Proper Resonance Depiction of Acylium Cation: A High-Level and Student Computational Investigation

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ABSTRACT: The electronic and molecular structure of the acylium cation ([CH₃CO]+, 1) receives varied treatment in undergraduate textbooks and online resources. The overall structure of 1 is typically represented as an equal combination of resonance structures containing C=O triple and double bonds, the latter structure occasionally being shown with a bent C−C−O bond angle. This description is inconsistent with available experimental and theoretical data, all of which indicate that 1 is a linear molecule containing a C≡O bond, and can lead students to a false conception of structure, conjugation, and charge distribution. A set of simple computational exercises is reported that allows students to calculate and rationalize the most accurate resonance representation of 1.

KEYWORDS: Second-Year Undergraduate, Curriculum, Organic Chemistry, Misconceptions/Discrepant Events, Computational Chemistry, Covalent Bonding, Molecular Modeling, Reactive Intermediates, Resonance Theory

INTRODUCTION

The acylium cation ([CH₃CO]+, 1) is commonly encountered in the undergraduate organic chemistry curriculum because of its role as the prototypical electrophile in Friedel–Crafts acylation reactions and as a signature fragment in the electron-pushing mechanism of a Friedel–Crafts acylation, presumably to highlight the electrophilicity of the carbon atom by drawing attention to the formal positive charge. It is the methyl analogue of the formylium cation ([HCO]+), the equilibrium geometry of which has been determined in the gas phase via microwave spectroscopy. Analogous to the formylium cation, 1 is a C₃ᵥ symmetric molecule featuring a linear C−C−O moiety as determined by X-ray crystallography and infrared spectroscopy. The C−O bond distance (1.108(15) Å) and the IR C−O stretching frequency (2294 cm⁻¹) are consistent with a C−O triple bond. Unfortunately, the electronic and molecular structures of 1 are often misrepresented in contemporary organic chemistry textbooks and online resources. A survey of available undergraduate texts revealed an inconsistent treatment of 1, typically using some combination of resonance structures 1a−1c (Figure 1).

Only a minority of the texts surveyed show exclusively 1a or correctly highlighted the dominant contribution of 1a to the overall resonance hybrid while they depicted the resonance structures 1a and 1b. The majority of texts depict the overall resonance hybrid of 1 as comprising the two resonance contributors 1a and 1b but neglect discussion of their relative contributions. This omission leads the reader to assume either an ambiguous or approximately equal contribution of each resonance form. A number of textbooks exclusively employ 1b in the electron-pushing mechanism of a Friedel–Crafts acylation, presumably to highlight the electrophilicity of the carbon atom by drawing attention to the formal positive charge. The most inaccurate representations of 1 occur by showing 1b as the major contributor or by depicting a nonlinear molecule such as 1c. These depictions and theoretical descriptions create confusion among students and are not required in order to understand the structure and reactivity of 1.

Herein, the adoption of a resonance description of 1 is reported that is consistent with all available experimental and theoretical data and reduces student misconceptions regarding the bonding and structure of 1. First, the electronic structure of 1 is confirmed via a high-level computational study, and an accurate resonance depiction is provided via natural bond orbital (NBO) calculations. How the electronic structure and molecular geometry of 1 can be correctly determined by undergraduate students, using commonly available computational chemistry packages, is then demonstrated. The specific pedagogical goals of this activity are to provide students with a correct understanding of the molecular structure of 1, to explain the electrophilicity of 1 from a molecular orbital or...
charge distribution viewpoint, and to re-enforce the fact that formal atomic charges often misrepresent the true charge distribution in a molecule. The student exercises could be used either as supporting information for a lecture course or in combination with one of the many published Frieldel–Crafts laboratory experiments.\textsuperscript{27–33} The computational exercises have been performed by over 1500 students in a second-year undergraduate organic chemistry laboratory course as part of the lab report for the acylation of anisole.\textsuperscript{28}

\section*{COMPUTATIONAL METHODS}

Several levels of theory and basis sets were used to demonstrate that the correct representation of 1 is independent of the computational approach and is accessible with resources that are available at many undergraduate institutions. Each computational method produces similar structural parameters (Table 1), all of which are in close agreement with the C\textsubscript{3v} description of the overall geometry and electronic structure of 1. As shown below, a more accessible computational approach involving analysis of atomic charges and molecular orbitals of 1 can be employed to lead students to the same conclusion.

