

Partial Proton Transfer in the Gas Phase: A Spectroscopic and Computational Analysis of the Trifluoroacetic Acid – Trimethylamine Complex

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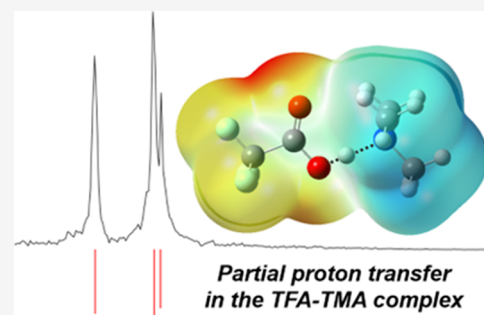
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ABSTRACT: The 1:1 complex formed from trifluoroacetic acid (TFA) and trimethylamine (TMA) has been observed in the gas phase by rotational spectroscopy and further investigated by DFT and MP2 methods. Spectra of both the parent form and the $-OD$ isotopologue have been obtained. The complex is structurally similar to a hydrogen bonded system, with the O–H bond directed toward the nitrogen of the TMA. However, both the spectroscopic and computational results indicate that it is intermediate between a hydrogen bonded complex and a proton-transferred ion pair. Two metrics are used to assess the degree of proton transfer from the acid to the base. The first is based on experimental ^{14}N nuclear quadrupole coupling constants. Specifically, the component of the ^{14}N nuclear quadrupole coupling tensor along the c -inertial axis of the complex, χ_{cc} , is 31% of the way between that of free TMA (no proton transfer) and that of TMAH^+ (complete proton transfer). A second metric, adapted from that of Kurnig and Scheiner [*Int. J. Quantum Chem. Quantum Biol. Symp.* 1987, 14, 47–56], is based on calculated O–H and H–N distances and corroborates this description. These results indicate that the degree of proton transfer in TFA–TMA is very similar to that in the TMA complex of HNO_3 , which has been previously studied and for which the proton affinity of the conjugate anion (NO_3^-) is almost identical to that of CF_3COO^- . While the solid salt, $\text{TMAH}^+\cdot\text{CF}_3\text{COO}^-$, is an ionic plastic above 307 K and exhibits free rotation of the ions, no such motion is observed in the cold 1:1 gas phase adduct.



INTRODUCTION

Gas phase clusters form the bridge between molecular and bulk descriptions of matter.¹ For homogeneous systems, this means tracking the properties of aggregates as the sequential addition of molecules morphs molecular clusters into small samples of liquid or solid. Similarly, for heterogeneous systems, a gradual increase in cluster size offers the possibility of following the emergence of solvation. A particularly interesting situation arises when the formation of bulk matter is accompanied by chemical change. Simple examples involve systems which undergo a transition from hydrogen bonded B–HA complexes in the gas phase to ionic salts BH^+A^- in the solid state.

Our laboratory has long been interested in studying proton transfer in Brønsted–Lowry acid–base pairs using microwave spectroscopy and computational methodologies. A goal of this work has been to identify and understand gas phase adducts with varying degrees of proton transfer, i.e., to explore systems that are best described as hydrogen bonded, that are best described as ion pairs, or for which neither limiting case provides a proper description. For bases such as NH_3 and H_2O , most common mineral acids form hydrogen bonded complexes in the gas phase. Notably, Legon and coworkers have shown² that complexes of ammonia or trimethylamine with hydrogen halides are hydrogen bonded systems, with the

exception of the adducts of $(\text{CH}_3)_3\text{N}$ with HBr or HI , which are best described as trimethylammonium halide ion pairs. In our laboratory, we have shown that the complexes $\text{HNO}_3\text{--NH}_3$,³ $\text{HNO}_3\text{--}(\text{H}_2\text{O})_{n=1-3}$,⁴⁻⁶ and $\text{H}_2\text{SO}_4\text{--H}_2\text{O}$ ⁷ are also hydrogen bonded systems, though $\text{HNO}_3\text{--}(\text{H}_2\text{O})_3$ shows some features of incipient proton transfer. The complex of HNO_3 with $\text{N}(\text{CH}_3)_3$, however, is neither a hydrogen bonded system nor a *bona fide* ion pair and is best described as a system with “partial proton transfer”.⁸ Intuitively, increasing the strength of the acid should further increase the degree of proton transfer to any given base. Indeed, with the superacid triflic acid ($\text{CF}_3\text{SO}_3\text{H}$), complete or near-complete proton transfer been demonstrated in a 1:1 complex with $\text{N}(\text{CH}_3)_3$ ⁹ and in its complex with three water molecules.¹⁰

