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Computational Analysis of Azine-N-Oxides as Energetic Materials

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A BKW equation of state in a 1-dimensional hydrodynamic simulation of the cylinder test can be used to estimate the performance of explosives. Using this approach, the novel explosive 1,4-diamino-2,3,5,6-tetrazine-2,5-dioxide (TZX) was analyzed. Despite a high detonation velocity and a predicted CJ pressure comparable to that of RDX, TZX performs relatively poorly in the cylinder test. Theoretical and computational analysis shows this to be the result of a low heat of detonation. A conceptual strategy is proposed to remedy this problem. In order to predict the required heats of formation, new *ab initio* group equivalents were developed. Crystal structure calculations are also described that show hydrogen-bonding is important in determining the density of TZX and related compounds.

ZND theory identifies the Chapman-Jouget (CJ) state as uniquely characteristic of an explosive (1). Consequently, the detonation velocity and pressure associated with this state are frequently cited as figures of merit for an explosive. This state point is found as the point of tangency of the Rayleigh line, the slope of which is related to the detonation velocity, and the Hugoniot of the detonation products, as shown in Figure 1. (A more complete description may be found in Reference 1.) Thus, in this simple one-dimensional model, the explosive is shocked up the solid Hugoniot and decomposes as it decays down the Rayleigh line to the CJ state. The explosive products then expand from this state along an isentrope.

With this theory, it is possible to use BKW (2) or many other chemical equations of state to locate the CJ state and compute a variety of explosive product properties, including their shock hugoniots and expansion isentropes. The detonation velocity, D_{CJ} , is especially important as it is the steady propagation rate of the detonation and can be accurately measured. Thus, a knowledge of a candidate explosive's composition, bulk density, and heat of formation is

Figure 1. Simple model of 1-D plane detonation. Explosive is shocked up the solid Hugoniot (—) then decomposes as it decays down the Rayleigh line (straight —) to the CJ state, where the decomposition is complete. The CJ state can be found as the point of tangency between the Rayleigh line and the detonation product Hugoniot (curved —). The explosive expands along the isentrope (— — —) through the CJ state.

sufficient to allow the use of BKW for its characterization. This emphasizes the need for accurate models of heats of formation and crystal density.

Although the ZND model and the thermodynamic quantities it employs are important, as are their accurate calculation, the performance of an explosive is usually measured experimentally by its ability to push metal. Thus, an assessment of the performance of an explosive requires further consideration. The cylinder test is one experimental measure of the ability of an explosive to push metal (3). Typically a foot long one-inch i.d. copper cylinder with a .1 inch thick wall is loaded with HE. The explosive is initiated at one end and a detonation propagates along the cylindrical axis causing the walls to expand radially. The wall velocity is measured at several distances of expansion. It has become standard practice to refer to the wall velocities at 5 and 19 mm expansion as a measure of the performance of an explosive. These values have been tabulated for common explosives(4).

Two-dimensional hydrodynamic simulations of the cylinder test have been performed using chemical equations of state. The simulation proceeds by finite-difference solution of partial differential equations derived from consideration of the conservation of mass, momentum, and energy and yields the time evolution of an initial configuration. Using this approach, Sours and Kury find (5) that.

when appropriately scaled, BKWR (6) gives the best fit of the experimental data compared with JCZ3 (7) and CHEQ (8). Kerley and Christian-Frear (9) have used the PANDA model (10) to realistically simulate cylinder tests.