\textbf{Implementation in the Undergraduate Curriculum}

Students in the introductory organic chemistry laboratory course investigated the structure of 1 by obtaining the B3LYP/6-31G(d) optimized structure and performing a subsequent NBO calculation. The optimized structure was of C\textsubscript{3v} symmetry and was isoelectronic with acetonitrile (computational data for acetonitrile are included in the Supporting Information for those who wish to make this comparison explicitly with students). Performance of an NBO calculation on an optimized geometry in Gaussian09 required that a molecular orbital (MO) calculation was performed simultaneously. The output of the MO calculation allowed students to view the molecular orbitals, NBOs, Mulliken and natural population analysis (NPA)\textsuperscript{36} charges, and an electrostatic potential map of 1. Students rationalized the dominant contribution of 1a to the structure of 1 by viewing the two π and one σ NBOs of the C≡O unit. The carbon and oxygen atoms are connected by one σ bond (BD(1)C1−O2) and two π bonds (BD(2)C1−O2 and BD(3)C1−O2) as shown in Table 4, each with an occupancy of ~2 electrons. Students observed that these orbitals contain a total of ~6 shared electrons (5.99 e\textsuperscript{−}), a value that invalidates the assumption of a large contribution from 1b to the overall structure of 1. This observation caused a disequilibrium for many of the students who relied upon the formal positive charge on the carbon atom of 1b to justify the electrophilicity of 1, a situation that must be addressed in order

\begin{table}[h]
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\begin{tabular}{|c|c|c|c|c|}
\hline
Table 1. Calculated and Experimental Structural Parameters of 1\textsuperscript{4}
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Structural Parameter\textsuperscript{a} & B3LYP/6-31G(d) & B3LYP/6-311G**(2d,p) & MP2/cc-pVTZ & CCSD(T)/ANO2 & Exp \hline
R\textsubscript{c} C–O (Å) & 1.124 & 1.113 & 1.126 & 1.116 & 1.108(15)\textsuperscript{5} \hline
R\textsubscript{c} C–C (Å) & 1.434 & 1.427 & 1.433 & 1.441 & 1.385(16)\textsuperscript{5} \hline
R\textsubscript{c} C–H (Å) & 1.101 & 1.098 & 1.092 & 1.093 & \hline
Ac. C–H (°) & 108.587 & 108.355 & 107.933 & 107.687 & \hline
\hline
v\textsubscript{CO} (cm\textsuperscript{−1}) & 2373.3 & 2369.7 & 2289.5 & 2349.2 & 2294\textsuperscript{4} \hline
\hline
\end{tabular}
\end{table}

\textsuperscript{4}The nature of the theoretical structures as energy minima was confirmed by harmonic vibrational frequency calculation.

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Table 2. NBO 6.0/NRT Bond Orders of 1 Using Various Computational Methods
\hline
Level of Theory & C–C Bond Order & C–O Bond Order \hline
B3LYP/6-31G(d) & 1.09 & 2.91 \hline
B3LYP/6-311G**(2d,p) & 1.09 & 2.91 \hline
MP2/cc-pVTZ & 1.16 & 2.84 \hline
CCSD[T]/ANO2 & 1.06 & 2.94 \hline
\hline
\end{tabular}
\end{table}

These data, again, indicate that resonance structure 1b does not contribute in any meaningful sense to the overall structure of 1. Each of 1d–1f, which are not typically considered during a simple analysis of 1, contributes more to the overall structure than does 1b. Resonance structures 1d–1f arise from hyperconjugation of the three C–H donor orbitals with the two π\textsuperscript{a} C–O acceptor orbitals. In light of the above analyses, it is clear that resonance structure 1a is the most accurate

