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Third Time is a Charm – Protonating Tricarboxybenzenes

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Triprotonation of the three constitution isomers of tricarboxybenzene was accomplished. Furthermore, the preparation of selected mono- and dications showed the sequence of protonation steps. The cations were mostly isolated as $[SbF_6]$ and $[AsF_6]$ species, which were characterized by Raman and NMR spectroscopy as well as X-ray structure determination. To further elucidate the experimental results, quantum chemical calculations are employed, especially in regard to charge distribution with NPA charges and aromaticity by NICS(0) values. Thermal decomposition of the compounds was investigated in order to explore the possibility of acyl cation formation. The influence of the aromatic system, substitution pattern and anomeric effect concerning the properties of the respective compounds was thus explained.

Introduction

Olah and White[1] prepared protonated carbonic acid and various other hydroxycarbenium ions,[1–2] which were extensively studied by low temperature NMR spectroscopy. Furthermore, the correlation between π-electron densities and ^{13}C chemical shifts was investigated, performing rudimentary quantum chemical calculations to describe experimental findings. Early works were initiated amongst others by Spiesecke and Schneider,[3] who described the substituent effects in monosubstituted benzenes on ^{13}C and ^{1}H NMR shifts, relating measured values to electronegativity or Hammet constants. Farnum[4] later described general relations between NMR data and charge density. Although a correlation of electron density to NMR shielding is present, a more complex description by paramagnetic and diamagnetic shielding for NMR shifts as correction is needed. In this work, early correlations regarding aromaticity are made, as the ring current is a criterion of that exceptional state. Olah and co-workers[5] prepared various antiaromatic 9-fluoroenyl cations, evaluating the obtained NMR data and employing quantum chemical calculations to explain their results. Although no direct correlation between the antiaromatic nature and NMR data was found, Schleyer continued working on this topic and introduced the Nucleus-Independent Chemical Shift (NICS). NICS is a suitable scale for aromaticity,[6] relating aromatic character, observed for example by reactivity, to quantum chemical calculations. Combined with magnetic susceptibility exaltations data computed via an increment scheme, an appropriate scale for aromaticity is obtained. Apart from the NICS(0) value, commonly abbreviated as NICS, which measures the ring current in the plane of an aromatic systems other probing positions, for example above the investigated system, can be evaluated.[7]

Apart from smaller, aliphatic hydroxycarbenium ions, protonation of benzoic acid with FSO_3H/SbF_5 was achieved by Birchall and Gillespie[8] in 1965. The presence of an $=OH^+$ group was confirmed by ^{1}H NMR spectroscopy, clearly observable by integration. Olah and Westerman have reported the ^{13}C NMR data of protonated mono- and dicarboxylic acid esters, where they correlate the deshielding of certain ^{13}C resonance with substituent effects in other hydrogen carbons.[9] They also report the diprotonation of oxalic acid in this study, generally emphasizing the utility of ^{13}C over ^{1}H NMR shifts for structural determination. The contribution of mesomeric structures is related to shielding or deshielding of specific ^{13}C resonances of the cation. It was only in 1977 that Bruck and Rabionvitz[10] reported the protonation of benzene dicarboxylic acids in magic acid-SO_2. Diprotonation of the three constitution isomers is achieved at low temperatures. Depending on the substitution pattern, the dicarboxonium ions undergo decomposition upon warming up, forming carboxonium acylium dications.

Interestingly, the behavior of tricarboxybenzenes in superacidic media has not been investigated so far. Apart from the simple question, if those systems are basic enough to achieve triprotonation, possible formation of acylium ions was considered, as well if any selectivity regarding site and sequence of protonation and acylium formation is given.

Herein we report the triprotonation of all three constitution isomers of tricarboxybenzene, elucidating on the sequence of protonation and discussing the particular effect on the aromaticity of the systems.

