

THE AROMATICITY OF MESOIONIC COMPOUNDS:

SYDNONES AND MÜNCHNONES

by

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(Under the Direction of Paul Schleyer)

ABSTRACT

Magnetic (dissected NICS) and energetic (Indene/Iso-indene type evaluations of aromatic stabilization) criteria confirm that the closed forms of sydnone and münchnone, are indeed aromatic, comparable to benzene, furan, or pyrrole. While CH₃, NH₂, OH, F, CN, and NO₂ substituents on nitrogen have nearly the same effects on the energy differences (ΔE) between closed and open forms of both sydnones and münchnones, all the sydnones prefer cyclic minima, whereas some of the münchnones (including the parent) favor open structures. Aromaticity stabilizes the closed forms of münchnones, while amide resonance stabilizes the open forms to a comparable extent. Sydnones prefer the closed form more than münchnones because the energy of the N=O bond of open sydnones is far less favorable than that of the C=O amide bond in open münchnones. For sydnones and münchnones, the ΔE values plot best against Taft σ inductive (rather than Hammett σ) constants.

INDEX WORDS: Mesoionic, Aromaticity, Sydnone, Münchnone

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CHAPTER 1

INTRODUCTION, LITERATURE REVIEW, AND STATEMENT OF PROBLEM

In the IUPAC definition, mesoionic¹ compounds are “Dipolar five- (and possibly six-) membered heterocyclic compounds in which both the negative and positive charges are delocalized, for which a totally covalent structure cannot be written, and which cannot be represented satisfactorily by any one polar structure. The formal positive charge is associated with ring atoms, and the formal negative charge is associated with ring atoms or an exocyclic nitrogen or chalcogen atom.” Mesoionic compounds have found a variety of uses including ligands for Grubb’s catalyst,² proton-conducting gels,³ pharmaceutical agents and drugs,⁴ and nonlinear optical materials.⁵

Two representative members of the class of mesoionic compounds are sydnone and münchnone. Sydnone (from “SYDney” + “lactONE”) was first synthesized by Earl and Mackney in 1935⁶ (see Figure 1). The related münchnone was first prepared by Lawson and Miles in 1958.⁷ Rolf Huisgen et al. established the structure and reactivity of münchnones (from “MÜNCHeN”, German for Munich, + “lactONE”).⁸ Since then, recent reviews of mesoionic compounds in general⁹ and sydnone specifically¹⁰ have appeared in the literature.

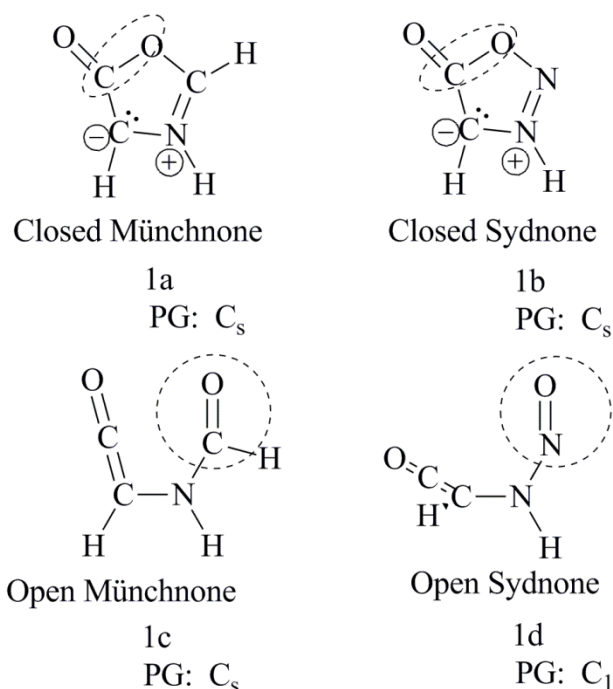


Figure 1. Open and closed forms of the parent münchnone and sydnone. The endocyclic C-O bonds mentioned in this study are circled. The amide C=O bond of open münchnone and N=O bond of open sydnone are selected as well. Point groups (PG) are given below each molecule.

Aromaticity is generally determined by chemical behavior (a preference for electrophilic aromatic substitution over addition reactions), structure (bond length equalization due to cyclic delocalization), energetic (enhanced stability, e.g. a large resonance energy), and magnetic (ring current effects induced in a magnetic field).¹¹ Whether or not mesoionic compounds like sydnone and münchnone are aromatic is still controversial. Sydnones and münchnones have significant differences in bond lengths around the ring, but do have six π electrons in a delocalized environment (Hückel's $(4n + 2)$ π electrons and do participate in electrophilic aromatic substitution reactions.^{10,12} The magnetic criteria of aromaticity has been applied to mesoionic compounds in limited studies in the form of Nucleus-Independent Chemical Shifts. Aromatic stabilization energies (ASE's) are yet to be applied to mesoionic compounds. Before studying this

class of compounds, it is important to examine the background scientific literature on the subject of aromaticity in mesoionic compounds sydnone and münchnone.

What are arguments against aromaticity in mesoionic compounds based on structural criteria? “Are mesoionic compounds aromatic?”¹³ According to Simas et al.¹³, “The combination of the synthetic and kinetic studies indicates clearly that the mesoionic systems studied [in general] have well-separated positive and negative regions able to act independently as electron-deficient and electron-rich functions. This is tantamount to indicating that mesoionic compounds should not be considered aromatic.” Sydnones can be divided into an ylide unit (with negative and positive charges balanced to make an overall neutral unit) and a neutral CO₂ unit (see Figure 2). This division into two parts has no relevance to aromaticity. The ylide part can be separated from the CO₂ portion in chemical reactions.

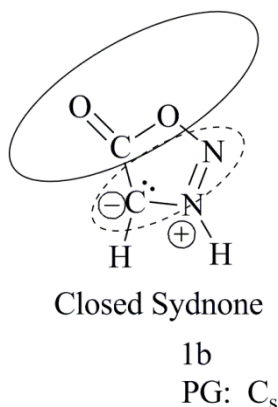
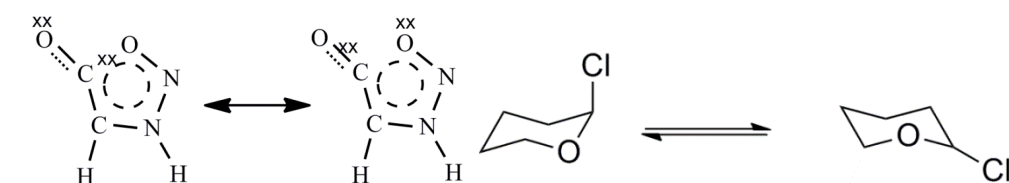


Figure 2. Sydnone ylide unit (dotted circle) and CO₂ unit (solid circle).

Furthermore, “the unusually long endocyclic C-O bond” (actually 1.407 Å¹⁴) has “little or no π character” (compared to furan’s length of 1.362 Å¹⁴). “These [x-ray studies] indicated clearly the existence of two regions in each of which bond distances correspond to the existence of electron and charge delocalization and that these two regions are

separated by what are essentially single bonds.” The anomeric effect is likely responsible for the longer sydnone C-O bond, although the length is between that for a single and double bond, as expected for an aromatic system. The typical lengths of C-O single and double bonds are 1.42 and 1.21 Å respectively.¹⁵ The bond length here has little to do with aromaticity of sydnone. “This delocalization appears to lend extra p character to the carbon orbital associated with the ring oxygen, thereby lengthening that bond, and to detract p character from the other two orbitals of carbon, shortening those bonds and widening the angle between them.¹⁴” An examination of the π character follows in the Results and Discussion Section. The computed bond lengths for the indicated C-O bond of sydnone is 1.472 Å, consistent with the anomeric effect.¹⁶ Figure 16 shows bond lengths for sydnone and münchnone in this study. It is longer than the aromatic C-O bond in furan due to the anomeric effect. The anomeric effect involves a preference for the axial position for polar groups in sugars due to overlap of the σ lone pair on oxygen with the π^* antibonding orbital of the C-Cl bond (for example).



PG: C_s

Figure 3. Anomeric effect for sydnone and cyclic ether.

How has the structural criterion been applied to mesoionic compounds in general to demonstrate aromaticity? Irshaidat studied the submolecular charge distribution of the compound shown in Figure 4 by means of Mulliken, NPA, APT, and ChelpG atomic charge schemes and the aromaticity through a variant of HOMA (Harmonic Oscillator

Model of Aromaticity).¹⁷ The aromaticity of the system ranged from 0.83 to 0.86 depending on the substituents R, where that of benzene is 1.00 on this scale. The distribution of electron density was determined in a positively charged model system lacking the sulfur substituent. The aromatic p-orbitals charge was controllable in the model compound (see Figure 4, 4b).

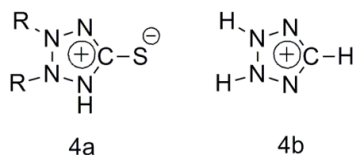


Figure 4. SCN_4R_2 (4a) system examined by Irshaidat.¹⁷ R = Methyl, Ethyl, Propyl, or Phenyl.

Bird¹⁸ created a structural aromaticity (I_5) index that ranked mesoionic compounds from a low of 0 to a high of 88 (where furan was 43 and pyrrole was 59 for reference). Bird's index was based upon the "statistical degree of uniformity of the bond orders of the ring periphery."¹⁸ This I_5 index is a measure of the structural criterion of aromaticity, where idealized aromatic systems feature bond length equalization (100 on Bird's scale). The bond orders were calculated from bond lengths using the Gordy relationship from Bird's paper ($N = a/R^2 - b$, where N = bond orders, R = bond length, and a and b are constants from Table 1).¹⁸ This geometric index could not be used to compare different ring sizes. Bird found that his I_5 index tracked qualitatively with experimental resonance energies (ERE). Refer to Table 2 for a listing of these resonance energies and aromaticity index (I_5) values. The wide range of uncertainty in the experimental resonance energies prevents the establishment of a quantitative relationship. These resonance energies were evaluated in the 1970s and vary widely. The fact that several of the I_5 Bird index values

given in Figure 5 are relatively high contradicts Simas's argument that mesoionic compounds are not aromatic on the basis of the bond lengths.

Table 1. Gordy relationship a and b constants.

Bond	a	b
C-C	6.80	1.71
C-N	6.48	2.0
C-O	5.75	1.85
C-S	11.9	2.59
N-N	5.28	1.41
N-O	4.98	1.45
N-S	10.53	2.50
O-S	17.05	5.58
S-S	19.30	3.46

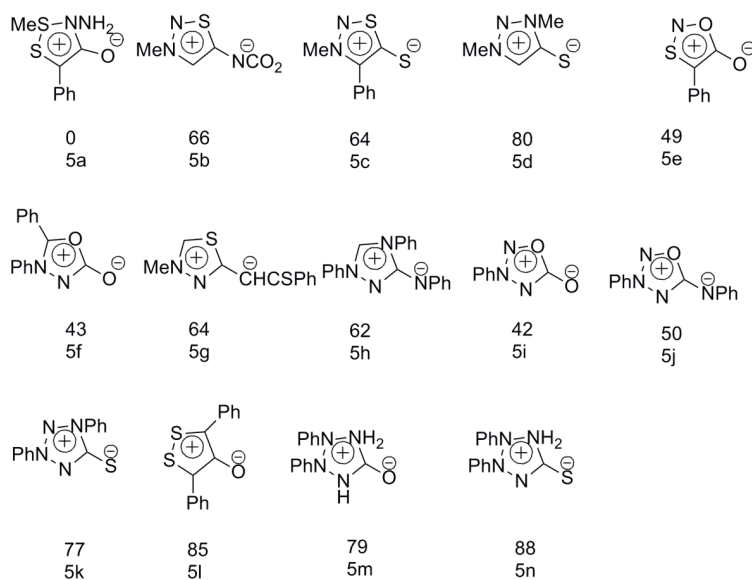


Figure 5. Bird aromaticity (I_5) values for mesoionic compounds.¹⁸ Pyrrole and furan were 59 and 43 respectively.

Table 2. Comparison of aromaticity indices [I_5] with experimental resonance energies (ERE).

Heterocycle	Aromaticity Index	ERE (experimental resonance energies) kJ/mol
Furan	43	34-96
Isoxazole	47	4-46
1,3,4-Oxadiazole	50	167
Pyrrole	59	59-130
Imidazole	64	51-134
Thiazole	64	42-50
Thiophene	66	84-117
Tetrazole	72	231-293
Pyrazole	73	112-174

The discussion of prior literature featuring the magnetic criterion is based on NICS indices (Nucleus-Independent Chemical Shifts).¹⁹⁻²⁰ Isotropic NICS(0), computed at the ring heavy atom center, includes significant contamination from the σ bond framework and does not differentiate the directionality of aromatic π bonds well (contamination from xx and yy tensors).¹⁹⁻²⁰ Negative NICS values denote aromaticity, positive NICS values denote antiaromaticity, and values near zero denote nonaromatic systems.¹⁹⁻²⁰ NICS(1)zz is the NICS magnetic tensor in the zz-direction as calculated 1 Å above the ring center, which reduces contamination from the σ framework.¹⁹⁻²⁰ Fabian et al.²¹ computed Nucleus-Independent Chemical Shifts (NICS(0)) isotropic calculations of -5.4 and -10.1 for two sulfur-containing mesoionic compounds, one of which was more aromatic than benzene (see Figure 6). NICS(0) isotropic for benzene is -7.97.²²

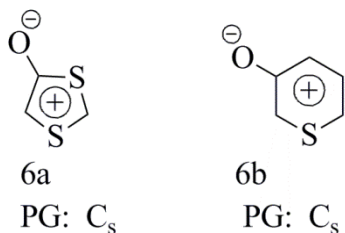


Figure 6. Sulfur-containing mesoionic compounds in Fabian's study.²¹

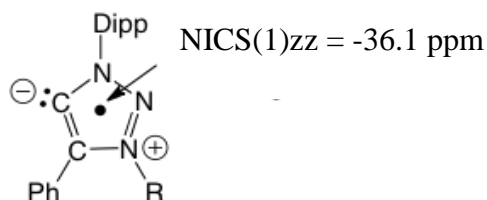
Bouffard et al.^{2b} found that a mesoionic ligand (see Figure 7) used to enhance the performance of Grubb's catalyst was aromatic with a NICS(0) of -14.9 ppm and NICS(1)zz of -36.1 ppm. In comparison, NICS(1)zz for benzene is -29.0¹⁹ and NICS(0) is given above.

NICS(0) isotropic at ring

center and NICS(1)zz at

1 Å above ring center

NICS(0) = -14.9 ppm and



PG: C₁

Figure 7. NICS (Nucleus Independent Chemical Shifts) diagram of mesoionic carbene ligand used in Grubb's catalyst.^{2b} (Dipp = 2,6-Diisopropylphenyl; R= methyl or isopropyl) Dipp, Ph, and R are all = H for the NICS calculation on the parent mesoionic carbene in the study above.