In this paper, we report a microwave and computational study of the complex formed from trifluoroacetic acid (F_3CCOOH , TFA) and trimethylamine ($\text{N}(\text{CH}_3)_3$, TMA).

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Table 1. Observed and Calculated Constants for the Parent Form of TFA-TMA

	observed value	MP2/6-311++G(df,pd) value	average calculated value ^a
A [MHz]	2176.8392(40)	2192	2181(19)
B [MHz]	480.88929(20)	482	479.8(35)
C [MHz]	463.55898(20)	464	462.3(36)
Δ_J [kHz]	0.02048 (22)		
Δ_{JK} [kHz]	0.1262(14)		
δ_J [kHz]	0.00031(29)		
δ_K [kHz]	−0.147(73)		
χ_{aa} (¹⁴ N) [MHz]	−3.4020(80)	−3.76	−3.86(12)
$(\chi_{bb} - \chi_{cc})$ (¹⁴ N) [MHz]	−0.495(22)	−0.48	−0.56(9)
$ \mu_a $ [D]		5.81	6.02(18)
$ \mu_b $ [D]		0.66	0.70(6)
$ \mu_c $ [D]		0.00	0.00(0)
$ \mu_{TOT} $ [D]		5.85	6.06(18)
ΔE [kcal/mol] ^b		−20.2	−19.6(4)
$r(\text{OH})$ [Å]		1.072	1.081(9)
$r(\text{NH})$ [Å]		1.476	1.470(1)
$\angle(\text{OHN})$ [°]		179.5	178.9(9)
N^c	314(209)		
RMS [kHz]	3.3		

^aAverage of the values obtained from the six levels of theory tested. The number in parentheses is the standard deviation among the values. ^bEnergy of the complex relative to the sum of the energies of the free monomers. ^cNumber not in parentheses is the number of transitions in the fit. Number in parentheses is the number of distinct frequencies in the fit.

Trimethylamine is a strong amine base and TFA is a stronger acid than most carboxylic acids ($pK_a = 0.47$ at 298 K from an average of several literature values).¹¹ Thus, it is of interest to explore the degree of proton transfer in their 1:1 gas phase adduct. An unusual feature of this system is that, while the product of their bulk phase reaction is, as expected, the ionic compound trimethylammonium trifluoroacetate, $(\text{CH}_3)_3\text{NH}^+ \text{CF}_3\text{COO}^-$, X-ray powder diffraction, ¹H NMR, ¹⁹F NMR, and differential scanning calorimetry indicate several distinct phases, with two solid phase transitions occurring at 307 and 330 K.¹² Remarkably, in the two phases above 307 K, both the positive and negative ions undergo isotropic rotation and self-diffusion, rendering the solid a member of class of substances that has been termed “ionic plastics”. Here, we show that the 1:1 gas phase complex exhibits what is best described as partial proton transfer, but offers no indication of the rotational nonrigidity displayed in the solid.

EXPERIMENTAL METHODS AND RESULTS

A pulsed-nozzle Fourier transform microwave spectrometer with both cavity¹³ and broadband¹⁴ capabilities was used to collect spectra. Details of the instrument have been provided elsewhere.^{15,16} The TFA-TMA complex was formed via on-the-fly mixing as previously described.¹⁷ Briefly, a 0.5% mixture of TMA in argon was pulsed through a 0.080 in diameter orifice at a stagnation pressure of ~ 0.3 atm. TFA was continually injected into the expansion by bubbling argon through a sample the liquid and then passing the resulting gas mixture through a 0.016 in ID stainless steel needle situated so as to introduce the gas along the axis of the expansion. Measurement uncertainties were approximately 10 and 2 kHz for the transitions observed on the broadband and cavity spectrometers, respectively.

