The R 3 O + ⋯H + Hydrogen Bond: Toward a Tetracoordinate Oxadionium(2+) Ion

7 AUTHORS, INCLUDING:

Evgenii S Stoyanov
University of California, Riverside
70 PUBLICATIONS   1,050 CITATIONS

SEE PROFILE

Gorkem Gunbas
University of California, Berkeley
25 PUBLICATIONS   900 CITATIONS

SEE PROFILE

Nema Hafezi
Northwestern University
10 PUBLICATIONS   100 CITATIONS

SEE PROFILE

Christopher A. Reed
University of California, Riverside
257 PUBLICATIONS   14,518 CITATIONS

SEE PROFILE

The R₃O⁺···H⁺ Hydrogen Bond: Towards a Tetracoordinate Oxadionium(2+) Ion

Evgenii S. Stoyanov[*,†], **Gorkem Gunbas**[‡], **Nema Hafezi**[‡], **Mark Mascal**[*,‡], **Irini V. Stoyanova**[†], **Fook S. Tham**[†], and **Christopher A. Reed**[*,†]

[†]Department of Chemistry, University of California Riverside, 900 University Avenue, Riverside, California 92521-0403

[‡]Department of Chemistry, University of California Davis, 1 Shields Avenue, Davis, California 95616-5270

Abstract

Oxatriquinanes are tricyclic oxonium ions which are known to possess remarkable solvolytic stability compared to simple alkyl oxonium salts. Their rigid, hemispherical structure presents an oxygen at the apex of three fused five-membered rings. While trivalent oxygen species like these have been well described in the literature, the ability of oxygen to enter into a fourth covalent bonding relationship has been visited in theory and suggested by the outcome of certain reactions conducted in superacidic media, but has never established by the characterization of a stable, persistent R_3OH^{++} or R_4O^{++} ion. In this study, the nucleophilicity of the oxatriquinane oxygen was evaluated first by a series of protonation studies using the Brønsted superacid $H(CHB_{11}Cl_{11})$ both in the solid state and in liquid HCl solution. The interaction of the oxatriquinane oxygen with a bridging carbocation was also examined. A strong case could be made for the occurrence of hydrogen bonding between $H(CHB_{11}Cl_{11})$ and oxatriquinane using IR spectroscopy. Under the most forcing protonation conditions, the oxatriquinane ring is cleaved to give a bridged, dicationic protonated tetrahydrofuran-carbenium ion.

1. Introduction

It has been known for nearly a century that dialkyl ethers can be protonated to give isolable species in which there are three covalent bonds to oxygen.[1] The products, which have a formal +1 charge on oxygen, are acids of moderate strength, with a pK_a of approximately −3.5.[2] In recent times, several examples of stable, crystalline R_2OH^+ salts with non-coordinating counterions, such as $B[3,5-(CF_3)_2C_6H_3]_4$,[3] $B(C_6F_5)_4$,[4] $CHB_{11}H_5X_6$ (X = Cl, Br),[5] and $Al[OC(CF_3)_3]_4$[6] have been described.

Ethers likewise can be alkylated to give R_3O^+ oxonium ions, the first examples of which were described by Meerwein in 1937.[7–9] Like the above-described acids, trialkyloxonium salts can be isolated when the counterion is inert, and have found widespread synthetic use as powerful alkylating agents.[10]

SUPPORTING INFORMATION
^{1}H- and ^{13}C-NMR spectra and synthetic details for the preparation of **6a**, **6b** and **7**, photograph of the IR cell, and details of the X-ray crystallography of **21**. This material is available free of charge via the Internet at http://acs.pubs.org.

Although considerable speculation has been made regarding the potential for oxygen to enter into a fourth covalent bonding relationship, to date tetracoordinate oxygen species have only been implicated as reactive intermediates,[11] or visited in theory.[12,13] Thus, Olah and coworkers produced indirect evidence for the intermediacy of H_4O^{2+} in superacid-activated H^+/D^+ exchange reactions of the hydronium ion,[14] and likewise for R_3OH^{2+} in the alkylation of aromatics with R_3O^+ salts.[15,16] The arguments were supported by gas-phase computational modeling, which indicated that while H_4O^{2+} was 61.9 kcal mol^{-1} higher in energy than H_3O^+, a significant deprotonation barrier nonetheless implied kinetic stability. On the other hand, Me_3OH^{2+} was found to be more stable than Me_3O^+ by 27.6 kcal mol^{-1}. However, the exchange and substitution reactions which led to the advancing of these intermediates took place not in the gas phase, but in the superacid solutions 1:1 HF/SbF_5 and 2:1 $CF_3SO_3H/B(CF_3SO_3)^3$, respectively, and taking medium effects into account can change the picture dramatically. For example, H_4O^{2+} is no longer a minimum energy structure in reaction fields with $\varepsilon \geq 3$ in a continuum solvent model.[17] Also, examination of the reported, energy minimized structure of Me_3OH^{2+} reveals C–O bond lengths of 1.67 Å. The analogous Et_3OH^{2+}, which has also been implicated in the alkylation of aromatics,[15] has even less plausible C–O bond lengths of 1.74 Å and does not optimize to a minimum energy structure in the gas phase. Ultimately, no evidence for complete proton transfer to oxygen was given for either of these reactions, and the authors themselves recognized that the reactivity of oxonium salts in superacid media might be a matter of "electrophilic assistance,"[12] or in other words, activation via transient H-bonding interactions, rather than discrete, tetravalent oxygen intermediates.

More likely examples of R_4O^{2+} species have been advanced recently by Schneider and Werz.[13] Using DFT and MP2 calculations, they have proposed that tetracoordinate chalcogens could be stabilized by caging them within polycycles of the type represented by structure **1**. These dications, which embody the fusion of four triquinane ring systems with a common apex, were found to be energy minima, and the C–O bond distance where X = O is 1.62 Å. Further modeling in the presence of tetraphenylborate counterions suggested a real possibility of observing such species in an inert medium.[13] A dication of sulfur, R_4S^{2+}, having two coordinating biaryl substituents, has been isolated and characterized by Sato and coworkers.[18]
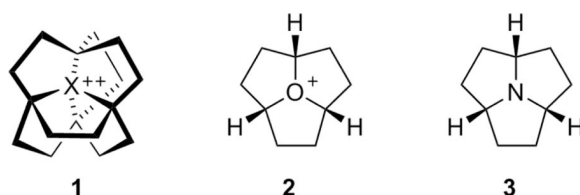
Recently, we described the preparation of oxatriquinane **2**,[19] an oxonium analogue of the previously reported azatriquinane **3**.[20] The fused, tricyclic framework of **2** was found to impart remarkable stability compared to other cyclic oxonium species,[21] such that salts of **2** could be recrystallized from boiling water or even chromatographed. The structural correspondence between **2** and **3** is proposed to be significant in the sense that **3** has been described as the most basic trialkyl amine known, the conjugate acid of which has a pKa value *ca.* 0.5 pK_a units greater than that of quinuclidine.[22] This effect has been attributed in part to the acute pyramidalization of the apical nitrogen, and is further supported by the low ionization potential of its lone pair.[23] By analogy, **2** might then be considered to be the most "basic" trialkyloxonium ion. The availability of the lone pair in **2**, while contracted in comparison with that in **3**, nevertheless led us to the question of whether a persistent, valence shell expanded R_3OH^{2+} or R_4O^{2+} derivative might be generated in this system. Herein, we report on efforts both to protonate and alkylate the oxatriquinane framework.

2. Theory

Ab initio modeling of the protonated or alkylated core of **2** was an essential starting point for determining whether the concept of a tetracoordinate oxygen species based on **2** was grounded in theory, or otherwise. The most obvious experiment is to simply attach a proton or a methyl group to the oxygen of **2** and determine whether an energy minimum can be located. In the case of protonation, a stationary point is found with a normal O–H bond length of 0.98 Å, but with C–O bond lengths of 1.74 Å, compared to 1.53–1.54 Å in **2** itself. Analogous to Et_3OH^{2+}, the structure is not an energy minimum, having two negative frequencies which correspond to C–O bond stretches. Manual displacement of this C_3 symmetric structure in the direction of one of these bond stretches followed by re-optimization results in the cleavage of a C–O bond to give the bridged, protonated THF structure **4**, which is an energy minimum. As with protonation, the methylation of **2** results in a structure with a credible O–CH_3 bond (1.52 Å, within the typical range for oxonium salts), but substantially elongated C–O bonds within the oxatriquinane framework (1.72 Å). The structure, while a potential energy minimum, appeared nevertheless an unlikely target for synthesis. In both cases, the calculated bond lengths suggest that triquinane-based oxadionium species can be likened to HO or CH_3O fragments participating in fractional bonds with three partially charged carbons in a crown-configured cyclononane ring (**5**). This model intuitively suggests that alkyl substitution at the positions α to the oxygen would result in a more stable structure, which prompted the inclusion of substituted *oxatriquinanes **6** in this study.
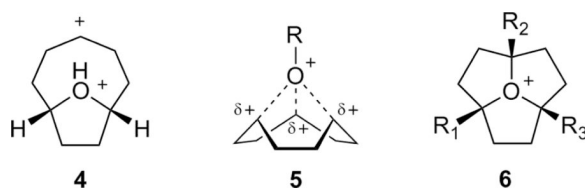
Given that the protonation of **2** is at least possible, even if it were to eventually lead to ring cleavage, the next question that arises is whether any known acid would be capable of protonating it. The modeling of acidity is a difficult problem for theoretical methods, particularly for strong-weak conjugate pairs, due in part to uncertainties in methods of determining free energy of solvation when a change of charge state accompanies a reaction. Nevertheless, protonation within a homologous series can give an indication of relative proton affinity. Hence, we calculated the protonation energy of **2** and **6** alongside related species, some of which are also weakly basic (Table 1). The first thing to note is that the protonation of positively charged species to give dications is energetically very unfavorable in the gas phase. The use of a solvent model, in this case the conductor-like polarizable continuum model (CPCM)[24] of dichloromethane (ε = 8.93), provides a more realistic energy comparison. All the same, monoprotic species should only be compared in series with other monoprotic species (entries 1–6) and likewise diprotic species only with other diprotic species (entries 7–10).