Evidence for the open form of münchnones has appeared in the literature. Huisgen had trapped "the amidoketene intermediate (see Figure 1) with certain imines in [2 + 2] cycloadditions at 100 degrees Celsius."²³ Dewar et al.²⁴ found through MINDO/3 calculations that the N-methyl ketene valence tautomer was 31 to 36 kJ/mol (7.4 to 8.6 kcal/mol) higher than the N-methyl closed form of münchnone. Both forms can be reached in a chemical reaction, although they do not equilibrate. Apparently, münchnone has both open and closed forms. Fabian et al.²¹ computed both closed and open forms for the mesoionics shown in Figure 6. "The ring-opening is endothermic, with a noticeable barrier, whereas the ring-closure is exothermic with a very low reaction barrier."²¹ Whether or not the mesoionic compounds sydnone and münchnone are aromatic and an examination of the factors that control conversion between open and closed forms are the subjects of this thesis.

CHAPTER 2

METHODS

All geometries were optimized at the MP2(fc)/cc-pvdz level as implemented in Gaussian 03²⁵ followed by harmonic vibrational frequencies at the same level to establish the nature of the stationary points. All MP2(fc) zero-point vibrational energies (ZPVE) were scaled by 0.9784 as recommended by Sinha et al²⁶ for the cc-pvdz basis set and 0.9557 for the aug-cc-pvtz basis set. The NICS(0) _{π zz} data, the most sophisticated and highly recommended NICS(0) _{π zz} index, where negative (diatropic) values generally denote aromaticity, positive (paratropic) values antiaromaticity, and values near zero denote nonaromaticity, were computed using the localized molecular orbital (LMO)²⁷ dissection at the PW91/IGLO-III DFT level with the individual gauge for localized orbitals (IGLO) method²⁸ (as implemented in the deMon NMR program²⁹) utilizing the Pipek-Mezey localization algorithm.³⁰ The LMO dissection separates the total NMR shielding tensors into individually localized MO contributions of bonds and lone pairs. The NBO analysis involved Natural Resonance Theory³¹ using the NBO 5.0 program,³² as implemented in Gaussian 98³³ at the B3LYP/cc-pvdz//MP2(fc)/cc-pvdz and MP2(fc)/cc-pvdz//MP2(fc)/cc-pvdz levels of theory. ASE's (aromatic stabilization energies) were computed by means of the Indene/Iso-indene method (see Figure 11 for a pictorial description).³⁴ Block Localized Wavefunction³⁵ (BLW) computations, designed for evaluating resonance energies for both cyclic and acyclic conjugated molecules without additional reference compounds (the compounds themselves serve as the references),

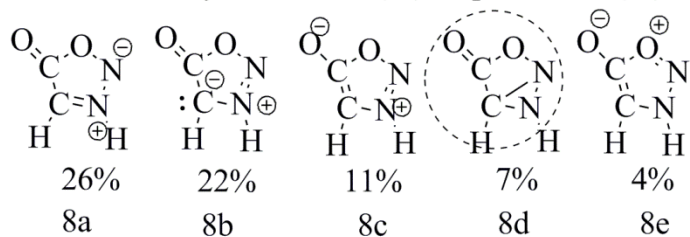
were performed at the B3LYP/6-31G* level as implemented in the GAMESS R5 version.³⁶ Block Localized Wavefunction Resonance Energies (BLW RE's) adopt the Pauling-Wheland³⁷ definition and are the computed total energy difference between the completely delocalized conjugated molecule and that of its most stable resonance contributor.³⁵

CHAPTER 3

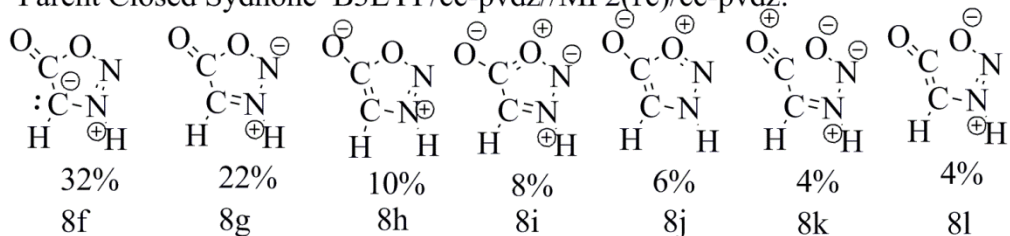
RESULTS AND DISCUSSION

The IUPAC definition¹ for mesoionic compounds, as quoted on page 1, is incomplete and incorrect, as covalent forms of the parent sydnone and münchnone can be drawn (see circled sydnone and münchnone in Figure 8). NRT, Natural Resonance Theory,³¹ analysis for the open forms of sydnone and münchnone are shown in Figure 9, where it should be noted that these forms are not mesoionic. Natural Resonance Theory is a means of determining both Lewis and non-Lewis structures for a compound and the weight each carries. NBO,³² (Natural Bond Orbital) a suite for calculating molecular properties of molecules such as the hybridization of individual atoms, analysis reveals that the endocyclic C-O bond (closest to the exocyclic carbonyl) has significant p character, and therefore is at least a partial π bond (münchnone: 73% p on the endocyclic oxygen and 81% p on the endocyclic carbon and sydnone: 70% p on the endocyclic oxygen and 78% p on the endocyclic carbon). Thus Simas's argument that the endocyclic C-O bond had little or no π character is refuted.¹³

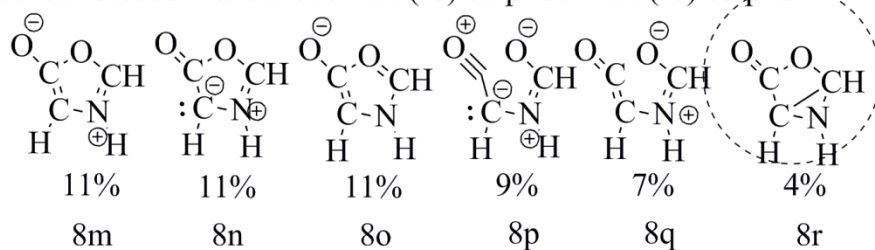
Parent Closed Sydnone MP2(fc)/cc-pvdz//MP2(fc)/cc-pvdz:



Parent Closed Sydnone B3LYP/cc-pvdz//MP2(fc)/cc-pvdz:



Parent Closed Münchnone MP2(fc)/cc-pvdz//MP2(fc)/cc-pvdz:



Parent Closed Münchnone B3LYP/cc-pvdz//MP2(fc)/cc-pvdz:

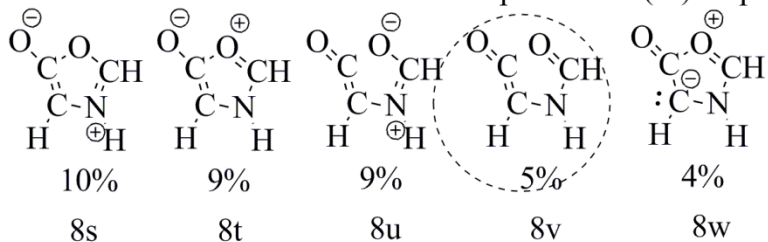


Figure 8. The leading NRT³¹ (Natural Resonance Theory) contributors for closed sydnone and münchnone. Covalent forms for each are circled.

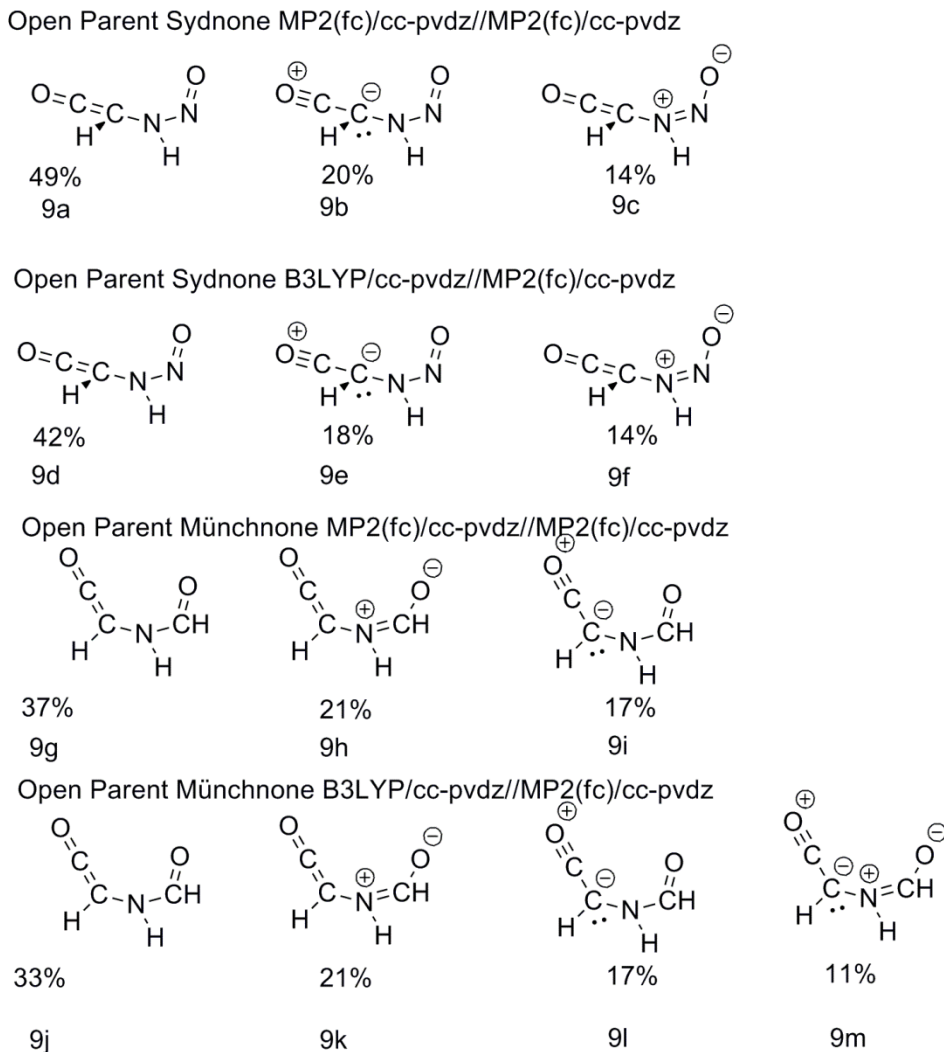


Figure 9. The leading NRT³¹ (Natural Resonance Theory) contributors for open sydnone and münchnone.

Are sydnone and münchnone aromatic? The LMO NICS(0)_{πzz} 6π totals (Table 3) for sydnone and münchnone are less than that of benzene, furan, and pyrrole. Figure 10 shows the individual contributions of bonds and lone pairs to LMO NICS(0)_{πzz}. The benzene value compares favorably to that previously published.³⁸ It is important to note that sydnone and münchnone have four π MO's, of which the HOMO is that of the exocyclic carbonyl π orbital and is excluded in the ring aromaticity. Sydnone and münchnone are nearly as aromatic as benzene energetically (ASE—aromatic stabilization energy); where the value for benzene compares to that previously published (see Figure

11 for how the ASE's are calculated).^{34b} Figure 12 reveals the anti-syn butadiene difference of 3.6 kcal/mol.^{34a} There are two such mismatches for benzene (for a correction of 7.2 kcal/mol) and 1 for both pyrrole and furan (3.6 kcal/mol correction). Mesoionic compounds sydnone and münchnone have no syn-anti mismatches and therefore do not need to be corrected (listed as uncorrected in Figure 11). The ASE's are a measure of a change from an aromatic to a nonaromatic isomer.^{35b} Contrary to Simas's argument¹³ that systems such as sydnone and münchnone are not aromatic due to well-defined but separate, non-overlapping regions of positive and negative charge, mesoionic compounds are indeed aromatic (see Figure 2 for a division of sydnone into CO₂ and ylide portions).

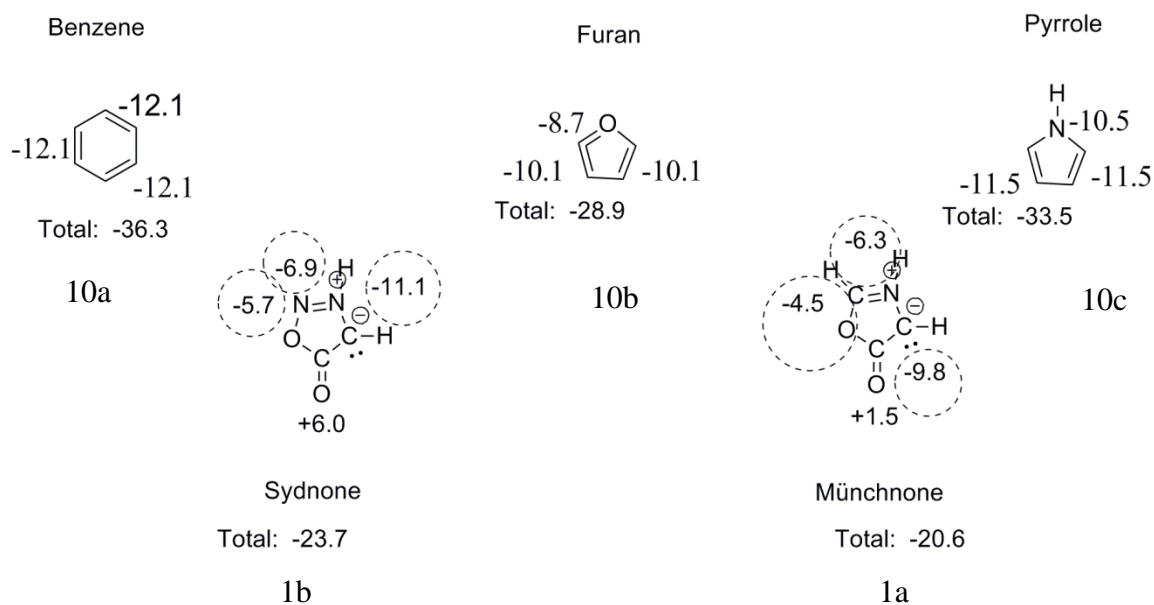


Figure 10. Computed dissected LMO NICS(0)_{πzz} for benzene, sydnone, and münchnone at PW91PW91/IGLO-III//MP2(fc)/cc-pvdz. The circled contributions are added together to derive the NICS(0)_{πzz} 6π totals for sydnone, münchnone, and benzene.²⁷

Table 3. NICS(0) $_{\pi_{zz}}$ 6π and ASE's for benzene, furan, pyrrole, sydnone, and münchnone*

