COMPUTATIONALLY BASED DESIGN AND SCREENING OF HYPERGOLIC MULTIAMINES

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ABSTRACT

Seeking to identify structural features of saturated, (all) tertiary, alkyl multiamines (STAMs) that correlate with hypergolic ignition delays, conformers of STAMS whose ignition delays have been measured were established through density functional theory-based calculations. Examined from the standpoint of lone pair/(C-N and C-C) bond orientations, a correlation is suggested. Conformers of 1,3-dimethylimidizolidine (DMIZ), a notional hypergol whose synthesis and testing was originally recommended for other reasons, were therefore characterized. On the basis of the characterization, it is expected to have a short ignition delay. Moreover, estimates of DMIZ's density specific impulse indicate that its performance will be competitive with hydrazine-based fuels. The lowest energy structure of a second notional hypergol—1,3-dimethylhexahydropyrimidine (DMHHP)—has a lone pair/lone pair orientation unlike any found in previously tested STAMs. The results suggest that the potential of STAMs as replacements for hydrazines in hypergolic propulsion systems may not yet be fully realized, and that the synthesis and testing of DMIZ and DMHHP should be pursued.

1. INTRODUCTION

Hydrazine-based hypergols being acutely toxic and suspected carcinogens, the US Army Aviation and Missile Research, Development and Engineering Center (AMRDEC) has been searching for alternatives, with recent efforts devoted to testing the hypergolicity of commercial-off-the-shelf (COTS) multiamines; i.e., variously substituted amines with two or more amine sites (Stevenson et al., 2004). The potential of multiamines for hypergolic propulsion was recognized and extensively examined in the early-to-mid 1950's by the Phillips Petroleum Co. (PPC) (Phillips Petroleum Co., 1956). PPC reports performance related properties for over 40 different multiamines, and 6 of them were tested in rocket motor firings. As summarized by Clark (Clark, 1972),

> "They were good fuels. Ignition was hypergolic and fast, combustion was good and performance was respectable, and the saturated ones, at least, were quite stable to heat and suitable for regenerative cooling. [But they] were obsolete at birth. … Hydrazine was the name of the big game."

A view apparently shared by the propellant development community; a literature search for other (more recent) information on multiamine hypergols suggests that research into and development of them effectively ceased with the PPC effort.

Given this history, the PPC results were scrutinized to assess the prospects for designing and developing a multiamine-based fuel that, if not meeting or exceeding the performance of hydrazine or its derivatives, at least approaches it. Hoping to develop a hypergol made primarily with jet fuel (JP-4), PPC studied multiamines as "ignition enablers". To assess a multiamine's potential in this application, the ignition delays of blends were measured as a function of temperature and multiamine concentration. "Overwhelming proportions" of multiamine additive were found needed to make JP-4 hypergolic (Clark, 1972), so only neat multiamines were fired in the rocket motor tests. Of multiamines tested by PPC, saturated compounds (i.e., no multiple bonds) with tertiary amine sites (only) were considered to have the most promise. This conclusion still judged to be valid, only the prospects for saturated, (all) tertiary, alkyl multiamines (STAMs) were considered further.

The STAMs synthesized and tested by PPC included 9 linearly branched (acyclic) diamines, 2 linearly

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branched triamines, a linearly branched tetraamine, and 2 compounds having an ethylene chain with a heterocyclic ring attached at each end. Fig. 1 provides schematic renderings of selected members of this group. Of all the compounds tested by PPC, the linearly branched diamines N,N,N',N'-tetramethylbutane-1,3-diamine (TMB13DA) and N,N,N',N'-tetramethylethane-1,2-diamine (TMEDA) were considered to have the most promise, their ignition delays (including temperature insensitivity) and freezing points separating their performance from all the other STAMs evaluated. They were, however, observed to have significantly longer ignition delays than unsymmetrical dimethylhydrazine (UDMH). Higher densities and shorter ignition delays (at 298 K) were observed for the two STAMs with heterocyclic rings: 1,2- di(1-piperidyl)ethane (DPipE) and 1,2-di(1-pyrrolidyl)ethane (DPyrE), but the relatively high freezing points of these two compounds precluded interest in them.