Importantly, it emerges that the protonation of oxatriquinane **2** is more energetically favorable than that of Et_3O^+, in line with the increased basicity expected from the triquinane effect (*cf.* **3** vs Et_3N). Also, the stabilizing influence of alkyl groups in **6** ($R_1=R_2=R_3=CH_3$) is apparent, particularly in the gas phase, where charge is distributed over the three carbon sites to a greater extent than in **2**.[23] As discussed earlier, the protonation of H_3O^+ is seen to be endothermic in the gas phase, while optimization of structure of H_4O^{++} does not converge at all in solvent.

While the question of whether any existing acid has the capacity to protonate **2** remained a matter of speculation, prior work in the Reed laboratory had shown that the carborane acid $H(CHB_{11}Cl_{11})$[24] is currently the strongest isolable Brønsted acid.[25,26] It has been used to protonate weakly basic molecules such as benzene, sulfur dioxide, and even chlorocarbons.[27] Traditional superacid media, which are mixtures of Brønsted and Lewis acids (e.g. HSO_3F/SbF_5), have the disadvantage of putting the substrate into a competition between protonation and Lewis adduct formation ("basicity suppression")[28] and of exposing the substrate to potentially deleterious SbF_5 redox chemistry. $H(CHB_{11}Cl_{11})$ was therefore regarded as the acid of choice for attempting the protonation of **2** and **6**.

Regarding the alkylation of **2**, the fact that the modeled O-methyloxatriquinane dication does not dissociate into **2** and CH_3^+ suggests that, at least in the gas phase, it can be produced if a sufficiently reactive methylating agent could be employed. The most powerful methylating agent appears to be the methyl carborane $CH_3(CHB_{11}Cl_{11})$,[29] which has been used to produce the hexamethyldihydrazinium dication, $Me_6N_2^{2+}$.[30] The methylation of **2** with $CH_3(CHB_{11}Cl_{11})$ was however not attempted here, because a potentially more attractive option emerged in this case. Although the hexacyclic species **1** described by Schneider and Werz can be seen as synthetically challenging to say the least, the corresponding pentacycle **9** could, in principle, be derived from the more accessible bridged oxatriquinane **7** via an intramolecular alkylation (Scheme 1). In fact, modeling shows that **9**, like **1** (X = O) is also an energy minimum structure in the gas phase.

The principal objectives of this study were therefore established to be the following: *a)* to attempt the protonation of oxatriquinane **2** (and alkylated analogues **6**) with the carborane acid $H(CHB_{11}Cl_{11})$ and *b)* to determine whether the protonation of alkene **7** results in the formation the tetraalkyl oxygen(2+) species **9**.

3. Materials and Methods

3.1. Oxatriquinanes

The synthesis of **2** has been previously described.[17] Two alkylated derivatives were also studied, **6a**: $R_1 = R_2 = H$, $R_3 = n\text{-}C_3H_7$ and **6b**: $R_1 = R_2 = R_3 = n\text{-}C_3H_7$, the propyl groups being chosen to aid solubility of the oxonium salts. The synthesis of these compounds is shown in Scheme 2, and the synthesis of alkene-bridged oxonium salt **7** is described in Scheme 3. For IR measurements, the counterions were exchanged for $CHB_{11}Cl_{11}^-$ by anion metathesis.

3.2. Computational Modeling

Geometry optimizations were performed either at the B3LYP density functional level of theory[31] or the MP2 (second order Møller-Plesset) level of theory[32] using the 6–31+G(d,p) basis set. Symmetry constraints were used where possible to simplify calculations. Any species optimizing to structures other than minima were re-optimized in the absence of symmetry constraints to ensure that the imposition of symmetry was not preventing minimization. Vibrational analyses were performed in order to characterize stationary points as either minima, transition states, or higher order saddle points on the potential energy surface and to apply zero-point energy corrections. Reported frequencies are unscaled. Redundant internal coordinates were modified where partial optimizations were carried out. For calculations performed in a solvent model, the method used was the conductor-like polarizable continuum model (CPCM)[22] with the molecular cavity specified by the United Atom Topological Model (UAKS) on radii optimized for the PBE0/6-31(d) level of theory. All calculations were done using the Gaussian 03 program, using default SCF convergence criteria.[33]

3.3. Interaction of Oxatriquinanes with Crystalline H(CHB11Cl11)

This was carried out by finely grinding the solids in an approximate 1:1 molar ratio in an agate mortar in a drybox at room temperature for about 5 min. $H(CHB_{11}Cl_{11})$ (hereafter abbreviated $H\{Cl_{11}\}$) was prepared as previously described.[29] Its IR spectrum is unchanged by grinding, indicating retention of its polymeric structure.

3.4. Interaction of Oxatriquinanes with Sublimed H{Cl$_{11}$}

This was carried out in a specially designed IR cell with silicon windows (see Supporting Information). In a drybox, a few drops of the oxatriquinane salt in dichloromethane solution were evaporated on the window of the IR cell, forming a thin layer. A small quantity of freshly prepared $H\{Cl_{11}\}$ was placed in the bottom of the cell. The cell was then evacuated and immersed in an oil bath to just below the level of the silicon windows. Upon heating to 150 °C at 10^{-5} bar, the acid sublimed onto the windows, the temperature of which was *ca.* 120 °C.

3.5. Interaction of Oxatriquinanes with H{Cl$_{11}$} in Liquid HCl Solution

In a drybox, weighed quantities of oxatriquinanes and $H\{Cl_{11}\}$ were placed in a thick-walled Schlenk tube. The tube was evacuated and the lower part cooled in liquid nitrogen. High purity HCl gas was then condensed onto the solids. After disconnecting from the HCl supply, the sealed tube was allowed to warm to 0 °C (*ca.* 23 atm. pressure) to melt the HCl. After stirring for *ca.* 15 min, the HCl was allowed to escape slowly until the tube reached atmospheric pressure at room temperature.

3.6. IR Spectra

These were recorded on a Perkin Elmer Spectrum-100 spectrometer in transmission or ATR mode (4000-380 cm^{-1}) and the data were manipulated using GRAMS/AI (7.00) software from Thermo Scientific.

3.7. X-ray Crystallography of 21

Details are provided in the Supporting Information.[34]

4. Results and Discussion

4.1. Synthesis

The synthetic route to substituted oxatriquinanes **6** starts with the known ketone **10**.[35] Propylation was carried out using allylmagnesium bromide in order to avoid reduction of the ketone by hydride donation. Hydrogenation of the double bond of **11** and closure of the triquinane ring with trifluoromethanesulfonic acid (TfOH) gave the triflate salt of **6a**, whose counterion was exchanged for PF_6^-.

Alternatively, direct ring closure of **11** gave allyloxatriquinane **13**. Ring opening of **13** at an unsubstituted position with acetate ion gave the bicyclic acetate ester, which was hydrolyzed to alcohol and oxidized with chromium(VI) oxide to give ketone **14**. A second Grignard addition and ring closure gave diallyl oxatriquinane **15**. A final round of ring opening with acetate, hydrolysis of the ester, and oxidation gave **16**, which was converted into **6b** by a third Grignard addition, hydrogenation of the double bonds, and ring closure to the oxatriquinane, followed by counterion exchange with PF_6^-.

The approach to **7** is closely related to that of **6**, starting from **14** and reacting in this case with homoallylmagnesium bromide in the presence of $LaCl_3 \cdot 2LiCl$[36] to give **17** (Scheme 3). Ring closure gave the asymmetrically disubstituted oxatriquinane **18**, which was re-opened

at an unsubstituted position with acetate to give ester **19**. Olefin metathesis with the first generation Grubbs catalyst then gave the cyclic alkene **20**, final ring closure of which gave the tetracyclic oxatriquinane **7** as a PF_6^- salt. Where necessary, anion exchange to prepare **7**{Cl_{11}} was carried out using the cesium carborane salt in dichloromethane/water.

4.2. IR Considerations

The COC stretching vibrations of oxatriquinanes are expected to be the most useful indicators of protonation at the O atom, so their characteristics were investigated to establish baseline data. Experimental and calculated frequencies are listed in Table 2.

The C_3 symmetric parent oxatriquinane **2** and its tri-*n*-propyl derivative **6b** show a single, intense, doubly degenerate $\nu_{as}COC$ band in the 700–770 cm^{-1} region. In the less symmetric mono-*n*-propyl derivative **6a** and the alkene-bridged tetra-cycle **7** this band is split and that arising from the symmetric stretch becomes active, leading to three observed bands. The experimental spectra are very close to those calculated for the free cations in the gas phase, indicating a weak interaction between the O-atom of the C_3O^+ motif and the carborane anion in the condensed phase. This is consistent with $CHB_{11}Cl_{11}^-$ being one of least coordinating anions.[25]

Despite the fact that the calculations indicate the COC vibrations are coupled to other vibrations in oxatriquinane cations, their frequencies are nevertheless indicative of C–O bond strength. Thus, with increasing electron donor properties of the alkyl substituents (3R > R > H) and increasing the average C–O bond length (Table 2), $\nu_{as}COC$ decreases more or less in the same order.

In a related manner, the CO stretching vibrations are expected to be sensitive to electron density loss at the O-atom via H-bonding. The relationship between $\nu_{as}COC$ and H-bonding to the parent oxatriquinane **2** was investigated computationally by modeling its interaction with HCl at fixed distances from the oxygen. The results are shown in Figure 1. The $\nu_{as}COC$ frequency is observed to have an approximately linear relationship with H-bonding distance and, by implication, with H-bonding strength.

4.3. Hydrogen-Bonding in Co-ground Solids (Mechanoactivation)

When an oxatriquinane salt and the H{Cl_{11}} carborane acid were finely ground together, the ATR IR spectrum showed bands from a new compound. Subtraction of the spectrum of free oxatriquinane and H{Cl_{11}} (ground in the same manner) allowed isolation of the spectra of the products. These spectra show $\nu_{as}COC$ bands similar to those of initial oxatriquinanes, but shifted to lower frequencies (Table 3), indicating a $C_3O^+\cdots$H{Cl_{11}} interaction without disruption of the C_3O^+ motif.