Initial experiments employed broadband scans in the region between 6 and 15 GHz and 30 transitions were immediately assigned and fit using the DAPPERS package.¹⁸ ¹⁴N nuclear quadrupole hyperfine splittings were not resolved at this stage.

However, the fit proved to be predictive and allowed additional transitions with resolved nuclear hyperfine structure to be measured on the cavity instrument. No evidence of internal motion was observed. A total of 314 rotation-hyperfine transitions (209 distinct frequencies, mostly *a*-type but also including some *b*-type lines) with J'' and K_{-1}'' values ranging from 4 to 13 and 0 to 7, respectively, were observed and fit to Watson's A-reduced Hamiltonian in the I' representation¹⁹ using Pickett's SPFIT package.²⁰ Transition frequencies and residuals from the least-square fit are provided in the Supporting Information and the spectroscopic constants are given in Table 1. A sample spectrum is shown in Figure 1.

As a check, spectra were also obtained using deuterated TFA, d-TFA. The deuterated acid was formed by reacting trifluoroacetic anhydride with D₂O and was introduced into the spectrometer as described above. As expected, the spectra

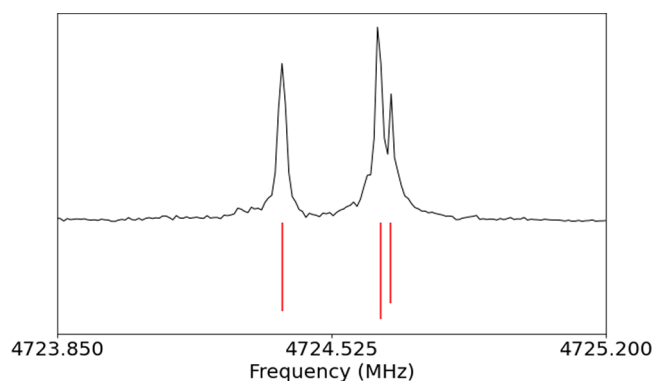


Figure 1. Sample cavity spectrum for the $S_{23}-4_{22}$ transition, with the $F = 5-4$, $6-5$, and $4-3$ hyperfine transitions shown in that order. Inverted red lines are predicted peaks. This spectrum is the result of averaging 3000 free induction decay signals using the cavity spectrometer. The horizontal axis is in units of MHz and the vertical axis is in arbitrary units.

Table 2. Observed Spectroscopic Constants and Isotope Shifts of d-TFA-TMA

	obs	observed isotope shift ^a	calculated constant ^b	calculated isotope shift ^b
A [MHz]	2174.226(40)	−2.6132(40)	2189.7	−2.4
B [MHz]	478.73860(20)	−2.15069(21)	480.8	−0.7
C [MHz]	461.37621(20)	−2.18277(21)	463.0	−0.7
Δ_J [kHz]	0.02370(23)			
Δ_{JK} [kHz]	0.1218(18)			
δ_J [kHz]	0.00048(16)			
δ_K [kHz]	−0.233(82)			
χ_{aa} (¹⁴ N) [MHz]	−3.537(15)			
$(\chi_{bb} - \chi_{cc})$ (¹⁴ N) [MHz]	−0.44(11)			
N^c	241(158)			
RMS (kHz)	2.9			

^aThe observed shift is the constant for the deuterated complex minus that for the parent complex. ^bCalculated at the MP2/6-311++G(df,pd) level/basis set. ^cNumber not in parentheses is the number of transitions in the fit. Number in parentheses is the number of distinct frequencies in the fit.

were considerably more congested due to the presence of both the ¹⁴N and deuterium nuclei, and the deuterium hyperfine structure was not resolved. A total of 241 *a*-type rotation-hyperfine transitions arising from the ¹⁴N nucleus (158 distinct frequencies) were observed and are also given in the Supporting Information. *J*" and *K*_{−1}" values ranged from 3 to 14 and 0 to 6, respectively. The fitted spectroscopic constants are given in Table 2. Further isotopic substitution was not pursued, as the agreement between the experimental and theoretical spectroscopic constants (see below) was sufficient to confirm the identity of the complex.

