

Extreme Oxatriquinanes: Structural Characterization of α -Oxyoxonium Species with Extraordinarily Long Carbon–Oxygen Bonds

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S Supporting Information

ABSTRACT: The first stable α -oxyoxonium species have been synthesized and characterized. Strong donation of nonbonding electrons on oxygen into the adjacent $\sigma^*(\text{C}-\text{O}^+)$ orbital was predicted by modeling to result in unheard of carbon–oxygen bond lengths. The kinetic stability of the triquinane ring system provides a platform upon which to study these otherwise elusive species, which are evocative of intermediates on the acetalization reaction pathway. Crystallographic analysis of the α -hydroxy and α -methoxy oxatriquinane triflates reveals 1.658 and 1.619 Å C–O⁺ bond lengths, respectively, the former of which is a new record for the C–O bond.

Recently, we published an account describing the combined effects of steric repulsion and strong contributions of adjacent C–H and C–C bonds into $\sigma^*(\text{C}-\text{O})$ orbitals on C–O bond distances.¹ The outcome of that study can be summarized by Figure 1, where incremental effects of charge, annulation, and degree of substitution can clearly be seen. By exploiting the robust nature of the oxatriquinane ring system, we were able to push the covalent C–O bond length to a record 1.622 Å in **5**.¹

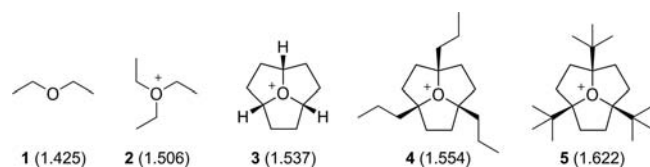


Figure 1. Crystallographic C–O bond lengths (Å) of ether² and a series of oxonium ions.

While enhanced hyperconjugative effects can lead to unusual bonding outcomes like those in Figure 1, conjugate electron contribution by an n -donor such as oxygen into an electrophilic σ^* orbital would involve a correspondingly much greater effect on the C–O bond. In acetal **7** for example, the contribution of O1 into the adjacent $\sigma^*(\text{C}-\text{O})$ orbital would have the effect of lengthening the C2–O3 bond while at the same time contracting the O1–C2 bond. Since O3 contributes into $\sigma^*(\text{C2}-\text{O1})$ in the same way, these effects are held in balance, and the overall result is actually a slight decrease in C–O bond distance compared to the ether analogue **6**. A bond lengthening effect is not exhibited until one oxygen can be identified as the

Table 1. Modeled (MP2/6-31**) C–O Bond Lengths (Å) in **6–10** (Crystallographic Data Are Given in Parentheses)

	O1–C2	C2–O3
6	1.425	–
7	1.409	1.409
8	1.390 (1.369) ³	1.432 (1.448) ³
9	1.387 (1.378) ⁴	1.456 (1.466) ⁴
10	1.331	1.594

principal electron donor in a mixed acetal, such as in literature compounds **8** and **9**, the result of which can be seen in Table 1.

While bond distances indicate that the σ^* orbitals of C2–O3 bonds of **8** and **9** are good electron acceptors, a strong enhancement of the effect would be expected where one of the oxygen sites of an acetal is positively charged. The protonated dioxolane **10**, for example, has a much shorter C–O “donor” bond and longer C–O “acceptor” bond than those in **8** and **9**. While completely intuitive, this effect can be quantified using second order perturbation theory analysis of the Fock matrix in the Natural Bond Order (NBO) basis.⁵ Thus, while the mutual contributions of the oxygen lone pairs into the adjacent σ^* orbitals in **7** are worth 16.0 kcal mol^{−1}, the delocalization of the O1 lone pair into $\sigma^*(\text{C2}-\text{O3})$ in the charged analogue **10** is significantly more favorable at 44.0 kcal mol^{−1}. However, **10** would in no way be expected to be a stable molecule.