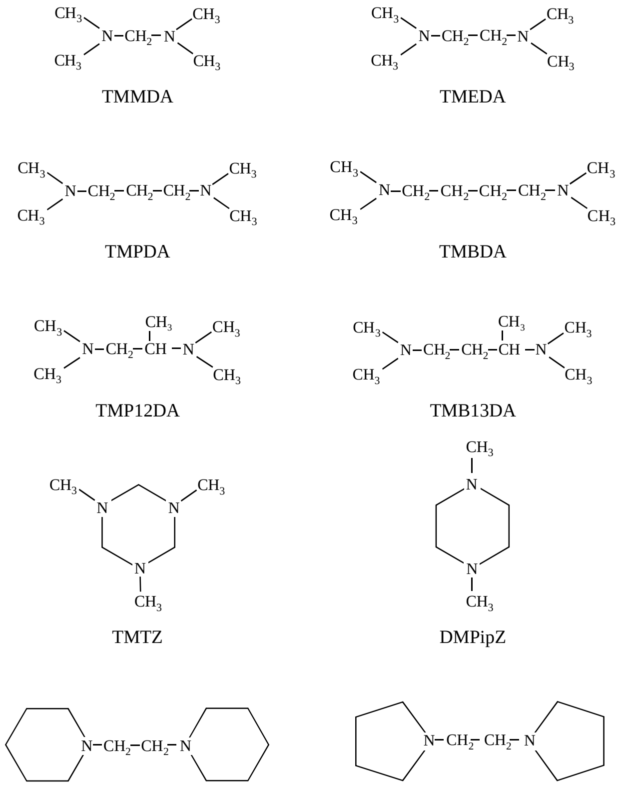
TMMDA
TMEDA
TMPDA
TMBDA
TMP12DA
TMB13DA
TMTZ
DMPipZ
DPipE
DPyrE

Fig. 1. Schematic renderings of STAMs whose hypergolicity with IRFNA has been tested.

The recent experimental results reported by AMRDEC (Stevenson et al., 2004) corroborate the PPC results. The AMRDEC results indicate a smaller ignition delay difference between UDMH and the best-performing STAMs, but it is not certain which group's results will have the best correlation with the ignition delays realized in a rocket motor. Regardless, given the large number of saturated, acyclic diamines synthesized and tested by PPC and the insight PPC researchers had regarding hypergolicity in this class of compounds, the limit of performance, if not already attained, has surely been closely approached for linearly branched compounds. Thus, AMRDEC's newer experimental results (alone) do not offer much justification for undertaking a more concerted development effort; i.e., one that involves synthesizing new compounds.

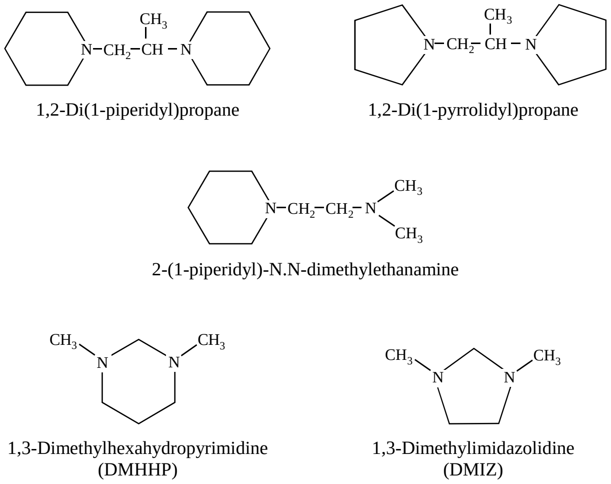
1,2-Di(1-piperidyl)propane
1,2-Di(1-pyrrolidyl)propane
2-(1-piperidyl)-N.N-dimethylethanamine
1,3-Dimethylhexahydropyrimidine (DMHHP)
1,3-Dimethylimidazolidine (DMIZ)

Fig. 2. Schematic renderings of notional STAM hypergols.

On the other hand, consideration of AMRDEC's results for 1,4-dimethylpiperazine (DMPipZ), coupled with the PPC results for DPipE and DPyrE, suggest that further investigation of multiamines with heterocyclic rings might be warranted. Though DPipE and DPyrE have high freezing points and temperature sensitive ignition delays, (the latter a property PPC associates with high freezing point compounds,) PPC does not appear to have pursued the synthesis of variations of them that might have had lower freezing points. This is surprising because they recognized that (acyclic) diamines with branched alkyl chains connecting the amine sites had lower freezing points than diamines with unbranched connecting chains. For example, the "symmetric" molecules TMEDA and N,N,N',N'-tetramethylpropane-1,3-diamine (TMPDA) have freezing points of 216 K (-70^{o}F) and 191 K (-115^{o}F), respectively, while the "reduced symmetry" N,N,N',N'-tetramethylpropane-1,2-diamine (TMP12DA) has a freezing point of 158 K (-175^{o}F). Thus one would expect that the freezing points of 1,2-di(1-piperidyl)propane and 1,2-di(1-pyrrolidyl)propane, which are shown in Fig. 2, are lower than their ethane counterparts. Alternately, reduced freezing points (and hopefully ignition delay temperature sensitivities) might be produced by synthesizing compounds with different end groups—e.g., 2-(1-pyrrolidyl)-N,N-dimethylethanamine. This report, however, explores a third possibility—mono-heterocyclic variations of DMPipZ.