Using the correlation in Figure 1, the experimental $\nu_{as}COC$ value of 751(2) cm^{-1} for the **2**$\cdots$H{Cl_{11}} interaction corresponds to a **2**$\cdots$HCl distance of ca. 2.1 Å. Since both are strong acids, the H-bonding interaction strengths of **2** with H{Cl_{11}} and HCl can be taken as roughly comparable. The sum of the van der Waals radii for O and H is 2.61 Å, so the hydrogen bond between **2** and H{Cl_{11}} indicated by the $\Delta\nu_{as}COC$ is of good quality.[37] Compared with **2**, the $\Delta\nu_{as}COC$ value for *n*-propyloxatriquinane **6a** is the same (−19 cm^{-1}). For tri-*n*-propyloxatriquinane **6b**, the $\Delta\nu_{as}COC$ is approximately half this value (11 cm^{-1}), suggesting that its H-bond with H{Cl_{11}} is roughly half as strong. This can be rationalized by the more hindered steric approach of H{Cl_{11}} to the oxygen of the bulky **6b** cation.

The alkene bridged tetracycle **7** behaved quite differently. Upon grinding with H{Cl_{11}}, a quantitative reaction took place. The spectrum of the product showed the absence of the weak, sharp band of $\nu C=C$ at 1643 cm^{-1}, a strong decrease in the molar intensity of all C–H

stretch vibrations and the appearance of the band at 2753 cm^{-1} characteristic of carbocations (Figure 2).[38]

In addition, there was a significant decrease in the intensity of all low frequency bands, including the C–O stretches (Figure 2) which could nevertheless be detected as weak bands with average Δv of *ca.* -5 cm^{-1} (Table 3). These results indicate that the double bond in **7** is protonated to form carbocation **8** which does not proceed to **9**, suggesting that the carbenium ion center coordinates more effectively to the counterions than the C_3O^+ group. This condensed phase result stands in contrast with the modeled gas-phase behavior of the isolated dication. This reaction was also investigated in benzene solution. As a carborane salt, alkene **7** reacts quantitatively in a 1:1 mole ratio with the benzenium ion in $[C_6H_7^+]$ $[CHB_{11}Cl_{11}{}^-]$ to precipitate a colorless solid whose low solubility suggested an ionic formulation. As expected for the protonation of an alkene, the IR spectrum of this solid does not show a C=C stretching vibration band at 1643 cm^{-1}. However, new bands characteristic of a phenyl group appeared. Otherwise, the spectral features of the C_3O^+ group were essentially unchanged, indicating that this moiety was intact and the phenyl group was remotely situated.

The product had insufficient solubility for NMR characterization but single crystals, having the same IR spectrum as the initial precipitate, could be grown from the reaction mixture. X-ray diffraction analysis showed the new compound to be the product of the electrophilic addition of carbocation **8** to benzene (Figure 3).

Given that the cation could have formed at either carbon of the double bond, the oxygen lone pair may be considered to have had a role in the regiochemistry of the protonation of **7**, leading to the observed product as the only Ph-substituted isomer. The stereochemical outcome of the reaction may also be significant in that the phenyl group adds exclusively from the side opposite the oxygen, suggesting a proximity, even if transient, between O^+ and C^+.

Attempts to avert the reaction of dication **8** with solvent by carrying out the protonation in liquid SO_2Cl_2 were unsuccessful. Gradual decomposition was observed with the evolution of gaseous products. The use of liquid HCl as solvent (at 0 °C and 26 atm) led to precipitation of a solid having a similar IR spectrum to that obtained in the solid state reaction. This compound was stable for several days in contact with dichloromethane but did not yield single crystals for X-ray analysis.

4.4. H-bonding Using Sublimed Acid

Crystalline H{Cl$_{11}$} acid is known from its X-ray structure to be a linear polymer with short, strong, symmetrical H-bonding between Cl atoms of the carborane anions.[24] However, the freshly sublimed acid has been shown to be a mixture of H{Cl$_{11}$} monomers and dimers with weaker intermolecular H-bonding,[24] implying a higher acidity than the polymer. Thus, H{Cl$_{11}$} acid was freshly sublimed onto samples of the oxatriquinanes with the expectation that a stronger interaction would be observed.

Due to the configuration of the IR cell, experiments with the freshly sublimed acid required thin layers of solid oxatriquinane to be held at 120 °C. Since alkene **7** decomposes at this temperature, it was not studied by this technique. However, the IR spectra of parent oxatriquinane **2** and the mono-*n*-propyl derivative **6a** are essentially unchanged upon heating to 120 °C. When H{Cl$_{11}$} was sublimed onto them, new spectra were observed and isolated by computer subtraction of unreacted starting materials.

For the parent oxatriquinane **2**, the spectrum of the new product differs significantly from those calculated for **2**·HCl or **2**·H$^+$. The existence of only two νCH$_2$ stretching vibrations at 3026 and 2905 cm^{-1} indicates that the oxatriquinane has retained its high symmetry, which is only possible if H{Cl$_{11}$} interacts with the O atom. This interaction is corroborated by the significant increase in the frequencies of these νCH$_2$, indicating equal increase of positive charge over all CH$_2$ groups. The intensities of the δ_sCH$_2$ bending vibrations in the 1440–1472 cm^{-1} region decrease so much that they cannot be reliability determined. Most important is the appearance of two very broad and intense bands centered at ca. 1075 and 985 cm^{-1} and another at a lower frequency (795 cm^{-1}) (Figure 4).

These bands are diagnostic of short, strong, symmetrical (or nearly symmetrical) H-bonding.[5] They differ from those of {Cl$_{11}^-$}-H$^+$-{Cl$_{11}^-$} anion in both frequency and in molar intensity, and are assigned to proton vibrations of the C$_3$O$^+$···H$^+$···{Cl$_{11}^-$} group of the **2**·H{Cl$_{11}$} adduct. In the low frequency region, a new band at 717 cm^{-1} is assigned to ν_{as}CO in the C$_3$O$^+$···H$^+$···{Cl$_{11}^-$} group. This compares to 770 cm^{-1} in **2** and 740 cm^{-1} calculated for the H-bonded **2**·HCl at an O···H distance of 1.75 Å. Thus, the value of 717 cm^{-1} observed for **2**·H{Cl$_{11}$} is consistent with H$^+$ more or less equally shared by the C$_3$O$^+$ group and {Cl$_{11}$}$^-$ ion, as graphically interpreted in Figure 5.

Very similar results were observed when the monopropyl oxatriquinane **6a** was treated under the same conditions with the freshly sublimed H{Cl$_{11}$} acid. A new, strong band at 718 cm^{-1} was observed and assigned to the asymmetric CO stretch in the C$_3$O$^+$···H$^+$···{Cl$_{11}^-$} group, and a second weaker band at 685 cm^{-1} could be attributed to the symmetric CO stretch, becoming IR active due to the lower symmetry of **6a** compared to **2**.

We note that the IR spectra of **2**·H{Cl$_{11}$} and **6a**·H{Cl$_{11}$} both show the same relatively intense overtones of {Cl$_{11}$}$^-$ anion bands at 2072, 1956 and 1918 cm^{-1} which are also observed in the spectrum of polymeric H{Cl$_{11}$} acid. This commonality may reflect structural similarity in their short, strong, symmetrical (or nearly symmetrical) H-bonding involving the anion.

4.5. Protonation Reactions in Solution

The solid state reactions described above may be slow, incomplete and subject to lattice energy considerations, but they have significant advantages over solution phase studies. Reactions with solvent, such as the electrophilic addition of carbocation **8** to benzene described above, are excluded. In addition, solvent basicity does not compete with oxatriquinane basicity, and solvent leveling of the acidity does not diminish the carborane acid strength.

Experience shows that carborane acids dissolve only in solvents that can be protonated. For solvents with a heteroatom such as ethers, liquid SO$_2$ and possibly *o*-dichlorobenzene, the form of the proton is a *di*solvate, [solv···H$^+$···solv].[5] For arenes such as benzene, *mono*-protonated arenium ions are formed, probably having significant ion pairing and C-H···anion H-bonding, as seen in the X-ray structure of [C$_6$H$_7$][CHB$_{11}$Me$_5$Br$_6$].[39]

The ideal solvent for H{Cl$_{11}$} would be one whose basicity is comparable to the basicity of the carborane anion (to minimize the effect of solvent leveling) and whose reactivity is simply the solvation of H$^+$. Liquid SO$_2$ and related oxyhalides such as SO$_2$Cl$_2$ and SO$_2$ClF might seem attractive choices since they have been widely used in traditional superacid chemistry. Nevertheless, acidity leveling in these solvents appears to be significant and no apparent interaction between oxatriquinane cations and H{Cl$_{11}$} was observed in liquid SO$_2$, consistent with the acidity modeling described in Table 1, which indicated that SO$_2$

would be more basic than the oxatriquinanes. Beyond this, these solvents are not always innocent as nucleophiles.

The low basicity of chlorocarbon and fluorocarbon solvents might also seem attractive, but carborane acids are so strong that they instantly decompose chlorocarbons[27] and do not dissolve in fluorocarbons. Acting on the notion that liquid HCl might be a useful but unrecognized low-basicity solvent whose working conditions are manageable in heavy-walled glassware (P = 26 atm at 0 °C), we decided to explore this solvent as a medium for protonating oxatriquinanes.