COMPUTATIONAL METHODS AND RESULTS

Calculations of the rotational constants, quadrupole coupling constants, dipole moment components, and binding energies relative to the free monomers were performed using Gaussian 16.²¹ All combinations of three methods (B3LYP-D3(BJ), MP2, and M06-2X) and two basis sets (6-311++G(d,p) and 6-311++G(df,pd)) were tested. Overall, the MP2/6-311++G(df,pd) showed the best agreement with experiment, especially for the quadrupole coupling constants. Results using this level of theory are included in Table 1 and a complete table of calculated results for all six methods is given in the Supporting Information. Cartesian coordinates from the MP2/6-311++G(df,pd) calculations are also included. To provide a measure of the consistency of the calculated results, Table 1 also includes the average values along with the standard deviation among the calculations, and it is clear from the latter that good agreement among the calculations was obtained.²² Using the 6-311++G(df,pd) basis set, the MP2, M06-2X, and B3LYP-D3(BJ) calculations give hydrogen bond distances of 1.476, 1.481, and 1.482 Å, respectively, while the calculated values of the OHN angle are 179.5, 177.6, and 179.5°, respectively. The minimum energy structure is shown in Figure 2 and an electrostatic potential map with an isovalue of 0.0004 a.u. is shown in Figure 3. Calculated binding energies relative to the free monomers ranged from −19.1 to −20.2 kcal/mol among the calculations, with the MP2/6-311++G(df,pd) value being the largest in magnitude (−20.2 kcal/mol).

For the quadrupole coupling constants, the MP2/6-311++G(df,pd) calculations again gave the best agreement with experiment, with the χ_{aa} value about 10% in error and the $(\chi_{bb} - \chi_{cc})$ value within 4% of that observed. Because the MP2/6-311++G(df,pd) calculations performed best when compared with experiment, subsequent discussion of the

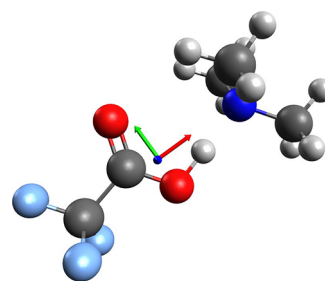


Figure 2. Structure of the TFA-TMA complex calculated at the MP2/6-311++G(df,pd) level of theory. The system is shown in its inertial axis system. The red and green arrows are the *a*- and *b*-axes, respectively.

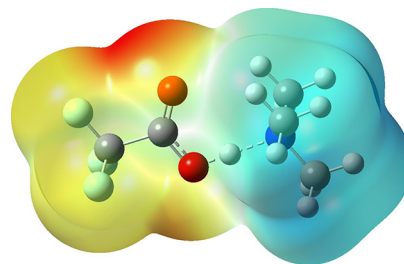


Figure 3. Electron density map of the TFA-TMA complex calculated at the MP2/6-311++G(df,pd) level of theory. Regions of positive and negative charge are indicated in blue and red, respectively. The isovalue is 0.0004 a.u.

theoretical results will employ values obtained from those calculations.

For d-TFA-TMA, the MP2/6-311++G(df,pd) calculations also gave excellent agreement with experiment, and the results for A, B, and C are included in Table 2. Also included in the table are the observed and calculated isotope shifts upon deuteration. Both the observed and calculated shifts in these constants upon deuterium substitution are quite small, with experimental values between −2.1 and −2.4 MHz. The calculated shifts in B and C are somewhat less, about −0.7 MHz. This discrepancy is acceptable, however, because the shifts are small and differences in vibrational averaging are not accounted for in these equilibrium structures. As noted above, overall agreement between theory and experiment is within expectation and therefore supports the assignment of the observed spectra to the TFA-TMA complex.