A one-dimensional hydrodynamic simulation of the cylinder test can be quickly and easily performed to obtain wall velocities at various expansions. In order to make the simulation one-dimensional, the initial state of the explosive is taken to be completely burned at its initial density. In Figure 1, this corresponds to a vertical Rayleigh line and infinite detonation velocity. This procedure neglects the portion of the expansion isentrope above the initial density of the explosive. In addition to providing quantities directly comparable with experiment, the simulation also samples a large proportion of the expansion isentrope, effectively measuring the work performed by the explosive over many volume expansions. This approach also gives consideration to the initial density of the explosive, the number and kinds of gas molecules produced, and the energy of decomposition. All these factors influence the description of the isentrope and hence the performance of an explosive. These hydrodynamic simulations provide a different measure of an explosive's performance as opposed to consideration of the CJ state, which is only a single point on the expansion isentrope, but is weighted more heavily in small volume expansions and in other geometries. Because the hydrodynamic simulation is one-dimensional, the absolute values of the wall velocity are not expected to be realistic. Nonetheless, the relative ordering of the wall velocities at 19 mm expansion proves to be a useful measure of explosive performance.

An interesting case history in the development of explosives is provided by 1,4-diamino-2,3,5,6-tetrazine-2,5-dioxide (TZX), which was first synthesized by M.D. Coburn at LANL. It has been discussed previously (11). Its structure is shown in Figure 2, along with those of some common HE's. Consideration of the CJ state alone for TZX, however, proves to be very misleading in terms of its performance in the cylinder test. In this report, the use of one-dimensional hydrodynamic simulations using a BKW equation of state is described. The performance of TZX is accurately described using this approach. A conceptual strategy is outlined to improve the performance of some nitrogen containing heterocycles. In order to facilitate assessments of such explosives, methods for obtaining their heats of formation and crystal density are examined and extended.

Methods and Results

BKW and Hydrodynamic Simulations: Some observed and calculated properties of TZX and RDX are shown in Table I. Comparison of these quantities shows that TZX has a higher predicted CJ pressure and detonation velocity than RDX, which is an explosive of considerable practical importance. In addition, TZX has a higher density and heat of formation than RDX. Another characteristic of an explosive is its heat of detonation. An idealized value of this quantity for C,H,N,O containing explosives can be obtained by assuming a standard set of detonation products (4). First, it is assumed that as much water

Figure 2. Structures of explosives referred to in this work.

(as a gas, $H_f = -57.5$ kcal/mol) as possible is formed; the remaining oxygen is then used to create carbon dioxide ($H_f = -94.05$ kcal/mol). The remaining atoms are combined to yield the elements in their standard states. Calculation of this quantity for HMX, RDX, and TZX yields: 1.48, 1.48, and 1.07 kcal/g, respectively. Thus, TZX compares unfavorably with other high-performance HE's on this basis.

The computer code SIN (2) was used in the manner described in the introduction to perform the hydrodynamic simulations. The explosives shown in Table II were studied. Sample BKW and SIN input decks are shown in appendixes A and B for reference. In the BKW calculations, the RDX parameter set and identical molecular co-volumes were used throughout. SIN produced plots of the cylinder wall velocity versus time. Wall velocities at 19 mm expansion were determined from these plots and are shown for the explosives examined in Table II under V_{19}^{calc} .

Experimentally measured D_{CJ} and P_{CJ} have been compared before with those computed using BKW and are not repeated in Table II (2). The calculated values are listed there for reference. For TNT, the calculations were also performed using the TNT parameter set in the BKW run. As shown in Table II, this had a noticeable effect on the CJ state, but a much lesser one

Table I. Observed and calculated quantities for TZX and RDX

	TZX	RDX
Observed Density (g/cc)	1.86	1.80
Observed H_f (kcal/mol)(c)	39.0	14.7
D_{CJ} (mm/ μ s)		
Obs.		8.75
BKW Calc.	8.85	8.75
BKW Calculated P_{CJ} (kbar)	354	347
BKW Calculated T_{CJ} (K)	1702	2587

on $V_{19}^{calc.}$. HNB also deserves comment because its calculated CJ parameters are in remarkably poor agreement with those observed: $D_{CJ} = 9.34$ mm/ μ s and $P_{CJ} \approx 400$ kbar (12).