The parent oxatriquinane $2\{Cl_{11}\}$ was insoluble in liquid HCl and showed no sign of reaction with a solution of $H\{Cl_{11}\}$ upon standing. On the other hand, the mono-*n*-propyl **6a** and tri-*n*-propyl **6b** carborane salts were soluble and reacted in two steps. The first step occurs at a 1:1 oxatriquinane: $H\{Cl_{11}\}$ molar ratio. The solid isolated from this solution with **6b** shows an IR spectrum with essentially unchanged oxatriquinane bands, although the COC stretching bands are slightly broadened and their molar intensities decreased. This suggests only a change in the cation-anion electrostatic interaction. The intensities of the anion bands are doubled and a new broad band appears at 1280 cm^{-1}. Subtraction of the spectrum of the anion reveals two additional broad bands at 1010 and 933 cm^{-1} (Figure 6) that are characteristic of a proton disolvate with a short, strong, symmetrical hydrogen bond.[5] This compound is therefore formulated as a salt with an unchanged oxatriquinane cation and the complex counterion, $\{Cl_{11}{}^-\}\cdots H^+ \cdots \{Cl_{11}{}^-\}$. The same conclusion follows from the ^1H NMR of this solid dissolved in CD_2Cl_2. Signals of the cation exactly coincide with those of **6b**·PF_6 and a new signal integrating for a single proton appeared at 4.09 ppm.

At a 1:2 mole ratio of **6b** and $H\{Cl_{11}\}$, a secondary interaction takes place in HCl solution. The IR spectrum of the precipitated product shows no absorptions from free acid, suggesting protonation of the oxatriquinane cation. All the distinctive absorptions of the $\{Cl_{11}\text{-}H^+\text{-}Cl_{11}\}^-$ complex anion are preserved but the absorptions of the cation are changed significantly. In the frequency region below 900 cm^{-1}, the usually intense $\nu_{as}COC$ bands of the C_3O^+ group, as well as other weaker bands of cation, are not observed. These spectral properties, whereby vibrations of molecular groups adjacent to H^+ either vanish or have greatly diminished intensity, are a characteristic of symmetrical proton disolvated cations of the type L-H^+-L (L=ether, ketone, etc.).[5,40] The intensities of the C-H stretching vibrations are also greatly decreased and hardly visible, indicating a distribution of positive charge over the C-H bonds.[41] The bending CH vibrations, better observed than the stretching, are combined in one complex band near 1457 cm^{-1}.

Evidence of carbocation formation can be derived from the appearance of a new strong doublet at 2788 and 2740 cm^{-1}. This region is characteristic for C-H stretching modes in hyperconjugatively stabilized carbocations, *e.g. t*-butyl.[38] In the lower frequency region, a very broad band centered at 1490 cm^{-1} is consistent with that expected for a protonated ether.[5] Thus, the product of the reaction of **6b**·$\{Cl_{11}\}$ with 2 equivalents of $H\{Cl_{11}\}$ is formulated as the mixed carbocation/oxonium ion dication **21** resulting from acidic cleavage of one of the C–O bonds of the C_3O^+ unit.

21
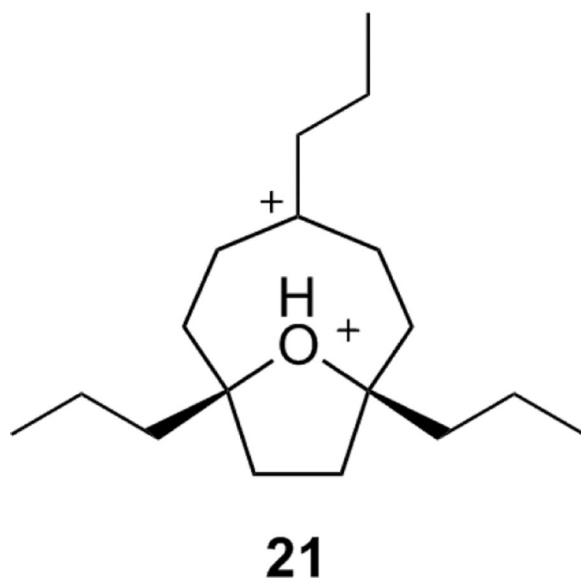
This is entirely consistent with the calculations described earlier that showed protonation of **2** giving rise to the protonated tetrahydrofuran **4**.

The salt of **21** dissolves well in dichloromethane and its ^{1}H NMR spectrum shows the expected narrow signal at 4.09 ppm from the $\{Cl_{11}\text{-}H^+\text{-}Cl_{11}\}^-$ anion. The spectrum of the cation is drastically changed from that of **6b**, appearing as very broad signals at room temperature which do not change on cooling to −40 °C, a common characteristic of carbocations in dichloromethane solution. The NMR spectrum evolved over time, indicating gradual decomposition. After 3 days, small crystals appeared which were shown by X-ray analysis to be the *t*-butyl salt, $[(CH_3)_3C]\{Cl_{11}\}$, a decomposition product often observed in carbocation chemistry.

The mono-propyl derivative **6a** behaved in a similar manner to **6b**. At 1:2 mole ratio of oxatriquinane to carborane acid, the IR spectrum of the isolated solid showed the same bands at 1263, 1008 and 928 cm^{-1} due to $\{Cl_{11}\}\text{-}H^+\text{-}\{Cl_{11}\}$ complex anion formation, as well as greatly diminished intensities in the lower frequency range from vibrations of the dication (Figure 7).

5. Conclusion

The inescapable conclusion from this work is that R_3O^+ oxonium cations have experimentally verifiable basicity, at least in oxatriquinanes. With three covalent bonds to oxygen in a rigid, fused, tricyclic ring system, the remaining lone pair of electrons in the valence shell octet is both stereochemically available and chemically "basic," despite the overall positive charge. In the absence of solvent, the lone pair can engage not only in conventional H-bonding with a strong acid but also in short, strong, nearly symmetrical H-bonding with a superacid, in this instance the monomeric form of the carborane acid $H(CB_{11}Cl_{11})$. In liquid HCl, a novel, weakly basic solvent, complete proton transfer from the carborane acid occurs but the resulting R_3OH^{2+} dication is unstable with respect to C–O bond cleavage, in agreement with calculations. The existence of a tetravalent oxygen(2+) dication has yet to be established. H-bonding to oxonium cations is now a matter of fact and provides an adequate explanation for experimental data that have invoked tetravalent intermediates in superelectrophile dication chemistry.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

REFERENCES

1. Meerwein H. Sitzber. Ges. Beforder. Naturw. Marburg. 1930; 64:119.

2. Arnett EM, Wu CY. J. Am. Chem. Soc. 1960; 82:4999.

3. Brookhart M, Grant B, Volpe AF. Organometallics. 1992; 11:3920.

4. Jutzi P, Muller C, Stammler A, Stammler HG. Organometallics. 2000; 19:1442.

5. Stasko D, Hoffmann SP, Kim KC, Fackler NLP, Larsen AS, Drovetskaya T, Tham FS, Reed CA, Rickard CEF, Boyd PDW, Stoyanov ES. J. Am. Chem. Soc. 2002; 124:13869. [PubMed: 12431118]

6. Krossing I, Reisinger A. Eur. J. Inorg. Chem. 2005:1979.

7. Meerwein H, Hinz G, Hofmann P, Kroning E, Pfeil E. J. Prakt. Chem. 1937; 147:257.Meerwein H, Battenberg E, Gold H, Pfeil E, Willfang G. J. Prakt. Chem. 1939; 154:83.Meerwein H, Eisenmenger U, Matthiae H. Liebigs Ann. Chem. 1950; 566:150.

8. Meerwein H. Org. Synth. 1966; 46:113.

9. Olah GA. Angew. Chem. Int. Ed. Engl. 1993; 32:767.

10. Hartz N, Rasul G, Olah GA. J. Am. Chem. Soc. 1993; 115:1277.

11. Schneider TF, Werz DB. Org. Lett. 2010; 12:772. [PubMed: 20085316]

12. Olah GA, Prakash GKS, Barzaghi M, Lammertsma K, Schleyer PV, Pople JA. J. Am. Chem. Soc. 1986; 108:1032.

13. Olah GA, Rasul G, Burricher A, Prakash GKS. Proc. Natl. Acad. Sci. USA. 1998; 95:4099. [PubMed: 9539696]

14. Olah GA, Demember JR, Mo YK, Svoboda JJ, Schillin P, Olah JA. J. Am. Chem. Soc. 1974; 96:884.

15. Houk KN, Takano Y. J. Chem. Theory Comput. 2005; 1:70.

16. Sato S, Ameta H, Horn E, Takahashi O, Furukawa N. J. Am. Chem. Soc. 1997; 119:12374.

17. Mascal M, Hafezi N, Meher NK, Fettinger JC. J. Am. Chem. Soc. 2008; 130:13532. [PubMed: 18798616]

18. Mascal M, Hext NM, Shishkin OV. Tetrahedron Lett. 1996; 37:131.

19. Haley MM. Angew. Chem. Int. Ed. Engl. 2009; 48:1544. [PubMed: 19152391]

20. Hext NM, Hansen J, Blake AJ, Hibbs DE, Hursthouse MB, Shishkin OV, Mascal M. J. Org. Chem. 1998; 63:6016. [PubMed: 11672206]

21. Galasso V, Hansen J, Jones D, Mascal M. J. Mol. Struct. (THEOCHEM). 1997; 392:21.

22. Cossi M, Rega N, Scalmani G, Barone V. J. Comput. Chem. 2003; 24:669. [PubMed: 12666158]

23. Atomic charge modeling (MP2/6–31+G**) using natural population analysis and vibrational frequency-dependent atomic polar tensor-based methods shows a greater positive charge on the α carbons of protonated **6** than protonated **2**.

24. Stoyanov ES, Hoffmann SP, Juhasz M, Reed CA. J. Am. Chem. Soc. 2006; 128:3160. [PubMed: 16522093]

25. Stoyanov ES, Kim KC, Reed CA. J. Am. Chem. Soc. 2006; 128:1948. [PubMed: 16464096]

26. Meyer MM, Wang XB, Wang LS, Kass SR, Reed CA. J. Am. Chem. Soc. 2009; 131:18050. [PubMed: 19950932]

27. Stoyanov ES, Stoyanova IV, Reed CA. J. Am. Chem. Soc. 2011; 133:8452. [PubMed: 21568318]

28. Reed CA. Chem. Commun. 2005:1669.

29. Reed CA. Accounts. Chem. Res. 2010; 43:121.

30. Zhang Y, Reed CA. Dalton. Trans. 2008:4392. [PubMed: 18698440]

31. Becke AD. J. Chem. Phys. 1993; 98:5648.Becke AD. J. Chem. Phys. 1993; 98:1372.Lee CT, Yang WT, Parr RG. Phys. Rev. B. 1988; 37:785.Stephens PJ, Devlin FJ, Chabalowski CF, Frisch MJ. J. Phys. Chem. 1994; 98:11623.