Molecule	NICS(0) $_{\pi_{zz}}$ ppm	ASE(uncorrected in parentheses) kcal/mol	Point Group
Benzene (8a)	-36.3	(23.8)31.0	D _{6h}
Pyrrole(8b)	-33.5	(13.1)16.7	C _{2v}
Furan(8c)	-28.9	(8.9)12.5	C _{2v}
Sydnone (1b)	-23.7	27.0	C _s
Münchnone (1a)	-20.6	28.2	C _s

*The LMO²⁷ NICS(0) $_{\pi_{zz}}$ is the best NICS index for evaluating aromaticity because it divides the shielding tensors in the zz-direction into individual contributions from π bonds and lone pairs (computed at PW91PW91/IGLO-III//MP2(fc)/cc-pvdz). ASE's at the RMP2(fc)/cc-pvdz//RMP2(fc)/cc-pvdz + scaled ZPVE (0.9784²⁶). Correction of 7.2 was applied to the benzene ASE model due to the presence of anti-syn diene mismatches.^{34a}

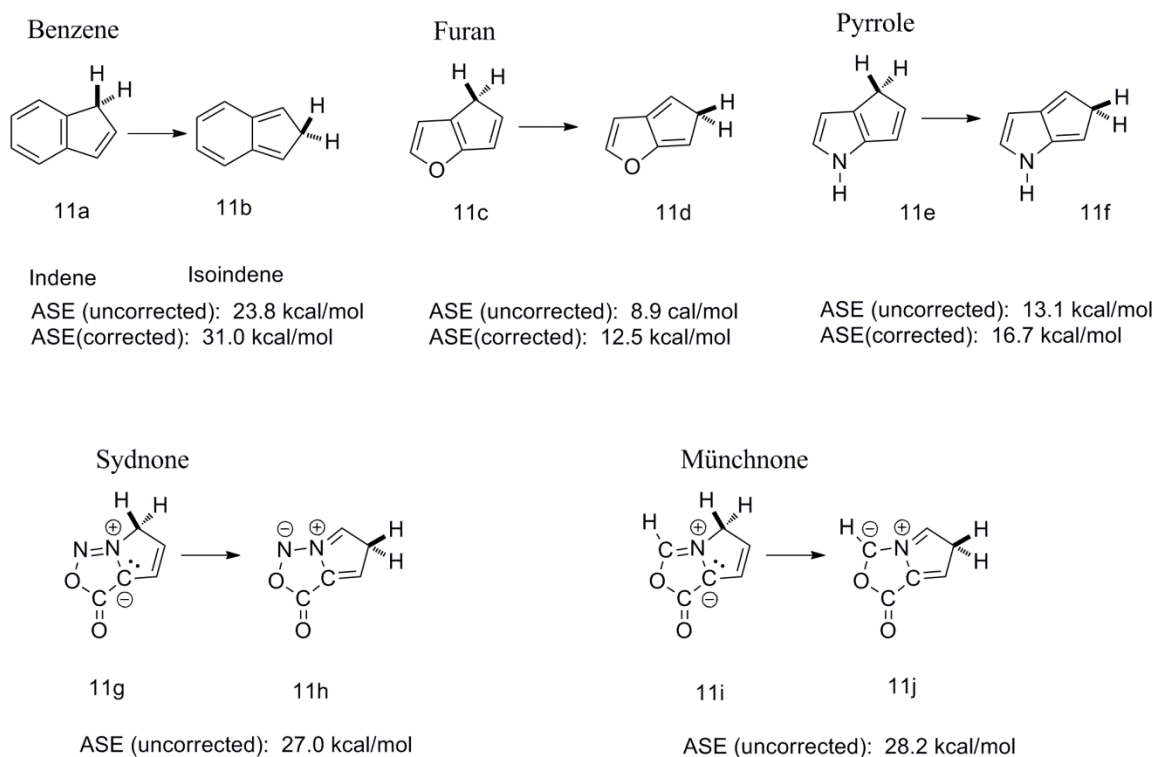


Figure 11. Indene/Iso-indene ASE computations. Correction of 7.2 applied to benzene due to two syn-anti butadiene mismatches and 3.6 applied to both pyrrole and furan due to one such mismatch.^{34a}

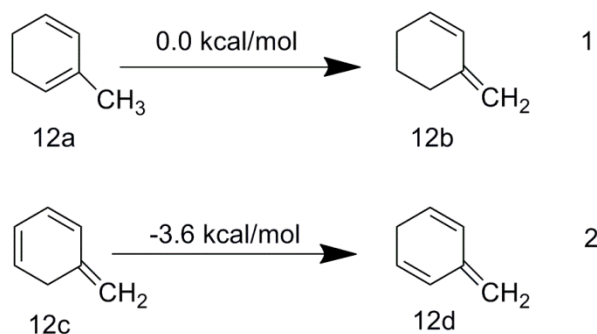
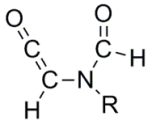
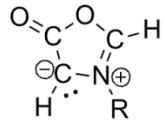


Figure 12. Equation 1 and Equation 2 show the 3.6 kcal/mol correction needed because of the anti-syn butadiene energy difference.^{34a}

Contrary to the expectation that resonance effects would dominate certain interactions, the substituent effects are mostly of an inductive nature. CH_3 , NH_2 , OH , F , CN , and NO_2 substituent effects were computed for open and closed forms of both sydnone and münchnone (ΔE values in Table 4 and 5). Their R^2 values show that these substituents plot best against Taft (σ_I) Sigma Inductive parameters (Figures 13 and 14). This shows that inductive effects dominate. The unit slope of Figure 15 shows that the substituents affect the energy difference ΔE in nearly the same way for both sydnones and münchnones.

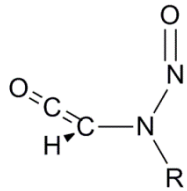
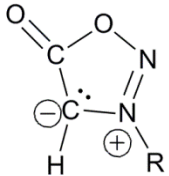
Table 4. Computed energy differences (total electronic energy) for substituted münchnones in kcal/mol*

R	Total Electronic Energy (a.u.) Open  (compound identification number in parentheses) Point Group	Total Electronic Energy (a.u.) Closed  (compound identification number in parentheses) Point Group	ΔE kcal/mol**	Relative ΔE kcal/mol	Most Stable Form
H	-320.41910 (1c) C_s	-320.41774 (1a) C_s	0.9	0.0	Open
CH ₃	-359.59558 (t4a) C_s	-359.59727 (t4b) C_s	-1.0	-1.9	Closed
NH ₂	-375.58705 (t4c) C_1	-375.58719 (t4d) C_s	-0.1	-1.0	Closed
OH	-395.40181 (t4e) C_1	-395.39937 (t4f) C_1	1.5	0.6	Open
F	-419.37028 (t4g) C_1	-419.35868 (t4h) C_s	7.2	6.3	Open
CN	-412.40354 (t4i) C_s	-412.38996* (t4j) C_s	8.5	7.6	Open
NO ₂	-524.41545 (t4k) C_s	-524.40136* (t4l) C_s	8.8	7.9	Open

*Z-matrix (as given in Appendix A) was used with an endocyclic C-O bond length fixed at 1.551 Å (the value for the closed münchnone) for substituted münchnones (closed CN and NO₂) that have no closed form minima.

** ΔE is calculated as the difference between the total electronic energy of the open form and the total electronic energy of the closed form at the MP2(fc)/cc-pvdz//MP2(fc)/cc-pvdz level of theory without ZPVE for all cases.

Table 5. Computed energy differences (total electronic energy) for substituted sydnones in kcal/mol*

R	Total Electronic Energy (a.u.) Open  (compound identification number in parentheses) Point Group	Total Electronic Energy (a.u.) Closed  (compound identification number in parentheses) Point Group	ΔE kcal/mol	Relative ΔE kcal/mol	Most Stable Form
H	-336.35633 (1d) C_1	-336.40197 (1b) C_s	-28.6	0.0	Closed
CH ₃	-375.53582 (t5a) C_1	-375.58443 (t5b) C_s	-30.5	-1.9	Closed
NH ₂	-391.52830 (t5c) C_1	-391.57483 (t5d) C_1	-29.2	-0.6	Closed
OH	-411.33958 (t5e) C_1	-411.38948 (t5f) C_s	-31.3	-2.7	Closed
F	-435.30970 (t5g) C_1	-435.34606 (t5h) C_s	-22.8	5.8	Closed
CN	-428.34012 (t5i) C_1	-428.37102 (t5j) C_s	-19.4	9.2	Closed
NO ₂	-540.35101 (t5k) C_1	-540.38465 (t5l) C_s	-21.1	7.5	Closed

* ΔE is calculated as the difference between the total electronic energy of the open form and the total electronic energy of the closed form at the MP2(fc)/cc-pvdz//MP2(fc)/cc-pvdz level of theory without ZPVE.

Table 6. Substituent σ constants

Substituent	Hammett Sigma Para (σ_p) ³⁹	Hammett Sigma Meta (σ_m) ³⁹	Taft Sigma Inductive (σ_I) ⁴⁰
CH ₃	-0.17	-0.07	-0.01
NH ₂	-0.66	-0.16	0.17
OH	-0.37	0.12	0.24
F	0.06	0.34	0.54
CN	0.66	0.56	0.57
NO ₂	0.78	0.71	0.67

³⁹Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165.

⁴⁰Datta, D. *J. Phys. Org. Chem.* **1991**, *4*, 96.

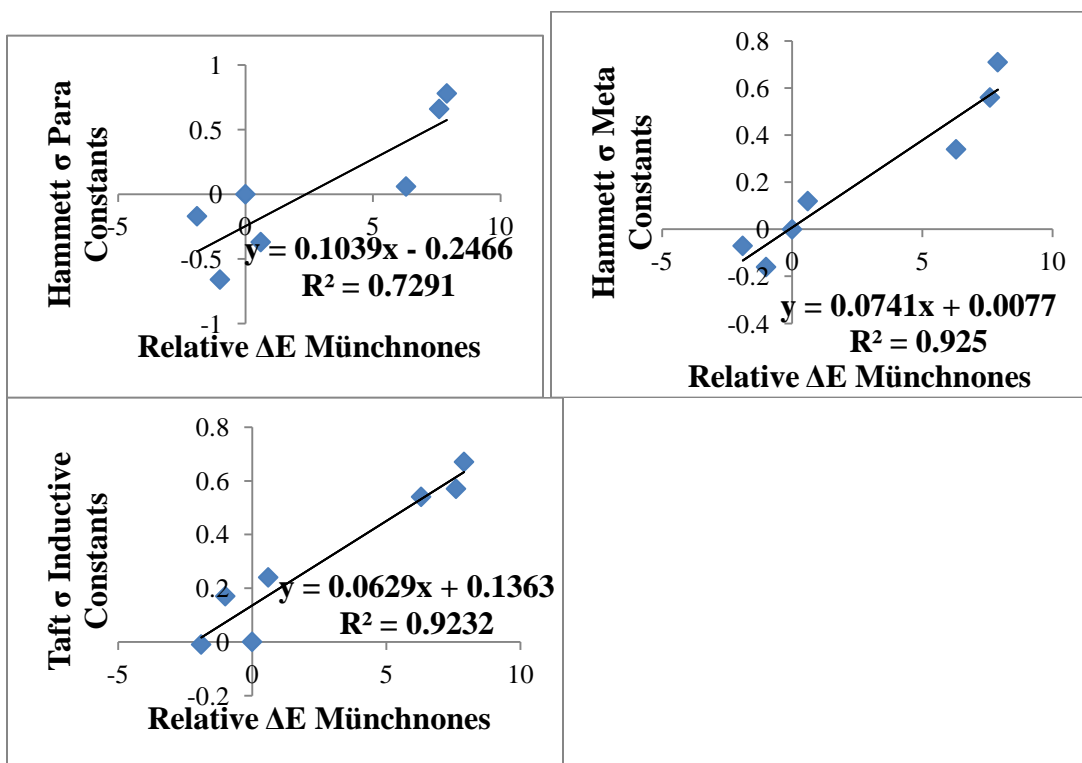


Figure13. Plot of Hammett Sigma Para (σ_p) (top left), Sigma Meta (σ_m) (top right) and Taft Sigma Inductive (σ_I) (bottom left) Parameters versus Relative ΔE column (kcal/mol) of Table 2 for Münchnones.

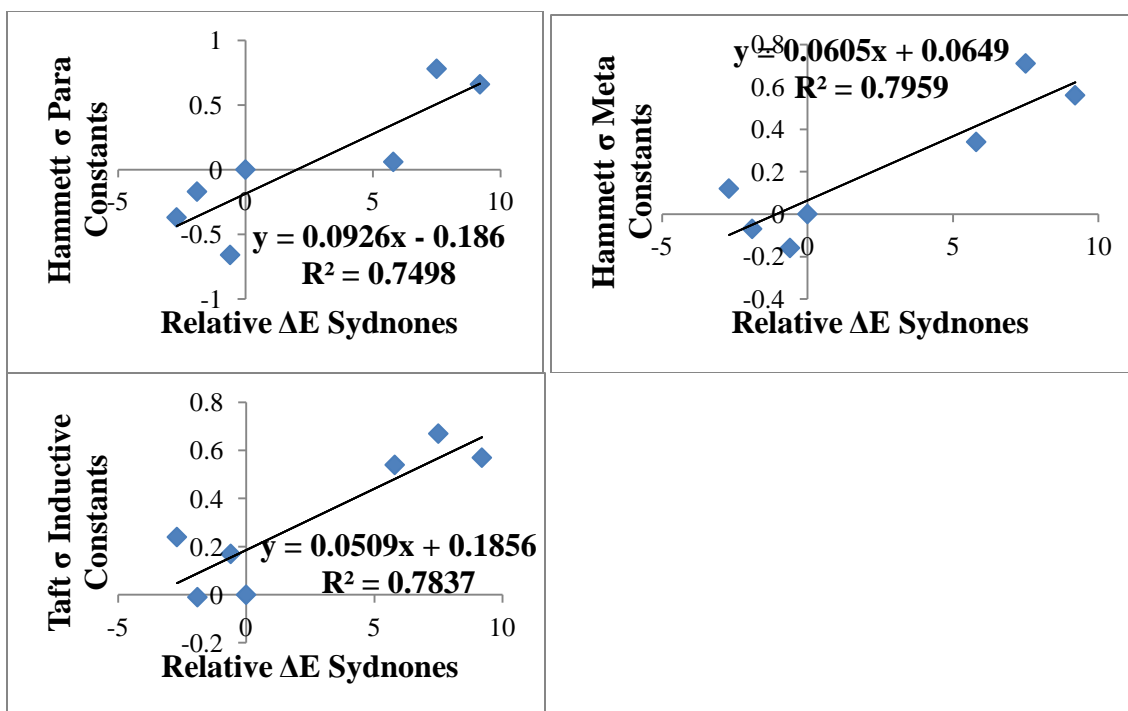


Figure 14. Plot of Hammett Sigma Para (σ_p) (top left), Sigma Meta (σ_m) (top right) and Taft Sigma Inductive (σ_I) (bottom left) Parameters versus Relative ΔE column (kcal/mol) of Table 3 for Sydnonnes.

