

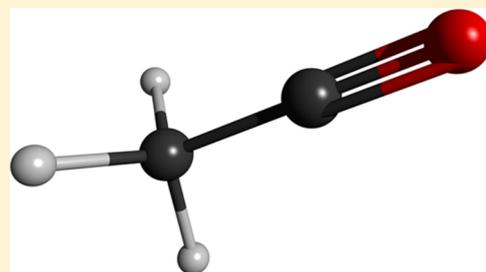
Proper Resonance Depiction of Acylium Cation: A High-Level and Student Computational Investigation

Brian J. Esselman* and Nicholas J. Hill

Department of Chemistry, University of Wisconsin–Madison, 1101 University Avenue, Madison, Wisconsin 53706, United States

S Supporting Information

ABSTRACT: The electronic and molecular structure of the acylium cation ($[\text{CH}_3\text{CO}]^+$, **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 $\text{C}\equiv\text{O}$ 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**.



Acylium Cation, $[\text{CH}_3\text{CO}]^+$

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

INTRODUCTION

The acylium cation ($[\text{CH}_3\text{CO}]^+$, **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-impact mass spectra of methyl ketones.^{1,2} It is the methyl analogue of the formylium cation ($[\text{HCO}]^+$), the equilibrium geometry of which has been determined in the gas phase via microwave spectroscopy.^{3,4} Analogous to the formylium cation, **1** is a C_{3v} symmetric molecule featuring a linear C–C–O moiety as determined by X-ray crystallography and infrared spectroscopy.^{5,6} The C–O bond distance (1.108(15) Å)⁵ and the IR C–O stretching frequency (2294 cm^{-1})⁶ 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^{7–26} 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**⁷ or correctly highlighted the dominant contribution of **1a** to the overall resonance hybrid while they depicted the resonance

structures **1a** and **1b**.^{8–12} 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.^{13–21} 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.^{14,16,18–22} The most inaccurate representations of **1** occur by showing **1b** as the major contributor^{22,23} or by depicting a nonlinear molecule such as **1c**.^{8,10,24–26} 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

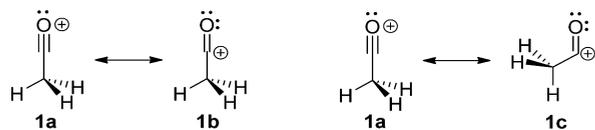


Figure 1. Resonance structures of **1** commonly employed in undergraduate textbooks.

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 Friedel–Crafts laboratory experiments.^{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.²⁸

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_{3v}

Table 1. Calculated and Experimental Structural Parameters of **1**^a

Structural Parameter ^a	B3LYP/6-31G(d)	B3LYP/6-311G+(2d,p)	MP2/cc-pVTZ	CCSD[T]/ANO2	Exp
 R _{C–O} (Å)	1.124	1.113	1.126	1.116	1.108(15) ⁵
R _{C–C} (Å)	1.434	1.427	1.433	1.441	1.385(16) ⁵
R _{C–H} (Å)	1.101	1.098	1.092	1.093	
A _{C–C–H} (°)	108.587	108.355	107.933	107.687	
$\nu_{C=O}$ (cm ^{–1})	2373.3	2369.7	2289.5	2349.2	2294 ⁶

^aThe nature of the theoretical structures as energy minima was confirmed by harmonic vibrational frequency calculation.

geometry of **1**⁵ (details of each computational method and a summary of the output files are provided in the Supporting Information). These data indicate that resonance structures **1b** and **1c** do not contribute significantly to the overall resonance hybrid of **1**.^{8–20,22–26,34}

This fact is further illustrated by NBO/natural resonance theory (NRT) calculations to determine the C–O and C–C bond orders of **1**. The NRT method allows the NBO calculation to estimate the individual contribution of each valid resonance structure to the overall resonance hybrid. Calculated C–C and C–O bond orders and % contributions of each resonance structure to the overall structure of **1** are shown at various levels of theory in Tables 2 and 3, respectively.