32. Møller C, Plesset MS. Phys. Rev. 1934; 46:0618.

33. Gaussian 03, Revision D.01. Wallingford CT: Gaussian, Inc.;

34. CCDC 847149 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

35. Mascal M, Hafezi N, Toney MD. J. Am. Chem. Soc. 2010; 132:10662. [PubMed: 20681692]

36. Krasovskiy A, Kopp F, Knochel P. Angew. Chem. Int. Ed. Engl. 2006; 45:497. [PubMed: 16397856]

37. Rowland RS, Taylor R. J. Phys. Chem. 1996; 100:7384.

38. Kato T, Reed CA. Angew. Chem. Int. Ed. Engl. 2004; 43:2908. [PubMed: 15170300]

39. Reed CA, Kim KC, Stoyanov ES, Stasko D, Tham FS, Mueller LJ, Boyd PDW. J. Am. Chem. Soc. 2003; 125:1796. [PubMed: 12580605]

40. Stoyanov ES, Reed CA. J. Phys. Chem. A. 2006; 110:12992. [PubMed: 17134158]

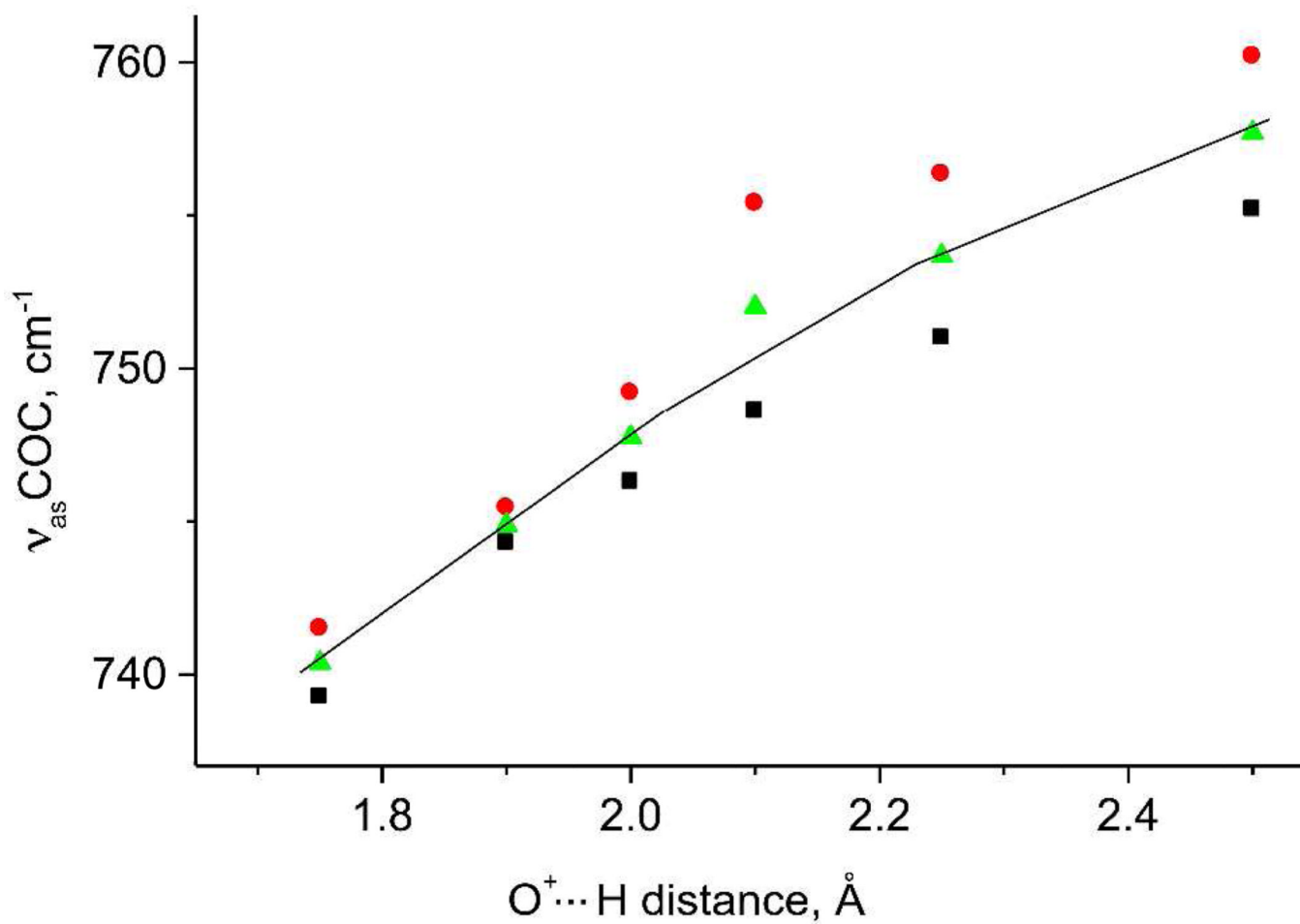41. Stoyanov ES, Stoyanova FV, Reed CA. Chem. Eur. J. 2008; 14:3596. [PubMed: 18327756]