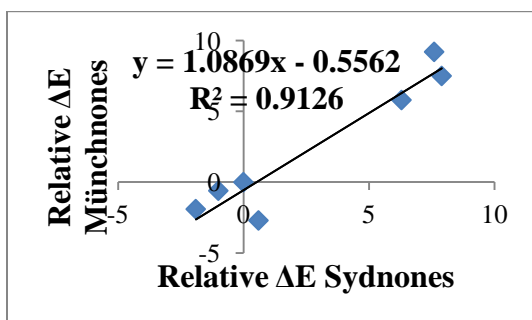
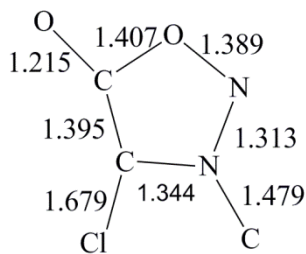
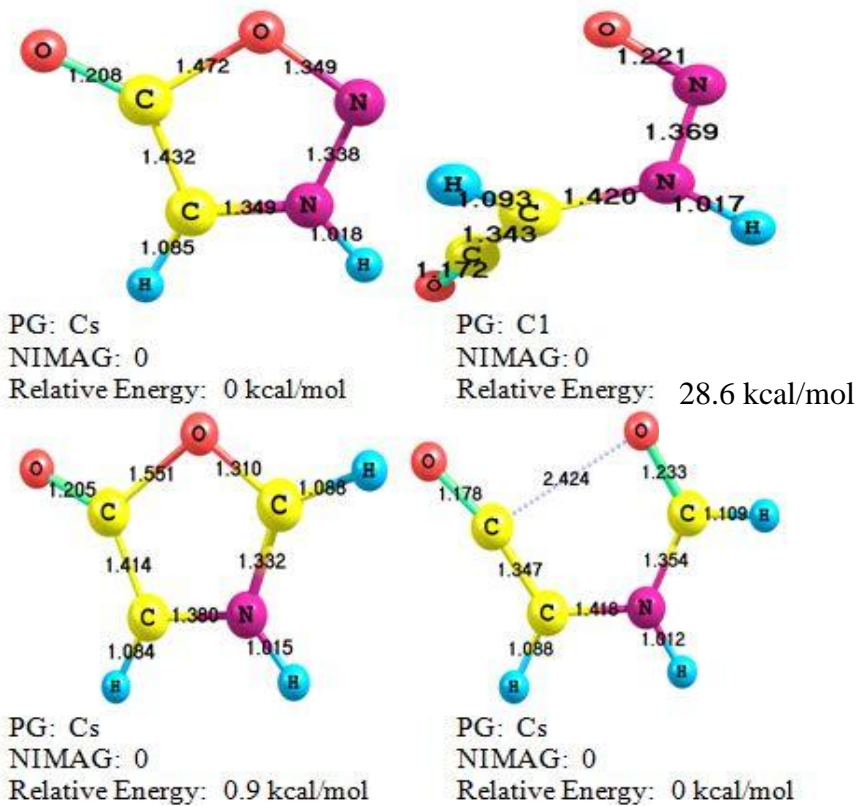


Figure15. Relative ΔE Münchnones versus Relative ΔE Sydnonnes in kcal/mol. Note the direct 1 to 1 relationship between substituent effects on sydnone and münchnone. Substituents in this study affect both münchnone and sydnone in the same way.

Figure 16 shows closed and open forms of both sydnone and münchnone. In comparing sydnone at the MP2(fc)cc-pvdz level to the x-ray structure, there appears to be a discrepancy at this level of theory, possibly due to the small basis set size. The O-CH (1.31 Å) and C-C (1.41 Å) bond lengths for closed münchnone are not “essentially single.” The O-C single bond length is 1.42 Å and that for a C-C single bond is about

1.53 to 1.54 Å in length.¹⁵ The calculated bond lengths between the CO₂ and ylide portion of münchnone are not single as Simas et al. had stipulated.¹³

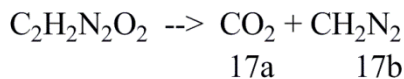


Closed Sydnone X-ray Structure¹⁴

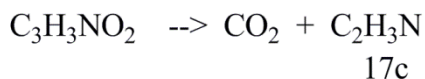
Figure 16. Bond lengths in Å for the closed and open sydnone (top) and münchnone forms (middle) at MP2(fc)/cc-pvdz. Closed sydnone x-ray structure (bottom).

Figure 17 shows the energetics of the division of sydnone and münchnone into CO₂ and ylide fragments. This division is energetically unfavorable, adding credence to the idea

of aromaticity in these systems and further revoking the arguments about this division by Simas et al.¹³



Sydnone: 90.2 kcal/mol



münchnone: 97.1 kcal/mol

Figure 17. Simple Equations showing the separation of sydnone and münchnone into CO₂ and ylide fragments. Note that 17b and 17c are ylide fragments.

The difference between open and closed forms of the parent münchnone is 0.9 kcal/mol. The Cs open form of münchnone shown in Figure 16 was of lower energy than any twisted open forms. Why does münchnone favor the open form? Figure 18 shows that amide resonance stabilizes the open form and aromaticity stabilizes the closed form (ASE of 28.2 kcal/mol).

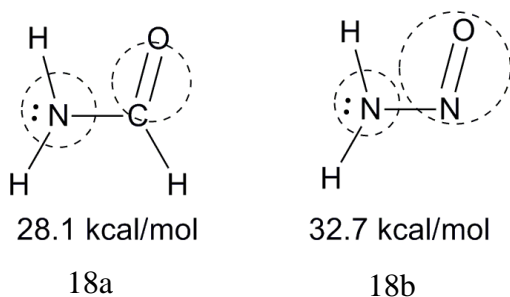
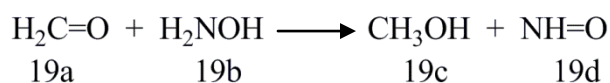


Figure 18 $\pi \rightarrow \pi^*$ electrons in circled groups were blocked in H₂NCHO and H₂NNO in the BLW calculation. Adiabatic BLW values, like those provided above, include optimization under the BLW localization constraint. The BLW localization constraints form a wavefunction for which selected electron groups are prevented from conjugating. The fully conjugated, relaxed molecule is also calculated, and the energy difference between these two molecules is the resonance energy of the system.³⁵

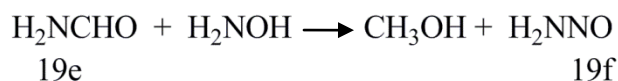
Why do sydnones prefer the closed form more than münchnones at the MP2(fc) level of theory? Simple equations reveal that part of this difference is due to the greater

strength of C=O bonds in the amide bond of open münchnones (see Figure 1 for which C=O bond is indicated) compared to sydnones' N=O (see Figure 1). The remainder of the effect is due to the σ bond framework. In order to examine these effects, experimental values for the first equation of Figure 19 were taken from the CCCBD database.⁴¹ The C=O bond energy from a standard bond energies table⁴² is 179 kcal/mol compared to 143 kcal/mol for a N=O bond. The CH bond energy is 99 kcal/mol, and the NH is 93 kcal/mol. The difference in C=O and N=O is 36 kcal/mol. Subtracting the 6 kcal/mol energy difference between C-H and N-H bonds, one arrives at 30 kcal/mol which is close to the 28.7 kcal/mol energy difference below, confirming that the amide C=O bond of open münchnone is more favorable than the N=O bond of open sydnone.



Experimental: 15.5 kcal/mol

MP2: 16.0 kcal/mol



MP2: 28.7 kcal/mol

Figure 19. Equations comparing relative energies of C=O (found in open form of münchnone) and N=O (found in open form of sydnone). These nonisodesmic reactions compare the tautomerization between closed and open forms of münchnone and sydnone. MP2(fc)/aug-cc-pvtz//MP2(fc)/aug-cc-pvtz + scaled²⁷ ZPVE level of theory.

CHAPTER 4

CONCLUSIONS

In contrast to the major arguments of Simas et al¹³ (the endocyclic C-O bond with little or no π character and the fact that mesoionic compounds had well-separated regions of negative and positive charges separated by what were essentially single bonds), sydnones and münchnones are aromatic and are comparable to the aromaticity of benzene, furan, and pyrrole by magnetic (NICS(0) $_{\pi zz}$) and energetic (ASE) criteria (Table 3). The NICS(0) $_{\pi zz}$ and ASE data nicely complement the structural criteria of aromaticity deduced by Bird¹⁸ and magnetic criteria data of Bouffard^{2b} for a mesoionic. The more refined NICS(0) $_{\pi zz}$ data presented here confirms mesoionic systems' aromaticity in consideration of the cruder NICS(0) isotropic data of Fabian.²¹ The closed form of münchnone is stabilized by aromaticity (Table 3) to about the same degree that the open form is stabilized by amide resonance (Figure 18). Finally, sydnone prefers the closed form more strongly than münchnone due to the stronger C=O amide bond in the open münchnone compared to the N=O bond in open sydnone (see Figure 19 for a comparison of the strengths of C=O versus N=O).

REFERENCES

- (1) Moss, G. P.; Smith, P. A. S.; Tavernier, D. *Pure Appl. Chem.* **1995**, *67*, 1307.
- (2) (a) Keitz, B. K.; Bouffard, J.; Bertrand, G.; Grubbs, R. H. *J. Am. Chem. Soc.* **2011**, *133*, 8498. (b) Bouffard, J.; Keitz, B. K.; Tonner, R.; Guisado-Barrios, G.; Frenking, G.; Grubbs, R. H.; Bertrand, G. *Organometallics* **2011**, *30*, 2617.
- (3) Wieczorek, W.; Zukowska, G.; Ostrovskii, D.; Florjańczyk, Z. *J. Phys. Chem. B.* **2001**, *105*, 9686.
- (4) (a) Bhosale, S. K.; Deshpande, S. R.; Wagh, R. D. *J. Chem. Pharm. Res.* **2012**, *4*, 1185. (b) Nithinchandra, N.; Kalluraya, B.; Aamir, S.; Shabaraya, A. R. *Eur. J. Med. Chem.* **2012**, *54*, 597.
- (5) Moura, G. L. C.; Simas, A. M.; Miller, J. *Chem. Phys. Lett.* **1996**, *257*, 639.
- (6) Earl, J. C.; Mackney, A. W. *J. Chem. Soc.* **1935**, 899.
- (7) Lawson, A.; Miles, D. H. *Chem. Ind. (London)* **1958**, 461.
- (8) Huisgen, R.; Gotthardt, H.; Bayer, H. O.; Schaefer, F. C. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 136.
- (9) Gribble, G. W. Mesoionic Ring Systems. In *The Chemistry of Heterocyclic Compounds, Volume 59: Synthetic Applications of 1,3-Dipolar Cycloaddition Chemistry Toward Heterocycles and Natural Products*; Padwa, A.; Pearson, W. H., Eds.; John Wiley and Sons, Inc.: New York, 2002, 59, 681.
- (10) Browne, D. L.; Harrity, J. P. A. *Tetrahedron* **2010**, *66*, 553
- (11) Schleyer, P. v. R.; Jiao, H. *Pure Appl. Chem.* **1996**, *68*, 209.
- (12) Badami, B. V. *Resonance.* **2006**, 40.
- (13) Simas, A. M.; Miller, J.; de Athayde-Filho, P. F. *Can. J. Chem.* **1998**, *76*, 869.
- (14) Thiessen, W. E.; Hope, H. *J. Am. Chem. Soc.* **1967**, *89*, 5977.
- (15) Reed Organic Chemistry Online.
http://academic.reed.edu/chemistry/roco/Geometry/bond_distances.html (accessed March 2013).

- (16) Anomeric Effect Wikipedia. http://en.wikipedia.org/wiki/Anomeric_effect. (accessed March 2012).
- (17) Irshaidat, T. *J. Phys. Org. Chem.* **2010**, *23*, 67.
- (18) Bird, C. W. *Tetrahedron.* **1985**, *41*, 1409.
- (19) Fallah-Bagher-Shaidaei, H.; Wannere, C. S.; Corminboeuf, C.; Puchta, R.; Schleyer, P. v. R. *Org. Lett.* **2006**, *8*, 863.
- (20) Chen, Z.; Wannere, C. S.; Corminboeuf, C.; Puchta, R.; Schleyer, P. v. R. *Chem. Rev.* **2005**, *105*, 3842.
- (21) Fabian, J.; Hess, B. A. *Int. J. Quantum Chem.* **2002**, *90*, 1055.
- (22) Okazki, T.; Laali, K. K. *Org. Biomol. Chem.* **2006**, *4*, 3085.
- (23) (a) Huisgen, R.; Funke, E.; Schaefer, F. C.; Knorr, R. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 367. (b) Bayer, H. O.; Huisgen, R.; Knorr, R.; Schaefer, F. C. *Chem. Ber.* **1970**, *103*, 2581. (c) Funke, E.; Huisgen, R. *Chem. Ber.* **1971**, *104*, 3222.
- (24) Dewar, M. J. S.; Turchi, I. J. *J. Chem. Soc., Perkin Trans. 2.* **1976**, 548.
- (25) Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.
- (26) Sinha, P.; Boesch, S. E.; Gu, C.; Wheeler, R. A.; Wilson, A. K. *J. Phys. Chem. A* **2004**, *108*, 9213.
- (27) Schleyer, P. v. R.; Manoharan, M.; Wang, Z. X.; Kiran, B.; Jiao, H.; Puchta, R.; Hommes, N. J. R. v. E. *Org. Lett.* **2001**, *3*, 2465.
- (28) Kutzelnigg, W. *Isr. J. Chem.* **1980**, *19*, 193.

