Monoaza-analogs † of trimethylenemethane. Isoelectronic similarities and differences

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Calculations employing multireference second-order perturbation theory and density functional theory have been carried out for a series of monoaza-analogs of trimethylenemethane (TMM). Trimethyleneammonium is predicted to have multiplet splittings very similar to TMM. Iminoallyl, also isoelectronic with TMM but with heteroatomic perturbation at a terminal position, is a ground-state triplet like TMM but its corresponding closed-shell singlet state is stabilized relative to the triplet by about 7 kcal mol^{-1}. Protonation of iminoallyl generates iminiumdimethylenemethane and the latter system has a singlet ground state in violation of Ovchinnikov's rule. Aqueous medium effects on the singlet and triplet states of iminiumdimethylenemethane are calculated to reduce the singlet–triplet splitting by 1.6 kcal mol^{-1} using Solvation Model 5.4/AM1.

Organic molecules characterized by high-spin ground states are of interest for many reasons, including their potential use as spin reservoirs in ferromagnetic organic materials.[1–3] For the design of high-spin organic molecules having an even number of electrons, one typically tries to take advantage of Hund's rule[4] in constructing systems biased towards having triplet ground states. That is, one attempts to design a molecule where the frontier molecular orbitals (MOs) are degenerate (or nearly so), in which case the preferred occupation of those orbitals may be expected to generate, for the case of two electrons, the diradical triplet state.

Trimethylenemethane (TMM) in D_{3h} symmetry is an example of such an organic molecule. TMM is a non-Kekulé hydrocarbon (non-Kekulé implying that no resonance structure can be drawn placing its $2n$ pi electrons into n double bonds) characterized by two degenerate non-bonding π frontier MOs (Fig. 1). Coulson[5] credited Moffitt with first having appreciated this unusual (for an organic molecule) feature of TMM, and shortly thereafter Longuet–Higgins[6] provided a theoretical analysis of the orbital properties of non-Kekulé hydrocarbons in general.

In spite of having been the subject of considerable theoretical study, however, TMM remained 'undiscovered' until 1966, when Dowd[7] successfully synthesized TMM and observed its EPR spectrum in a frozen matrix; later experiments confirmed the ground state of TMM to be the triplet.[8] A recent photoelectron spectroscopy experiment quantitated the separation between the $^3A'_2$ ground state and the excited $^1A_1$ state as 16.1 ± 0.1 kcal mol^{-1} in the gas phase.[9] High level theoretical calculations are in good agreement with this splitting.[10] Although a small molecule, TMM proves a challenging test case for different theoretical models—achieving equivalent accuracies for different spin states in molecules having nearly degenerate frontier orbitals is not trivial. For best results, multireference wavefunctions corrected for dynamical correlation effects are required; a summary of prior theoretical work on TMM is available.[10]

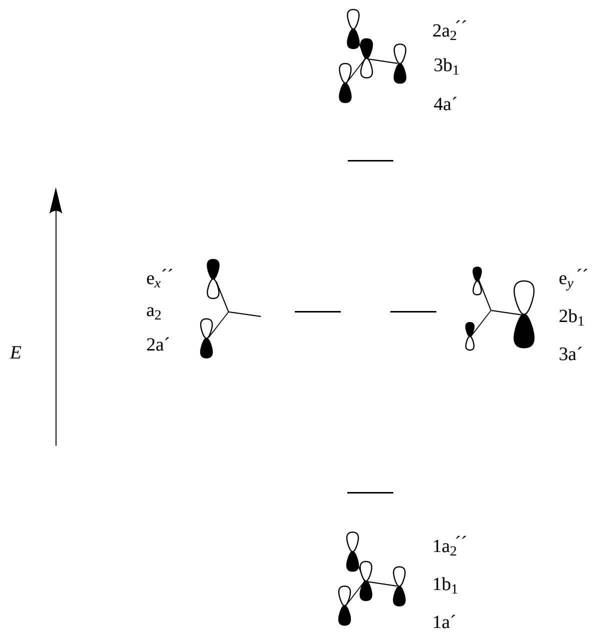

Fig. 1 Schematic diagram of the π orbitals in TMM and its aza analogs, into which must go four π electrons. The orbitals are labeled from top to bottom according to their irreducible representations in D_{3h}, C_{2v}, and C_s symmetry. Although the second and third orbitals are rigorously degenerate in D_{3h} symmetry, in lower symmetries this is not a requirement. Similarly, the orbitals drawn are for D_{3h} symmetry; as symmetry is lowered, participation from p orbitals on other atoms than those indicated may be allowed.