Observing from NASA–Lewis thermochemical code calculations that the specific impulses of diamines (and amine azides) were inversely proportional to their carbon to nitrogen (C/N) ratio, fuels with lower symmetries and/or C/N ratios than those found in the tested compounds were sought. DMPipZ's C/N ratio being relatively low, reduced symmetry variations that might have lower freezing points than it were postulated. Of those imagined, two were considered particularly intriguing: 1,3-N,N'-dimethylhexahydropyrimidine (DMHHP) and 1,3-dimethylimidazolidine (DMIZ). (See Fig. 2.) DMHHP is stoichiometrically equivalent to DMPipZ, and (at least schematically) is less symmetric than DMPipZ. Moreover, having the 3-carbon atom separation found in hypergols with short ignition delays, such as TMB13DA and TMPDA, it seemed likely it would have a short ignition delay too. And eliminating stoichiometry as a factor (Schalla and Fletcher, 1956), the difference between DMHHP's and DMPipZ's ignition delay might yield insight into the correlation between amine-separating CH_2 chain lengths and ignition delay observed by PPC. DMIZ, which has the reduced symmetry of DMHHP, has the (presumably) added benefits of a lower C/N ratio and the "optimal" 2-carbon atom separation between amine nitrogens found in TMEDA and DMPipZ. Neither DMIZ nor DMHHP appears to be a commercial-off-the-shelf (COTS) item, but both would appear to be relatively easy to synthesize (Hutchins et al., 1968). Thus, it was recommended that AMRDEC make and test these two compounds (McQuaid, 2003).

Putting this recommendation in perspective, however, are the results for another compound that the first author recommended for testing—1,3,5-trimethylhexahydro-1,3,5-triazine (TMTZ, Fig. 1) (McQuaid, 2003). As would be expected for a multiamine with such high degree of (schematic) symmetry, it has a relatively high freezing point (246 K, -17^{o}F). But it has an extremely low C/N ratio for a STAM (C/N=2.0) and is a COTS item. Therefore, AMRDEC obtained and tested it. Somewhat surprisingly, they found that it is not hypergolic.

Both PPC and AMRDEC find that TMMDA, which has a 1-carbon atom separation of its nitrogen atoms, has a much longer ignition delay than compounds with 2-carbon atom separations such as TMEDA, TMP12DA and DMPipZ. Thus it might have been guessed that TMTZ, which has only 1-carbon separations between its nitrogen atoms, would have a relatively long ignition delay. (That it is not hypergolic is nonetheless surprising.) And given (1) the 1-carbon atom separations in DMHHP and DMIZ and (2) the lack of any true understanding of how the various carbon atom separations impact ignition delay, it can be argued that the ignition delays for DMIZ and DMHHP will be long. Coupled with the difficulty and cost of synthesizing and testing notional compounds, even when their synthesis is expected to be relatively simple, it is difficult to justify the effort.

Initially motivating the study summarized in this paper were two publications discovered during a literature search for synthesis routes and properties of DMHHP. In the first (Nelsen and Buschek, 1974), features of the gas-phase photoelectron spectra (PES) of DMHHP, DMPipZ and some other cyclic multiamines are attributed to configuration-dependent lone pair "through-bond" and "through-space" interactions. Based on DMPipZ's PES, the carrier of the spectrum was attributed to a conformer with anti-parallel, axially oriented lone pair sets (aa')—a conclusion consistent with that derived from a solution NMR study (Lett et al., 1970). In the case of DMHHP, the PES evidence was considered ambiguous, but the spectrum was believed to be carried by either aa and/or ae forms—conformations indicated by a solution NMR study (Eliel et al., 1971). In addition to the indications that DMHHP's and DMPipZ's lone pair orientations are different, the ionization potential (IP) of DMHHP is 0.66 eV lower than DMPipZ's, suggesting that these compounds might have different reactivities.

The other publication motivating the study summarized here reports the H-2 NMR frequency (shifts) of 2-methyl- and 2-ethyl-1,3-diazanes (Hutchins et al., 1968). The shifts are observed to be a strong function of substituent-dependent lone pair alignments. Given the postulated importance of H-atom abstraction reactions in the ignition of hydrazine-IRFNA systems (Sawyer and Glassman, 1967)—and by extension STAM-IRFNA systems—the phenomenon was taken as another suggestion that reactivity differences in a family of similar STAMs might be indicated on the basis of lone pair alignments.