- (29) Malkin, V. G.; Malkina, O. L.; Casida, M. E.; Salahub, D. R. *J. Am. Chem. Soc.* **1994**, *116*, 5898.
- (30) Pipek, J.; Mezey, P. J. *J. Chem. Phys.* **1989**, *90*, 4916.
- (31) (a) Glendening, E. D.; Weinhold, F. *J. Comput. Chem.* **1998**, *19*, 593. (b) Glendening, E. D.; Weinhold, F. *J. Comput. Chem.* **1998**, *19*, 610. (c) Glendening, E. D.; Badenhoop, J. K.; Weinhold, F. *J. Comput. Chem.* **1998**, *19*, 628.
- (32) NBO 5.X. Glendening, E. D., Badenhoop, J. K.; Reed, A. E.; Carpenter, J. E.; Bohmann, J. A.; Morales, C. M., and F. Weinhold (Theoretical Chemistry Institute, University of Wisconsin, Madison, WI, 2003); <http://www.chem.wisc.edu/~nbo5>. Foster, J. P.; Weinhold, F. *J. Am. Chem. Soc.* **1980**, *102*, 7211.
- (33) Gaussian 98, Revision A.9, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 1998.
- (34) (a) Schleyer, P. v. R.; Pühlhofer, F. *Org. Lett.* **2002**, *4*, 2873-2876. (b) Wannere, C. S.; Moran, D.; Allinger, N. L.; Hess, B. A.; Schaad, L. J.; Schleyer, P. v. R. *Org. Lett.* **2003**, *5*, 2983.
- (35) (a) Mo, Y.; Peyerimhoff, S. D. *J. Chem. Phys.* **1998**, *109*, 1687. (b) Mo, Y.; Zhang, Y.; Gao, J. *J. Am. Chem. Soc.* **1999**, *121*, 5737. (c) Mo, Y.; Subramanian, G.; Ferguson, D. M.; Gao, J. *J. Am. Chem. Soc.* **2002**, *124*, 4832. (d) Mo, Y.; Wu, W.; Song, L.; Lin, M.; Zhang, Q.; Gao, J. *Angew. Chem.* **2004**, *116*, 2020. *Angew. Chem. Int. Ed.* **2004**, *43*, 1986. (e) Mo, Y. *J. Chem. Phys.* **2003**, *119*, 1300. (f) Mo, Y.; Song, L.; Wu, W.; Zhang, Q. *J. Am. Chem. Soc.* **2004**, *126*, 3974. (g) Mo, Y. *J. Org. Chem.* **2004**, *69*, 5563. (h) Mo, Y.; Song, L.; Lin, Y. *J. Phys. Chem. A* **2007**, *111*, 8291.
- (36) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S. J.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. Gamess (Version R5) *J. Comput. Chem.* **1993**, *14*, 1347.
- (37) (a) Pauling, L. C.; Wheland, G. W. *J. Chem. Phys.* **1933**, *1*, 362. (b) Pauling, L. C. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960. (c) Wheland, G. W. *J. Am. Chem. Soc.* **1941**, *85*, 431. (d) Wheland, G. W. *The Theory of*

Resonance; Wiley: New York, 1944. (e) Wheland, G. W. *Resonance in Organic Chemistry*; Wiley: New York, 1955.

(38) Wu, J. I.; Pülhofer, F. G.; Schleyer, P. v. R.; Puchta, R.; Kiran, B.; Mauksch, M.; Hommes, N. J. R. v. E.; Alkorta, I.; Elguero, J. *J. Phys. Chem. A* **2009**, *113*, 6789-6794.

(39) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165.

(40) Datta, D. *J. Phys. Org. Chem.* **1991**, *4*, 96.

(41) Computational Chemistry Comparison and Benchmark Database. <http://cccbdb.nist.gov> (accessed August 2012).

(42) Michigan State University Standard Bond Energies Table. <http://www.cem.msu.edu/~reusch/OrgPage/bndenrgy.htm>. (accessed March 2013).

APPENDIX A

SUPPORTING INFORMATION

Coordinates, Point Groups (PG), Total MP2(fc) Energies (RMP2(fc)/cc-pvdz//RMP2(fc)/cc-pvdz) (Hartrees), Unscaled Zero Point Energies (ZPVE) in kcal/mol, Lowest Real Frequency (cm^{-1}), Number of Imaginary Frequencies (NIMAG)

Note: The number to the left of each compound name designates the Figure in the text (example 1a denotes Figure 1 compound a) or table (t3a = table 3 compound a) in which it first appears.

1a Closed Münchnone

Geometry:

O	-1.1249465446	-0.1739567282	0.0000000000
C	0.0023267023	0.8916714724	0.0000000000
O	-0.3001784819	2.0585106688	0.0000000000
C	1.1554304501	0.0724877339	0.0000000000
N	0.7655567739	-1.2514352868	0.0000000000
C	-0.5618138898	-1.3571682029	0.0000000000
H	1.3959315260	-2.0473537403	0.0000000000
H	2.1957580725	0.3767095158	0.0000000000
H	-1.1252463796	-2.2876863137	0.0000000000

PG: Cs

Lowest Real Frequency: 250.31 cm^{-1}

ZPVE (unscaled): 38.84 kcal/mol

MP2(fc) Energy: -320.41774 Hartrees

NIMAG: 0

1b Closed Sydnone

Geometry:

O	-1.087818966	-0.180774181	0.000000000
C	-0.043906746	0.857619675	0.000000000
O	-0.323140185	2.032518432	0.000000000
C	1.144505495	0.059096852	0.000000000
N	0.744824958	-1.229455997	0.000000000
N	-0.577922168	-1.429334915	0.000000000
H	1.328922952	-2.063816474	0.000000000

H 2.186838234 0.361099676 0.000000000

PG: Cs

Lowest Real Frequency: 261.01 cm⁻¹

ZPVE (unscaled): 31.86 kcal/mol

MP2(fc) Energy: -336.40197 Hartrees

NIMAG: 0

1c Open Münchnone

Geometry:

O 0.8332328457 -1.2575099217 0.0000000000

C -1.2143109537 0.0394303387 0.0000000000

O -2.1040808384 -0.7324359363 0.0000000000

C -0.3963060599 1.1099907213 0.0000000000

N 1.0162148360 0.9877188761 0.0000000000

C 1.5516055152 -0.2554986518 0.0000000000

H 1.5931126778 1.8192498542 0.0000000000

H -0.8466038239 2.1002816790 0.0000000000

H 2.6608402260 -0.2775312519 0.0000000000

PG: Cs

Lowest Real Frequency: 73.30 cm⁻¹

ZPVE (unscaled): 37.61 kcal/mol

MP2 (fc) Energy: -320.41910 Hartrees

NIMAG: 0

1d Open Sydnone

Geometry:

O 1.6942216128 -0.9130511014 -0.6481333268

C -0.8555363784 1.2706163223 0.0514050543

O -1.5581816172 2.0029677950 -0.5353324788

C -0.0899917638 0.4271857824 0.7629908223

N -0.1702144761 -0.9595831761 0.4706031001

N 0.8363082259 -1.6357282545 -0.1658162715

H -0.7528123455 -1.5833256689 1.0243498450

H 0.6750049857 0.8443595050 1.4234935387

PG: C1

Lowest Real Frequency: 38.99 cm⁻¹

ZPVE (unscaled): 29.64 kcal/mol

MP2 (fc) Energy: -336.35633 Hartrees

NIMAG: 0

10a Benzene

Geometry:

C 0.0000000000 1.4057320000 0.0000000000

C -1.2173996229 0.7028660000 0.0000000000

C 1.2173996229 0.7028660000 0.0000000000

H -2.1658868084 1.2504753319 0.0000000000

H	2.1658868084	1.2504753319	0.0000000000
C	-1.2173996229	-0.7028660000	0.0000000000
C	1.2173996229	-0.7028660000	0.0000000000
H	-2.1658868084	-1.2504753319	0.0000000000
H	2.1658868084	-1.2504753319	0.0000000000
C	0.0000000000	-1.4057320000	0.0000000000
H	0.0000000000	-2.5009506637	0.0000000000
H	0.0000000000	2.5009506637	0.0000000000

PG: D6h

Lowest Real Frequency: 400.89 cm⁻¹

ZPVE (unscaled): 63.08 kcal/mol

MP2(fc) Energy: -231.50645 Hartrees

NIMAG: 0

10b Furan

Geometry:

C	-0.9708783420	-0.7181922394	0.0000000000
C	-0.9708783420	0.7181922394	0.0000000000
C	0.3543978912	1.0945975275	0.0000000000
O	1.1678776460	0.0000000000	0.0000000000
C	0.3543978912	-1.0945975275	0.0000000000
H	-1.8310168620	-1.3863310296	0.0000000000
H	-1.8310168620	1.3863310296	0.0000000000
H	0.8583889832	2.0585220092	0.0000000000
H	0.8583889832	-2.0585220092	0.0000000000

PG: C2v

Lowest Real Frequency: 599.15 cm⁻¹

ZPVE (unscaled): 44.05 kcal/mol

MP2 (fc) Energy: -229.35223 Hartrees

NIMAG: 0

10c Pyrrole

Geometry:

C	-0.9927132742	-0.7134496966	0.0000000000
C	0.3388475912	-1.1291953290	0.0000000000
N	1.1245272371	0.0000000000	0.0000000000
C	0.3388475912	1.1291953290	0.0000000000
C	-0.9927132742	0.7134496966	0.0000000000
H	-1.8620388166	-1.3708005441	0.0000000000
H	0.7806180887	-2.1244642569	0.0000000000
H	0.7806180887	2.1244642569	0.0000000000
H	-1.8620388166	1.3708005441	0.0000000000
H	2.1375389924	0.0000000000	0.0000000000

PG: C2v

Lowest Real Frequency: 480.44 cm⁻¹

ZPVE (unscaled): 51.90 kcal/mol

MP2 (fc) Energy: -209.52583 Hartrees
NIMAG: 0

11a Benzene ASE Compound 1

Geometry:

C	1.8613250560	-1.3633218355	0.0000000000
C	0.4910000836	-1.6754989566	0.0000000000
C	2.2966899374	-0.0218717970	0.0000000000
H	0.1567521758	-2.7189609861	0.0000000000
H	3.3697109180	0.1977562979	0.0000000000
C	-0.4385090097	-0.6197940388	0.0000000000
C	1.3670378440	1.0354881208	0.0000000000
H	1.7114557520	2.0760961513	0.0000000000
C	-0.0000001290	0.7298810000	0.0000000000
H	2.6022011273	-2.1700877700	0.0000000000
C	-1.2093962093	1.6381888931	0.0000000000
C	-2.3647131231	0.6624627910	0.0000000000
C	-1.9090230095	-0.6225971687	0.0000000000
H	-1.2306462676	2.2978168912	0.8881520000
H	-2.5297179299	-1.5234402236	0.0000000000
H	-3.4155781498	0.9653806981	0.0000000000
H	-1.2306462676	2.2978168912	-0.8881520000

PG: Cs

Lowest Real Frequency: 188.52 cm⁻¹

ZPVE (unscaled): 88.00 kcal/mol

MP2 (fc) Energy: -346.66577 Hartrees

NIMAG: 0

11b Benzene ASE compound 2

Geometry:

C	-2.2962700636	-0.0111482379	0.0000000000
C	-1.4205751511	1.0492078344	0.0000000000
C	-1.8289789499	-1.3884641993	0.0000000000
H	-1.7871032364	2.0819028041	0.0000000000
H	-2.5720038835	-2.1935912607	0.0000000000
C	-0.0000001290	0.7816409516	0.0000000000
C	-0.4888529244	-1.6971300887	0.0000000000
H	-0.1514728384	-2.7397080609	0.0000000000
C	0.4756769867	-0.6204850091	0.0000000000
H	-3.3758250790	0.1755716730	0.0000000000
C	1.8558369872	-0.6271488952	0.0000000000
C	2.3403638699	0.7942001448	0.0000000000
C	1.0908888012	1.6270140417	0.0000000000
H	2.5038810599	-1.5074878417	0.0000000000
H	1.0692017110	2.7199290399	0.0000000000
H	2.9723928522	1.0086321970	0.8858860000

H 2.9723928522 1.0086321970 -0.8858860000
PG: Cs
Lowest Real Frequency: 173.04 cm⁻¹
ZPVE (unscaled): 86.81 kcal/mol
MP2 (fc) Energy: -346.62579 Hartrees
NIMAG: 0

11c Furan ASE 1

Geometry:

O	1.2150480000	1.2088139107	0.0000000000
C	2.1222400000	0.1719979107	0.0000000000
C	1.4980020000	-1.0644810893	0.0000000000
C	0.0000000000	0.6092959107	0.0000000000
C	0.0928720000	-0.7688930893	0.0000000000
C	-1.4087160000	1.1010009107	0.0000000000
C	-1.2816970000	-1.2926700893	0.0000000000
C	-2.1495070000	-0.2338020893	0.0000000000
H	-1.5707570000	-2.3465060893	0.0000000000
H	-3.2401340000	-0.3055800893	0.0000000000
H	-1.6624490000	1.7021399107	0.8920910000
H	-1.6624490000	1.7021399107	-0.8920910000
H	3.1686580000	0.4703489107	0.0000000000
H	2.0075830000	-2.0277440893	0.0000000000

PG: Cs

Lowest Real Frequency: 162.76 cm⁻¹
ZPVE (unscaled): 69.15 kcal/mol
MP2 (fc) energy: -344.49280
NIMAG: 0

11d Furan ASE 2

Geometry:

O	1.2702700000	1.2062130179	0.0000000000
C	2.1039770000	0.0982310179	0.0000000000
C	1.4626280000	-1.1104619821	0.0000000000
C	0.0000000000	0.6734790179	0.0000000000
C	0.0433620000	-0.7870279821	0.0000000000
C	-1.2699420000	1.1638160179	0.0000000000
C	-1.2437520000	-1.2593949821	0.0000000000
C	-2.1676940000	-0.0571729821	0.0000000000
H	-2.8313720000	-0.0684479821	0.8875770000
H	-2.8313720000	-0.0684479821	-0.8875770000
H	-1.5850410000	-2.2967439821	0.0000000000
H	-1.6076160000	2.2001110179	0.0000000000
H	3.1679280000	0.3378050179	0.0000000000
H	1.9538390000	-2.0827889821	0.0000000000

PG: Cs

Lowest Real Frequency: 221.59 cm⁻¹
ZPVE (unscaled): 68.64 kcal/mol
MP2 Energy: -344.47782 Hartrees
NIMAG: 0

11e Pyrrole ASE 1

Geometry:

N	1.2776657524	1.1283100186	0.0000000000
C	2.1680129015	0.0657431435	0.0000000000
C	1.4422250696	-1.1321219583	0.0000000000
C	-0.0000001786	0.6363018393	0.0000000000
C	0.0646760174	-0.7604701516	0.0000000000
C	-1.4139082483	1.1333926409	0.0000000000
C	-1.3183529128	-1.2575423457	0.0000000000
C	-2.1744340625	-0.1907214658	0.0000000000
H	-1.6230847655	-2.3077073885	0.0000000000
H	-3.2661050546	-0.2475366190	0.0000000000
H	-1.6678953330	1.7365526052	0.8917950000
H	-1.6678953330	1.7365526052	-0.8917950000
H	3.2432488768	0.2418922944	0.0000000000
H	1.8803582097	-2.1304758969	0.0000000000
H	1.5484016153	2.1050620566	0.0000000000

PG: Cs

Lowest Real Frequency: 152.77 cm⁻¹
ZPVE (unscaled): 77.01 kcal/mol
MP2 Energy: -324.66820 Hartrees
NIMAG: 0

11f Pyrrole ASE 2

Geometry:

N	-1.3377857685	1.1135122816	0.0233468929
C	-2.1437149327	-0.0287256026	-0.0312961071
C	-1.4018490995	-1.1889347092	-0.0008581071
C	-0.0094308282	0.6984080906	-0.0030871071
C	-0.0076620398	-0.7738159096	0.0217398929
C	1.2627932445	1.2043209078	-0.0189491071
C	1.2951828974	-1.2105540969	0.0381828929
C	2.1901550727	0.0085847745	0.0079748929
H	2.8555900696	-0.0127093212	-0.8787101071
H	2.8545960768	0.0372946789	0.8952488929
H	1.6590357494	-2.2402771492	0.0597888929
H	1.5857443944	2.2464508613	-0.0394551071
H	-3.2302029169	0.0811585536	-0.0581961071
H	-1.8110002446	-2.1985926504	0.0137158929
H	-1.6621086358	2.0363883282	-0.2380641071

PG: C1

Lowest Real Frequency: 182.41 cm⁻¹
ZPVE (unscaled): 76.05 kcal/mol
MP2 Energy: -324.64577 Hartrees
NIMAG: 0 Cs form had 1 imaginary frequency that led to C1 form above.