Figure 1.
Dependence of ν_{as}COC stretches (red, black; average green) on O···H distance in calculated 2···HCl pairs.
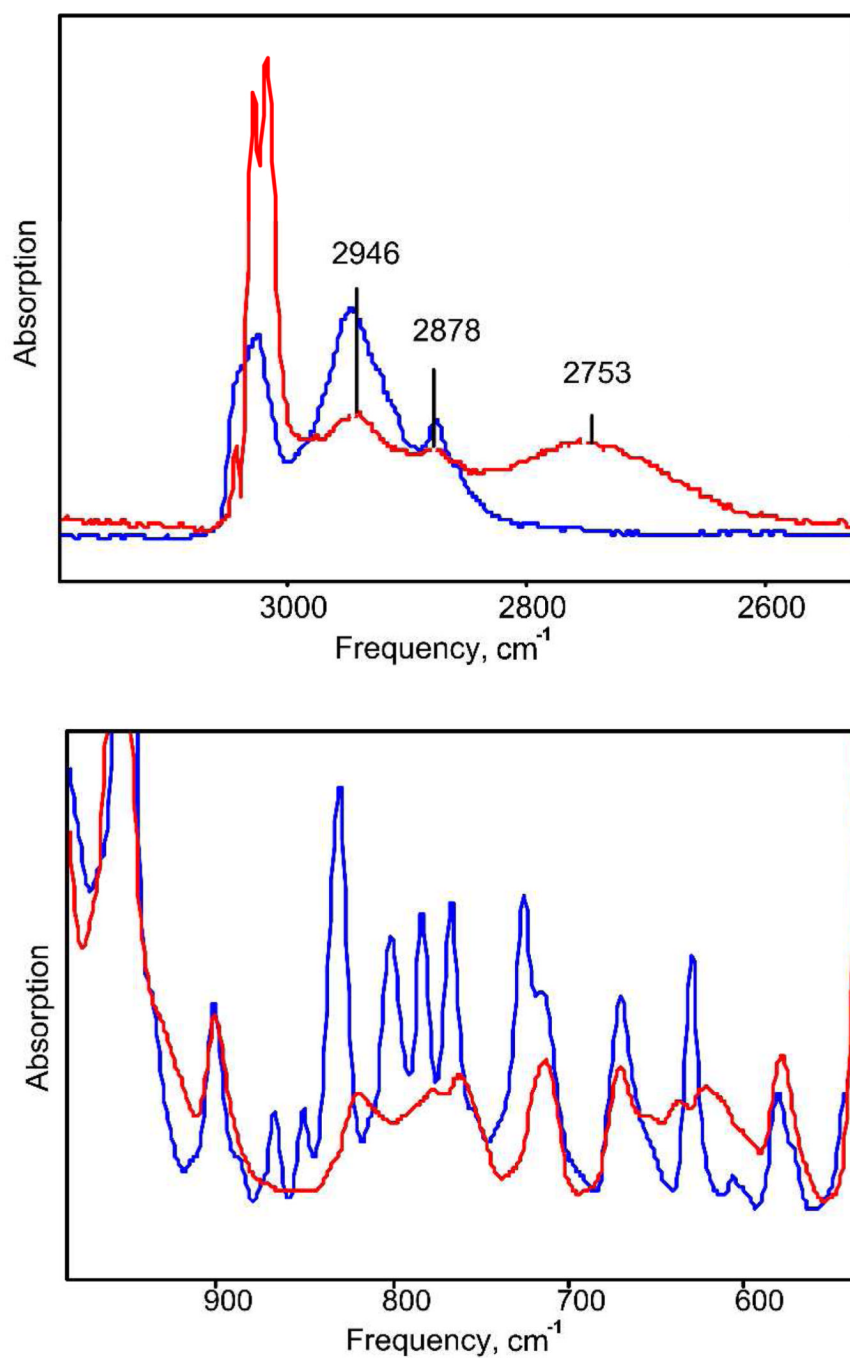
Figure 2.
IR spectra (normalized to unit intensity of the carborane anion) of alkene 7 before (blue) and after (red) grinding with H{Cl$_{11}$}.
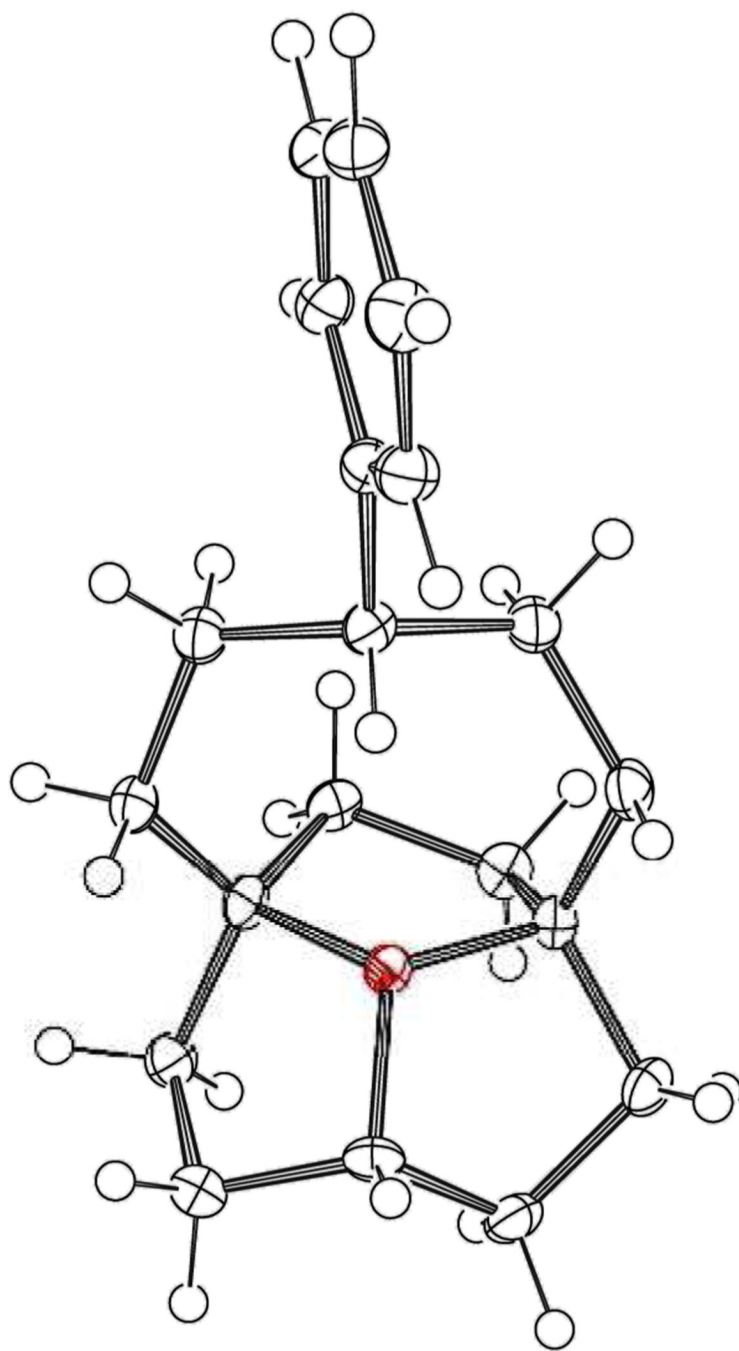
Figure 3.
X-ray crystal structure of the C_6H_6 addition product to cation 8. The counterion is omitted for clarity.
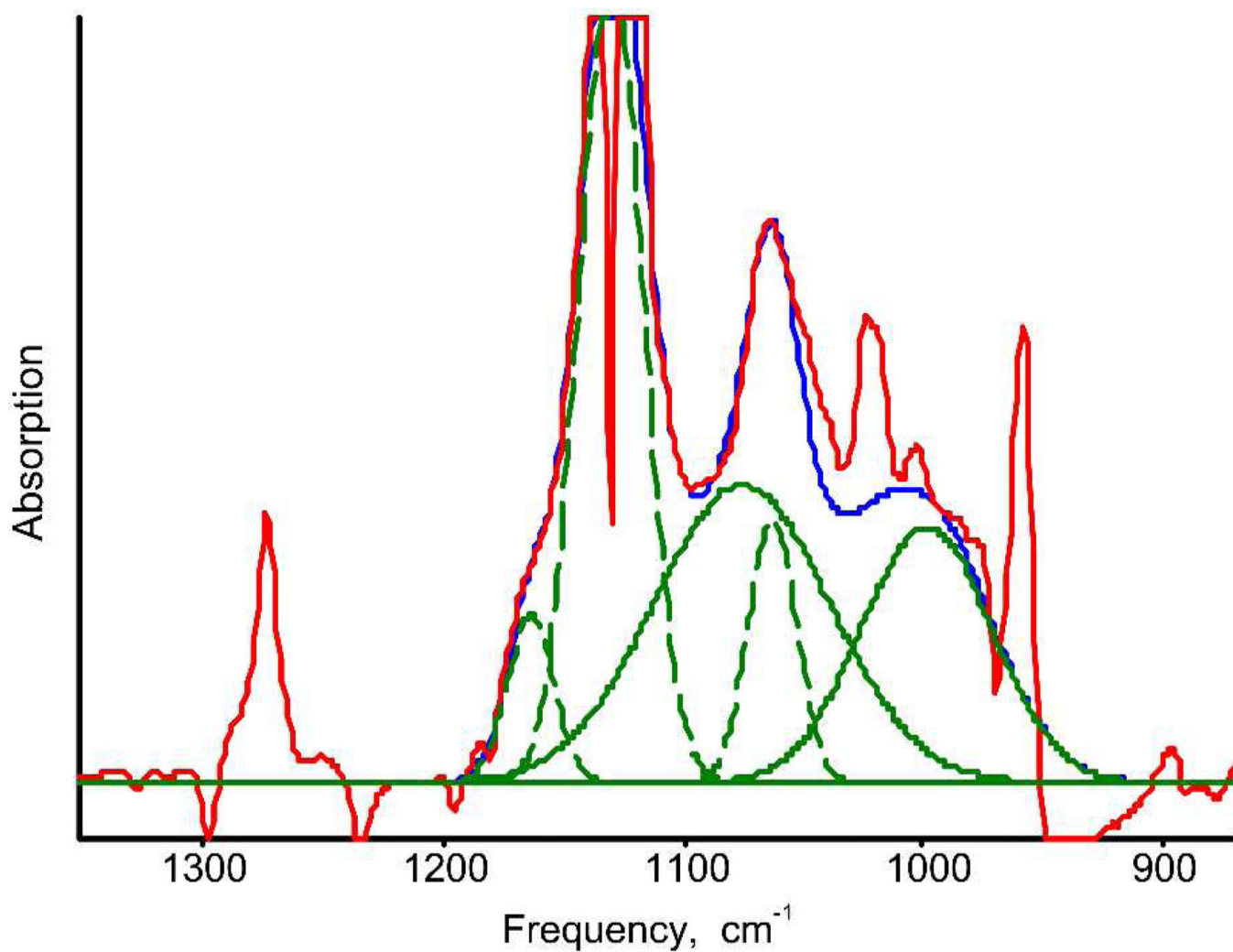
Figure 4.
Deconvolution (green), with summation (blue), of the spectrum of $2 \cdot H\{Cl_{11}\}$ with absorptions of $\{Cl_{11}\}$ anion subtracted (red) showing broad bands at 1075 and 985 cm^{-1} assigned to bridging proton vibrations (solid green).
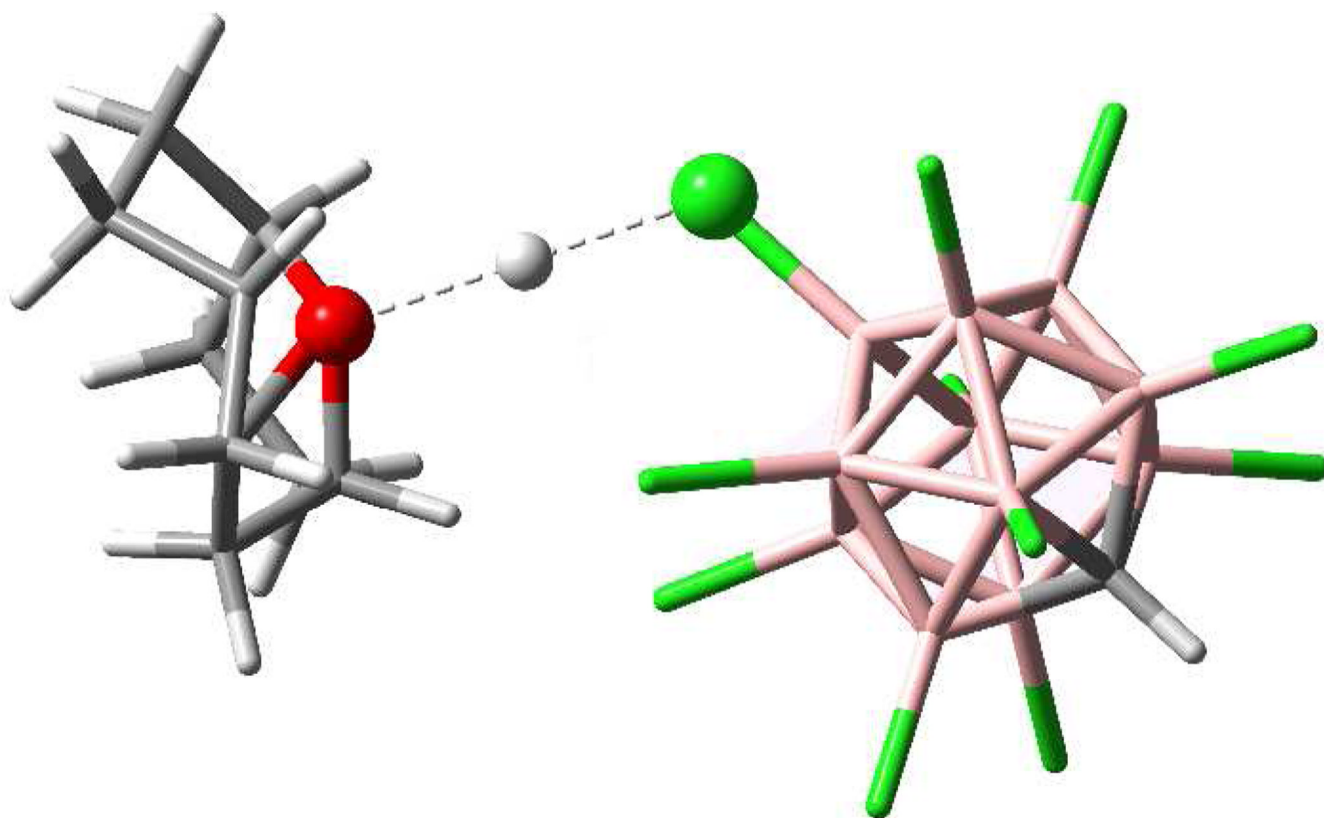
Figure 5.
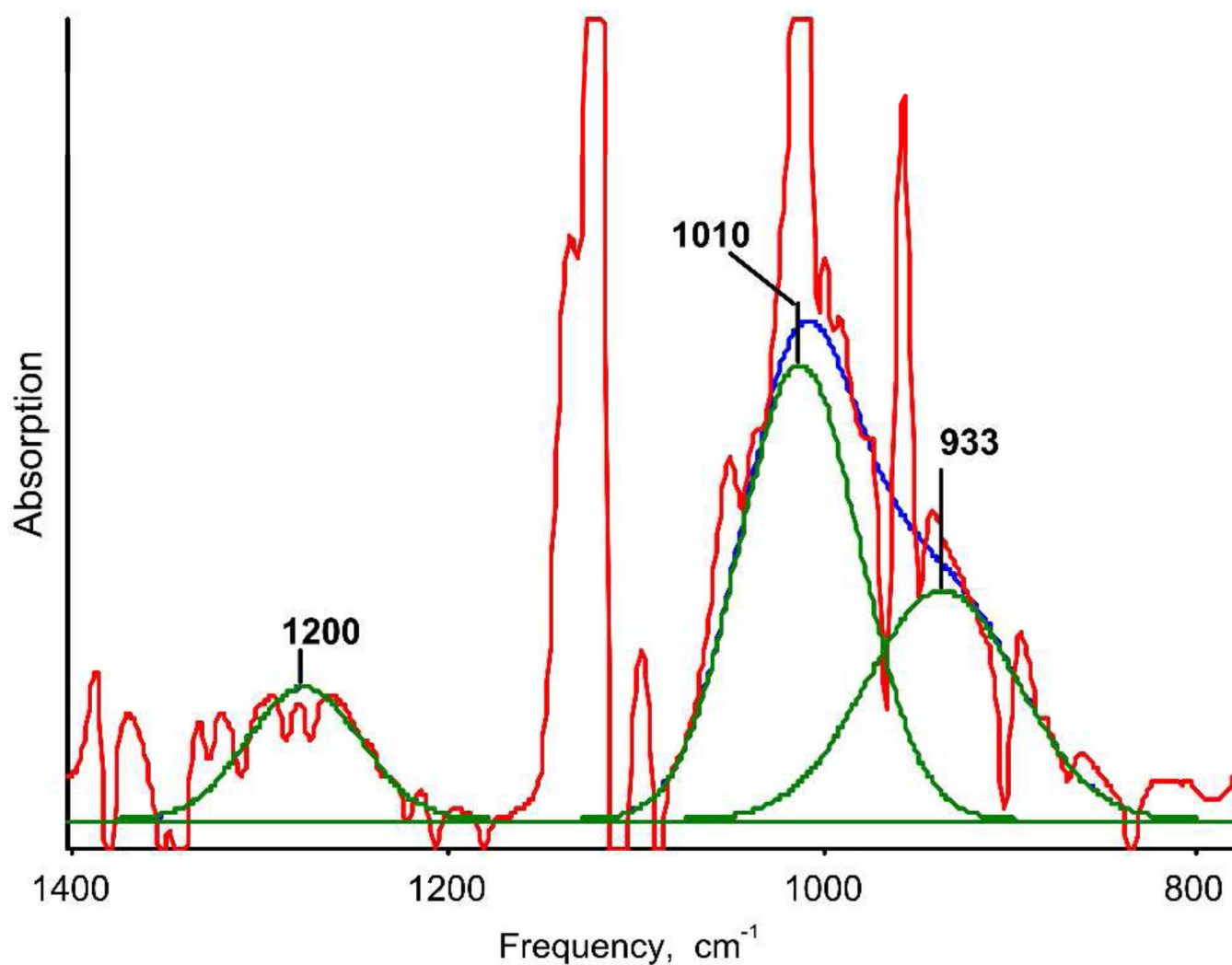Graphical depiction of the experimental results described in Section 4.4.