Finally, for the purpose of comparisons discussed in the next section, MP2/6-311++G(df,pd) calculations were also performed for the $\text{H}_2\text{O}-\text{NH}_3$ complex. This system is taken as representative of an $\text{O}-\text{H}\cdots\text{N}$ hydrogen bonded complex, with the $\text{O}-\text{H}$ and $\text{N}\cdots\text{H}$ distances determined to be 0.971 and 1.948 Å, respectively. The calculated binding energy at this level of theory is 7.5 kcal/mol. Additionally, a value of the ^{14}N quadrupole coupling constant for free TMAH^+ was calculated and gave $\chi_{\perp} = 0.1180$ MHz, where $\chi_{\perp}$ is the component of the quadrupole coupling tensor along an axis perpendicular to the symmetry axis. This value is in good agreement with the 0.1322 MHz value obtained by Legon and co-workers²³ from B3LYP calculations.

DISCUSSION

It is of interest to interpret the above results in a way that casts some intuitive light on the degree to which the acidic proton of the TFA is transferred to the TMA. In this regard, we note that the notion of “partial proton transfer” is inherently imprecise insofar as protons cannot be split and, moreover, there is no sharp boundary between the acid and the base. Thus, the “degree” of proton transfer is only defined by the method used to measure it. Nevertheless, in previous work, we have used two quantities to provide an intuitive understanding. The first is based on nuclear quadrupole coupling constants and is primarily an experimental metric related to electronic structure. The second is structurally based and, while determinable from experimental data if the requisite isotopologues have been observed, it is most easily derived from computed bond distances.

Nuclear Quadrupole Coupling Analysis. The ^{14}N nuclear quadrupole coupling tensor is related to the electric field gradient at the nitrogen nucleus resulting from all charges external to that nucleus. Thus, its components are a measure of electronic structure. The constants χ_{aa} , χ_{bb} , and χ_{cc} are the components of that tensor in the inertial axis system of the complex. For complexes with a plane of symmetry such as TFA-TMA, χ_{cc} can be used as a means of comparison between complexes because the c -inertial axis is perpendicular to the plane regardless of how different moieties orient the a - and b -axes. On this basis, we have previously defined a proton transfer parameter, Q_{PT}^B ,⁸ where the superscript B indicates that reporting nucleus is located on the base:

$$Q_{\text{PT}}^B = \frac{\chi_{cc}^{\text{complex}} - \chi_{\perp}^{\text{TMA}}}{\chi_{\perp}^{\text{TMAH}^+} - \chi_{\perp}^{\text{TMA}}} \times 100\% \quad (1)$$

Thus, Q_{PT}^B expresses where the perpendicular component of the electric field gradient lies between the limiting forms of TMA (no proton transfer) and TMAH^+ (full proton transfer). The subscript $\perp$ refers to the component of the quadrupole coupling tensor of free TMA or TMAH^+ that is perpendicular to its symmetry axis. (The symmetry axes of TMA or TMAH^+ lie in the ab plane of the complex.) As in previous work⁸ we use $\chi_{\perp}^{\text{TMA}} = 2.7512(13)$ MHz (derived from the experimental value of $\chi_{cc} = -5.5024(25)$ MHz).²⁴ For $\chi_{\perp}^{\text{TMAH}^+}$ we use the 0.1180 MHz value noted above. The value of $\chi_{cc}^{\text{complex}}$ is easily derived from the measured values of χ_{aa} and $(\chi_{bb} - \chi_{cc})$ using the traceless feature of the quadrupole coupling tensor, i.e., $\chi_{cc} = -\left(\frac{1}{2}\right)[\chi_{aa} + (\chi_{bb} - \chi_{cc})] = 1.9485(43)$ MHz. Applying these values in eq 1 gives $Q_{\text{PT}}^B = 31\%$. Thus, the c -component of the electric field gradient at the ^{14}N nucleus is about 31% of

the way from that of TMA to that of TMAH^+ . Note that although a computed value of $\chi_{\perp}^{\text{TMAH}^+}$ is used in this calculation, the result is primarily experimental, because the 0.1180 MHz value introduces a relatively small correction to the denominator of eq 1. Interestingly, the 31% value of Q_{PT}^B for TFA-TMA is identical to that derived for HNO_3 -TMA.⁸