Towards examining the possibility, quantum mechanics-based (QM) calculations were performed to corroborate the experimentally derived conclusions as to the nature of the equilibrium geometries (and corresponding lone pair orientations) of DMHHP and DMPipZ. Finding their lowest energy structures to be those indicated experimentally, structural determinations for a wider set of known STAM hypergols were undertaken to more fully explore the possibility of a correlation between STAM lone pair orientations and their ignition delays.

In addition to the structural characterizations, QM methods were employed to predict DMIZ's and DMHHP's gas-phase heats of formation; and their condensed phase densities and heats of vaporization were estimated via molecular dynamics (MD) simulations. These results were then employed as a basis for calculating their density specific impulse. Results for the notional compounds are compared to those for hydrazines and for diamines tested by AMRDEC.

2. COMPUTATIONAL METHODS

The Gaussian 03 (G03) implementation (Frisch et al, 2003) of PBEPBE/6-311++G(d,p) (Perdew et al., 1996; Perdew et al., 1997; Miehlich et al., 1989; Clark et al., 1983; McLean and Chandler, 1980; Krishnan et al., 1980) was employed to identify equilibrium molecular structures. Conformer searches for a given molecule were conducted by starting geometry optimizations from all of the structures that can be hypothesized for it based on presumed dihedral angle preferences. Normal mode frequencies were calculated for all identified structures to confirm that they were indeed equilibrium structures. The normal mode calculations also provided the zero-point vibrational energies employed to obtain the zero-point corrected electronic energies that were the basis for comparing the energies of a molecule's conformers and to estimate conformer statistical weights in a vapor sample at 298 K.

Gas-phase heats of formation at 298 K [$\Delta H_f(298)$] were derived from the heats of reaction [$\Delta H_r(298)$] calculated for "isodesmic" reactions at 298 K (Foresman and Frisch, 1996). G03 calculations of reactant, product and reference molecule enthalpy differences at 298 K and 0 K [$H(298)$-$H(0)$] were employed (unscaled) to derive $\Delta H_f(298)$ from the QM results.

Condensed-phase densities [$\rho(298)$)] and heats of vaporization [$\Delta H_v(298)$] were estimated via molecular dynamics (MD) simulations. Performed with the *Discover* program (Accelrys, Inc.) and employing the COMPASS force field (Sun, 1998), the simulation methodology was the same as that employed by the first author for previous studies, and the interested reader is referred to one of them (McQuaid, 2002) for details.

3. RESULTS

3.1 Equilibrium Structures

The equilibrium structures of TMMDA, TMEDA, DMPipZ, TMTZ, DMHHP, and DMIZ were found via conformational searches that involved starting geometry optimizations from every configuration that can be postulated based on presumed dihedral angle preferences. In a number of cases, the equilibrium configuration generated by an optimization started with one postulated structure ended up being the same as that obtained from another postulated starting configuration. In all of these cases, the result could be attributed to interference between N-methyl and N'-methyl groups and it is assumed that a low energy conformer corresponding to the originally postulated structure does not exist. (Conformers with energies more than 3 kcal /mol above the lowest energy conformer have negligible populations in a vapor sample at 298 K.)

In the subsections that follow, conformer lone pair/(C-N or C-C) bond orientations are described with respect to one another. Lone pairs are assumed to project from nitrogen atoms along a vector that makes equal angles with the three adjacent N-C bonds. In discussing the results, configurations are referred to as "aligned" or "unaligned" based on simple angle differences (ΔSA) and dihedral angles (DA). ΔSA is defined to be (1) $|\text{SA1 - (180-SA2)}|$ when the corresponding dihedral angle is in the range $-90^o \le \text{DA} \le 90^o$, and (2) $|\text{SA1 - SA2}|$ when the corresponding dihedral angle is outside the range $-90^o \le \text{DA} \le 90^o$. A configuration is referred to as "unaligned" if (1) either ΔSA or $|\text{DA}|$ is in the range 90 ± 20^o, or if (2) both ΔSA and $|\text{DA}|$ are in the range 90 ± 55^o. All other configurations are referred to as "aligned". A completely aligned lone pair and C-N (or C-C) bond will have either (1) complementary simple angles ($\text{SA1} + \text{SA2} = 180^o$) and a dihedral angle of $\pm0^o$, or (2) identical simple angles (SA1 and SA2) and a dihedral angle of $\pm180^o$.

