.10^{-3}$ | |
| ***C(2)–OH*** | | | | |
| $\nu$(O–H) | 3215 | 3213 | ~3213 | 3237 |
| $\beta$(COH) + $Bz_{14}$ | ~1364 | 1364 | 1381, 1364, 1215 | 1384, 1211 |
| $\gamma$(COH) | | | ~684sh | ~650sh |
| ***COOH monomer*** | | | | |
| $\nu$(O–H) | 3531 | 3531 | 3531 | 3508sh |
| $\nu$(C=O) | 1696 | 1696 | 1696 | ~1681sh |
| $\gamma$(C=O) | 644 | 643 | 643 | ~640sh |
| $\beta$(COH) | 1414 | 1415 | 1416 | 1406 |
| $\nu$(C–O) + $Bz_{13}$ | 1185 | 1185 | 1184 | 1191 |
| ***COOH dimer*** | | | | |
| $\nu$(O–H) | – | 3200-2400 | 3200-2400 | 3300-2200 |
| $\nu$(C=O) out-of-phase | – | 1662 | 1662 | 1659 |
| $\gamma$(C=O) | – | 661 | 659 | 660 |

| | | | | |
|---|---|---|---|---|
| $\beta$(COH) + $\nu$(C–O) | – | 1441, 1298 | 1441, 1299 | 1445, 1296 |
| $\gamma$(COH) | – | | 893 | 893 |
| monomer : dimer | M>>D | 5 : 1 | 1 :1 | M<<D |

**Table S2** Experimental vibrational frequencies of tetrabutylammonium 2-hydroxybenzoate **2** ($cm^{-1}$)

| Solvent | $CCl_4$ | $CCl_4$ | $CHCl_3$ | $CHCl_3$ |
|---|---|---|---|---|
| *c* mol $l^{-1}$ | $3.10^{-4}$ | $3.10^{-3}$ | $3.10^{-3}$ | $\sim 5.10^{-1}$ |
| $\nu$(O–H) | ~3333, 3195 | 3346, 3195 | ~3341, 3191 | 3355, 3205 |
| $\nu_{as}(CO_2^-)$+$Bz_{8b}$+$Bz_{8a}$ | 1633 | 1634, 1589 | 1631, 1588 | 1631, 1588 |
| $\nu_s(CO_2^-)$+$\delta_s(CH_3)$ | ~1407sh, 1382, ~1360sh | ~1410sh, 1382, ~1360sh | ~1409sh, 1383, ~1360sh | ~1409sh, 1384 |
| $\beta_s(CO_2^-)$+$\beta_{as}(CH_2)$ | | 882 | 886sh, 880 | 881 |

**Table S3** Experimental vibrational frequencies of 2-aminobenzoic acid **3** ($cm^{-1}$)

| Solvent | $CCl_4$ | $CCl_4$ | $CCl_4$ | $CCl_4$ | KBr | Deuterated |
|---|---|---|---|---|---|---|
| *c* mol $l^{-1}$ | $1.10^{-5}$ | $1.10^{-4}$ | $1.10^{-2}$ | saturated | | Nujol |
| | ***C(2)–NH₂*** | | | | | |
| $\nu_{as}(NH_2)$ | 3510 | 3511 | 3512 | 3512 | 3473 | 2532 |
| $\nu_s(NH_2)$ | 3377 | 3378 | 3387 | 3387 | 3374 | 2460 |
| $\nu_{as} - \nu_s$ | 133 | 133 | 125 | 125 | 99 | 72 |
| $\beta_{as}(NH_2)$ | | 1092 | 1092 | 1093 | 1114 | 880sh |
| | | ~1058 | 1060 | 1060 | 1060 | |
| $\beta_s(NH_2)$+$Bz_{8b}$+$Bz_{8a}$ | 1617 | 1618, 1596 | 1617, 1590, 1560 | 1617, 1590, 1560 | 1618, 1588, 1564 | 1615, 1588, 1556, ~1190 |