Results and Discussion

Triprotonation of 1,3,5-tricarboxybenzene was achieved in the superacidic systems HF/SbF_5 and HF/AsF_5. The starting material began dissolving at $-20\,°C$, achieving a complete solution at $0\,°C$. Removal of the solvent at $-78\,°C$ led to the formation of colorless solids, respectively (Scheme 1).
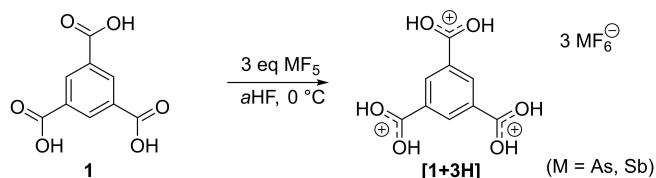
Using single crystal X-ray diffraction analysis $[1+3H]$ $[(SbF_6)_3]\cdot 3HF$ could be identified. Raman spectroscopy showed

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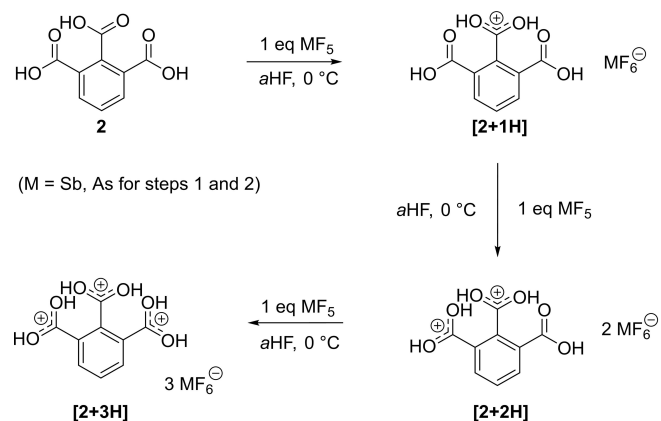European Chemical Societies Publishing

Scheme 1. Protonation of 1,3,5-tricarboxybenzene.

only marginal thermal decomposition at room temperature over several hours. Upon decomposition, no formation of acylium ions was observed, but that of diprotonated and monoprotonated species, e.g. carboxonium salts.

In a similar fashion, protonation of 1,2,3-tricarboxybenzene was carried out. Mono-, di- and triprotonation were achieved by using the respective stoichiometry of antimony pentafluoride in *a*HF. Excess amounts of arsenic pentafluoride in *a*HF at most enabled diprotonation, showing the boundaries of the acidity of HF/AsF$_5$ (Scheme 2).

NMR spectroscopy confirmed the sequence shown in Scheme 2, in case of the trication, 2D NMR spectra enabled a complete assignment of chemical shifts. Unequivocal proof was accomplished by single crystal X-ray diffraction with the determination of **[2+1H][SbF$_6$]·HF** and **[2+3H][(SbF$_6$)$_3$]** as the monoprotonated and triprotonated species, showing the first site of protonation to be the carboxy group in position 2. While the respective mono- and diprotonated salts were stable at room temperature over several hours, the tricationic species decomposed within minutes at room temperature into the partially protonated species.

Likewise, protonation of 1,2,4-tricarboxybenzene was investigated. Notably, the usage of one equivalent of Lewis acid results in an intramolecular hemiprotonation, with the proton being located between the carboxy groups in positions 1 and 2. The system HF/BF$_3$ is acidic enough to form the monocation, while HF/GeF$_4$ at most leads to the dication. This diprotonation occurs at the carboxy group in position 4. Similar to 1,2,3-tricarboxybenzene, HF/AsF$_5$ is not acidic enough to break the

intramolecular hemiprotonation, which is required to form the trication (Scheme 3).

Single crystal X-ray diffraction confirmed the sequence shown in Scheme 3, identifying **[3+1H][AsF$_6$]·HF** as the monoprotonated and **[3+3H][(Sb$_2$F$_{11}$)(SbF$_6$)$_2$]** as the triprotonated species. Salts containing the mono- and diprotonated species were stable at room temperature, while the tricationic salts decomposed within minutes into the partially protonated species, thus being the most unstable tricationic species compared to the other two isomers.

First and foremost, the crystallographic data enabled clear identification of site of protonation, but also effects of protonation on the bond lengths of all types of bonds. The complete list of crystallographic details can be found in the Supporting Information (Section 3).

In **[1+3H][(SbF$_6$)$_3$]·3HF**, in contrast to the starting material,[11] the C–O bonds are with 1.270(4) and 1.272(3) Å (Figure 1) equally long, ranging between a C–O single and double bond, which is typical for carboxonium ions.[12] The C–C bond between the carboxonium and tertiary arylic carbon is slightly shortened by around 0.025 Å due to the protonation, while no detectable change of the aromatic CC bond lengths occurs. The carboxonium groups are slightly tilted against the ring by 6.4(4)°.