Table 2. NBO 6.0/NRT Bond Orders of **1** Using Various Computational Methods

Level of Theory	C–C Bond Order	C–O Bond Order
B3LYP/6-31G(d)	1.09	2.91
B3LYP/6-311G+(2d,p)	1.09	2.91
MP2/cc-pVTZ	1.16	2.84
CCSD[T]/ANO2	1.06	2.94

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 $\sigma_{C–H}$ donor orbitals with the two $\pi^*_{C–O}$ acceptor orbitals. In light of the above analyses, it is clear that resonance structure **1a** is the most accurate

Table 3. Contribution of Important Resonance Structures of **1** Obtained from NBO 6.0/NRT Calculations Using Various Computational Methods

Level of Theory	 1a	 1d	 1e	 1f	 1b
B3LYP/6-31G(d)	90% ^a	3%	3%	3%	0%
B3LYP/6-311G+(2d,p)	90%	3%	3%	3%	< 0.01% ^b
MP2/6-311G* ³⁵	82%	3%	3%	3%	^d
MP2/cc-pVTZ	81%	4%	4%	4%	0%
CCSD[T]/ANO2 ^c	93%	2%	2%	2%	< 0.17% ^b

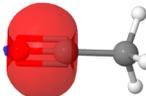
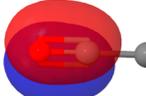
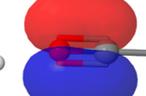
^aThe % contribution of each resonance structure to the overall resonance hybrid is rounded to the nearest whole number. ^bThis resonance structure is not explicitly listed in the NRT output but may be present in a summation of very low % contribution resonance structures. Both **1a** and **1b** were explicitly input as reference structures, though **1b** was rejected because of very low contribution. ^cThe keyword density = current is not available for this method in Gaussian09. ^dPrevious work with NBO 3.1 did not indicate the inclusion of **1b** as a reference structure.³⁵

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.

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_{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)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 $C\equiv O$ 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

Table 4. Acylium (**1**) C–O Natural Bond Orbitals

NBO Designation	Orbital e^- Occupancy	BD(1)C1–O2	BD(2)C1–O2	BD(3)C1–O2
	1.9995		1.9959	
		1.9995	1.9959	1.9959

occupancy of ~ 2 electrons. Students observed that these orbitals contain a total of ~ 6 shared electrons ($5.99 e^-$), 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

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–O π^* 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

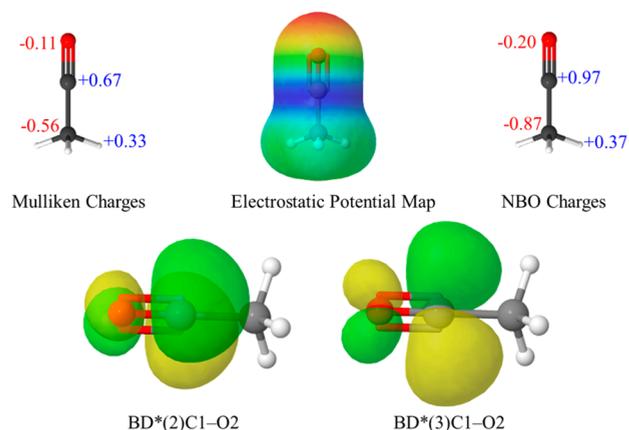


Figure 2. Carbon atom electrophilicity of **1** illustrated by atomic charges and molecular orbitals.

NBO π^* 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 π^* 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–O π^* 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>.

AUTHOR INFORMATION

Corresponding Author

*E-mail: besselman@chem.wisc.edu.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We gratefully acknowledge funding from the National Science Foundation for the support of shared departmental computing resources (CHE-0840494). We thank the students and teaching assistants of the CHEM 344 laboratory course for their feedback, and Frank Weinhold and Clark R. Landis for insightful discussions. We thank J. R. Schmidt, Desiree M. Bates, and Paul B. McGuire for their computational assistance.