| | | | | | | |
|---|---|---|---|---|---|---|
| | ***COOH monomer*** | | | | | |
| $\nu$(O–H) | 3544 | 3544 | 3544 | ~3545 | – | 2603 |
| $\nu$(C=O) | 1709 | 1709 | 1707 | 1707 | – | – |
| $\gamma$(C=O) | 641 | 641 | 641 | 641 | – | – |
| $\beta$(COH) | 1335, 1354 | 1335, 1353 | ~1335 | ~1335 | – | – |
| $\nu$(C–O) | 1181 | 1181 | 1181 | 1181 | | |
| | ***COOH dimer*** | | | | | |
| $\nu$(O–H) | 3300-2300 | 3300-2300 | 3400-2300 | 3400-2300 | 3400-2300 | 2200-2000 |
| $\nu$(C=O) out-of-phase | – | 1671 | 1671 | 1671 | 1674 | 1668, 1650 |
| $\gamma$(C=O) | – | 658 | 658 | 658 | 660 | 642 |
| $\beta$(COH) + $\nu$(C–O) | ~1415, 1380 | 1418, 1300 | 1418, 1300 | 1418, 1300 | 1420, 1302 | 1034, 1044 1286, 1271 |
| $\gamma$(COH) | – | 912 | 916 | 916 | 918 | ~741 |
| monomer : dimer | M>>D | 2.5 : 1 | 1 : 9 | 1 : 13 | D | M<<D |

**Table S4** Experimental vibrational frequencies of tetrabutylammonium 2-aminobenzoate **4** ($cm^{-1}$)

| Solvent | $CCl_4$ | $CCl_4$ | $CHCl_3$ |
|---|---|---|---|
| $c$ mol $l^{-1}$ | $3.10^{-4}$ | $3.10^{-3}$ | $3.10^{-3}$ |
| $\nu_{as}(NH_2)$ | 3464 | 3461 | 3458 |
| $\nu_s(NH_2)$ | ~3380, 3219 | 3363, 3228 | 3262 |
| $\nu_{as} - \nu_s$ | 245 | 233 | 196 |
| $\beta_s(NH_2)$ | | 1542sh, 1530 | 1531 |
| $\nu_{as}(CO_2^-)$+$Bz_{8b}$+$Bz_{8a}$ | 1614 | 1614, 1582 | 1612, 1581 |
| $\nu_s(CO_2^-)$+$\delta_s(CH_3)$ | 1381, 1358 | 1380, 1360 | 1410, 1382sh, 1360 |
| $\beta_s(CO_2^-)$+$\beta_{as}(CH_2)$ | ~893 | 881 | 880, 889sh |

**Table S5** Experimental vibrational frequencies of 2-sulphonamidobenzoic acid **7** (in $cm^{-1}$)

| Solvent | $CCl_4$ | $CCl_4$ | $CCl_4$ | KBr |
|---|---|---|---|---|
| *c* mol $l^{-1}$ | $5.10^{-6}$ | $2.10^{-5}$ | saturated | |
| | ***$SO_2NH_2$*** | | | |
| $\nu_{as}(NH_2)$ | 3438-6 | 3437 | 3436 | 3351 |
| $\nu_s(NH_2)$ | 3319-7 | 3318 | 3318 | 3253 |
| $\nu_{as} - \nu_s$ | ~119 | 119 | 118 | 98 |
| $\beta_s(NH_2)$ | | | | 1594 |
| $NH_2$ intermol. H-bond? | ~3399-7 | 3398 | 3397 | |
| $\nu_{as}(SO_2)$ | | 1371, 1358 | 1371, 1355 | 1338, 1326 |
| $\nu_s(SO_2)$ | | | (1179, 1162sh) | 1161 |
| $\nu$(S–N) | | | | 909 |
| $\beta_s(SO_2)$ | | | | 595, 588sh |
| $\gamma_s(SO_2)$ | | | | 544 |
| | ***COOH monomer*** | | | |
| $\nu$(O–H) | ~3538 | 3529 | 3520 | |
| $\nu$(C=O) | | ~1755, 1743 | 1756, 1742 | |
| | ***COOH dimer*** | | | |
| $\nu$(O–H) | | | | 3300-2400 |
| $\nu$(C=O) | | 1709 | ~1712 | 1711 |
| $\gamma$(C=O) | | | | 651 |
| $\beta$(COH) + $\nu$(C–O) | | | | 1395, 1250 |
| $\gamma$(COH) | | | | 863 |
| monomer : dimer | M | M>>D | M>>D | D |