The bond lengths of mono- and triprotonated 1,2,3-tricarboxybenzene are summarized in Figure 2. In **[2+1H]**
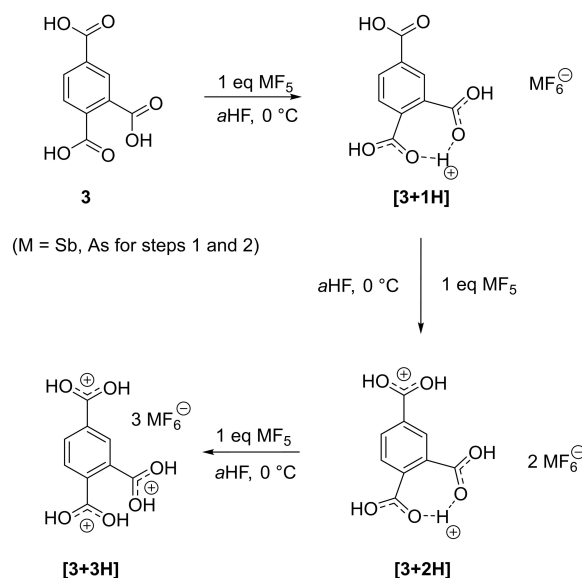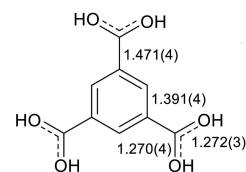

Scheme 3. Protonation of 1,2,4-tricarboxybenzene.

Scheme 2. Protonation of 1,2,3-tricarboxybenzene.

Figure 1. Bond distances of **[1+3H]** in Å.

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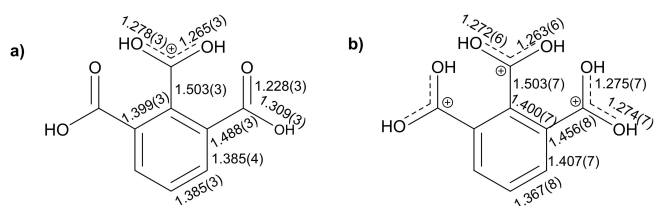European Chemical Societies Publishing

Figure 2. Selected bond distances of a) [2 + 1H] and b) [2 + 3H] in Å.

[SbF$_6$]·HF, the unprotonated carboxy groups in positions 1 and 3 are only slightly tilted against the ring plane by −8.8(3)° and −10.2(3)° respectively, and the carboxonium group in position 2 is oriented perpendicular to the ring.

Strong hydrogen bonds between the carboxy groups connect the cations in a zig-zag fashion, forming chains, while the anion and co-crystallized HF interlink the cations via the carboxonium groups, bridging the cation chains vertically.

In [2 + 3H][(SbF$_6$)$_3$], the torsions of the carboxonium groups are quite similar to the monoprotonated salt and the starting material.[13] No contacts between the cations exist, as they are fully enclosed by anions. When comparing the trication,
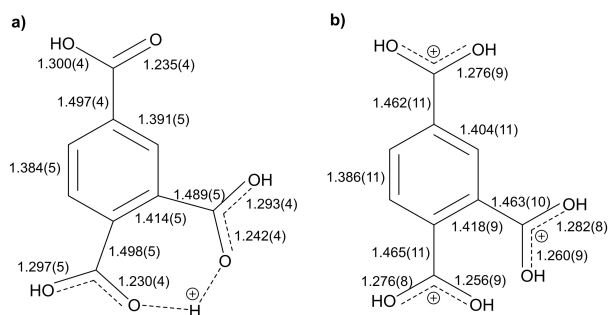

Figure 3. Selected bond distances of a) [3 + 1H] and b) [3 + 3H] in Å.

monocation and starting material, apart from the obvious change of the CO bond lengths, no significant changes in bond lengths are observed (Figure 2).

In [3 + 1H][AsF$_6$]·HF, all carboxy groups are only slightly tilted against the plane, with the group in position 4 being twisted by −4.9(5)° and the groups in position 1 and 2 by −10.9(5)° and 10.3(5)° respectively. The bridging nature of the proton between the two carboxy oxygens is reflected by the equisized C−O bond distances of the carboxy groups in positions 1 and 2 (Figure 3).