Dowd[11] and Berson[12] were both particularly active in expanding knowledge of the chemistry of TMM and substituted derivatives, and subsequent workers have continued to find new uses for TMM derivatives, *e.g.*, in the cleavage of double-stranded DNA.[13] Larger non-Kekulé systems have also been the subject of much study, particularly with respect to the development of models allowing the prediction of ground state spin.[14–23] For instance, the general class of non-Kekulé hydrocarbons can be divided into two subsets, so-called disjoint and non-disjoint diradicals.[14] The former are characterized by frontier MOs that are formed from disjoint sets of atomic orbitals (AOs), and, as a result, violations of Hund's rule can occur.[22] In the latter set of non-Kekulé hydrocarbons, on the other hand, the same AOs may contribute to both frontier MOs, and exchange repulsion guarantees a high-spin ground state if the orbitals are truly degenerate (exact degeneracy is typical for highly symmetric systems where the frontier orbitals belong to an irreducible representation of the molecular point group of dimension 2 or higher).

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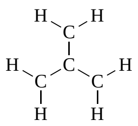
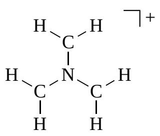
† IUPAC-preferred names: TMM, 2-methylenepropane-1,3-diyl; TMN$^+$, 2-methylene-2-azoniapropane-1,3-diyl; IA, 2-iminopropane-1,3-diyl; IDMM, 2-iminiopropane-1,3-diyl; 2-oxyallyl, 2-oxopropane-1,3-diyl; 2-hydroxyallyl cation, 2-oxoniumylidenepropane-1,3-diyl.

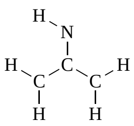
MO degeneracy, however, can be lifted in a number of ways. Closed-shell singlet TMM, for instance, undergoes Jahn–Teller distortion to lower the energy of the (formally) doubly occupied frontier orbital at the expense of the (formally) empty one.[17] Alternatively, rotation of one methylene group out of the remaining allyl plane lifts the orbital degeneracy and leads to the lowest energy TMM singlet (${}^1B_1$).[10] Finally, replacing one of the carbon atoms in TMM with a heteroatom may lift the orbital degeneracy.[20,24] This latter observation should in some sense seem trivial! For instance, although it does not appear ever to have been explicitly emphasized, the 2-hydroxyallyl cation is isoelectronic with TMM. This cation is a well known synthon employed in [4 + 3] cycloadditions[25,26]—there is no doubt that this molecule has a singlet ground state by a large margin. On the other hand, 2-oxyallyl is also isoelectronic with TMM and is a ground state triplet,[27,28] albeit with a much smaller splitting than TMM. This indicates that the nature of the heteroatom substitution and the overall electronegativity of that heteroatom (as possibly modified by protonation/coordination) may play a significant role in tuning the state energy splitting in a non-Kekulé system. The remainder of this article focuses on the effects of nitrogen-atom substitution to generate isoelectronic aza analogs of TMM, and in particular computationally characterizes various low-energy spin states of trimethyleneammonium (TMN$^+$), 2-iminoallyl (IA), and iminiumdimethylenemethane (IDMM$^+$) using multiconfiguration self-consistent field (MCSCF) and density functional (DFT) methods.



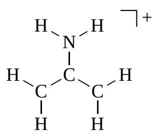
TMM



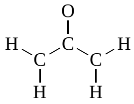
TMN$^+$



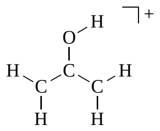
IA



IDMM$^+$



2-oxyallyl



2-hydroxyallyl cation

Computational methods

All geometries were fully optimized at the MCSCF and DFT levels of theory using the cc-pVDZ basis set of Dunning.[29] Single point energy calculations with the larger cc-pVTZ basis set[29] were also carried out. DFT calculations were done using the gradient-corrected functionals of Becke[30] for exchange and of Perdew *et al.*[31] for correlation.[32] Other functionals were examined cursorily and gave similar results, but are not described here. The MCSCF calculations for TMN$^+$ and IDMM$^+$ employed 10-electron/10-orbital active spaces, where the orbitals included were the 4 π orbitals and the three bonding and three antibonding heavy-atom–heavy-atom σ orbitals. For IA, this space was expanded to include the nitrogen lone pair, leading to a 12-electron/11-orbital active space. Dynamic correlation effects were accounted for using multireference second-order perturbation theory[33,34] (CASPT2). Previously published data[10] for TMM are included for comparison below; MCSCF calculations were for the same (10,10) active space as used for TMN$^+$ and IDMM$^+$ and DFT calculations were also the same except that an earlier correlation functional of Perdew[35] was employed (which is expected to have very little impact on the results, since we do not observe sensitivity of structures or energies to correlation functionals in general).