11g Sydnone ASE Compound 1

Geometry:

N	-0.4956433197	-1.6819295629	0.0000000000
O	-1.6516051147	-0.9575522357	0.0000000000
C	-1.4311877022	0.5003277019	0.0000000000
N	0.4392949489	-0.7327838274	0.0000000000
C	0.0000003125	0.5521482969	0.0000000000
O	-2.3574734823	1.2772659640	0.0000000000
C	1.9009329197	-0.8357892411	0.0000000000
C	1.1670265576	1.4182979666	0.0000000000
C	2.2851523357	0.6340316502	0.0000000000
H	1.1318278661	2.5085209766	0.0000000000
H	3.3219334321	0.9748753568	0.0000000000
H	2.2408797668	-1.3761053373	0.8986240000
H	2.2408797668	-1.3761053373	-0.8986240000

PG: Cs

Lowest Real Frequency: 148.06 cm⁻¹
ZPVE (unscaled): 57.15 kcal/mol
MP2 Energy: -451.54902 Hartrees
NIMAG: 0

11h Sydnone ASE Compound 2

Geometry:

N	-0.4142178269	-1.7239771072	0.0000000000
O	-1.6568919338	-0.9907812883	0.0000000000
C	-1.4697911325	0.3729167390	0.0000000000
N	0.5111200377	-0.7948369724	0.0000000000
C	-0.0000001562	0.5361989531	0.0000000000
O	-2.3661912507	1.1842446084	0.0000000000
C	1.8751410349	-0.7756257737	0.0000000000
C	1.0092087127	1.4358771002	0.0000000000
C	2.3045068255	0.6612952889	0.0000000000
H	2.9123287857	0.9347543775	0.8870310000
H	2.9123287857	0.9347543775	-0.8870310000
H	0.9054955544	2.5218370851	0.0000000000
H	2.4618051683	-1.6913276882	0.0000000000

PG: Cs

Lowest Real Frequency: 146.23 cm⁻¹
ZPVE (unscaled): 55.89 kcal/mol
MP2 Energy: -451.50398 Hartrees
NIMAG: 0

11i Münchnone ASE Compound 1

Geometry:

C	-0.5466166941	-1.6188302654	0.0000000000
O	-1.6974108791	-0.9708215940	0.0000000000
C	-1.4181573101	0.5389984857	0.0000000000
N	0.4689180606	-0.7593949755	0.0000000000
C	-0.0000003125	0.5472918906	0.0000000000
O	-2.3443105314	1.3140882213	0.0000000000
C	1.9404740763	-0.8144395554	0.0000000000
C	1.1528284383	1.4201192198	0.0000000000
C	2.2913516537	0.6657265448	0.0000000000
H	1.0998451271	2.5101742046	0.0000000000
H	3.3200665502	1.0282668385	0.0000000000
H	2.2971242287	-1.3483724536	0.8972980000
H	2.2971242287	-1.3483724536	-0.8972980000
H	-0.4820943839	-2.7052622470	0.0000000000

PG: Cs

Lowest Real Frequency: 138.75 cm^{-1}

ZPVE (unscaled): 64.24 kcal/mol

MP2 Energy: -435.56479 Hartrees

NIMAG: 0

11j Münchnone ASE Compound 2

Geometry:

C	-0.4436255129	-1.6914512586	-0.1353995828
O	-1.6813753592	-1.0203001893	-0.0050885417
C	-1.4784453850	0.3365578140	0.0076725263
N	0.5729151342	-0.8019162441	-0.0034844777
C	-0.0010365977	0.5090984842	-0.0101502805
O	-2.3601626572	1.1637024473	0.0357971756
C	1.9324245815	-0.6956655571	0.0751433711
C	0.9579388254	1.4600313241	-0.0103127917
C	2.2960745255	0.7612014959	0.0061783826
H	2.8985823242	1.1074807725	0.8709684123
H	2.8801052321	1.0297760414	-0.9008936966
H	0.7891557381	2.5379361898	-0.0049811710
H	2.5801385776	-1.5670129972	-0.0003527611
H	-0.4060663022	-2.7206181765	0.2151917399

PG: C1

Lowest Real Frequency: 143.91 cm^{-1}

ZPVE (unscaled): 63.47 kcal/mol

MP2 Energy: -435.51865 Hartrees

NIMAG: 0

Note: Cs form had 1 imaginary frequency that leads to C1 form above

Substituted Münchnones:

t4a CH₃ Open

Geometry:

O	-0.2308853341	-1.6504225805	0.0000000000
C	-1.4914769061	0.2908167156	0.0000000000
O	-2.6281893034	-0.0187076747	0.0000000000
C	-0.3138831933	0.9546720261	0.0000000000
N	0.9326681895	0.2789438423	0.0000000000
C	0.8628197614	-1.0716139709	0.0000000000
H	-0.3282331235	2.0429793613	0.0000000000
H	1.8457052810	-1.5855205290	0.0000000000
C	2.1663484192	1.0368050781	0.0000000000
H	2.2367569480	1.6739516152	-0.8977878625
H	2.2367569480	1.6739516152	0.8977878625
H	3.0100852334	0.3309939905	0.0000000000

PG: Cs

Lowest Real Frequency: 80.66 cm⁻¹

ZPVE (unscaled): 55.71 kcal/mol

MP2 (fc) Energy: -359.59558 Hartrees

NIMAG: 0

t4b CH₃ Closed

Geometry:

O	-0.6550452256	-1.2611048018	0.0000000000
C	-1.3033850738	0.1413727566	0.0000000000
O	-2.5065137074	0.2272986212	0.0000000000
C	-0.1604346751	0.9744780972	0.0000000000
N	0.9796322531	0.1927842112	0.0000000000
C	0.6462864018	-1.0973158540	0.0000000000
H	-0.1181290648	2.0586943365	0.0000000000
H	1.3529759828	-1.9259851351	0.0000000000
C	2.3421921182	0.7001006306	0.0000000000
H	2.5064329987	1.3131159004	-0.8985795959
H	2.5064329987	1.3131159004	0.8985795959
H	3.0393801499	-0.1497948186	0.0000000000

PG: Cs

Lowest Real Frequency: 143.84 cm⁻¹

ZPVE (unscaled): 56.58 kcal/mol

MP2 (fc) Energy: -359.59727 Hartrees

NIMAG: 0

t4c NH₂ Open

Geometry:

O	1.5496663523	-0.6485843998	-0.0087015001
C	-0.7282111431	-1.3346901470	0.0365657391
O	-0.7302361927	-2.5120501168	0.0298302359

C	-1.0147934971	-0.0160084926	0.0466522746
N	0.0006513862	0.9823441930	0.0295881675
C	1.2879646301	0.5577090158	-0.0213518433
H	-2.0529050962	0.2938037400	0.1525167961
H	2.0214902106	1.3856394211	-0.0678321441
N	-0.2940434188	2.3422521029	-0.0879729887
H	-0.8734067740	2.6148955959	0.7111366684
H	-0.8666353277	2.4765010468	-0.9273544799

PG: C1

Lowest Real Frequency: 172.25 cm⁻¹

ZPVE (unscaled): 29.72 kcal/mol

MP2 (fc) Energy: -375.58705 Hartrees

NIMAG: 0

t4d NH₂ Closed

Geometry:

O	0.6423116183	1.2564093619	0.0000000000
C	1.2825477681	-0.1626245679	0.0000000000
O	2.4844501223	-0.2527694409	0.0000000000
C	0.1333151506	-0.9840197689	0.0000000000
N	-0.9941071404	-0.1775162935	0.0000000000
C	-0.6586697714	1.1080827581	0.0000000000
H	0.0717342656	-2.0671366837	0.0000000000
H	-1.3755494375	1.9268103929	0.0000000000
N	-2.3398518243	-0.5780937983	0.0000000000
H	-2.4578624417	-1.1840764808	0.8181368687
H	-2.4578624417	-1.1840764808	-0.8181368687

PG: Cs

Lowest Real Frequency: 172.25 cm⁻¹

ZPVE (unscaled): 49.55 kcal/mol

MP2 (fc) Energy: -375.58719 Hartrees

NIMAG: 0

t4e OH Open

Geometry:

O	-1.6695904281	-0.5034996920	-0.5933841344
C	0.8257323709	-1.2843655916	0.2372663389
O	0.6426385494	-2.3754915117	0.6243267618
C	1.0879753388	-0.0600473416	-0.2532361213
N	0.0966882214	0.9524555579	-0.2878409243
C	-1.2526545830	0.6068643780	-0.3123590404
H	2.0441833733	0.0967923892	-0.7538900652
H	-1.8811733020	1.4900570164	-0.0716301557
O	0.3411712923	2.0591365613	0.5751730951
H	0.6800983100	2.7300901590	-0.0385461518

PG: C1

Lowest Real Frequency: 32.48 cm⁻¹
ZPVE (unscaled): 40.02 kcal/mol
MP2 (fc) Energy: -395.40181 Hartrees
NIMAG: 0

t4f OH Closed

Geometry:

O	-0.7339120858	-1.1795847785	0.1057014884
C	-1.2448600545	0.2671139807	0.0477109717
O	-2.4319248949	0.4703935290	0.0991487671
C	-0.0369938112	1.0036801398	-0.0556153761
N	1.0013676564	0.1006960052	-0.0679941990
C	0.5825578807	-1.1576892394	0.0311912192
H	0.1149717638	2.0647253278	-0.2191038682
H	1.2238944173	-2.0351614349	0.0407119632
O	2.3279378749	0.4240716446	-0.2180167199
H	2.5505289799	0.8678916233	0.6199621241

PG: C1

Lowest Real Frequency: 180.02 cm⁻¹
ZPVE (unscaled): 40.89 kcal/mol
MP2 (fc) Energy: -395.39937 Hartrees
NIMAG: 0

t4g F Open

Geometry:

O	-1.7175460557	-0.4729999359	-0.6506316772
C	0.9153965014	-1.2073314401	0.1540161554
O	0.7800018493	-2.2788309658	0.5997524105
C	1.0749954741	0.0065577308	-0.4155852775
N	0.0629248765	0.9704179833	-0.3319503794
C	-1.2890192507	0.5866133863	-0.2390882092
H	1.9744417930	0.1982319470	-1.0005530313
H	-1.8935666902	1.4060846722	0.1998091987
F	0.3078631183	1.9224851833	0.7261527344

PG: C1

Lowest Real Frequency: 58.52 cm⁻¹
ZPVE (unscaled): 31.95 kcal/mol
MP2 (fc) Energy: -419.37028 Hartrees
NIMAG: 0

t4h F Closed

Geometry:

O	-0.7331367366	-1.1683561115	0.0000000000
C	-1.2286295383	0.2702440921	0.0000000000
O	-2.4133075988	0.4885609946	0.0000000000
C	-0.0159957592	1.0168216650	0.0000000000

N	0.9957160325	0.1010040262	0.0000000000
C	0.5928664823	-1.1663436084	0.0000000000
H	0.1562894361	2.0865788210	0.0000000000
H	1.2289592184	-2.0458558573	0.0000000000
F	2.3029829659	0.4406974329	0.0000000000

PG: Cs

Lowest Real Frequency: 181.65 cm⁻¹

ZPVE (unscaled): 32.87 kcal/mol

MP2 (fc) Energy: -419.35868 Hartrees

NIMAG: 0

t4i CN Open

Geometry:

O	-0.9177393688	1.6446098356	0.0000000000
C	-1.6345622596	-0.7314633396	0.0000000000
O	-2.8089944569	-0.7018840224	0.0000000000
C	-0.3155708585	-0.9947795756	0.0000000000
N	0.6788679928	0.0353357101	0.0000000000
C	0.2689817486	1.3624755372	0.0000000000
H	0.0164623915	-2.0309740346	0.0000000000
H	1.1126666889	2.0807269000	0.0000000000
C	1.9942818430	-0.2892068159	0.0000000000
N	3.1505546764	-0.5601520253	0.0000000000

PG: Cs

Lowest Real Frequency: 47.39 cm⁻¹

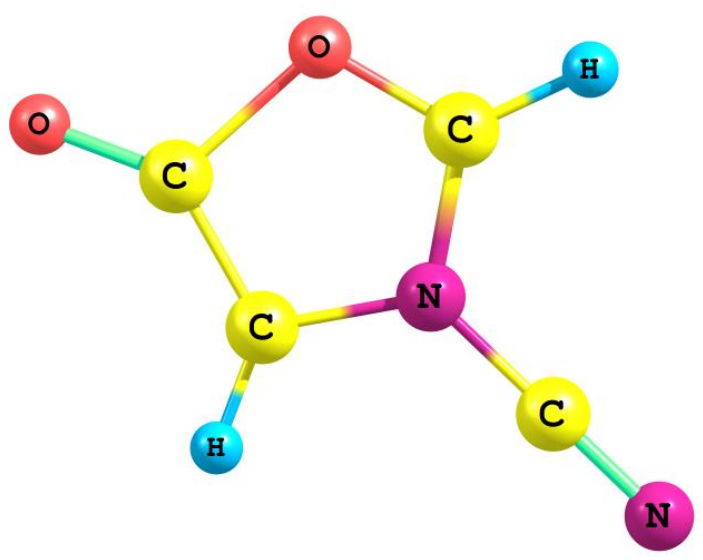
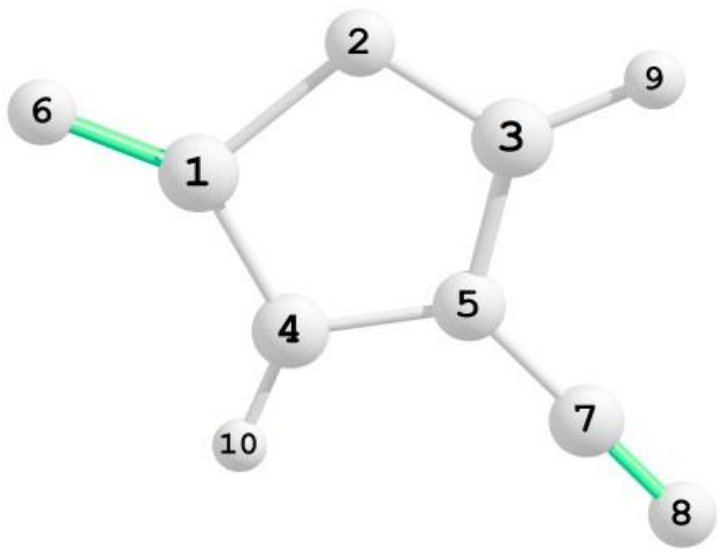
ZPVE (unscaled): 36.28 kcal/mol