**Table S6** Experimental vibrational frequencies of tetrabutylammonium 2-sulphonamidobenzoate **8** ($cm^{-1}$)

| Solvent | $CCl_4$ | $CCl_4$ | $CHCl_3$ |
|---|---|---|---|
| $c$ mol $l^{-1}$ | $1.10^{-4}$ | $1.10^{-3}$ | $3.10^{-3}$ |
| $\nu(NH_2)$ | 3384, ~3183 | 3389, 3308, 3173 | 3378, ~3200 |
| $\nu_{as} - \nu_s$ | 201 | 216 | 178 |
| $\beta_s(NH_2)$ | | 1524 | 1531, 1525 |
| $\nu_{as}(CO_2^-)$+$Bz_{8b}$+$Bz_{8a}$ | | 1607, ~1589sh | 1607, ~1589sh ~1565sh |
| $\nu_s(CO_2^-)+\delta_s(CH_3)$ | 1381, 1357 | 1380, 1360 | 1381sh, 1362 |
| $\beta_s(CO_2^-)+\beta_{as}(CH_2)$ | | 890, 882 | |
| $\nu_{as}(SO_2)$ | 1343 | 1329 | 1338 |
| $\nu_s(SO_2)$ | 1165 | 1158 | 1163 |
| $\beta_s(SO_2)$ | 586 | 586 | 586 |
| $\gamma_s(SO_2)$ | | 541 | 541 |
| $\nu$(S–N) | | | 831 |