DFT open-shell singlet energies were estimated using the 'sum method' as described by Ziegler *et al.*[36–38] This procedure makes use of the 50 : 50 determinant, eqn. (1), where 1 and 2 are

$$ {}^{50:50}\Psi = [\varphi_a(1)\alpha(1)\varphi_b(2)\beta(2) - \varphi_a(2)\alpha(2)\varphi_b(1)\beta(1)] \quad (1) $$

the indices of the unpaired electrons occupying orbitals φ_a and φ_b. The 50 : 50 superscript emphasizes that this configuration is an equal combination of the open-shell singlet and the $S_z = 0$ triplet, provided the two pure spin states are characterized by the same spatial orbitals. When the Hamiltonian contains no spin-dependent terms, the separation given in eqn. (2) may be

$$ \langle {}^{50:50}\Psi|H|{}^{50:50}\Psi\rangle = \tfrac{1}{2}(\langle {}^3\Psi_0|H|{}^3\Psi_0\rangle + \langle {}^1\Psi|H|{}^1\Psi\rangle) \quad (2) $$

accomplished. One may thus estimate the energy of the open-shell singlet from the readily calculated expectation value of the Kohn–Sham Hamiltonian operating on the 50 : 50 and triplet configurations.[10,39,40]

Aqueous solvation free energies were calculated for the different electronic states of IDMM$^+$ using gas phase (*i.e.*, unrelaxed) charge distributions and the SM5.4/AM1 solvation model.[41] The SM5.4/AM1 model uses Charge Model 1[42] (CM1) to map Austin Model 1[43] (AM1) zero-differential overlap Mulliken charges to higher-quality Class IV partial atomic charges (that accurately reproduce molecular dipole moments, for instance[42]); in this case the Mulliken charges were derived from AM1 calculations that included a full CI in the four-electron/four-orbital π subspace.

MCSCF and DFT calculations were carried out with the MOLCAS[44] and GAUSSIAN 94[45] electronic structure program suites, respectively. AM1-CI and SM5.4/AM1 calculations were accomplished using a locally modified version of the AMSOL[46] version 5.4.1 program suite.

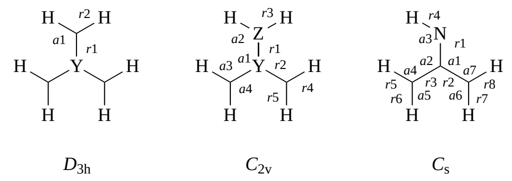
Results

The optimized geometries for the different electronic states at the DFT and MCSCF levels of theory are provided in Tables 1 and 2, respectively. The state energies relative to the triplet for all species at the CASPT2 and DFT levels are provided in Table 3. The triplet is the lowest energy state in every case but IDMM$^+$, where the ${}^1A_1$ state is lower in energy by about 9 kcal mol^{-1}.

For the ${}^1A_1$ states of TMM and TMN$^+$, the frontier π orbitals are very nearly degenerate (see Fig. 1). As discussed previously for TMM, this leads to wavefunctions that are dominated by two nearly equally contributing configurations, these being in the π space $|1b_1^2a_2^2\rangle$ and $|1b_1^22b_1^2\rangle$ (the weights of these two configurations in the MCSCF(10,10) wavefunctions for both TMM and TMN$^+$ are within 1% of each other). The energetic stabilization associated with the tendency of these wavefunctions to be multiconfigurational is called non-dynamical correlation. Since this multiconfigurational character is so nearly 50 : 50, the molecular wavefunctions are very poorly described by a single determinant method like DFT and give energies that are much too high relative to single-configuration states, even if smeared-density techniques are employed (*i.e.*, placing one electron's worth of paired spin density in both the a_2 and $2b_1$ orbitals).[10] Noting this inadequacy for the ${}^1A_1$ states of TMM and TMN$^+$, we present neither DFT geometries nor energies for these two cases.

In IDMM$^+$, on the other hand, the splitting between the a_2 and $2b_1$ orbitals is sufficiently large that the contributions of the $|1b_1^2a_2^2\rangle$ and $|1b_1^22b_1^2\rangle$ configurations to the MCSCF wavefunction are quite different (weights of 13% and 82%, respectively), and DFT successfully accounts for this reduced degree of multiconfigurational character (*vide infra*). The ability of DFT accurately to treat systems having small to moderate degrees of multiconfigurational character arising from non-dynamical correlation has been amply demonstrated in a number of single-center diradical cases,[39,40,47–61] *e.g.*, carbenes, nitrenes, nitrenium ions and silylenes.