MP2 (fc) Energy: -412.40354 Hartrees

NIMAG: 0

t4j CN Closed

Geometry (initial Z-matrix): First figure gives the atom numbers for z-matrix and second figure gives the compound with atoms labeled.



```

8
6 1 R12
6 1 R13      2 A213
6 2 R24      1 A124      3 D3124
7 4 R45      2 A245      1 D1245
6 5 R56      4 A456      2 D2456
7 6 R67      3 A367      1 D1367
1 3 R38      5 A538      4 D4538
1 4 R49      2 A249      1 D1249
8 2 R2_10    1 A12_10    3 D312_10
Variables:   Values:
R13          1.31000000
A213         108.000000
R24          1.41000000
A124         101.000000
D3124        0.00000000

```

R45	1.38000000
A245	108.980000
D1245	0.00000000
R56	1.47000000
A456	124.450000
D2456	180.000000
R67	1.16000000
A367	153.760000
D1367	180.000000
R38	1.08000000
A538	124.660000
D4538	180.000000
R49	1.08000000
A249	125.500000
D1249	180.000000
R2_10	1.20000000
A12_10	119.000000
D312_10	180.000000

Constants:

R12 = 1.551000000

Final Optimized Geometry (all variables but R12):

O	1.178389000	-1.109913000	0.000000000
C	-0.310240000	-1.545326000	0.000000000
C	1.239101000	0.185577000	0.000000000
C	-0.963063000	-0.292565000	0.000000000
N	0.000000000	0.713348000	0.000000000
C	-0.251939000	2.053951000	0.000000000
N	-0.474032000	3.218861000	0.000000000
H	2.160310000	0.766310000	0.000000000
H	-2.024152000	-0.070037000	0.000000000
O	-0.566026000	-2.719032000	0.000000000

PG: Cs

MP2 (fc) Energy: -412.38996 Hartrees

t4k NO₂ Open

Geometry:

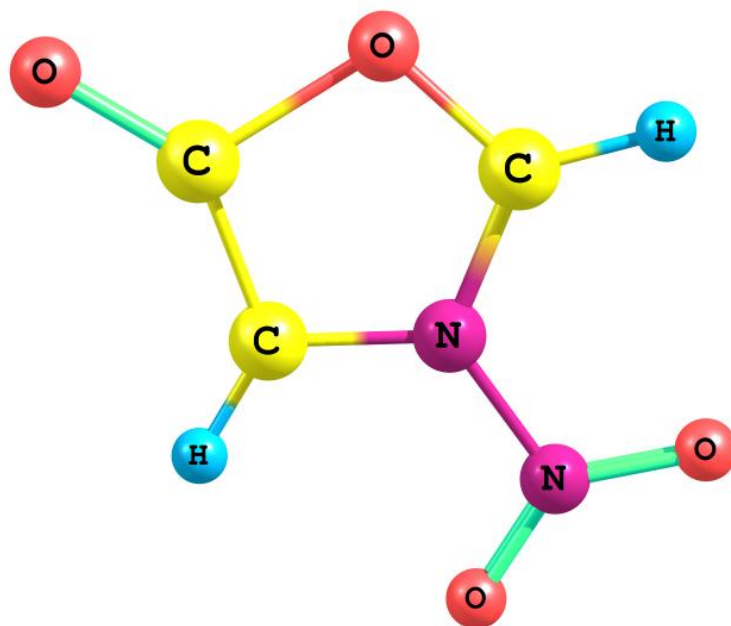
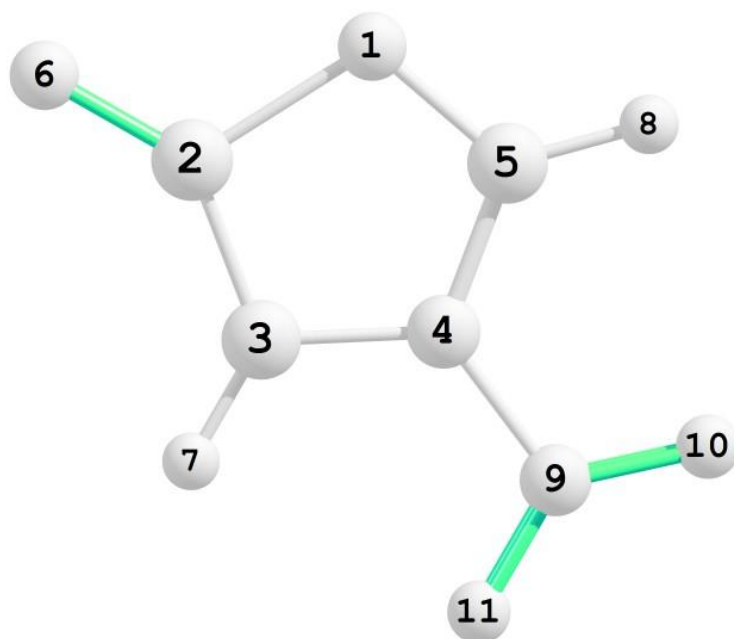
O	-1.2444108347	1.7040324300	0.0000000000
C	-1.9449585087	-0.6835213801	0.0000000000
O	-3.1192949272	-0.6584115700	0.0000000000
C	-0.6252720914	-0.9383508572	0.0000000000
N	0.3453386871	0.0996615052	0.0000000000
C	-0.0525228329	1.4330978945	0.0000000000
H	-0.2780030307	-1.9678996000	0.0000000000
H	0.7840294676	2.1503937232	0.0000000000
N	1.7138807550	-0.2577172974	0.0000000000
O	1.9507644543	-1.4576905113	0.0000000000
O	2.5149360658	0.6691374612	0.0000000000

PG: Cs

Lowest Real Frequency: 3.91 cm^{-1}
ZPVE (unscaled): 39.14 kcal/mol
MP2 (fc) Energy: -524.41545 Hartrees
NIMAG: 0

t4I NO₂ Closed

Geometry initial Z-matrix: First figure gives the atom numbers for z-matrix and second figure gives the compound with atoms labeled.



8
6 1 R12
6 2 R23 1 A123

7	3	R34	2	A234	1	D1234
6	4	R45	3	A345	2	D2345
8	2	R26	3	A326	4	D4326
1	3	R37	4	A437	5	D5437
1	5	R58	4	A458	3	D3458
7	4	R49	3	A349	2	D2349
8	9	R9_10	4	A49_10	3	D349_10
8	9	R9_11	4	A49_11	3	D349_11

Variables:	Values:
R23	1.41000000
A123	101.220000
R34	1.38000000
A234	108.980000
D1234	0.00000000
R45	1.33000000
A345	110.960000
D2345	0.00000000
R26	1.21000000
A326	139.920000
D4326	180.000000
R37	1.08000000
A437	125.510000
D5437	180.000000
R58	1.08000000
A458	124.550000
D3458	180.000000
R49	1.45000000
A349	124.520000
D2349	180.000000
R9_10	1.23000000
A49_10	117.680000
D349_10	180.000000
R9_11	1.23000000
A49_11	117.680000
D349_11	0.00000000

Constants:

R12 = 1.5510000000

Final Optimized Geometry (all variables but R12):

O	-1.389763000	-1.289397000	0.000000000
C	0.038428000	-1.894270000	0.000000000
C	0.842590000	-0.728585000	0.000000000
N	0.000000000	0.361667000	0.000000000
C	-1.292619000	0.011492000	0.000000000
O	0.155467000	-3.090603000	0.000000000
H	1.921689000	-0.634582000	0.000000000
H	-2.132288000	0.701794000	0.000000000
N	0.438431000	1.757767000	0.000000000
O	-0.457577000	2.576389000	0.000000000
O	1.643272000	1.899227000	0.000000000

PG: Cs
MP2 (fc) Energy: -524.40136 Hartrees

Substituted Sydnones:

t5a CH₃ Open

Geometry:

8	-2.416790375	0.191704973	0.064626837
6	1.252761513	-0.941846426	0.825395787
8	2.346124727	-1.302150141	1.074883898
6	0.000169860	-0.554594444	0.565744512
7	-0.304982058	0.427442374	-0.403233366
7	-1.585286107	0.784825157	-0.629748256
1	-0.847260874	-0.988434280	1.099543271
6	0.709901891	1.093497530	-1.190990178
1	1.409168348	1.644406423	-0.538596113
1	1.274258882	0.362940809	-1.795905509
1	0.184031278	1.796387219	-1.851204475

PG: C1

Lowest Real Frequency: 68.49 cm⁻¹

ZPVE (unscaled): 47.46 kcal/mol

MP2 (fc) Energy: -375.53582 Hartrees

NIMAG: 0

t5b CH₃ Closed

Geometry:

O	-0.8376892272	-1.0810949191	0.0000000000
C	-1.2490979917	0.3311587543	0.0000000000
O	-2.4158071381	0.6458274655	0.0000000000
C	0.0199925533	0.9899801604	0.0000000000
N	0.9722476605	0.0307817555	0.0000000000
N	0.5025056903	-1.2220890824	0.0000000000
H	0.2513830079	2.0507189947	0.0000000000
C	2.4197133793	0.1949477605	0.0000000000
H	2.7272270086	0.7437735665	-0.9017274150
H	2.7272270086	0.7437735665	0.9017274150
H	2.8552127964	-0.8134952629	0.0000000000

PG: Cs

Lowest Real Frequency: 111.72 cm⁻¹

ZPVE (unscaled): 49.48 kcal/mol

MP2 (fc) Energy: -375.58443 Hartrees

NIMAG: 0

t5c NH₂ Open

Geometry:

O	-2.3817559247	0.4718135457	0.1771511959
---	---------------	--------------	--------------

C	1.2280598653	-1.0333474014	0.7400989714
O	2.3035525701	-1.4779237895	0.9026509519
C	-0.0165401885	-0.5610657138	0.5966932949
N	-0.2878794446	0.4325505573	-0.3729315925
N	-1.5092061199	0.9440784057	-0.5671127705
H	-0.8482662940	-0.9134834682	1.2041617009
N	0.7768750240	0.8920604847	-1.1593953285
H	0.8314940414	1.9065080924	-1.0290756238
H	0.5147998789	0.7416774256	-2.1380198711

PG: C1

Lowest Real Frequency: 71.45 cm^{-1}

ZPVE (unscaled): 40.33 kcal/mol

MP2 (fc) Energy: -391.52830 Hartrees

NIMAG: 0

t5d NH₂ Closed

Geometry:

O	0.8011166682	-1.0564072751	0.2506727354
C	1.2327205873	0.3030272850	-0.1391561447
O	2.4031566290	0.5718645571	-0.2661431223
C	-0.0245621443	0.9704075704	-0.2632053938
N	-0.9803036651	0.0598181009	0.0287975568
N	-0.5418596205	-1.1613033508	0.3409756141
H	-0.2666908000	1.9935435139	-0.5294866796
N	-2.3569786934	0.3209963316	0.0208832902
H	-2.6949850404	0.0677776602	0.9543595185
H	-2.7675173476	-0.3624621001	-0.6226232120

PG: C1

Lowest Real Frequency: 42.75 cm^{-1}

ZPVE (unscaled): 42.28 kcal/mol

MP2 (fc) Energy: -391.57483 Hartrees

NIMAG: 0

t5e OH Open

Geometry:

8	-2.137676410	-0.078688757	-0.003769898
6	1.079058913	-1.118608845	0.741803970
8	1.726862358	-2.091723152	0.693689043
6	0.364621601	0.017852486	0.795261922
7	-0.100392115	0.548300936	-0.433723753
7	-1.451379762	0.664058268	-0.688605854
1	0.068411702	0.426409822	1.766159417
8	0.623351167	1.585971815	-1.022374480
1	0.431611427	2.367134652	-0.472604841

PG: C1

Lowest Real Frequency: 42.52 cm^{-1}

ZPVE (unscaled): 31.53 kcal/mol
MP2 (fc) Energy: -411.33958 Hartrees
NIMAG: 0

t5f OH Closed

Geometry:

O	0.8411702121	-1.0426724800	0.0000000000
C	1.1942451834	0.3898385312	0.0000000000
O	2.3469772899	0.7446301616	0.0000000000
C	-0.0947115041	1.0128165514	0.0000000000
N	-0.9820669021	-0.0012726463	0.0000000000
N	-0.5025668733	-1.2287432674	0.0000000000
H	-0.3911437029	2.0556544178	0.0000000000
O	-2.3333018795	0.1608589157	0.0000000000
H	-2.6523869253	-0.7640062947	0.0000000000

PG: Cs

Lowest Real Frequency: 187.35 cm⁻¹

ZPVE (unscaled): 33.83 kcal/mol

MP2 (fc) Energy: -411.38948 Hartrees

NIMAG: 0

t5g F Open

Geometry:

O	-2.1527229905	-0.0950567920	-0.0934859016
C	1.1220448364	-1.1346627739	0.6956524817
O	1.7876192407	-2.0935168576	0.6563817365
C	0.3536627636	-0.0303059550	0.7447850432
N	-0.0701955048	0.4712823760	-0.4988137178
N	-1.4770780625	0.7418361517	-0.6409436156
H	0.0793411048	0.4088574541	1.7075148398
F	0.5353509183	1.7330793803	-0.7638894816

PG: C1

Lowest Real Frequency: 65.89 cm⁻¹

ZPVE (unscaled): 23.33 kcal/mol

MP2 (fc) Energy: -435.30970 Hartrees

NIMAG: 0

t5h F Closed

Geometry:

O	0.8383085534	-1.0419169931	0.0000000000
C	1.1786072829	0.3946705037	0.0000000000
O	2.3241269953	0.7643978933	0.0000000000
C	-0.1199217390	1.0058329580	0.0000000000
N	-0.9754971248	-0.0308365847	0.0000000000
N	-0.5070436872	-1.2598753515	0.0000000000
H	-0.4367809477	2.0427710276	0.0000000000