Figure 6.
Deconvolution (green), with summation (blue), of IR spectrum of 6b[H{Cl$_{11}$}$_2$] with the spectrum of {Cl$_{11}$} anion subtracted (red).
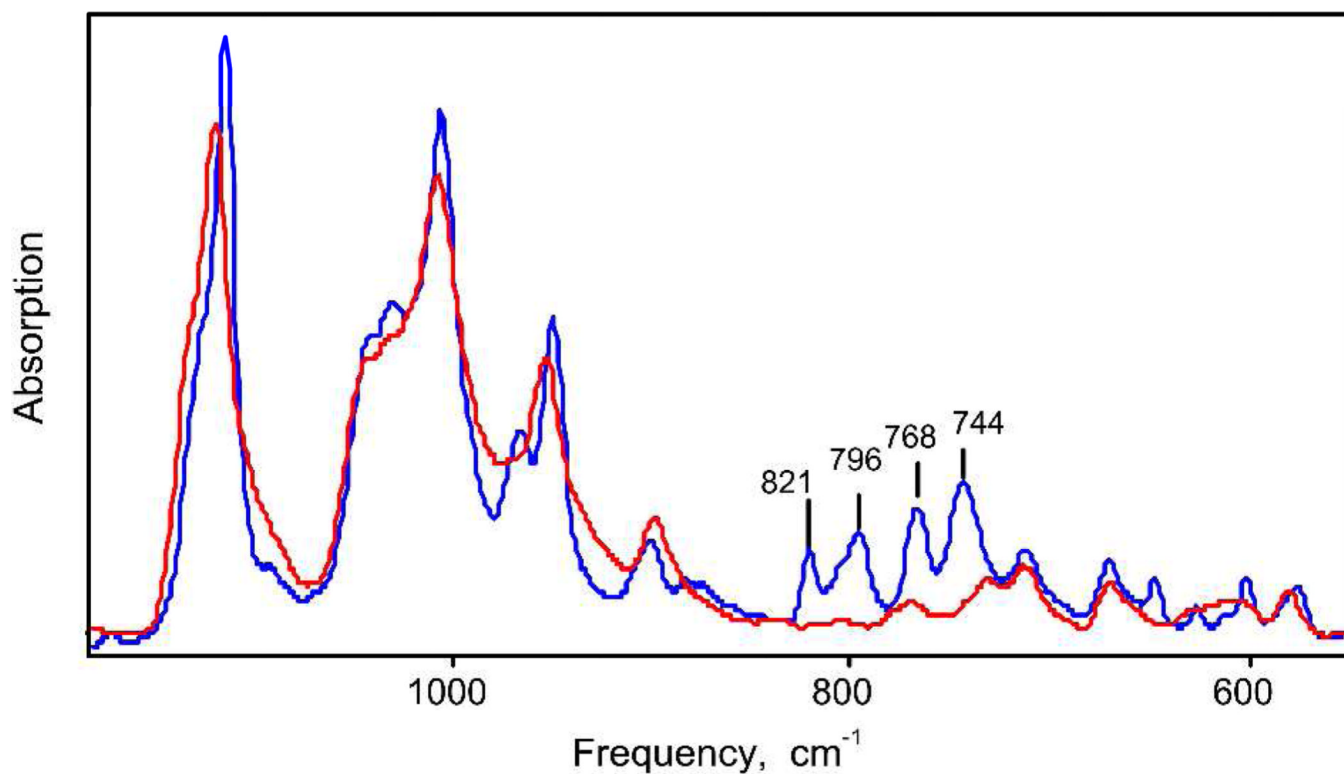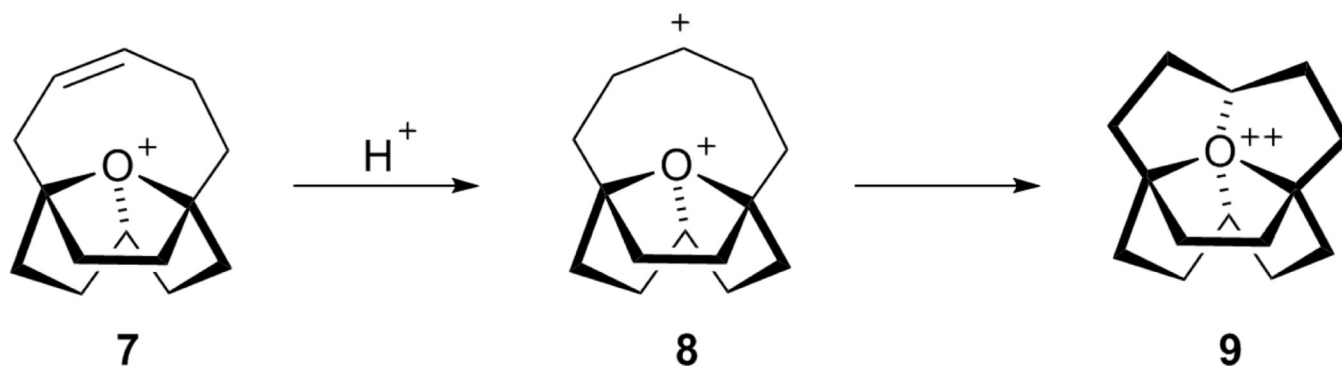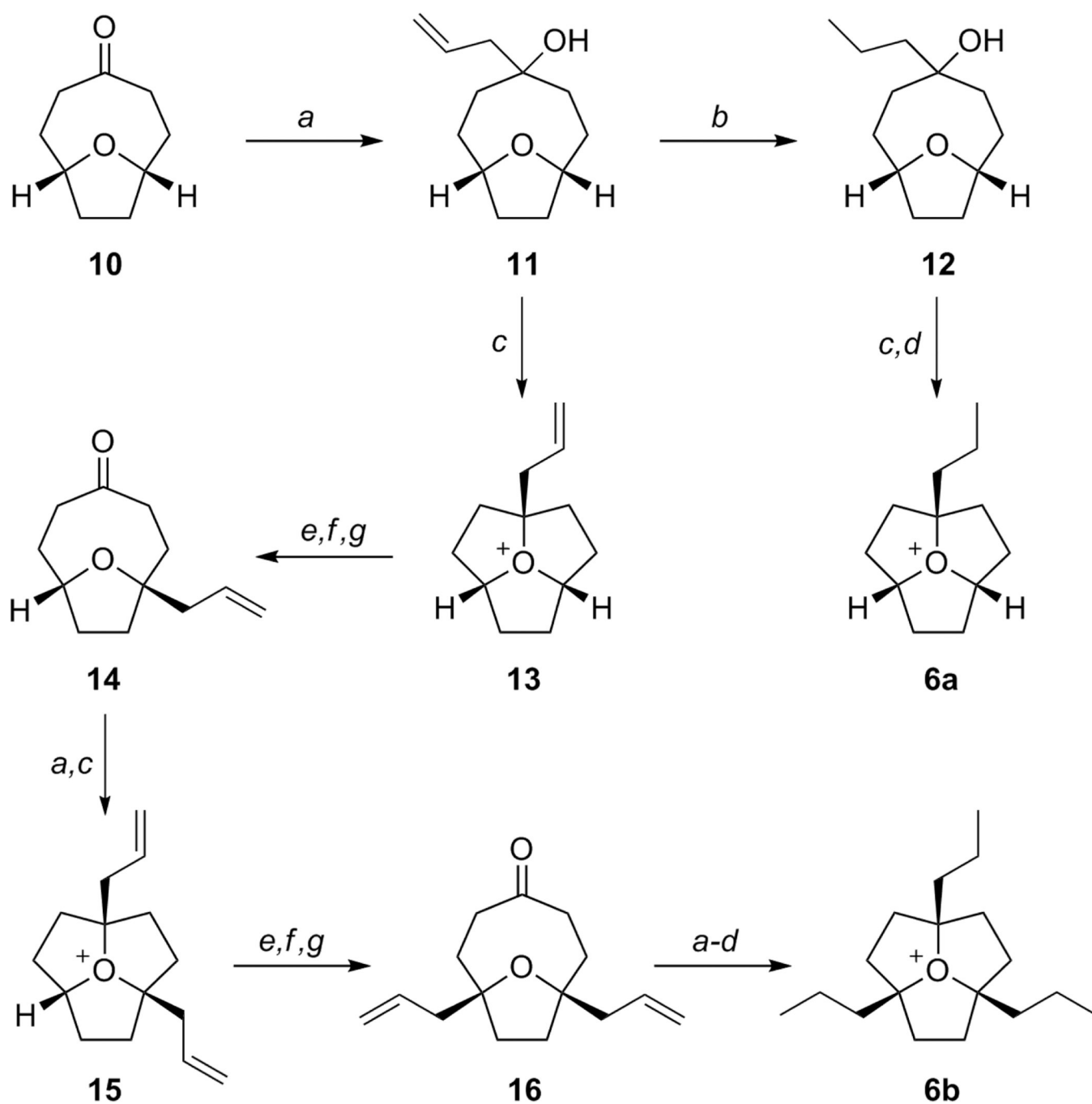
Figure 7.
IR spectrum of the product from 1:2 mole ratio of 6a{Cl$_{11}$} and H{Cl$_{11}$} in liq. HCl (red) compared to 6a{Cl$_{11}$} (blue)