Bond Length Analysis. Kurnig and Schiener have defined an alternate measure of proton transfer based on molecular structure (ρ_{PT}).²⁵ Their definition, adapted to the present case, is based on bond distances and has the following form:

$$\rho_{\text{PT}} = (r_{\text{OH}}^{\text{complex}} - r_{\text{OH}}^{\text{free}}) - (r_{\text{HN}}^{\text{complex}} - r_{\text{HN}}^{\text{free}}) \quad (2)$$

Here, $r_{\text{OH}}^{\text{complex}}$ and $r_{\text{OH}}^{\text{free}}$ are the OH distances in the complex and in free TFA, respectively, while $r_{\text{HN}}^{\text{complex}}$ and $r_{\text{HN}}^{\text{free}}$ are the NH distance in the complex and in TMAH^+ , respectively. As may be seen from eq 2, if there is no migration of the proton away from the TFA, the first term vanishes and ρ_{PT} has a negative value which is equal in magnitude to $r_{\text{HN}}^{\text{complex}} - r_{\text{HN}}^{\text{free}}$. Conversely, if the proton is transferred to the TMA such that the NH distance equals that in TMAH^+ , the second term vanishes and ρ_{PT} has a positive value equal to $(r_{\text{OH}}^{\text{complex}} - r_{\text{OH}}^{\text{free}})$. In the case of equal proton sharing, the lengthening of the OH bond equals that of the NH bond in TMAH^+ , and $\rho_{\text{PT}} = 0$ Å. At the MP2/6-311++G(df,pd) level of theory, the computed value of ρ_{PT} is -0.35 , while using the average value obtained from all calculations, $\rho_{\text{PT}} = -0.33$ Å. Interestingly, these results are very close to the -0.37 Å value previously reported for HNO_3 -TMA.⁸

Using both Q_{PT}^B and ρ_{PT} as indicators, the proton transfer in TFA-TMA is not “complete”. Rather, it is somewhat advanced relative to that in the $\text{H}_2\text{O}-\text{NH}_3$ complex, which is expected to be more representative of a hydrogen bond between an OH group and a nitrogen atom. Indeed, the calculated bond lengths for $\text{H}_2\text{O}-\text{NH}_3$ at the MP2/6-311++G(df,pd) level of theory noted above give a calculated value of $\rho_{\text{PT}} = -0.91$ Å. Both the 31% value of Q_{PT}^B , and the -0.35 Å value for ρ_{PT} for TFA-TMA are about midway between the values one would expect for a hydrogen bonded complex and a system with equal proton sharing. The electron density map in Figure 3 is visually consistent with this picture insofar as the proton lies slightly in the positive region of the complex, while the CF_3COO^- moiety supports the excess negative charge. As noted above, the hydrogen bond distance for TFA-TMA calculated at the MP2/6-311++G(df,pd) level is 1.48 Å, which is quite short for a hydrogen bond. (The average of the calculated values at all levels of theory used is 1.47 Å.)

The binding energy of the complex, computed at the MP2/6-311++G(df,pd) level of theory is -20.2 kcal/mol. This value is significantly larger than the -7.5 kcal/mol obtained at the same level for the $\text{H}_2\text{O}-\text{NH}_3$ complex, a “hydrogen bonded” system. It is, however, notably smaller than the -31.7 kcal/mol value similarly obtained for the triflic acid-TMA complex, which has been shown to be best described as a proton-transferred ion pair.⁹ Thus, insofar as the binding energy is between that of a hydrogen bonded system and an ion pair, the energetics are in accord with the above metrics.

The computed dipole moment of the complex at the MP2/6-311++G(df,pd) level is 5.9 D while the same level of theory gives 2.28 and 0.61 D for TFA and TMA, respectively. Thus, the dipole moment of the complex is almost exactly twice the sum of the monomer dipole moments. While a variety of factors can contribute to dipole moment of a complex, the

large enhancement is consistent with a significant migration of charge upon complexation. Interestingly, using the calculated dipole moment of 5.9 D and dividing by the center of mass separation between moieties determined from the MP2/6-311++G(df,pd) coordinates, gives opposing charges of 0.27 e[−] on each moiety. While such a point-dipole calculation is clearly overly simplistic, it is interesting to note that the result lies squarely between the values of zero (no charge transfer) and 0.5 (equal proton sharing).