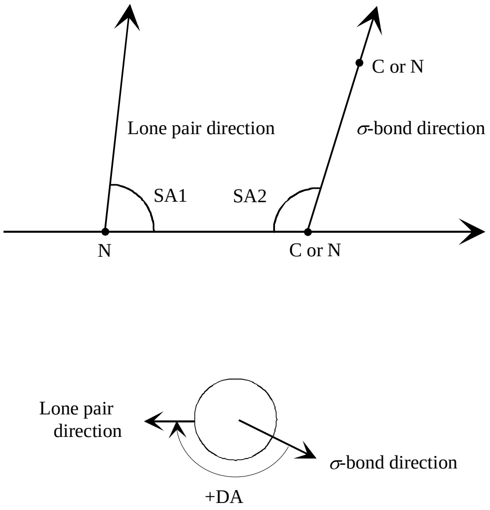

Fig. 3. Measures of lone pair/(C-N or C-C) bond orientations.

TMMDA. If it is assumed, as found in the study of DMAZ (McQuaid et al., 2002), that the dimethylamine fragment [$(CH_3)_2N$–] has only one (nominal) equilibrium configuration, 4 unique TMMDA conformers can be postulated. In the predominant configuration in a TMMDA vapor sample at 298 K, both lone pairs align fairly closely with an N-CH_3 bond of their amine neighbor. In the higher energy TMMDA conformers, the lone pairs are not as well aligned with C-N bonds as they are in the lowest energy conformer, but the orientations still meet the criteria that defines a lone pair/(C-N) bond orientation as being "aligned."

TMEDA. Assuming (as in the case of TMMDA) that only one nominal dimethylamine fragment orientation exists, 8 unique TMEDA structures can be postulated. A total of 7 were found. Of the 7 identified equilibrium TMEDA conformers, 4 have at least one lone pair that does not align well with either a C-N or C-C bond. When combined, the calculations indicate that the mole fraction of these 4 conformers in a TMEDA vapor sample at 298 K will approach 75%.

DMPipZ. Four equilibrium conformers were found for DMPipZ. They are distinguished by the orientation of the lone pair sites with respect to the plane of the ring. The lowest energy conformer has two axially oriented lone pair sites, and they are anti-parallel to one another (aa'). The second lowest energy conformer has one axially oriented lone pair and one equatorially oriented lone pair (ae). The conformers with (1) two equatorially oriented lone pairs (ee) and (2) two axially oriented, co-parallel lone pairs (aa) are considerably higher in energy. The low energy structures are those expected based on the analysis of solution-phase NMR spectra (Lett et al., 1970) and gas-phase PES (Nelsen and Buschek, 1974). The molecules in a vapor-phase DMPipZ sample at 298 K will be almost exclusively in the aa' form. In this form, neither lone pair aligns with either the N-CH_3 bonds or the C-C or C-N bonds in the ring.

TMTZ. Four equilibrium conformers of TMTZ were found. Three are chair form and one is boat form. The boat form (aaa') is much higher in energy than the three chair forms. The lowest energy conformer has a pair of axially oriented, co-parallel lone pairs and an equatorially oriented lone pair (aae). It is calculated to be more than 1 kcal/mol lower in energy than the other three conformers and the predominant structure in a vapor phase TMTZ sample at 298 K. The axially oriented lone pairs align with the N-CH_3 bond associated with the nitrogen with the equatorially oriented lone pair; and the equatorially oriented lone pair aligns with the C-N bonds in the ring. This is also the case for the aee conformer. Together, these two conformers will constitute 98% of the population of a 298 K sample. The remaining 2% will be in the aaa conformation. It has unaligned lone pairs.

DMHHP. Four equilibrium conformers of DMHHP were found. Like TMTZ, 3 are chair form (aa, ae, and ee) and 1 is boat form (aa'), and the boat form is much higher in energy than the chair forms. Conformers aa and ae are the lowest in energy, and the calculations indicate that they will be essentially the only two structures found in a DMHHP vapor sample at 298 K. In the predominant conformation (aa), the lone pairs do not align with any of the C-N or C-C bonds in the molecule. In the ae conformer, lone pair/(C-N) bond alignments are similar to those found in the two lowest energy TMTZ conformers.

DMIZ. There were 2 equilibrium DMIZ conformers found. In both conformers, both lone pairs are axially oriented, one conformer having a co-parallel set (aa) and the other having an anti-parallel set (aa'). Searches for conformations with equatorially oriented lone pairs were conducted, but optimizations started with such orientations invariably produced one of the 2 identified conformers. The results indicate that the aa' conformer is only about 0.5 kcal/mol lower in energy than the aa conformer and will be found in significant quantities in a 298 K DMIZ vapor sample. Neither conformer has lone pairs that align well with C-N or C-C bonds.