REFERENCES

- Nummela, J. A.; Carpenter, B. K. Nonstatistical Dynamics in Deep Potential Wells: A Quasiclassical Trajectory Study of Methyl Loss from the Acetone Radical Cation. *J. Am. Chem. Soc.* **2002**, *124* (29), 8512–8513.
- Zhou, J.; Schlegel, H. B. Dissociation of Acetone Radical Cation ($\text{CH}_3\text{COCH}_3^+ \rightarrow \text{CH}_3\text{CO}^+ + \text{CH}_3\cdot$): An Ab Initio Direct Classical Trajectory Study of the Energy Dependence of the Branching Ratio. *J. Phys. Chem. A* **2008**, *112* (50), 13121–13127.
- Dore, L.; Beninati, S.; Puzzarini, C.; Cazzoli, G. Study of Vibrational Interactions in DCO^+ by Millimeter-Wave Spectroscopy and Determination of the Equilibrium Structure of the Formyl Ion. *J. Chem. Phys.* **2003**, *118* (17), 7857–7862.
- Woods, R. C.; Dixon, T. A.; Saykally, R. J.; Szanto, P. G. Laboratory Microwave Spectrum of HCO^+ . *Phys. Rev. Lett.* **1975**, *35* (19), 1269–1272.
- Boer, P. F. Crystal Structure of a Friedel–Crafts Intermediate. Methyloxocarbonium Hexafluoroantimonate. *J. Am. Chem. Soc.* **1968**, *90* (24), 6706–6710.
- Olah, G. A.; Kuhn, S. J.; Tolgyesi, W. S.; Baker, E. B. Stable Carbonium Ions. II. Oxocarbonium (Acylium) Tetrafluoroborates, Hexafluorophosphates, Hexafluoroantimonates, and Hexafluoroarsenates. Structure and Chemical Reactivity of Acyl Fluoride: Lewis Acid Fluoride Complexes. *J. Am. Chem. Soc.* **1962**, *84* (14), 2733–2740.
- Clayden, J.; Greeves, N.; Warren, S. *Organic Chemistry*, 2nd ed.; Oxford University Press: New York, 2012; p 477.
- Brown, W. H.; Iverson, B. L.; Anslyn, E. V.; Foote, C. S. *Organic Chemistry*, 7th ed.; Brooks/Cole, Cengage Learning: Belmont, CA, 2014; pp 934–935.
- Carey, F. A.; Giuliano, R. M. *Organic Chemistry*, 8th ed.; McGraw-Hill: New York, 2011; p 490.
- Carey, F. A.; Giuliano, R. M. *Organic Chemistry*, 9th ed.; McGraw Hill: New York, 2014; Vol. 467, pp 486–487.
- Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry Part A: Structure and Mechanisms*, 5th ed.; Springer: New York, 2008; Vol. 809–811, p 1019.
- Dewick, P. M. *Essentials of Organic Chemistry: For Students of Pharmacy, Medicinal Chemistry, and Biological Chemistry*; John Wiley & Sons, Inc.: West Sussex, England, 2006; p 308.
- Hornback, J. H. *Organic Chemistry*, 2nd ed.; Thomson Brooks/Cole: Belmont, CA, 2006; p 696.
- Vollhardt, K. P. C.; Schore, N. E. *Organic Chemistry: Structure and Function*, 7th ed.; W. H. Freeman and Company: New York, 2014; Vol. 681–682, p 744.
- Solomons, T. W. G.; Fryhle, C. B.; Snyder, S. A. *Organic Chemistry*, 11th ed.; John Wiley & Sons, Inc.: Hoboken, NJ, 2014; Vol. 437, pp 679–680.