In previous work on the triflic acid-TMA complex, both Q_{PT}^B and ρ_{PT} indicated complete or near-complete proton transfer. A simplistic model based on the proton affinities of TMA and the triflate ion showed that, while direct proton transfer to produce isolated ions was endothermic, the Coulomb stabilization at the interionic distance in the complex was enough to make the ion pair formation favored over hydrogen bonding. Thus, the ionic nature of the complex could be rationalized. This assessment was aided by the structure of the ion pair obtained from MP2/6-311++G(df,pd) calculations, which provided a reasonable distance with which to calculate the Coulomb energy. In the case of TFA-TMA, the relevant proton affinities are 323.8 and 226.8 kcal/mol for CF₃COO[−] and TMA, respectively,²⁶ and thus the formation of isolated CF₃COO[−] and TMAH⁺ ions is endothermic by 97 kcal/mol. However, an ionic structure is not predicted computationally and it is unclear what distance should be used to compute the Coulomb energy. As a result, the model is not directly applicable. Nevertheless, we note that Kuchitsu et al.¹² have estimated the radii of rotating ions in the crystal to be 2.62 and 2.71 Å for CF₃COO[−] and TMAH⁺, respectively. Using the sum of these values as an approximation to the proper distance gives a Coulomb stabilization of −54 kcal/mol, which is smaller in magnitude than 97 kcal/mol and is, therefore, clearly insufficient to render the formation of an ion pair energetically favorable. Other distances, however (e.g., between the nitrogen and the oxygens of the CF₃COO[−]), give much larger Coulomb energies, in the −120 kcal/mol range, and would suggest that the ion pair should be more stable. Thus, uncertainties associated with the calculation of the Coulomb energy do not permit the simple model that has been previously applied to rationalize the nature of the complex in this case.

Despite the above uncertainty, we note that the superacidity of triflic acid (and the correspondingly low proton affinity of the triflate ion) was an important factor in driving the proton transfer to TMA.⁹ Interestingly, the values of Q_{PT}^B and ρ_{PT} for TFA-TMA are almost identical to those previously obtained for the HNO₃-TMA complex,⁸ and the proton affinities of CF₃COO[−] and NO₃[−] are also almost identical (323.8 and 324.5 kcal/mol, respectively).²⁶ Both are significantly higher than that of the triflate anion (305.4 kcal/mol).

The nature of the gas phase complex provides an interesting contrast with that in solid state where, as noted above, X-ray, NMR, and differential scanning calorimetry have characterized the system as an ionic plastic.¹² In each of two distinct solid phases, the compound is composed of CF₃COO[−] and (CH₃)₃NH⁺ ions that undergo isotropic rotation. The gas phase results presented here offer no indication of such motion. Rather, the system appears to acquire the directionality more characteristic of a hydrogen bond, albeit one in which a significant amount of proton transfer has occurred. (Note the OHN angle of near 180° in Table 1.) It is interesting that the limited number of interactions in the gas

phase give rise to more angular rigidity than is observed in the crystalline state, though surely temperature plays a role.

CONCLUSION

Microwave spectra and theoretical calculations establish that the 1:1 gas phase complex formed from trifluoroacetic acid and trimethylamine is best characterized as being intermediate between a hydrogen bonded system and a proton-shared adduct. Both nuclear quadrupole coupling data and theoretical bond lengths support this point of view. The system lies closer to a hydrogen bonded complex than an ion pair, with a computed hydrogen bond distance of only 1.48 Å, but some migration of the TFA proton toward the TMA is evident. In contrast with the isotropic rotation previously observed in the solid ionic crystal, the geometry of the gas phase adduct reflects the directionality normally associated with a hydrogen bond.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpca.3c06768>.

Computational results for the TFA-TMA complex from all levels of theory tested; par, var, lin, cat, and pform files for both isotopic species studied (PDF)

TFA-TMA supplemental files (ZIP)

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Notes

The authors declare no competing financial interest.

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