Table 1 DFT geometries for planar TMM and aza analogs



Electronic State Symmetry	TMM[a]			TMN$^+$			IA			IDMM$^+$		
	$^3A'_2$ D_{3h}	$^1A_1$[b] C_{2v}	$^1B_2$ C_{2v}	$^3A'_2$ D_{3h}	$^1A_1$[b] C_{2v}	$^1B_2$ C_{2v}	$^3A'$ C_s	1 $^1A'$ C_s	2 $^1A'$ C_s	$^3B_2$ C_{2v}	$^1A_1$ C_{2v}	$^1B_2$ C_{2v}
Bond lengths (Å)												
*r*1	1.424		1.459	1.378		1.426	1.359	1.309	1.325	1.348	1.350	1.379
*r*2	1.100		1.409	1.095		1.358	1.431	1.442	1.448	1.438	1.417	1.422
*r*3			1.100			1.093	1.431	1.470	1.454	1.027	1.018	1.028
*r*4			1.100			1.095	1.041	1.035	1.039	1.098	1.101	1.097
*r*5			1.100			1.096	1.096	1.102	1.097	1.096	1.096	1.098
*r*6							1.097	1.098	1.097			
*r*7							1.099	1.097	1.099			
*r*8							1.099	1.101	1.099			
Valence angles (deg)												
*a*1	121.0		119.6	118.4		119.2	116.2	121.3	118.0	117.8	123.9	117.0
*a*2			120.8			117.8	122.9	132.7	125.5	121.4	121.5	121.5
*a*3			121.2			118.7	107.6	109.1	108.4	120.0	119.8	120.1
*a*4			120.9			118.7	120.3	121.5	120.3	121.1	122.4	121.4
*a*5							121.8	121.3	121.7			
*a*6							121.8	121.8	121.7			
*a*7							118.7	119.7	118.8			

[a] Reference 10. [b] This state is not treated well by DFT and geometrical data are not provided; see the text.

Table 2 MCSCF geometries for planar TMM and aza analogs

Electronic State Symmetry	TMM[a,b]			TMN^{+b}			IA[c]		IDMM^{+b}		
	$^3A_{2'}$ D_{3h}	$^1A_1$ C_{2v}	$^1B_2$ C_{2v}	$^3A_{2'}$ D_{3h}	$^1A_1$ C_{2v}	$^1B_2$ C_{2v}	$^3A'$ C_s	1 $^1A'$ C_s	$^3B_2$ C_{2v}	$^1A_1$ C_{2v}	$^1B_2$ C_{2v}
Bond lengths (Å)											
*r*1	1.438	1.370	1.539	1.385	1.305	1.506	1.360	1.297	1.338	1.344	1.510
*r*2	1.081	1.496	1.411	1.077	1.457	1.354	1.447	1.495	1.457	1.437	1.403
*r*3		1.082	1.079		1.080	1.075	1.448	1.503	1.007	1.000	1.013
*r*4		1.080	1.081		1.076	1.077	1.013	1.011	1.080	1.082	1.080
*r*5		1.080	1.081		1.075	1.079	1.079	1.080	1.078	1.078	1.079
*r*6							1.080	1.080			
*r*7							1.081	1.080			
*r*8							1.080	1.080			
Valence angles (deg)											
*a*1	120.9	121.1	119.0	118.2	121.0	118.0	116.7	119.7	118.2	123.1	114.8
*a*2		121.2	120.3		119.4	116.4	122.8	125.5	121.1	121.0	121.2
*a*3		120.2	121.4		117.0	118.8	108.5	109.8	119.7	119.5	122.5
*a*4		120.9	120.6		117.3	118.6	120.5	120.3	120.6	121.7	119.0
*a*5							121.4	121.3			
*a*6							121.3	121.1			
*a*7							119.1	119.0			

[a] Reference 10. [b] (10,10) active space. (12,11) active space. [c] The 2 $^1A'$ state was not calculated.

Table 3 Relative state energies (kcal mol^{-1}) for planar TMM and aza analogs at optimized geometries

Electronic State	TMM[a,b]			TMN^{+b}			IA[c]			IDMM^{+b}		
	$^3A_{2'}$	$^1A_1$	$^1B_2$	$^3A_{2'}$	$^1A_1$	$^1B_2$	$^3A'$	1 $^1A'$	2 $^1A'$	$^3B_2$	$^1A_1$	$^1B_2$
CASPT2	0.0	19.1	19.1	0.0	18.8	17.9	0.0	12.7		0.0	−8.9	43.8
DFT	0.0		16.9[d]	0.0		19.8[d]	0.0	22.3	11.2[d]	0.0	−8.7	47.7[d]

[a] Reference 10. [b] (10,10) active space for CASPT2. [c] (12,11) active space for CASPT2. [d] Calculated using the sum method.

IA, being of lower symmetry (C_s), presents a set of different challenges with respect to the singlet states. In the C_{2v} systems, one may conveniently refer to closed-shell and open-shell singlets as distinct species. A closed-shell singlet may be defined as a linear combination of configurations in which all orbital occupancies are either zero or two, while an open-shell singlet has at least two orbitals that are occupied by single electrons that are spin-paired singlet. The irreducible representation (irrep) to which the lowest energy open-shell singlet belongs is determined[62] by taking the product of the irreps of the singly occupied frontier π orbitals (B_2). Closed-shell states, on the other hand, always belong to the totally symmetric irrep (A_1 in this case), so the two singlet states are easily distinguished and do not mix. In the case of IA, however, *all* π orbitals belong to the a″ irrep, and thus the product of the irreps of the frontier π orbitals *is* the totally symmetric irrep (here A′). As such, both the lowest energy singlet (1 ^{1}A′) and the first excited singlet (2 ^{1}A′) are free to adopt mixed degrees of open- and closed-shell character.