Comparison of the calculated and observed wall velocities shows the calculated values to be systematically too high. When the observed and calculated values of V_{19} are plotted, a good linear correlation between them is found, as shown in Figure 3. V_{19} is poorly predicted for TATB. In this instance, however, diameter effects are likely to be important. Thus the large deviation from that predicted has its basis in a real physical effect. Consequently, a correlation for ideally detonating explosives should neglect this point, until data at larger cylinder diameters becomes available. This was done in determining the correlation equation shown along the bottom of the plot. BTF has the next largest error in predicted and observed values. This was the only explosive examined in establishing the correlation that produces no water on detonation. The error in the predicted V_{19} is less than 3%.

After the correlation had been established, HNB was considered. The predicted wall velocity from the correlation equation is 1.91 mm/ μ s; the observed value is 1.95 mm/ μ s, a difference of less than 3%.

The cylinder test for X-0535, which contains predominately TZX, show that its performance is much less than that of RDX. This large difference cannot be accounted for by the fact that the comparison is performed for pure RDX versus a formulation containing TZX. Further information about the poor performance of TZX was obtained by performing calculations for two hypothetical forms of TZX, one in which the density was increased to 1.95 g/cc and one in which the heat of formation was raised to 102. kcal/mol, which results in a heat of detonation of 1.5 kcal/g. The artificial values used in these calculations are comparable to those of RDX and HMX. All other quantities were fixed at values corresponding to those of the real material. The BKW and SIN calculations were repeated and the results are summarized in Table III. The predicted V_{19} 's for both of these hypothetical forms show improvements over that found for

Table II. Particulars of 1D 1 in. cylinder test calculations performed with BKW EOS.

HE	Molar Composition				ρ (g/cc)	E_0^a (kcal/fw)	P_{CJ} (kbar)	D_{CJ} (mm/ μ s)	γ_{CJ}	$V_{19}^{calc.}$ (mm/ μ s)	$V_{19}^{obs.}$ (mm/ μ s)	Ref.
	C	H	N	O								
PBX-9501	1.470	2.855	2.602	2.689	1.834	10.8	358	8.85	3.0	1.93	1.78	b
Comp-B	2.092	2.619	2.129	2.651	1.717	9.6	283	8.06	2.9	1.76	1.63	c
HMX	4	8	8	8	1.891	36.3	389	9.11	3.0	1.99	1.86	b
RDX	3	6	6	6	1.800	33.5	347	8.75	3.0	1.93	1.78	c
X-0535 ^d	1.431	2.721	3.956	1.319	1.787	25.7	308	8.42	3.1	1.67	1.52	e
TATB	6	6	6	6	1.860	-13.9	311	8.28	3.1	1.70	1.45	b
TNT ^f	7	5	3	6	1.630	3.8	212	7.18	3.0	1.54	1.40	b
NM	1	3	1	2	1.140	-20.8	130	6.43	2.6	1.35	1.22	c
PETN	5	8	4	12	1.765	-103.5	315	8.39	2.9	1.88	1.77	c
PETN	5	8	4	12	1.266	-103.5	162	6.79	2.6	1.49	1.38	g
BTF	6	0	6	6	1.859	158.0	325	8.16	2.8	1.92	1.83	c
HNB ^h	6	0	6	12	1.965	39.7	362	8.51	2.8	2.04	1.95	i