We have promoted the triquinane ring system as a robust molecular platform for the stabilization of otherwise transient species, in particular threefold tertiary alkyl oxonium salts⁶ and tetravalent oxadionium (R_4O^{2+}) ions.⁷ Whereas sterics and hyperconjugation were previously used to push the C–O bonds in oxatriquinane to record distances (Figure 1), we considered the extent to which direct electron donation, like that described for **10** above, would affect the C–O bond length, and likewise the extent to which the resulting species, an α -oxyoxonium ion, could be stabilized within the triquinane framework. The literature shows that, while examples of O-alkylated acetals have been characterized at low temperatures in liquid SO_2 ,^{8,9}

Received: April 10, 2013

Published: May 17, 2013

manipulation under ambient conditions in common solvents, or in the solid state, is unknown.

To this end, mono-, di-, and trihydroxy and -methoxy oxatriquinanes **11**–**16** were conceptualized and modeled. Before long it was clear that, again, the system was leading toward some unusual bonding outcomes. Computed structural data for **11**–**16** are presented in Table 2. As can be seen, there

Table 2. Modeled (MP2/6-31G) C–O Bond Lengths (Å) in 11–16**

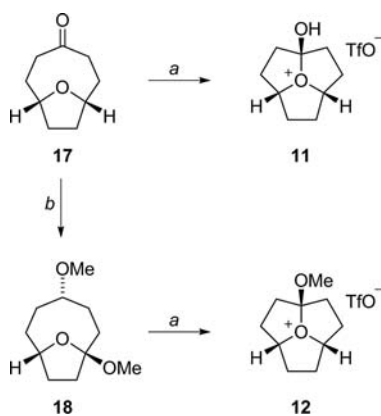
	O1–C2	C2–O3	O3 n → σ^* C2–O1, kcal mol ⁻¹
11 R=H	1.625	1.350	48.94
12 R=Me	1.650	1.342	53.08
13 R=H	1.585 ^a	1.357 ^a	43.81 ^a
14 R=Me	1.595 ^a	1.353 ^a	44.08 ^a
15 R=H	1.561	1.360	40.97
16 R=Me	1.565	1.360	39.25

^aAverage values.

appears to be significant potential for extraordinary C–O bond lengths, particularly in the monosubstituted oxatriquinanes **11** and **12**. Interestingly, the di- and trisubstituted analogues have shorter C–O bonds, such that the bonding in **15** is even comparable to that in tripropyloxatriquinane **4**. NBO analysis shows n -electron donation consistent with that of both the O1–C2 and C2–O3 bond length trends.

The prospect of achieving new record C–O bond lengths, as anticipated by Table 2, prompted attempts to synthesize **11**–**16**. In the case of **11** this turned out to be remarkably straightforward, whereby known ketone **17**⁶ was simply protonated with triflic acid to give **11** directly (Scheme 1). In the case of **12**, treatment of **17** with acid in methanol solution leads not to the expected acetal but dimethoxy bicycle **18**, presumably via **11** by ring-opening at an unsubstituted α -position with methanol followed by a glycosidation-like

Scheme 1^a

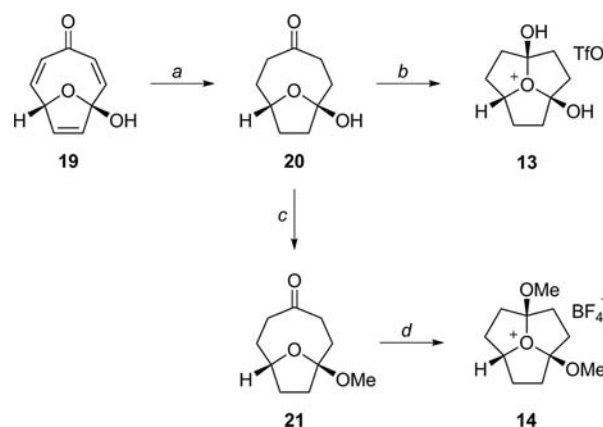


^aReagents and conditions: (a) F₃CSO₃H, CD₃CN; (b) *p*-MeC₆H₄SO₃H, (MeO)₃CH, K10 montmorillonite, MeOH, 89%.

reaction. Compound **18** is conveniently closed down with triflic acid to **12** (Scheme 1).