This poses unique difficulties for both the MCSCF and the DFT calculations. In the case of the MCSCF(12,11) calculations, it is straightforward to optimize a ^{1}A′ wavefunction that appears to be well described as a closed-shell singlet [the π space configurations $|(1a'')^2(2a'')^2\rangle$ and $|(1a'')^2(3a'')^2\rangle$ are weighted 34% and 58%, respectively]. Attempts to find the next higher energy singlet, however, were unsuccessful. Such a calculation is typically carried out by optimizing the wavefunction for the second eigenvalue of the ^{1}A′ CI matrix. However, since the orbitals that optimize the second root are *not* optimal for the first root, if the roots begin to be close to each other in energy then their relative positions can reverse during the calculation, and this leads to instabilities in the computation. We found this to be the case, and we further had no success optimizing for the second root using state-averaged orbitals. Attempts to start from geometries presumed optimal for the 2 ^{1}A′ state were similarly unsuccessful. Based on these results, we tentatively assign the optimized closed-shell-like wavefunction to be the 1 ^{1}A′ state, but emphasize that the open-shell-like singlet is very close in energy (as is also found for TMM and TMN$^+$, see Table 3), so the relative ordering of these two states cannot be definitively assigned.

DFT calculations are not helpful in resolving this dilemma. While they can be successfully carried out for a closed-shell singlet (by careful use of a restricted self-consistent-field procedure), the similarity of the two dominant weights in the MCSCF ^{1}A′ wavefunction (34% and 58%) suggests that DFT results for this state should be viewed with some suspicion, and indeed the relative energy calculated for this state at the DFT level is 10 kcal mol^{-1} higher than at the MCSCF level. Such an overestimation of the relative state energy by DFT is expected for a system subject to large non-dynamical correlation effects.

As for the open-shell singlet, the various approximations in the sum method (*e.g.*, the geometry optimization is for a mixed electronic state) render this method unsatisfactory for quantitative comparison of state energies. However, the DFT relative energy for the 2 ^{1}A′ state (11.2 kcal mol^{-1}) *is* found to be quite close to the MCSCF relative energy for the 1 ^{1}A′ state (12.7 kcal mol^{-1}), supporting the qualitative notion that these two states are narrowly separated in energy.

The analysis of IA is further complicated because no formal proof exists for the applicability of DFT to molecular excited states in the general case. The Hohenberg–Kohn theorem[63] *has* been proven to generalize to the lowest energy state for each irrep in a symmetric system,[37,64,65] so there is no formal ambiguity in calculating multiplet splittings between lowest-energy states belonging to different irreps (*e.g.*, $^3B_2$ and $^1A_1$). For IA, however, all *three* states we are interested in belong to the same A′ irrep, so DFT results must be analyzed with caution.

Discussion

We begin by comparing DFT and MCSCF geometries for molecular electronic states where both were computed. There is generally good to excellent agreement between these two levels of theory for all of the triplets, which is certainly expected insofar as the triplets are dominated by a single configuration and pose no particular theoretical challenge in terms of their wavefunctions. One small discrepancy is that there is a consistent trend for DFT to predict C–H bond lengths to be about 0.02 Å longer than the MCSCF predictions. For the $^1A_1$ state of IDMM$^+$, there is also good agreement between the two levels of theory, consistent with this state being dominated by a single configuration (*vide supra*). For the open-shell singlets of TMM, TMN$^+$, and IDMM$^+$, on the other hand, there is rather poor geometrical agreement between DFT and MCSCF. Of course, the DFT geometries are optimized for the 50 : 50 mixed singlet/triplet state, so one expects them to be roughly midway between the DFT triplet and the MCSCF open-shell singlet, and this expectation is qualitatively borne out. However, we have noted previously that, in spite of the large differences in geometry between the DFT and MCSCF structures for the $^1B_2$ state of TMM, the DFT energies for these two geometries differ by only 0.2 kcal mol^{-1}.[10] This small sensitivity to geometry seems to be maintained in the open-shell singlets of TMN$^+$ and IDMM$^+$, based on the reasonably good comparisons of MCSCF and DFT relative energies for these states found in Table 3.