3.2 Gas-phase Heat of Formation Estimates

Table 1 shows $\Delta H_f(298)$ estimates for the geometrically characterized STAMs and various monoamines with well-established $\Delta H_f(298)$ values. Based on the good agreement between established and estimated values for the monoamines, the estimates for the STAMs are expected to be reasonably accurate. As expected, the $\Delta H_f(298)$ estimates for DMPipZ and DMHHP are similar. The estimate of DMIZ's $\Delta H_f(298)$ is higher than either DMPipZ's or DMHHP's, which is also in line with expectations.

Table 1. Gas-phase Heat of Formation Estimates (kcal/mol) for Various Molecules.

Compound	$\Delta H_f(298)$ Literature	$\Delta H_f(298)$ Calculated
Ethane	-20.0	-20.1
Propane	-25.0	-24.2
Methylamine	-5.5	-5.9
Dimethylamine	-4.7	-4.6
Trimethylamine	-5.7	-5.5
TMEDA		0.6
TMMDA		0.7
TMTZ		21.6
DMPipZ		6.0
DMHHP		6.7
DMIZ		15.6

3.3 Condensed-phase Property Estimates and Specific Impulse Predictions

Table 2 presents MD-based *ρ(298)* and $\Delta H_v(298)$ estimates for TMEDA, DMPipZ, DMHHP, and DMIZ. The *ρ(298)* estimates for TMEDA and DMPipZ are in good agreement with literature values. As expected, the estimate of DMHHP's density is very similar to that of DMPipZ. The density of DMIZ (0.83 g/cc) is lower than the other two mono-heterocycles, but higher than TMEDA's (0.775 g/cc) and other acyclic diamines – e.g. TMB13DA (0.795 g/cc).

Table 2 also compares the specific impulses (I_{sp}) calculated for 2 known diamine hypergols (TMEDA and DMPipZ), two notional compounds (DMIZ and DMHHP) and hydrazines (UDMH, hydrazine, MMH, and A-50). (A-50 is a 50/50 wt % mixture of hydrazine and UDMH.) Exceptions to the previously noted correlation between a compound's I_{sp} and C/N ratio are observed, e.g. (1) TMEDA (C/N=3.0) vs. DMIZ (C/N=2.5) and (2) N_2H_4 (C/N=0.0) vs. all other compounds in the table. These exceptions are undoubtedly due to differences in molecule H/N ratios. As found by PPC, the specific impulses of the hydrazines are slightly higher than those of the STAMs, and even TMEDA has a higher value than the notional compounds. But having relatively high densities, when $\rho{*}I_{sp}$ is considered as the performance standard, both DMHHP and DMIZ exceed TMEDA and fall in the range between UDMH and MMH.

Table 2. Condensed-phase Property and I_{sp} Estimates for Various Diamines.

Compound	*ρ(298)* (g/cc)	ΔH_v (kcal/mol)	$I_{sp}{}^a$ (lb_f-s/lb_m)	$\rho{*}I_{sp}$ (lb_f-s/ft^3) ($x10^{-3}$)
Diamines				
TMEDA	0.78	10.4	280.6	13.7
DMIZ	0.83	9.3	279.8	14.5
DMPipZ	0.87	10.6	278.7	15.1
DMHHP	0.88	11.1	278.7	15.2
Hydrazines				
UDMH			285.9	14.0
N_2H_4			252.3	15.7
MMH			288.3	15.7
A-50			289.5	16.3

a. I_{sp} calculated via the NASA-Lewis thermochemical code. The value reported corresponds to that for the optimal fuel to oxidizer ratio.

4. DISCUSSION

A correlation is observed between the fraction of a fuel's conformers in a 298 K vapor sample with "aligned" lone pair/(C-N or C-C) bond orientations and the fuel's ignition delay—see Fig. 4. Comparing the linearly branched diamines TMEDA and TMMDA, whose ignition delay difference has not been satisfactorily explained based on traditional chemical insights, significantly different lone pair/(C-N) bond alignments are observed. In all of the conformers found for TMMDA, which, with only one methyl group separating the amines, has only 3 low-energy equilibrium conformers, both of the lone pairs align with C-N bonds. But in the case of TMEDA, which has more equilibrium conformers, 4 of the 6 significantly populated conformers have at least one lone pair that fails to align with a C-N or C-C bond. And the increasing number of equilibrium conformers for diamines with longer $(CH_2)_n$ chains (such as TMPDA and TMB13DA) though not searched and characterized, will certainly produce populations in which a significant fraction of molecules have unaligned lone pairs. Given TMMDA's relatively long ignition delay, a deleterious effect of lone pair/(C-N) bond alignment on ignition delay is indicated. The negative impact of lone pair/(C-N) bond alignment is also indicated by the results for the heterocycle-containing compounds DMPipZ and TMTZ. In (hypergolic) DMPipZ, the only significantly populated conformer has minimal lone pair/(C-N or C-C) bond alignment while in (non-hypergolic) TMTZ, the only two conformers with any significant population at 298 K have all three lone pairs aligning with C-N bonds.