In [3 + 3H][(Sb$_2$F$_{11}$)(SbF$_6$)$_2$], all carboxonium groups are twisted against the plane, in positions 1 and 2 by respectively −41(1)° and −32(1)° and in position 4 by −17(1)°. Throughout the different protonation levels, bond distances do not change drastically (Figure 3).

Comparing all three isomers, the level of protonation has no detectable effect on the CC bond lengths inside the ring. Apart from the carboxonium character of the [COOH$_2$] moiety, a sometimes detectable decrease in the bond length of C$_{carboxonium}$−C$_{aromatic}$ is observed. While the torsion angles of the [COOH$_{(2)}$] moieties of the 1,3,5- and 1,2,3-isomer do not drastically change, the 1,2,4-isomer undergoes variable geometries.

The protonation of the tricarboxybenzenes can also be traced by NMR spectroscopy, especially ^{13}C NMR data. The complete list of NMR data can be found in the Supporting Information (Section 4). Using ^{1}H NMR, the presence of C(OH)$_2^+$ groups is shown for all trications, which can be attributed to the aromatic hydrogens by integration, thus confirming triprotonation (see Table 1). The ^{1}H NMR spectrum of [1 + 3H] displays the carboxonium resonance at 13.06 ppm and the aromatic protons at 9.00 ppm. Three signals are also found in the ^{13}C NMR spectrum. For [3 + 3H], the C(OH)$_2^+$ groups adjacent to each other are magnetically equivalent, occurring at 9.48 ppm, while the group in position 4 exhibits an even more deshielded signal at 12.91 ppm. The ^{13}C NMR spectrum also

Table 1. ^{1}H and ^{13}C NMR shifts of triprotonated tricarboxybenzenes.[a–c]

	[1 + 3H]	[2 + 3H]	[3 + 3H]
δ (^{1}H) (COOH$_2$)	13.06	9.86	12.91 (Pos. 4) 9.48 (Pos. 1, 2)
δ (^{1}H) (aromatic)	9.00	8.66 (H-7/H-9) 8.01 (H-8)	8.50 (H-5) 8.30 (H-9) 7.79 (H-8)
δ (^{13}C) (carboxylic)	178.14	185.53 (C-2) 176.50 (C-1/C-3)	182.43 (C-3) 178.34 (C-1) 178.17 (C-2)
δ (^{13}C) (C–H aromatic)	135.54	143.58 (C-7/C-9) 137.11 (C-8)	141.72 (C-9) 136.32 (C-5) 133.67 (C-8)
δ (^{13}C) (tertiary, arylic)	133.07	129.52 (C-5) 122.77 (C-4/C-6)	132.17 (C-4) 129.45 (C-6) 123.52 (C-7)

[a] All shifts in ppm. [b] Measured at 0 °C in aHF with acetone-d$_6$ as external reference. [c] [Sb$_x$F$_y$] as anions.

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features three distinct signals in the expected regions. [**2**+**3H**] shows only one signal for the $C(OH)_2^+$ groups at 9.86 ppm in the ^1H NMR spectrum, while the ^{13}C NMR spectrum exhibits two resonances, at 176.50 ppm for the position 1 and 3 carbons and another resonance at 185.53 ppm for the position 2 carbon.

Generally, upon protonation, the sequence of carbon signals for all three isomers is quite similar. All carboxylic and C–H aromatic carbons are deshielded, which mostly increases with the level of protonation (see Figure 4 and Figure 5), while the tertiary arylic carbons are shielded. For **1**, the carboxylic carbons shifts are deshielded by 7 ppm due to protonation. The C–H aromatic carbon resonances are shifted downfield by 6 ppm, the tertiary arylic carbon resonances upfield by 3 ppm.

The ^{13}C spectra of the respective trications therefore show an ordered structure with the distinct sequence of carboxylic, C–H aromatic and tertiary arylic carbon signals (from low to high field), irrespective of the substitution pattern.

To evaluate NMR shifts and the charge localization and to quantify the aromatic character to some extent, quantum chemical calculations are performed. The full list of calculations is given in the Supporting Information (Section 5). For all isomers and the respective protonation levels, optimization and frequency calculations were conducted on the DFT, B3LYP/6-311G++(3d2f, 3p2d) level of theory. Furthermore, NICS(0) values of the previously optimized species were calculated on the same level. As stated before, correlations between ^{13}C NMR data and charge density can be applied for structural analyses,[4,9] so NPA charges of the various species were calculated. Okazaki and Laali[14] investigated pyrene and its protonation/oxidation cations by using DFT, GIAO and NICS calculations, which showed a correlation between ^{13}C NMR shifts, calculated and measured, as well as the NPA charges. NICS values were calculated to examine aromaticity of the respective compounds.