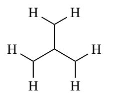
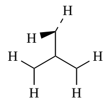
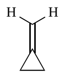
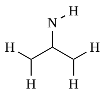
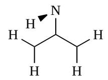
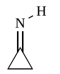
In the case of IA, the DFT 1 ^{1}A′ geometry is in fair agreement with the MCSCF structure, but shows a reduced degree of Jahn–Teller-like distortion from the triplet geometry. As noted above, the 2 ^{1}A′ geometry could not be obtained at the MCSCF level, and the DFT structure is for a mixed state, so little more can be said about this electronic state.

With respect to electronic state energies, the most striking result from the calculations is that, at both levels of theory, protonation of IA to form IDMM$^+$ is predicted to invert the preferred spin state from triplet to singlet. This is similar to Dougherty's observation of ground state reversal in the conjugate acid and base forms of pyridine-based *m*-xylylenes, which are also non-Kekulé systems.[66] And, as noted in the introduction, while never previously pointed out, the same reversal is found for 2-oxyallyl and 2-oxyallyl cation. Dougherty has emphasized that one may explain this phenomenon using either valence bond formalisms or molecular orbital arguments.

In the molecular orbital analysis, one need only consider the frontier π orbitals (Fig. 1) and recognize that the energy of the $2b_1$ orbital (using the C_{2v} symmetry labels) will be lowered relative to the a_2 orbital when a single atom of higher electronegativity is at one of the terminal positions. Under such conditions, one expects the p orbital of that atom to be the one making the dominant contribution to the $2b_1$ orbital, thereby localizing electron density onto the more electronegative atom at the expense of the other two termini. One means to evaluate this computationally is to consider orbital energies for the two singly occupied π molecular orbitals (SOMOs) calculated at the unrestricted Hartree–Fock (UHF) level for the triplet state. This choice of state and level of theory is motivated by the single-determinant nature of the triplet, the greater reliability of orbital energies for occupied orbitals compared with virtual orbitals, and the availability of energy eigenvalues for the UHF orbitals. The calculated splittings between the two SOMOs for TMM, TMN$^+$, IA, 2-oxyallyl, IDMM$^+$, and 2-hydroxyallyl cation are 0.0, 0.0, 1.9, 2.6, 2.9 and 3.8 eV, respectively. There is a direct correlation between the singlet–triplet energy splittings in these systems and the magnitude of this orbital gap, as expected. The trend is also consistent with respect to the electronegativity of oxygen *vs.* nitrogen, orbital splittings being larger for the former and hence S–T gaps being smaller for the same group charge.

The valence bond analysis is most simply demonstrated for IDMM$^+$, for which three resonance structures are presented in Fig. 2. The left-most structure is a typical diradical mesomer, and available to both spin states. The singlet state, however, can spin-pair the highest energy electrons on a single atom, with the obvious choice being the more electronegative nitrogen atom, thereby creating 2-aminoallyl cation mesomers (we note that in

Table 4 Relative state energies (kcal mol^{-1}) for planar and rotated IA and iminocyclopropane[a,b]

						
	$^3A'_2$	$^1A_1$	$^1B_2$	$^3B_1$	$^1B_1$	$^1A_1$
BP86/cc-pVDZ	0.0(−155.972 21)	23.0	17.1	13.6	15.4	−26.1
MCSCF(10,10)/cc-pVDZ	0.0(−154.995 09)	19.2	19.5	13.8	15.9	−18.9
CASPT2/cc-pVDZ	0.0(−155.425 36)	19.1	19.1	13.9	15.7	−20.9
MCSCF(10,10)/cc-pVTZ	0.0(−155.035 62)	18.9	19.3	13.8	15.8	−19.8
CASPT2/cc-pVTZ	0.0(−155.630 73)	19.1	19.1	14.4	16.1	−21.9
						
	$^3A'$	$1\,^1A'$	$2\,^1A'$	$^3A''$	$^1A''$	$^1A'$
BPW91/cc-pVDZ	0.0(−171.949 24)	22.3	11.2	13.8	14.4	−30.4
MCSCF(12,11)/cc-pVDZ	0.0(−171.004 73)	12.2	*c*	15.2	16.9	−22.8
CASPT2/cc-pVDZ	0.0(−171.436 00)	12.7	*c*	15.2	16.1	−22.8
MCSCF(12,11)/cc-pVTZ	0.0(−171.049 60)	11.4	*c*	14.9	16.6	−23.3
CASPT2/cc-pVTZ	0.0(−171.652 39)	12.0	*c*	14.5	16.0	−24.1

[a] TMM results are from reference 10. [b] DFT energies are at DFT/cc-pVDZ geometries; MCSCF and CASPT2 energies are at MCSCF/cc-pVDZ geometries. Absolute energies (hartrees) are provided for the planar triplets. [c] An MCSCF solution for this state was not found.