Analyzed from the standpoint of lone pair/(C-N or C-C) bond orientations, DMHHP and DMIZ, which were recommended for synthesis and testing based on the hope of obtaining DMPipZ-like ignition delays with compounds having lower freezing points and

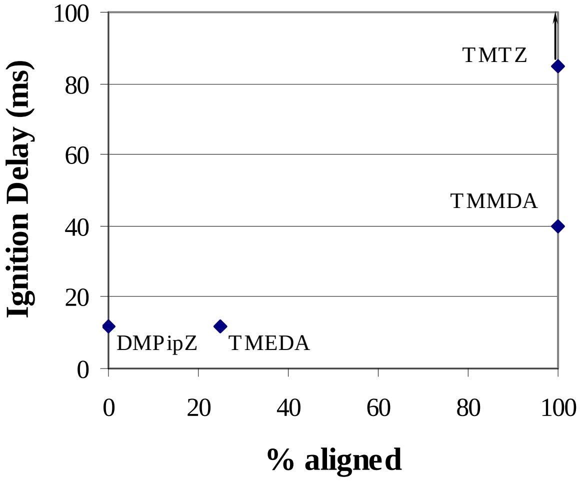

Fig. 4. Ignition delay vs. % of conformers with "aligned" lone pairs.

equal (or better) ρ^*I_{sp}, appear to have promise. Of the two DMHHP conformers with significant populations at 298 K, one (ae) has both of its lone pairs aligned with C-N bonds. Thus it would be expected that if a DMHHP sample was exclusively in this configuration, it would have a long ignition delay. However, the lone pairs in the lowest energy conformer (aa), like DMPipZ, do not align with C-N or C-C bonds. In contrast to DMPipZ, however, the lone pairs are co-parallel rather than anti-parallel. No other tested diamine has been observed to have (or is expected to have) this trait. Thus, its ignition delay may be found to be anomalously fast.

DMIZ was found to have only two low energy conformers, and its lone pairs do not align with C-N or C-C bonds in either configuration. The lowest energy conformer has the anti-parallel lone pair alignment found in DMPipZ, and on this basis, and noting the strain energy in the ring, it is expected that DMIZ will have an ignition delay as short as or shorter than DMPipZ. Moreover, on the basis of ρ^*I_{sp}, calculations, its performance will be competitive with UDMH.

Should the hypothesized correlation between structure and ignition delay be borne out in DMIZ and/or DMHHP, a more fundamental basis for designing and screening notional STAM fuels will be established. And should this be the case, computational chemistry will prove valuable for assessing modifications that may be proposed to address unforeseen shortcomings, such as melting points that are still too high.

CONCLUSION

Seeking to identify STAM structural features that correlate with hypergolic ignition delays, equilibrium configurations of 4 compounds with experimentally ranked delays were established through DFT-based calculations. Examined from the standpoint of lone pair/(C-N and C-C) bond orientations, a correlation with ignition delay is indicated. Conformers of DMIZ, a notional hypergol whose synthesis and testing was originally recommended based on benefits expected from reducing the symmetry and C/N ratio of an otherwise promising hypergol (DMPipZ), were therefore characterized and found to have the “unaligned” lone pair orientations of compounds with short ignition delays. Thus, it is expected to have the same property. Moreover, an estimate of its ρ^*I_{sp} indicates its performance will be competitive with hydrazine-based fuels. DMHHP, a notional hypergol with the same stoichiometry as DMPipZ, but with less symmetry, has co-parallel rather than anti-parallel lone pairs in its lowest energy conformer. A feature not found in any previously tested compound, it could have ignition delays shorter than other STAMs. Thus, it is considered that the potential of STAMs as hypergols may not yet be fully realized, and the synthesis and testing of DMIZ and DMHHP is recommended.

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REFERENCES

Clark, J. D., 1972: *Ignition! An Informal History of Liquid Rocket Propellants*. New Brunswick, NJ: Rutgers University Press.

Clark, T.; Chandrashakar, J.; Spitznagel, G. W.; and Schleyer, P. V. R., 1983: Efficient Diffuse Function-Augmented Basis-Sets for Anion Calculations. 3. The 3-21+G Basis Set for 1st-Row Elements, Li-F. *J. Comp. Chem.*, **4,** 294-301.