The di-O-substituted oxatriquinanes **13** and **14** were approached via a hydroxy-substituted version of **17**, i.e. **20**, which could be obtained by hydrogenation of literature compound **19**, itself 12 steps from commercial 1,5-cyclooctadiene.¹⁰ Thus, protonation of **20** with triflic acid gave **13**, while submission to acetalization conditions gave the methoxy substitution product **21**, which could be alkylated with Me₃O⁺ to provide **14** (Scheme 2).

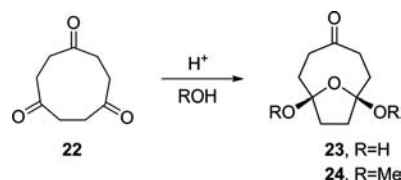
Scheme 2^a



^aReagents and conditions: (a) H₂, Pd/C, MeOH, 93%; (b) F₃CSO₃H, CD₃CN, -20 °C; (c) *p*-MeC₆H₄SO₃H, (MeO)₃CH, K10 montmorillonite, MeOH, 85%; (d) Me₃O⁺BF₄⁻, CD₃CN, -10 → 5 °C.

Finally, analogous attempts were made to produce **15** and **16** from literature compounds **23** and **24**, which are prepared from 1,4,7-cyclononatriene **22** (Scheme 3).¹¹ It can be envisaged that, like **17** and **20**, diol **23** could simply be protonated to give **15**. However, this reaction does not occur in aqueous acid, and in the absence of water, **23** quickly dehydrates back to **22**. Unlike **23**, compound **24** can in fact be isolated. Unfortunately, treatment of **24** with Me₃O⁺ in CD₃CN also leads back to **22**, presumably via alkylation at one of the OMe groups instead of the ketone.

Scheme 3



While dioxyoxatriquinanes **13** and **14** were prone to decomposition on standing at room temperature, X-ray quality crystals of **11** and **12** could be grown by dilution of their acetonitrile solutions with dry ether. Crystallographic analysis of **11** (Figure 2) revealed an O1–C2 bond distance of 1.658 Å, substantially greater than predicted by modeling (*cf.* Table 2), and displacing **5** as the C–O bond length record holder. Interestingly, the crystal structure of **12** showed an O1–C2 bond distance of 1.619 Å which, while still exceptional, was less than predicted. The C2–O3 bond of **11** is also correspondingly shorter (1.339 Å), and that of **12** longer (1.358 Å), than the modeled values. Although simple gas-phase calculations have

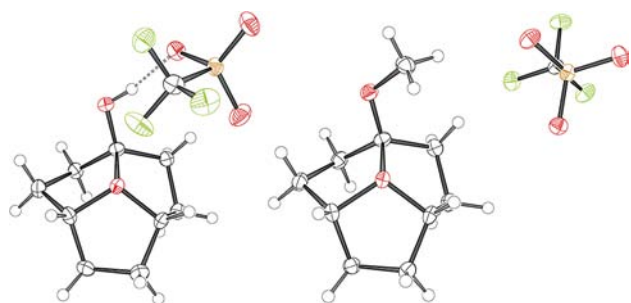


Figure 2. X-ray crystal structures of 11·OTf (left) and 12·OTf (right).

been used to predict the crystallographic C–O bond lengths of oxatriquinanes such as 3–5 with high accuracy,¹ it was proposed that in the present cases the absence of the counterion in the model was affecting the results, particularly for 11, which is involved in strong hydrogen bonding with a triflate oxygen. The computed bond lengths of interest for the triflate salts of 11 and 12 are given in Table 3, which show a

Table 3. Experimental and Calculated (MP2/6-31G**) C–O Bond Lengths (Å) for 11·OTf and 12·OTf

	model of 11·OTf ^a	crystal data for 11·OTf	model of 12·OTf ^a	crystal data for 12·OTf
O1–C2	1.668	1.658	1.624	1.619
C2–O3	1.334	1.339	1.351	1.358
O1–C4	1.501	1.501	1.514	1.521
O1–C5	1.498	1.498	1.508	1.510

^aSelf-consistent reaction field optimization in the conductor-like polarizable continuum model (CPCM) of ether ($\epsilon = 4.24$).

much closer agreement to the experimental data than those in Table 2. It is also noteworthy that, as the O1–C2 bond elongates, the bonds from O1 to the other two carbons (C4 and C5) contract, becoming even shorter than those of the parent oxatriquinane 3.