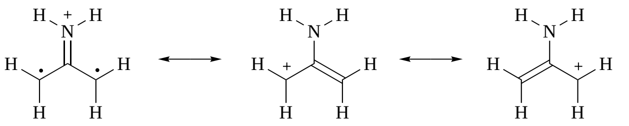


Fig. 2 Three resonance structures for IDMM$^+$. The right-most two are available only to the singlet state.

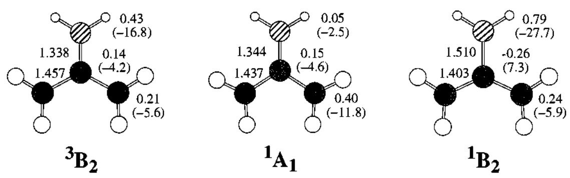


Fig. 3 Bond lengths, group CM1A partial charges, and SM5.4/AM1 aqueous solvation free energies (the latter in parentheses) for the three lowest electronic states of IDMM$^+$

this paper we have chosen *not* to refer to IDMM$^+$ as the 2-aminoallyl cation precisely because the small S–T gap in this system suggests that the diradical mesomer is a non-trivial contributor). In a neutral system, like TMM, this same spin-pairing would create a zwitterionic structure, with a carbanion at one terminus and a carbenium ion at another. Such zwitterionic states are very high in energy (particularly in the gas phase), so they contribute little to the character of TMM. However, when a formal positive charge is already present, a group of higher electronegativity, like NH_2 or OH, will be greatly stabilized by spin-pairing on that atom. As noted by Coolidge *et al.*[28] and Ichimura *et al.*,[67] even isoelectronic singlets bearing *zero* net charge can benefit from these resonance structures provided other factors stabilize the zwitterionic mesomers; thus, 1,3-dialkyl-2-oxyallyls are ground state singlets even though 2-oxyallyl itself is a ground state triplet because, in addition to oxygen being sufficiently electronegative to carry a partial negative charge, substituent hyperconjugation can stabilize partial positive charge on the allyl termini.[68]

Finally, it is of some interest to consider from a more mathematical standpoint why it is that Ovchinnikov's rule[15] fails for IDMM$^+$. To briefly recapitulate that rule, one takes a conjugated system and labels each heavy atom either with a star or lack of a star in such a way that every atom's neighbors are labeled differently. Ovchinnikov's rule is that the ground state for such a system has spin $|n - n^*|/2$.[15] This derives from assuming that the energy of the conjugated system may be approximated by a Heisenberg Hamiltonian [eqn. (3)], where *i* and *j*

$$H = \sum_{i,j}^{\text{neighbors}} J_{ij}(S_iS_j - \tfrac{1}{4}) \qquad (3)$$

run over all pairs of neighbors, J_{ij} is the Heisenberg exchange integral (positive for a hydrocarbon π system), and S_i is a spin operator returning values of +1/2 and −1/2 for α and β spins, respectively. Assuming one spin on all atoms, this Hamiltonian is minimized when all neighbors have opposite spins, which implies that all starred atoms have one spin and all unstarred atoms the other, and hence the ground state has a net spin as indicated above. The key effect of heteroatomic substitution and/or charge polarization is that the assumption of equal spin density on all atoms breaks down, and the simple Hamiltonian is no longer adequate.

Further analysis of the electronic structures of the various states of IDMM$^+$ is of particular interest because it is a charged system. As such, it would be expected to interact strongly with a surrounding medium, and that interaction may be different for the different electronic states. This will especially be the case if the charge distribution varies significantly over the different electronic states (which is certainly plausible given the extended π system present in a non-Kekulé molecule). Fig. 3 presents the summed group charges calculated from the CM1A model[42] for the terminal groups and the central carbon for each of the three states of IDMM$^+$ in the gas phase. The figure also provides the groupwise contributions to the aqueous solvation free energies of these states as calculated using the quantum statistical SM5.4/AM1 solvation model and the frozen gas-phase charge density.[41]

One immediately notices substantial differences in the charge distributions of the states. Based on the localization of positive charge, it would appear that the triplet state might best be described as an iminium cation diradical (consistent with the dominance of that resonance structure noted above for this state), while the closed-shell singlet would be better described as a 2-amino substituted allyl cation (also consistent with the ionic delocalization rationalized as providing VB stabilization to this state). Finally, the open-shell singlet resembles a 2-aminyl-cation-substituted allyl radical (and is, of course, very high in energy relative to the other two states). Since the singlet-coupled unpaired electrons do not enjoy any exchange stabilization (as they would were they to be triplet-coupled) there is some driving force for them to separate over different regions of the molecule, and this resonance contributor is expected to be more relevant for the open-shell singlet than the triplet.