Eliel, E. L.; Kopp, L. D.; Dennis, J. E.; and Evans, S. A.**,** 1971: Conformation Of Alkyl Groups in N,N'-Dialkyl-1,3-diazanes. *Tetrahedron Letters*, 3409.

Foresman, J. B and Frisch, A., 1996: *Exploring Chemistry with Electronic Structure Methods, 2^{nd} ed.* Pittsburgh, PA: Gaussian Inc.

Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A.; Vreven, T., Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M., Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A., 2003: Gaussian 03, Revision B.05, Pittsburgh PA: Gaussian, Inc.

Hutchins, R. O.; Kopp, L.D.; and Eliel, E. L., 1968: Repulsion of *syn*-Axial Electron Pairs. The "Rabbit Ear Effect. *J. Amer. Chem. Soc.*, **90**, 7174-7175.

Krishnan, R.; Binkley, J. S.; Seeger R.; and Pople, J. A., 1980: Self-Consistent Molecular-Orbital Methods. 20. Basis Set for Correlated Wave-Functions., *J. Chem. Phys.*, **72,** 650-654.

Lett, R. G.; Petrakis, L.; Ellis, A. F.; and Jensen, R. K., 1970: Nuclear Magnetic Resonance Spectral Parameters and Ring Interconversion of a Series of Piperazines. *J. Phys. Chem.*, **74,** 2816.

McLean, A. D. and Chandler, G. S., 1980: Contracted Gaussian-Basis Sets For Molecular Calculations. 1. 2nd Row Atoms, Z=11-18. *J Chem. Phys.*, **72,** 5639-5648.

McQuaid, M. J., 2003: Email communication to W. H. Stevenson and D. M. Thompson.

McQuaid, M. J., 2002: Computational Characterization of 2-Azidocycloalkanamines: Notional Variations on the Hypergol 2-Azido-N,N-Dimethylethanamine. ARL-TR-2806, Aberdeen Proving Ground, MD.

McQuaid, M. J.; McNesby, K. L.; Rice, B. M.; and Chabalowski, C. F., 2002: Density Functional Theory Characterization of the Structure and Gas-phase, Mid-infrared Absorption Spectrum of 2-Azido–N,N-dimethylethanamine (DMAZ). *J. of Mol Struct. (Theochem)*, **587,** 199-218.

Miehlich, B.; Savin, A.; Stoll, H.; and Preuss, H., 1989: Results Obtained With the Correlation-Energy Density Functionals of Becke And Lee, Yang and Parr. *Chem. Phys. Lett.*, **157,** 200-206.

Nelsen, S. F. and Buschek, J. M., 1974: Photoelectron Spectra of Some Cyclic Di- and Polyamines. Lone Pair-Lone Pair Interactions in 1,3- and 1,4-Diamines. *J. Amer. Chem. Soc.*, **96,** 7930-7934.

Perdew, J. P.; Burke, K.; and Ernzerhof, M., 1996: Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.*, **77,** 3865-3868.

Perdew, J. P.; Burke, K.; and Ernzerhof, M., 1997: Generalized Gradient Approximation Made Simple (vol 77, pg 3865, 1996). *Phys. Rev. Lett.*, **78,** 1396.

Phillips Petroleum Co., 1956: Petroleum Derivable Nitrogen Compounds as Liquid Rocket Fuels. Research Division Report 1478-56R, Phillips Petroleum Co., Bartlesville, OK.

Sawyer, R. F. and Glassman, I., 1967: Gas-Phase Reactions of Hydrazine with Nitrogen Dioxide, Nitrogen Oxide, and Oxygen. *Proceeding of the 11th Symposium (International) on Combustion*, 861-869.

Schalla, R. L. and Fletcher, E. A., 1956: The Behavior of the System Triethylamine-White Fuming Nitric Acid Under Conditions of Rapid Mixing. *Proceedings of the 6th Symposium (International) on Combustion*, Pittsburgh, PA: The Combustion Institute.

Stevenson, W. H.; Arkoosh, G. R.; Slocum-Wang, Z.; and Felton, L. D., 2004: Factors Influencing Ignition Delay of Fuels With Inhibited Red Fuming Nitric Acid. *1st JANNAF Liquid Propellant Subcommittee Meeting,* Las Vegas, NV.

Sun, H., 1998: COMPASS: An Ab Initio Force-field Optimized for Condensed-phase Applications - Overview With Details on Alkane and Benzene Compounds. *J. Phys. Chem. B*., **102,** 7338-7364.