The chemical nature of the synthesized compounds 11–14 is peculiar. Similar in concept and yet distinct from the protonated hemiacetals and protonated acetals that appear as familiar intermediates in acetalization reactions (or acetal hydrolysis), cations 11 and 12 describe an O-alkylated hemiacetal and O-alkylated acetal, respectively. The former embodies an intermediate one might expect if attempting the acetalization of a ketone with acid and R₂O, while the latter would occur in an analogous acetalization with R₂O in the presence of an R₃O⁺ catalyst—reactions which, although plausible on paper, are not known to us. For 13 and 14, even less likely descriptions arise, i.e., the product of the addition of a hemiacetal to a protonated ketone (13), and the product of the addition of an acetal to an O-alkylated ketone (14).

An analogy can also be drawn between α -oxyoxonium species and α -aminoammonium salts, which also show considerable heteroatom-carbon-heteroatom bond length alternation.¹² However, the likeness ends there, since quaternized aminals are relatively stable, represented in the literature by about 140 X-ray crystal structures,¹³ while O-alkylated acetals are practically unknown. A side-by-side comparison of these species is only possible using modeling, since no aza analogues of 11–16 have been structurally characterized. Optimization of the simple formaldehyde acetal 25 and aminal 26 in a charged

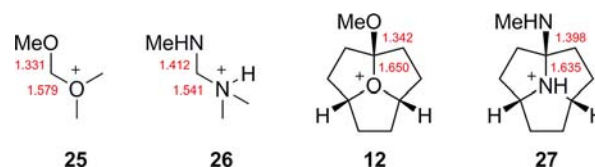


Figure 3. Modeled (MP2/6-31G**) formaldehyde and triquinane-based α -oxyoxonium and α -aminoammonium species, with bond lengths in Å.

(+1) state, as well as the protonated amino azatriquinane 27 alongside 12, gives the results shown in Figure 3. Here, we see that the more electronegative oxygen consistently produces a larger α effect, elongating the C–O⁺ bond to a relatively greater extent than does the nitrogen donor the C–N⁺ bond (CSD mean values for C–O and C–N are 1.42 Å and 1.47 Å, likewise for C–O⁺ and C–N⁺ 1.49 and 1.52 Å, respectively).¹⁴

In conclusion, we have previously studied the influence of sterics, ring strain, charge, coordination, and hyperconjugation effects on the nature of C–O bonding in oxonium salts. Here, we exploit conjugate electron donation within a robust oxatriquinane framework to achieve a new record C–O bond length. α -Oxy- and α,α' -dioxyoxatriquinanes were conveniently synthesized from known precursors. Attempts to prepare symmetric α,α',α'' -trioxyoxatriquinanes were however unsuccessful. Characterization of α -hydroxy and α -methoxy oxatriquinanes by X-ray crystallography revealed C–O⁺ bond distances of 1.658 and 1.619 Å, respectively, which outcome was consistent with modeling when the counterion was included in the calculation. α -Oxyoxonium ions are chemically eccentric species that represent frozen intermediates on the acetalization reaction landscape. Within the context of the oxatriquinane ring system, however, extremes in bonding such as these become freely observable.

■ ASSOCIATED CONTENT

Supporting Information

Detailed experimental procedures and ¹H and ¹³C NMR spectra for compounds 11–14, 18, 20, and 21; X-ray crystallographic files in CIF format for 11·OTf and 12·OTf; computed data (coordinates and energies) for 6–16 and 25–27. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was financially supported by National Science Foundation Grant CHE-0957798.

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