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Table 3. Contribution of Important Resonance Structures of 1 Obtained from NBO 6.0/NRT Calculations Using Various Computational Methods
\hline
Level of Theory & 1a & 1b & 1d & 1f \hline
B3LYP/6-31G(d) & 90% & <0.01% & 3% & 3% \hline
B3LYP/6-311G**(2d,p) & 90% & <0.01% & 3% & 3% \hline
MP2/cc-pVTZ & 82% & 4% & 4% & 4% \hline
CCSD[T]/ANO2 & 93% & 2% & 2% & 2% \hline
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\end{tabular}
\end{table}

\textsuperscript{5}The % contribution of each resonance structure to the overall resonance hybrid is rounded to the nearest whole number. \textsuperscript{6}This resonance structure is not explicitly listed in the NRT output but may be present in a summation of very low % contribution resonance structures. Both 1a and 1b were explicitly input as reference structures, though 1b was rejected because of very low contribution. \textsuperscript{5}The keyword density = current is not available for this method in Gaussian09. \textsuperscript{5}Previous work with NBO 3.1 did not indicate the inclusion of 1b as a reference structure.

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Table 4. Acylium (1) C–O Natural Bond Orbitals
\hline
NBO Designation & Orbital e\textsuperscript{−} & Occupancy \hline
BD(1)C1−O2 & 1.9995 \hline
BD(2)C1−O2 & 1.9959 \hline
BD(3)C1−O2 & 1.9959 \hline
\hline
\end{tabular}
\end{table}

\textsuperscript{4}Previous work with NBO 3.1 did not indicate the inclusion of 1b as a reference structure.
for these students to adopt a correct conception of the acylium cation.

Students were led to rationalize the electrophilicity of the carbon atom in 1 by calculating the atomic charges in the molecule and viewing the two degenerate C-\(\pi^*\) molecular orbitals. Both the Mulliken and NBO charges indicated that the carbon atom is positively charged and the oxygen atom is negatively charged (Figure 2). Additionally, visualization of the NBO \(\pi^*\) acceptor orbitals (BD*(2)C1-O2 and BD*(3)C1-O2) (Figure 2) showed the largest lobes to be located on the C atom, corresponding to its electrophilicity. These computational data, again, undermine the perceived importance of resonance structure 1b and also reminded students that formal charges are not necessarily indicative of the true charge distribution in a molecule.

### CONCLUSIONS

Computational studies at various levels of sophistication revealed that 1a is the most appropriate resonance structure for rationalizing the structure and reactivity of 1. The commonly invoked structure 1b makes no significant contribution to the overall resonance hybrid. This was unsurprising given that 1b requires the occupied 2p orbital of the O atom to remain unconjugated to the \(2p \pi^*\) orbital localized on the adjacent C atom. In reality, these orbitals are strongly conjugated because of their favorable overlap and similar size and symmetry. The electrophilicity of 1 was rationalized by recognition of the relative electronegativities of oxygen and carbon, by estimation of the individual atomic charges (either Mulliken or NBO charges, with the latter being more accurate), and visualization of the relative sizes of the C-\(\pi^*\) orbital lobes. The common argument that 1b assists students with understanding the correct charge and electrophilicity of the carbon atom is not necessary. In view of the data, it is recommended that discussion of the structure and reactivity of 1 does not include the insignificant resonance structure 1b, but instead uses exclusively structure 1a.

### ASSOCIATED CONTENT

#### Supporting Information

Summaries of geometry optimizations and harmonic vibrational frequency calculations from Gaussian09 and CFOUR, NBO/NRT analysis of acetone radical cation dissociation, instructions for use of WebMO/Gaussian, instructor notes, sample questions for students, and model answers. This material is available via the Internet at http://pubs.acs.org.

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**Notes**

The authors declare no competing financial interest.

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#### REFERENCES