**Table S7** Some calculated geometric parameters and vibrational frequencies of *ortho* substituted benzoic acids

| Structure and conformation | | Bond lengths | | Bond angles | | $\nu$(O–H) | $\nu$(N–H) |
|---|---|---|---|---|---|---|---|
| | | C1–C(O) | C1–C2 | C-C1-C2 | C1-C2-X | $cm^{-1}$ | $cm^{-1}$ |
| 2-OH | **1a** | 1.464 | 1.417 | 118.9 | 123.0 | 3768 | 3474 |
| | **1b** | 1.476 | 1.415 | 124.8 | 124.8 | 3768 | 3691 |
| | **1c** | 1.505 | 1.405 | 125.6 | 118.4 | 3672 | 3839 |
| | **1d** | 1.490 | 1.411 | 126.0 | 120.3 | 3758 | 3883 |
| | **1e** | 1.485 | 1.412 | 121.5 | 119.8 | 3778 | 3819 |
| 2-OH Ph-anion[a] | **2a** | 1.491 | 1.443 | 120.3 | 122.0 | 2460 | |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | **2c** | 1.457 | 1.469 | 124.5 | 125.9 | 2340 | | | |
| | **2d** | 1.452 | 1.471 | 120.7 | 125.6 | 3755 | | | |
| 2-OH Ca-anion[a] | **2b** | 1.529 | 1.418 | 120.3 | 120.6 | 3789 | | | |
| | **2e** | 1.547 | 1.403 | 123.0 | 118.2 | 3839 | | | |
| 2-$NH_2$ | **3a** | 1.466 | 1.425 | 120.2 | 122.4 | 3776 | | 3707 | 3549 |
| | **3b** | 1.476 | 1.423 | 125.6 | 124.0 | 3767 | | 3717 | 3597 |
| | **3c** | 1.511 | 1.409 | 124.7 | 119.8 | 3428 | | 3587 | 3497 |
| 2-$NH_2$ anion | **4a** | 1.550 | 1.421 | 123.3 | 120.6 | | | 3220 | 3613 |
| 2-COOH | **5a** | 1.491 | 1.407 | 120.6 | 124.0 | 3767 | 3757 | | |
| | | 1.501 | | | | | | | |
| | **5b** | 1.496 | 1.407 | 124.5 | 124.5 | 3761 | 3760 | | |
| | **5c** | 1.535 | 1.422 | 130-0 | 124.8 | 3363 | 3759 | | |
| | | 1.488 | | | | | | | |
| | **5d** | 1.494 | 1.406 | 120.8 | 121.4 | 3762 | 3757 | | |
| | | 1.498 | | | | | | | |
| 2-COOH anion | **6a** | 1.549 | 1.422 | 128.9 | 128.9 | 1727 | | | |
| | **6b** | 1.503 | 1.400 | 120.5 | 121.8 | 3775 | | | |
| | | 1.546 | | | | | | | |
| 2-$SO_2NH_2$ | **7a** | 1.494 | 1.408 | 123.3 | 123.6 | 3756 | | 3610 | 3476 |
| | **7b** | 1.498 | 1.407 | 126.2 | 123.5 | 3752 | | 3624 | 3510 |
| | **7c** | 1.517 | 1.410 | 127.8 | 124.0 | 3440 | | 3633 | 3514 |
| 2-$SO_2NH_2$ anion | **8a** | 1.557 | 1.408 | 128.1 | 124.0 | | | 3544 | 2901 |

[a] Phenolate and carboxylate anion, respectively.

**Table S8** Calculated energies of substituted benzoic acids and of some reference compounds, partly in fixed conformation

| Compound | Geometry constraints | *E*(DFT) a. u. |
|---|---|---|
| **1f** | $\phi_1$ 90° | –496.1831182 |
| **2f** | $\phi_1$ 90° | –495.6335427 |
| **3g** | $\phi_1$ 90° | –476.3137138 |

| | | |
|---|---|---|
| **4c** | $\phi_1$ 90° | –475.7677017 |
| **5f** | $\phi_1$ 90° | –609.5698253 |
| **6c** | $\phi_1$ 90° | –609.0274486 |
| **7d** | $\phi_1$ 90° | –1024.9505363 |
| **8b** | $\phi_1$ 90° | –1024.4259653 |
| 4-hydroxybenzoic acid | $\phi_1$ 90° | –496.1848894 |
| 4-hydroxybenzoate anion | $\phi_1$ 90° | –495.6329012 |
| 4-aminobenzoic acid | $\phi_1$ 90° | –476.3146925 |
| 4-aminobenzoate anion | $\phi_1$ 90° | –475.7616263 |
| 1,4-benzenedicarboxylic acid | $\phi_1$ 90° | –609.5732549 |
| 1,4-benzenedicarboxylic acid | $\phi_1$ 28°, $\phi_2$ 220° | –609.5778044 |
| 1,4-benzenedicarboxylic acid monoanion | $\phi_1$ 90° | –609.0296084 |
| 4-sulphonamidobenzoic acid | no constraints | –1024.9618549 |
| 4-sulphonamidobenzoic acid | $\phi_1$ 36°, $\phi_2$ 48° | –1024.9569097 |
| 4-sulphonamidobenzoic acid | $\phi_1$ 90° | –1024.9518985 |
| 4-sulphonamidobenzoate anion | no constraints | –1024.4281035 |
| 4-sulphonamidobenzoate anion | $\phi_1$ 39°, $\phi_2$ 57° | –1024.4199694 |
| 4-sulphonamidobenzoate anion | $\phi_1$ 90° | –1024.4227250 |
| benzenesulphonamide | | –836.3273776 |