For all tricarboxybenzenes, differences in NPA charges correlate to the differences in ^{13}C NMR shifts of the respective carbon atom after protonation. The electron density of all tertiary arylic carbons is increased, while that of all other carbons decreases, which influences the diamagnetic parameter, leading to the shielding and deshielding of the respective atoms (see Figure 6).

As NICS(0) calculations also give ^{13}C NMR shielding data, they were evaluated besides mentioned NPA charges. A complete list of calculated and measured ^{13}C NMR resonances for **1**, **2**, **3** and their triprotonated species is given in the Supporting Information (Section 5.11). For **1** and [**1**+**3H**], the resonances are predicted with a deviation of 5 ppm, only the C–H aromatic carbons in [**1**+**3H**] are predicted to be even more deshielded by 15 ppm compared to the experimentally
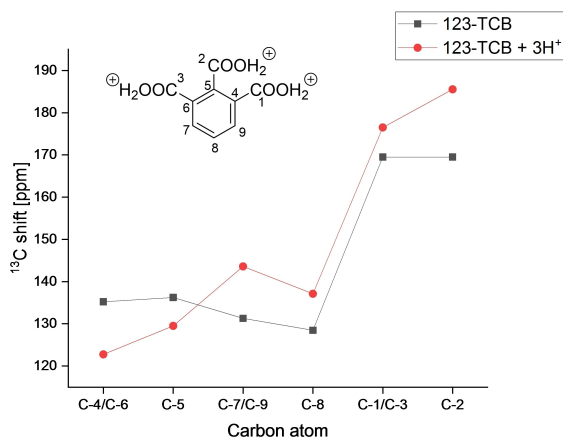

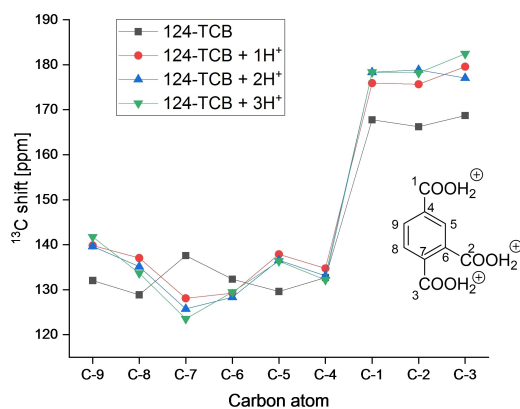**Figure 4.** Plot of ^{13}C NMR shifts of 1,2,3-tricarboxybenzene (**2**) in DMSO-d$_6$ and of [**2**+**3H**] in *a*HF.

Figure 5. Plot of ^{13}C NMR shifts of 1,2,4-tricarboxybenzene (**3**) in DMSO-d$_6$ and of [**3**+**1H**], [**3**+**2H**] and [**3**+**3H**] in *a*HF.

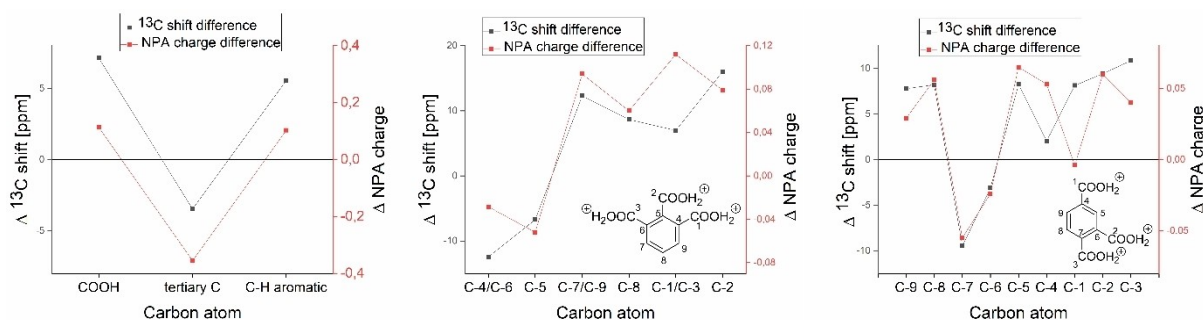**Figure 6.** Plot of the difference of the NPA charges of the carbon atoms and ^{13}C NMR shifts of **1** vs [**1**+**3H**] (left), **2** vs [**2**+**3H**] (middle) and **3** vs [**3**+**3H**] (right). DFT, B3LYP/6-311G++(3d2f, 3p2d).