- (16) McMurry, J. E. *Organic Chemistry with Biological Applications*; Brooks/Cole, Cengage Learning: Belmont, CA, 2011; p 334.
- (17) Loudon, M. G. *Organic Chemistry*, 5th ed.; Roberts and Company Publishers: Greenwood Village, CO, 2009; p 760.
- (18) Bruice, P. Y. *Organic Chemistry*, 7th ed.; Prentice Hall: Upper Saddle River, NJ, 2013; p 919.
- (19) Jones, M. J.; Fleming, S. A. *Organic Chemistry*, 5th ed.; W.W. Norton & Company: New York, 2014; pp 377–378, 710, 712, 775.
- (20) Karty, J. M. *Organic Chemistry: Principles and Mechanisms*, 1st ed.; W.W. Norton & Company, Inc.: New York, 2014; p 1078.
- (21) Wade, L. G. J. *Organic Chemistry*, 8th ed.; Pearson Education, Inc.: Glenview, IL, 2013; pp 782–783.
- (22) Klein, D. R. *Organic Chemistry*, 2nd ed.; John Wiley & Sons: Hoboken, NJ, 2012; pp 887–888.
- (23) Smith, M. B.; March, J. *March's Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*, 6th ed.; John Wiley & Sons, Inc.: Hoboken, NJ, 2007; p 243.
- (24) Wikipedia contributors. *Acyl*. <http://en.wikipedia.org/wiki/Acyl> (accessed December 2014).
- (25) Kürti, L.; Czakó, B. *Strategic Applications of Named Reactions in Organic Synthesis—Background and Detailed Mechanisms*; Elsevier Academic Press: Burlington, MA, 2005; p 176.
- (26) Smith, M. B. *Organic Synthesis*, 3rd ed.; Wavefunction, Inc: Irvine, CA, 2010; p 1204.
- (27) Jarret, R. M.; Keil, N.; Allen, S.; Cannon, L.; Coughlan, J.; Cusumano, L.; Nolan, B. Friedel–Crafts Acylation and Alkylation with Acid Chlorides. *J. Chem. Educ.* **1989**, 66 (12), 1056–1057.
- (28) Miles, W. H.; Nutaitis, C. F.; Anderton, C. A. Iron(III) Chloride as a Lewis Acid in the Friedel–Crafts Acylation Reaction. *J. Chem. Educ.* **1996**, 73 (3), 272.
- (29) French, L. G.; Stradling, S. S.; Dudley, M.; DeBottis, D.; Parisian, K. Introducing Environmentally Benign Synthesis into the Introductory Organic Lab—A Greener Friedel–Crafts Acylation. *Chem. Educ.* **2001**, 6 (1), 25–27.
- (30) Reeve, A. M. A Discovery-Based Friedel–Crafts Acylation Experiment: Student-Designed Experimental Procedure. *J. Chem. Educ.* **2004**, 81 (10), 1497–1499.
- (31) Bowman, D. C. Synthesis of 2-Acetylthiophene by the Acylation of Thiophene Using Acetic Anhydride and Iodine (A Revisiting after Almost Sixty Years). *Chem. Educ.* **2004**, 9 (3), 163–165.
- (32) Holden, M. S.; Crouch, R. D.; Barker, K. A. Formation of α -Tetralone by Intramolecular Friedel–Crafts Acylation. *J. Chem. Educ.* **2005**, 82 (6), 934–935.
- (33) Damkaci, F.; Dallas, M.; Wagner, M. A. Microwave-Assisted Friedel–Crafts Acylation of Toluene with Anhydrides. *J. Chem. Educ.* **2013**, 90 (3), 390–392.
- (34) Schupf, P. J. *Molecular Structure Calculations*. <http://www.colby.edu/chemistry/webmo/mointro.html> (accessed December 2014).
- (35) Xu, T.; Barich, D. H.; Torres, P. D.; Nicholas, J. B.; Haw, J. F. Carbon-13 Chemical Shift Tensors for Acylium Ions: A Combined Solid State NMR and Ab Initio Molecular Orbital Study. *J. Am. Chem. Soc.* **1997**, 119 (2), 396–405.
- (36) Reed, A. E.; Weinstock, R. B.; Weinhold, F. Natural Population Analysis. *J. Chem. Phys.* **1985**, 83 (2), 735–746.