F -2.3152256691 0.0899271727 0.0000000000
PG: Cs
Lowest Real Frequency: 186.46 cm⁻¹
ZPVE (unscaled): 25.98 kcal/mol
MP2 (fc) Energy: -435.34606 Hartrees
NIMAG: 0

t5i CN Open

Geometry:
O -2.1329081514 -0.4361744812 0.0214863165
C 0.8287029024 -1.3544399408 0.9157960579
O 1.2741310106 -2.4334006745 0.8495960748
C 0.3333525061 -0.1050872367 0.9933909838
N -0.1421596249 0.4926311589 -0.2019166181
N -1.5273243210 0.3678182651 -0.6298939122
H 0.2035804029 0.3635530798 1.9715816274
C 0.5489076245 1.4857207847 -0.8233103027
N 1.1553208781 2.3446772221 -1.3761182113
PG: C1
Lowest Real Frequency: 33.78 cm⁻¹
ZPVE (unscaled): 27.61 kcal/mol
MP2 (fc) Energy: -428.34012 Hartrees
NIMAG: 0

t5j CN Closed

Geometry:
O 1.1501594987 -1.0838666260 0.0000000000
C 1.5193470465 0.3627404467 0.0000000000
O 2.6675909199 0.7167719436 0.0000000000
C 0.2247184140 0.9746526022 0.0000000000
N -0.6907233327 -0.0291912110 0.0000000000
N -0.1715555638 -1.2994122406 0.0000000000
H -0.0560097451 2.0240010999 0.0000000000
C -2.0503583579 0.0964193865 0.0000000000
N -3.2303262776 0.2300151298 0.0000000000
PG: Cs
Lowest Real Frequency: 115.91 cm⁻¹
ZPVE (unscaled): 29.81 kcal/mol
MP2 (fc) Energy: -428.37102 Hartrees
NIMAG: 0

t5k NO₂ Open

Geometry:
O -2.3052261651 -0.3444822746 0.4297452850
C 0.7311732187 -1.7649261147 0.8321544230
O 1.1200081194 -2.8598601012 0.7030177203

C	0.2845156469	-0.5048341767	0.9853486393
N	-0.2308879316	0.1243184805	-0.1624702369
N	-1.6625619009	0.4025304320	-0.2561077107
H	0.2986769548	-0.0447255835	1.9765256537
N	0.5210120302	1.2733335668	-0.6898687405
O	1.5758377798	1.5103721829	-0.1276010483
O	0.0111620745	1.8267214402	-1.6454641084

PG: C1

Lowest Real Frequency: 43.02 cm⁻¹

ZPVE (unscaled): 30.25 kcal/mol

MP2 (fc) Energy: -540.35101 Hartrees

NIMAG: 0

t51 NO₂ Closed

Geometry:

O	1.4990942809	-1.1022124100	0.0000000000
C	1.8618854193	0.3341060132	0.0000000000
O	3.0119923146	0.6891679450	0.0000000000
C	0.5682313980	0.9591427532	0.0000000000
N	-0.3200606137	-0.0547368226	0.0000000000
N	0.1564378978	-1.3031938493	0.0000000000
H	0.2842846243	2.0062849724	0.0000000000
N	-1.8341446555	0.0932715674	0.0000000000
O	-2.4338776718	-0.9500442411	0.0000000000
O	-2.1872856647	1.2489432261	0.0000000000

PG: Cs

Lowest Real Frequency: 67.58 cm⁻¹

ZPVE (unscaled): 32.40 kcal/mol

MP2 (fc) Energy: -540.38465 Hartrees

NIMAG: 0

17a CO₂

Geometry:

C	0.0000000000	0.0000000000	0.0000000000
O	0.0000000000	0.0000000000	-1.1770838170
O	0.0000000000	0.0000000000	1.1770838170

PG: D*h

Lowest Real Frequency: 647.58 cm⁻¹

ZPVE(unscaled): 7.24 kcal/mol

MP2(fc) Energy: -188.13355 Hartrees

NIMAG: 0

17b CH₂N₂

Geometry:

C	-1.1173779673	0.0000000000	0.4668810094
N	0.0462837137	0.0000000000	-0.3345426053

N	1.1978933506	0.0000000000	0.1738305656
H	-0.0639760276	0.0000000000	-1.3753477242
H	-1.9409956186	0.0000000000	-0.3009540536

PG: CS

Lowest Real Frequency: 232.37 cm⁻¹

ZPVE(unscaled): 18.96 kcal/mol

MP2(fc) Energy: -148.12471 Hartrees

NIMAG: 0

17c C₂H₃N

Geometry:

C	-1.1819920700	0.0000000000	0.3737432647
N	0.0000000000	0.0000000000	-0.3238360390
C	1.1819920700	0.0000000000	0.3737432647
H	0.0000000000	0.0000000000	-1.3544898760
H	-1.9655233960	0.0000000000	-0.4317885135
H	1.9655233960	0.0000000000	-0.4317885135

PG: C_{2v}

Lowest Real Frequency: 332.36 cm⁻¹

ZPVE(unscaled): 26.70 kcal/mol

MP2(fc) Energy: -132.12944 Hartrees

NIMAG: 0

18a

H₂NCHO:

Amide BLW

Geometry:

N	-0.966857021	-0.592639567	0.000000000
H	-0.653124558	-1.548057226	0.000000000
H	-1.950056271	-0.387126831	0.000000000
C	0.028086057	0.453477995	0.000000000
O	1.206058819	0.246092465	0.000000000
H	-0.420330026	1.464948164	0.000000000

BLW energy (B3LYP/6-31G*): -169.75496 Hartrees

AmideaBLW (delocalized without BLW constraints)

Geometry:

N	-0.940686185	-0.561529851	0.000000000
H	-1.929386819	-0.358991252	0.000000000
H	-0.639621444	-1.527208968	0.000000000
C	0.002617379	0.421526637	0.000000000
H	-0.452679409	1.432212616	0.000000000
O	1.203872477	0.230869818	0.000000000

B3LYP/6-31G* energy (delocalized): -169.79976 Hartrees

18b

H2NNO:

BLW:

Geometry:

N	0.979521502	-0.455996058	0.000000000
H	1.931697915	-0.137800113	0.000000000
H	0.681632813	-1.419359762	0.000000000
N	-0.076110803	0.589103609	0.000000000
O	-1.156481427	0.105649324	0.000000000

BLW energy (B3LYP/6-31G*): -185.70190 Hartrees

aBLW (delocalized without BLW constraints):

Geometry:

N	0.938153007	-0.420743765	0.000000000
H	1.902070918	-0.119579967	0.000000000
H	0.662153531	-1.402504560	0.000000000
N	-0.000427645	0.530082767	0.000000000
O	-1.141689810	0.094342525	0.000000000

B3LYP/6-31G* energy (delocalized): -185.75398 Hartrees

Thermochemical Equation Evaluations (MP2(fc)/aug-cc-pvtz//MP2(fc)/aug-cc-pvtz + scaled (0.9557: Sinha, P.; Boesch, S. E.; Gu, C.; Wheeler, R. A.; Wilson, A. K. *J. Phys. Chem. A* 2004, 108, 9213-9217) ZPVE.

19a H₂C=O

Geometry:

C	0.000000000	0.000000000	-0.5341924511
O	0.000000000	0.000000000	0.6787490497
H	0.000000000	0.9360935343	-1.1124188453
H	0.000000000	-0.9360935343	-1.1124188453

PG: C_{2v}

Lowest Real Frequency: 1197.09 cm⁻¹

ZPVE (unscaled): 16.83 kcal/mol

MP2 (fc) Energy: -114.31641 Hartrees

NIMAG: 0

19b H₂NOH

Geometry:

N	-0.6782524790	0.1964709452	0.0000000000
O	0.7138389377	-0.1846687727	0.0000000000
H	1.1522429978	0.6722742474	0.0000000000
H	-1.0575935733	-0.2851103414	0.8093372891
H	-1.0575935733	-0.2851103414	-0.8093372891

PG: C_s

Lowest Real Frequency: 416.76 cm⁻¹

ZPVE (unscaled): 24.45 kcal/mol
MP2 (fc) Energy: -131.52245 Hartrees
NIMAG: 0

19c CH₃OH

Geometry:

C	0.6674996429	-0.0058804866	0.0000000000
H	1.0346881063	-0.5206779481	0.8893688775
H	1.0579893220	1.0074548977	0.0000000000
H	1.0346881063	-0.5206779481	-0.8893688775
O	-0.7515609001	0.1063273212	0.0000000000
H	-1.1198761914	-0.7814346518	0.0000000000

PG: Cs

Lowest Real Frequency: 290.65 cm⁻¹

ZPVE (unscaled): 32.55 kcal/mol

MP2 (fc) Energy: -115.52901 Hartrees

NIMAG: 0

19d HN=O

Geometry:

N	0.5695432558	-0.1693936794	0.0000000000
O	-0.6315190175	0.0535846150	0.0000000000
H	1.0653493491	0.7570788358	0.0000000000

PG: Cs

Lowest Real Frequency: 1475.80 cm⁻¹

ZPVE (unscaled): 8.70 kcal/mol

MP2 (fc) Energy: -130.28425 Hartrees

NIMAG: 0

19e H₂N-CHO

Geometry:

N	-1.0851439088	0.1451763901	0.0000000000
C	0.1636616948	-0.3876796795	0.0000000000
H	-1.1925257410	1.1449329218	0.0000000000
H	-1.8984870210	-0.4415092487	0.0000000000
H	0.1533574081	-1.4872558688	0.0000000000
O	1.1939615683	0.2617094427	0.0000000000

PG: Cs

Lowest Real Frequency: 130.36 cm⁻¹

ZPVE (unscaled): 28.51 kcal/mol

MP2 (fc) Energy: -169.62077 Hartrees

NIMAG: 0

19f H₂N-NO

Geometry:

N	0.9384039441	-0.4098535555	0.0000000000
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N	-0.0000005000	0.5277770000	0.0000000000
H	0.6652674063	-1.3854856849	0.0000000000
H	1.8918067954	-0.0959261039	0.0000000000
O	-1.1407372888	0.0819934596	0.0000000000

PG: Cs

Lowest Real Frequency: 89.53 cm^{-1}

ZPVE (unscaled): 20.29 kcal/mol

MP2 (fc) Energy: -185.56833 Hartrees

NIMAG: 0

APPENDIX B
PUBLICATIONS

1. Aromaticity in Group 14 Homologues of the Cyclopropenylum Cation, Fernández, I.; Duvall, M.; Wu, J. I. C.; Schleyer, P. v. R.; Frenking, G. *Chem. Eur. J.* **2011**, *17*, 2215.

Aromaticity in heavier Group 14 homologues of the cyclopropenylum cation were investigated at the BP86/TZ2p DFT level by energy decomposition analysis, Nucleus-Independent Chemical Shifts, and block localized wavefunction methods. All three methods indicate that the aromaticity decreases in the order C >> Si > Ge > Sn > Pb. My contribution was the calculations necessary for the data in Tables 7 and 8.

Table 7 gives NICS(0) π_{zz} (ring center) and NICS(1) zz (1 Å above the ring center) at the BP86/Def2-TZVPP level of theory. Table 8 gives ECRE's. Both NICS and ECRE's show the trend mentioned above

Table 7. NICS values (ppm)^a of D_{3h} E₃H₃⁺ cyclopropenylum ions.

	E = C	E = Si	E = Ge	E = Sn ^b	E = Pb ^c
NICS(0) _{πzz} ^a	-14.10	-9.03	-9.36	-8.34	-7.63
NICS(1) _{zz} ^a	-28.49	-7.12	-6.37	-9.75	-8.91

^aAll values were computed at the BP86/def2-TZVP//BP86/def2-TZVP level.

^bC_{3h} Sn₃H₃⁺ (NIMAG = 0).

^cC₃ Pb₃H₃⁺ (NIMAG = 0).

Table 8. Vertical and adiabatic resonance energies (RE) and extra cyclic resonance energies (ECRE) in kcal/mol computed with the BLW method at the B3LYP/Def2-TZVPP level of methylenecyclopropene analogues.

	E = C	E = Si	E = Ge	E = Sn	E = Pb
BLW Re ^a					
Vertical	92.2	62.5	42.4	34.8	25.7
Adiabatic	87.4	55.2	38.7	31.2	22.3
BLW RE ^b					
Vertical	58.2	48.3	30.5	24.9	19.6
Adiabatic	50.7	37.4	25.2	19.3	15.1
ECRE ^c					
Vertical	34.0	14.2	11.9	9.9	6.1
Adiabatic	36.7	17.8	13.5	11.9	7.2

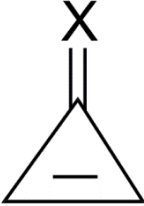
^aResonance energies of cyclic E₃H₃⁺ cations.

^bResonance energies of the corresponding allylic cations.

^cECRE calculated as the difference between RE (E₃H₃⁺) and RE (E₃H₅⁺).

2. Consistent Aromaticity Evaluations of Methylene-cyclopropene Analogues, Wang, Y.; Fernández, I.; Duvall, M.; Wu, J. I. C.; Li, Q.; Frenking, G.; Schleyer, P. v. R. *J. Org. Chem.* **2010**, *75*, 8252. Cyclopropene analogues (HC)₂C=X (with X = BH to InH, CH₂ to SnH₂, and NH to SbH) were examined by energy decomposition analysis, block localized wavefunction, and Nucleus-Independent Chemical Shifts. Electronegative X substituents increased aromaticity of the cyclopropene ring while electropositive substituents decreased aromaticity. The three methods investigated (Energy Decomposition Analysis, NICS(0) π_{zz} , and ECRE (Extra Cyclic Resonance Energies) correlated very well with each other. My contribution was the calculations necessary for NICS (as shown in Table 9).

Table 9. NICS(0), NICS(1) $_{zz}$, and NICS(0) π_{zz} (in ppm, BP86/def2-TZVPP//BP86/TZVPP)

								
	BH (C _{2v})	CH ₂ (C _{2v})	NH (C _s)	O (C _{2v})	AlH (C _{2v})	SiH ₂ (C _{2v})	PH (C _s)	S (C _{2v})
NICS(0)	-23.98	-20.66	-18.10	-14.69	-14.87	-18.83	-18.82	-15.71
NICS(0) π_{zz}	15.31	4.45	-1.85	-6.18	24.36	12.84	4.65	-2.14
NICS(1) $_{zz}$	-3.34	-10.68	-12.21	-12.50	4.70	-5.74	-11.57	-14.55
	GaH (C _{2v})	GeH ₂ (C _{2v})	AsH (C _s)	Se (C _{2v})	InH (C _{2v})	SnH ₂ (C _{2v})	SbH (C _s)	Te (C _{2v})
NICS(0)	-14.22	-17.06	-17.37	-15.37	-10.04	-14.17	-15.24	-14.56
NICS(0) π_{zz}	26.15	14.31	6.24	-0.76	30.42	17.59	8.75	1.54
NICS(1) $_{zz}$	7.37	-3.66	-10.23	-14.25	37.80	-0.60	-8.50	-13.67