observed difference of 6 ppm. For the other two isomers, the trends of shielded and deshielded carbons by triprotonation are satisfactorily expected in any case, although the relative values are in some cases over- or underestimated. While the carboxylic or carboxonium carbon resonances are accurately computed for all isomers, the discrepancy between measured and computed shifts for the aromatic carbon resonances is the most significant for [3+3H], but still adequately representing experimental observations.

A study by Vazquez also compared measured NMR shift to calculated ones with a comparable DFT method.[15] For the investigated pyramidal alkenes the computed ^{13}C NMR resonances are in good agreement with experimental data, although an under- or overestimation of certain shifts, similar to our work, was found. Regarding employed solvents, aHF and CD₃OD are protic and highly polar solvents, DMSO-d₆ is still polar, but aprotic and therefore the correct prediction of trends is particularly worth mentioning. As three positive charges are brought into each (aromatic) system, the NMR shifts together with NPA charges do predict and support experimental results. As either a magnetic or electrostatic probe, they give a good depiction of charge distribution and stabilization.

All in all, NICS(0) values decrease by protonation (see Figure 7), although all here examined systems do not become non-aromatic, as protonation never occurs at the ring. Thus the calculable effect is rather small, but still significant enough to be observed.

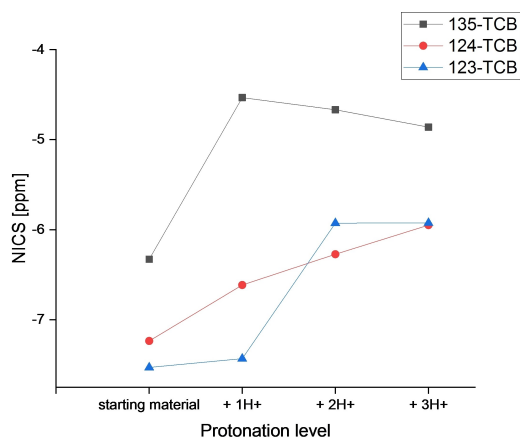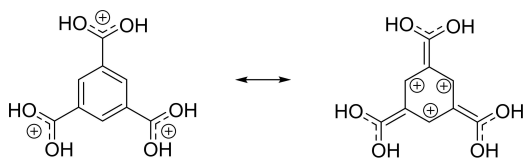For the trications, several resonance structures may be drawn. Exemplary, in Scheme 4 two structures of [1+3H] are

Figure 7. Plot of the NICS(0) values of 1,3,5-tricarboxybenzene (135-TCB), 1,2,4-tricarboxybenzene (124-TCB), 123-tricarboxybenzene (123-TCB) and their protonated derivatives. DFT, GIAO-B3LYP/6-311G++(3d2f, 3p2d).

Scheme 4. Selected resonance structures of [1+3H].

depicted. While in the left one the positive charges are located at the carboxonium groups, in the right one they are inside of the ring. The latter structure is obviously not of great importance as proximity of charges and non-aromatic character of the ring are highly unfavorable. That the right structure is still not to be excluded fully, is indicated by experimental data, as explained by ^{13}C shifts or even crystallographically found bond lengths. As NICS(0) quantifies ring current, the contribution of the right structure should decrease ring current, leading to a more positive value of NICS(0). The depicted resonance is for [2+3H] and [3+3H] only possible for two carboxonium groups, which are directed in meta position to each other. Naturally, stability of an aromatic compound does not depend on NICS(0), a quantum chemically calculated parameter. In case of the protonation of the tricarboxybenzenes, NICS(0) shows an explainable correlation with stability of the trications. Also NPA charges, as a more direct parameter compared to the before mentioned magnetic indicators, show the charge distribution occurring, as amongst other effects the C–H aromatic carbons become more positive.