Scheme 1.

Scheme 2.
Reagents and conditions: (*a*) H$_2$C=CHCH$_2$MgBr, ether; (*b*) H$_2$, Pd/C, MeOH; (*c*) TfOH, MeCN; (*d*) aq. KPF$_6$; (*e*) aq. NaOAc; (*f*) K$_2$CO$_3$, MeOH; (*g*) CrO$_3$, pyridine, CH$_2$Cl$_2$.
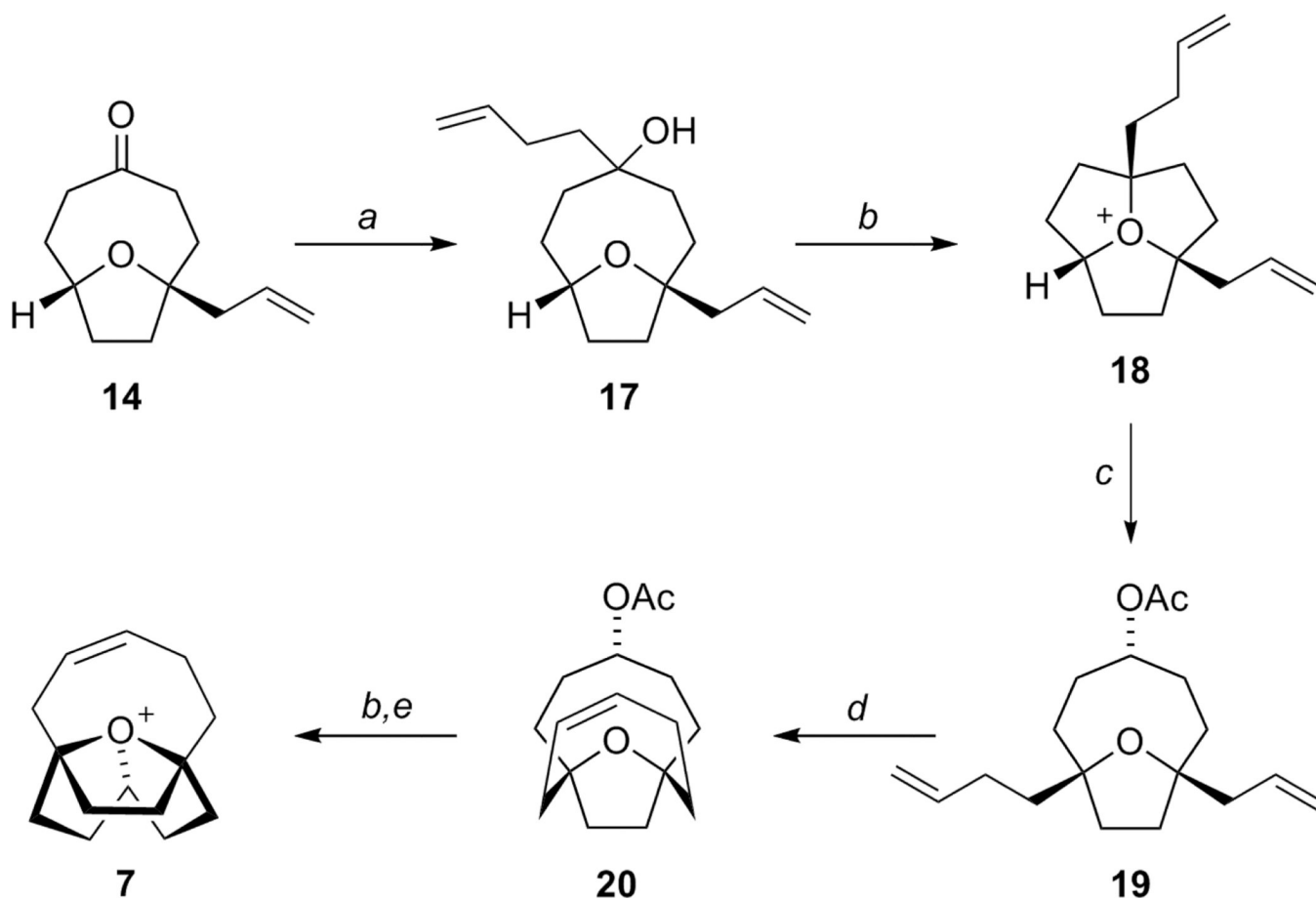
Scheme 3.
Reagents and conditions: (a) H$_2$C=CH(CH$_2$)$_2$MgBr, LaCl$_3$·2LiCl, THF; (b) TfOH, MeCN; (c) aq. NaOAc; (d) (PCy$_3$)$_2$Cl$_2$Ru=CHPh, benzene; (e) aq. KPF$_6$.

Table 1

Protonation energies (kcal mol^{-1}) in the gas phase (PE$_g$) and in a dichloromethane solvent model (PE$_s$) calculated at the B3LYP/6–31+G(d,p) level of theory.

entry	species	PE$_g$	PE$_s$
1	**3**	−239.8	−278.8
2	Et$_3$N	−233.2	−270.8
3	Et$_2$O	−196.9	−241.8
4	C$_6$H$_6$	−183.1	−225.7
5	SO$_2$	−153.3	−206.4
6	CO	−137.8	−196.5
7	**6**^{a}	−92.6	−195.1
8	**2**	−73.7	−192.2
9	Et$_3$O$^+$	−63.6	−177.7
10	H$_3$O$^+$	60.2	divergent

^{a}R$_1$=R$_2$=R$_3$=CH$_3$.

Table 2

Comparison of calculated νCOC values (as gas phase cations) versus experimental values (as solid state {Cl$_{11}$} salts).

Compound		ν$_{as}$COC (cm^{-1})	ν$_s$COC	C-O, Å
2	Exp.	770	*	1.537[17]
	Calc.	770 772		1.534
6a	Exp.	796 768	744	-
	Calc.	803 778	733	1.526, 1.577
6b	Exp.	729	*	-
	Calc.	732 735		1.555
7	Exp.	782 766	726	-
	Calc.	780 774 763		1.533

*
IR inactive

Table 3

IR frequencies (cm^{-1}) sensitive to H-bonding in co-ground oxatriquinane-H{Cl$_{11}$} samples.

Compound	vCOC (ΔvCOC**)			v$_{as}$*(Δv$_{as}$**)
2		770		821
2·H{Cl$_{11}$}		751 (−19)		804 (−17)
6a		768	744	821
6a·H{Cl$_{11}$}		749 (−19)	733 (−11)	806 (−15)
6b		729		758
6b·H{Cl$_{11}$}		718 (−11)		750 (−8)
7	782	766	726	830
7·H$^+$	776 (−6)	761 (−5)	721 (−5)	819 (−11)

*
vibration with minor contribution from COC stretch but nevertheless sensitive to H-bonding.

**
frequency shifts upon H-bonding to H{Cl$_{11}$} given in parentheses.