These differences in local charge lead to very large differences in groupwise contributions to the overall solvation free energy. For instance, the amino group contribution spans a range of 25 kcal mol^{-1}. However, since the majority of ionic solvation free energy is derived from long-range interactions that are not particularly sensitive to the localization of charge, but only to the existence of charge, these variations tend to cancel out over the whole molecule. As a result, the triplet and open-shell singlet have approximately the same aqueous solvation free energy, which is more negative (favorable) than that for the closed-shell singlet by about 1.6 kcal mol^{-1}. Such a difference, however, is of considerable interest, insofar as it does indicate a non-trivial medium effect on the relative state energies. Moreover, these solvation free energies were calculated for the frozen gas-phase charge distribution. Depending on relative polarizabilities, the differential solvation free energy might be expected to increase were the wavefunction allowed to relax. However, the SM5.4 model does not presently allow self-consistent reaction field calculations using CI-type wavefunctions, so this possibility remains to be tested.

Finally, because it has a high-spin ground state, we have carried out a more complete analysis for IA by calculating the energy for additional states/geometries/isomers. Table 4 provides DFT, MCSCF(12,11), and CASPT2 energies calculated with both the cc-pVDZ and cc-pVTZ basis sets for not only the planar $^3A'$ and $^1A'$ states, but also for iminocyclopropane and the $^3A''$ and $^1A''$ states derived from 90° rotation about the C–N bond. Attempted optimization of C_1 structures derived from 90° rotation about one of the C–C bonds inevitably led to one of the C_s structures. For comparison we provide prior results for similar calculations on TMM/methylenecyclopropane. Overall, the systems are remarkably similar for all diradical states except the closed-shell singlet (1 $^1A'$ for IA and $^1A_1$ for TMM), where the nitrogen heteroatom provides a stabilization relative to the triplet of about 7 kcal mol^{-1} at the MCSCF and CASPT2 levels. Noting that the experimental S–T splitting between these two states has been measured as 16.1 ± 0.1 kcal mol^{-1},[9] this suggests a good estimate for the splitting in IA to be about 9 kcal mol^{-1}.[32] Nitrogen substitution also stabilizes the substituted cyclopropane relative to the triplet by about 4 kcal mol^{-1}. Lastly, although the open-shell singlet that is lowest in energy for TMM has one methylene group rotated, it seems likely that in IA the planar geometry is slightly lower in energy, since otherwise the root switching that makes this state difficult to converge at the MCSCF level would not be expected and moreover the DFT energies for this state are expected to be reasonable based on precedent for TMM. We note that the various state energies appear well converged with respect to basis set size and, based on the small changes in relative state energies at the CASPT2 compared with the MCSCF level, that the chosen (12,11) active space is sufficiently robust for all states.

Conclusions

Trimethyleneammonium has an electronic structure very similar to trimethylenemethane, as expected given the small contribution of central atom atomic orbitals to the frontier π orbitals in these four-heavy-atom non-Kekulé molecules. Iminoallyl, which is also isoelectronic with TMM but now introduces heteroatomic perturbation at a terminal position, is a ground-state triplet with an electronic structure still roughly similar to TMM, except insofar as the closed-shell singlet state is stabilized relative to the triplet by about 7 kcal mol^{-1}. Protonation of iminoallyl, however, to generate iminiumdimethylenemethane, inverts the spin states, and this system thus violates Ovchinnikov's rule for ground states in conjugated molecules. This spin-state inversion illustrates the limitations of the Ovchinnikov Hamiltonian for systems having significant spin and/or charge polarization and can be rationalized using either molecular orbital or valence bond theory. Because of different charge localizations, medium effects are predicted to discriminate between the singlet and triplet states of iminiumdimethylenemethane, with the triplet interacting 1.6 kcal mol^{-1} more favorably with a surrounding aqueous solvent than the closed-shell singlet. Multiconfigurational theoretical models are more informative than density functional theory for most of the singlet diradicals studied here, although the latter level of theory can provide quantitatively useful energies in many cases, and in particular is sufficiently robust for electronic states characterized by only modest non-dynamical correlation effects within a Slater determinant formalism.

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68. A referee has pointed out that one might expand this valence bond analysis somewhat by considering the varying substituent group to have a perturbational interaction with the allyl cation. The symmetry of the perturbing group p orbital (b_1) requires it to mix with the lowest (and highest) energy π orbitals of the allyl cation. When the allyl cation is in its $^1A_1$ ground state, its π_1 orbital is doubly occupied, and the mixing is a destabilizing four-electron interaction. If the resonance (mixing) energy is large enough, however, it is energetically advantageous to promote an electron from π_1 to π_2 in the allyl cation, generating the $^3B_2$ state, thereby making the mixing event a stabilizing three-electron interaction. TMM's triplet ground state is thus rationalized by invoking a resonance interaction that is larger than the promotion energy in the allyl cation. Of course, both of these VB analyses are more useful qualitatively than quantitatively, and it is worth emphasizing that their utility derives not from any formal rigor but rather from their ability to speak to chemical intuition.

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