For the protonation of 1,3,5-tricarboxybenzene, the NICS(0) values first show a decrease in aromaticity for the monoprotonation with the shift being less negative, while di- and triprotonation again slightly increase the aromaticity of the system. The [COOH₍₂₎] groups are slightly twisted in 1 and its protonated derivatives, optimizing the overlap of the p-orbitals of the oxygens with the π-system of the ring, making [1+3H] the most stable of the here shown trications. In the 1,2,3-isomer, the carboxy groups in positions 1 and 3 are only slightly twisted against the ring for optimal overlap with the π-system, quite similar to the 1,3,5-isomer, while the carboxy group in position 2 is more tilted against the plane. Monoprotonation shows only a minor decrease in aromaticity, indicating a rather small contribution of the π-system, which suggests a rather isolated carboxonium ion.

As the configuration of the [COOH₍₂₎] moieties are found by X-ray characterization and quantum chemical calculation, solid state effects are deemed negligible for the consideration. In fact, NBO calculations indicate a stabilization by the carboxy groups in positions 1 and 3 specifically by the respective lone pair of the carbonyl oxygens via hyperconjugation to the empty p-orbital of carboxonium carbon in position 2 by 72.4 kcal/mol in total (see Figure 8).

A first protonation at position 2 is rather counterintuitive, as carboxy groups are commonly known to be meta directors, indicating an initial protonation at position 1. Diprotonation requires a twisting of all groups, leading to a disruption of the π-system, while triprotonation again results in a conformation similar to the monoprotonated species. Here, the stabilizing effect of the oxygen lone pairs as depicted in Figure 8 is no longer possible due to the carboxonium nature. Nevertheless, NBO calculations detect a donation of approximately 2–3 kcal/mol from the C–O bonds in positions 1 and 3 to the antibonding CO orbitals in position 2. In turn, electron density is donated to the carboxonium groups from the aromatic system (see Figure 8). Protonation of 1,2,4-tricarboxybenzene shows an almost linear decrease in aromaticity, indicating a consistent
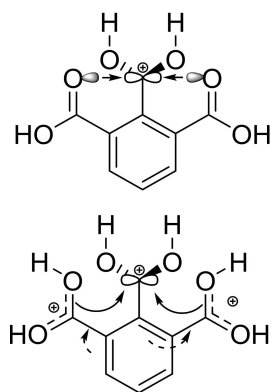
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Figure 8. Stabilization of [2+1H] and [2+3H].

increase in π-donation from the ring. NBO calculations detect no stabilizing effect as observed with [2+1H] and [2+3H], indicating that the conformation of the adjacent carboxonium groups in [3+3H] is predominantly caused by charge and steric nature. NBO calculations were further examined to quantify second order perturbations, exemplary donations from the bonding orbitals of the C–H bonds into the antibonding orbitals of $C_{(aromatic)}$-$C_{(carboxonium)}$ bonds were compared. While these donations amount for [1+3H] to 4.39 kcal/mol, for [2+3H] it is 3.42 kcal/mol and only 2.93 kcal/mol for [3+3H]. The stabilization by the aromatic system is most significant for the [1+3H] isomer.

Conclusion

In conclusion, triprotonated tricarboxybenzenes are small and surprisingly stable species, stabilized by the aromatic π-system and/or hyperconjugation, which highly depends on the respective substitution pattern. Triprotonated 1,3,5-tricarboxybenzene is the most stable isomer as the aromatic system can overlap most easily, with triprotonated 1,2,3-tricarboxybenzene being second most stable and triprotonated 1,2,4-tricarboxybenzene the least stable. Electron donation, i.e. migration of charge density is calculated and can be measured, especially by ^{13}C NMR spectroscopy, showing the donating effect of the aromatic system. Experimental NMR values fit astonishingly well to calculated data, especially the change in NPA charge. Aromaticity decreases as indicated by NICS(0) values, depending on the substitution pattern. Decomposition does not lead to acylium ions, but partially protonated cations.

Experimental Section

Caution! Avoid contact with any of these compounds. Hydrolysis might form HF, which burns skin and causes irreparable damage.

Apparatus and materials: Standard Schlenk technique with a stainless steel vacuum line was used to perform all reactions. All reactions in superacidic media were carried out in FEP/PFA reactors

closed with a stainless steel valve. HF was dried with F_2 prior to use. Raman spectra were recorded on a Bruker MultiRAM FT-Raman spectrometer with Nd:YAG laser excitation ($\lambda = 1064$ nm). For Raman measurements, samples of products were transferred into a cooled glass cell, which were evacuated afterwards. The educts were transferred into NMR tubes and measured at room temperature. NMR spectra were recorded either on a Jeol ECX400 NMR or a Bruker AV400 NMR instrument. The spectrometers were externally referenced to $CFCl_3$ for ^{19}F and to tetramethylsilane for ^{1}H and ^{13}C NMR spectra. The spectra were recorded inside 4 mm FEP NMR tube inliners. Acetone-d_6 was employed for external shimming, when aHF was used as solvent for the respective compounds. The educts were measured in 9 mm glass NMR tubes. The NMR samples were prepared by re-dissolving the respective protonated tricarboxybenzene at the designated measuring temperature in aHF and transferring the solution into a 4 mm FEP NMR tube inliner. The inliner was then frozen and flame sealed. The low-temperature X-ray diffraction of was performed with an Oxford X-Calibur3 equipped with a Kappa CCD detector, operating with Mo-K_α radiation ($\lambda = 0.71073$ Å) and a Spellman generator (voltage 50 kV, current 40 mA).

General procedure: In a typical experiment, the Lewis acid and aHF were condensed into a FEP reactor at $-196\,°C$. The mixture was reacted at $-40\,°C$ for 15 minutes and frozen to $-196\,°C$. The respective tricarboxybenzene (~0.1–0.8 mmol) is added under constant N_2-flow. The complete mixture was reacted at before mentioned temperature. The solution was cooled down to $-78\,°C$ and the solvent was removed *in vacuo*. Some material of the obtained colorless salts was used for Raman spectroscopy, the rest was redissolved in aHF. A part of the solution was transferred into a FEP NMR tube, the rest was used to grow crystals suitable for single crystal X-ray diffraction.

Crystallographic data: Deposition Numbers 2049675 (for [1+3H][(SbF6)3]·3HF), 2049673 (for [2+1H][SbF6]·HF), 2049672 (for [2+3H][(SbF6)3]), 204976 (for [3+1H][AsF6]·HF), and 2049674 (for [3+3H][(Sb2F11)(SbF6)2]) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

[1] G. A. Olah, A. M. White, *J. Am. Chem. Soc.* **1968**, *90*, 1884–1889.
[2] G. A. Olah, A. M. White, *J. Am. Chem. Soc.* **1967**, *89*, 3591–3594.
[3] H. Spiesecke, W. G. Schneider, *J. Chem. Phys.* **1961**, *35*, 731–738.
[4] D. G. Farnum in *Advances in Physical Organic Chemistry Vol. 11*, **1975**, 123–175.
[5] G. A. Olah, G. K. S. Prakash, G. Liang, P. W. Westerman, K. Kunde, J. Chandrasekhar, P. V. R. Schleyer, *J. Am. Chem. Soc.* **1980**, *102*, 4485–4492.
[6] P. V. R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao, N. J. R. Van Eikema Hommes, *J. Am. Chem. Soc.* **1996**, *118*, 6317–6318.
[7] H. Fallah-Bagher-Shaidaei, C. S. Wannere, C. Corminboeuf, R. Puchta, P. V. R. Schleyer, *Org. Lett.* **2006**, *8*, 863–866.
[8] T. Birchall, R. J. Gillespie, *Can. J. Chem.* **1965**, *43*, 1045–1051.
[9] G. A. Olah, P. W. Westerman, *J. Org. Chem.* **1973**, *38*, 1986–1992.
[10] D. Bruck, M. Rabionvitz, *J. Am. Chem. Soc.* **1977**, *99*, 240–241.
[11] Z.-Z. Fan, X.-H. Li, G.-P. Wang, *Acta Crystallogr. Sect. E* **2005**, *61*, 1607–1608.
[12] M. Schickinger, T. Saal, F. Zischka, J. Axhausen, K. Stierstorfer, Y. Morgenstern, A. J. Kornath, *ChemistrySelect* **2018**, *3*, 12396–12404.
[13] F. Takusagawa, A. Shimada, *Bull. Chem. Soc. Jpn.* **1973**, *46*, 2998–3004.
[14] T. Okazaki, K. K. Laali, *Org. Biomol. Chem.* **2004**, *2*, 2214–2219.
[15] S. Vázquez, *J. Chem. Soc. Perkin Trans. 2* **2002**, 2100–2103.