- a. $E_0 = H_f^{298} + \sum_i^{elements} k_i(H_f^{298} - H_f^0)_i$, where for formula $C_aH_bN_cO_d$, $k=a$ for C and $k=b/2$ for H, $k=c/2$ for N, $k=d/2$ for O. $(H_f^{298} - H_f^0)$ is closely approximated as .25 kcal/mol of C and 2 kcal/mol of H_2 , N_2 , and O_2 . So, for C,H,N,O explosives, $E_0(kcal/fw) = H_f^{298}(kcal/fw) + .25a + b + c + d$.
- b. *LASL Explosive Property Data*, Gibbs, T.R.; Popolato, A., Eds., University of California Press:Berkeley, 1980.
- c. *LLNL Explosives Handbook*, Dobratz, B.M., Ed.; UCRL-52997, 1981.
- d. 95/5 weight % TZX/FPC (polymeric binder). Composition also includes .0559 moles Cl and .0838 moles F.
- e. Dallman, J.C.; Explosive Technology Group, LANL, personal communication.
- f. TNT parameters gave $P_{CJ}=205$, $D_{CJ}=6.95$, $\gamma_{CJ} = 2.8$, and $V_{19}^{calc.} = 1.56$.
- g. LLNL Shot K260-261.
- h. Simpson, R.L., LLNL, provided density and heat of formation.
- i. Ref. 12, p.949.

Figure 3. Correlation between calculated and observed wall velocities.

the real material, but the improvement in performance is much larger when the heat of formation is increased. Thus, the poor performance of TZX is clearly due to a low heat of detonation, as the earlier argument above suggested.

Table III. Results of BKW Calculations for a Hypothetical TZX-like Explosive.

	High Density "TZX"	High Energy "TZX"
Assumed Density (g/cc)	1.95	1.86
Assumed H_f (kcal/mol)	39	102
Calculated P_{CJ} (kbar)	402	394
Calculated D_{CJ} (mm/ μ s)	9.23	9.12
Predicted ^a V_{19} (mm/ μ s)	1.71	1.87

^a Predicted value is found using calculated value in the equation shown in Figure 3. Predicted $V_{19} = 1.62$ mm/ μ s for pure TZX.

One means of improving the heat of detonation of TZX or other nitrogen-containing heterocycles is to introduce additional oxygen. This allows excess carbon to be oxidized to form carbon dioxide. TZX of course represents the embodiment of this strategy in that 1-4-diamino-2,3,5,6-tetrazine(DAT) is not expected to be an explosive. Thus simply converting aromatic nitrogen atoms

to the corresponding N-oxides is anticipated to raise the heat of detonation of a molecule, if it originally produced an excess of carbon. In this regard, molecules **I** (13) and **II** (14), below, are interesting to consider. These molecules contain adjacent N-oxides. They also have been synthesized. The crowding of the adjacent N-oxides is of interest because of the additional energy it is likely to impart to the molecule. An evaluation of this factor and an estimate of these and related molecules as energetic materials requires heats of formation and crystal densities. In order to obtain these quantities for the molecules under consideration, additional calculations were performed as described next.

I

II

Ab Initio Group Equivalents for Heats of Formation: Wiberg, Nakaji, and Breneman (15) derived *ab initio* group equivalents to estimate the gaseous heats of formation of azines. Equation 1 is used for this purpose, where E_{tot} is the total energy from the *ab initio* calculations and N_i is the number of groups corresponding to the energy equivalent E_i ; E_{tot} and E_i are in a.u., while H_f is obtained in kcal/mol.

$$H_f^{298} = 627.51 \times (E_{tot} - \sum_i (N_i \times E_i)) \quad (1)$$

We adopted the $C_{ar} - H$ and N_{ar} equivalents previously determined. In addition, we performed calculations using the MP4(SDTQ) method and developed group equivalents at this level. The $C_{ar} - H$ and N_{ar} MP4 equivalents were determined using only the observed heats of formation of benzene and pyridine. Thus the equivalents at this level are not as well calibrated as those at MP2 and MP3, which were determined using a larger experimental database. $N_{ar} - O$ and $C_{ar} - NH_2$ equivalents are required to calculate a H_f for TZX and other azine-N-oxides. Measured H_f 's of aniline and pyridine-N-oxide are available for this purpose. Unfortunately, this uniquely determines the equivalents, which is undesirable. The experimental values appear to be accurate, however, but it is likely that the resulting errors in the calculated H_f 's will be larger than those found in the earlier work.

Total calculated energies for several calibration compounds, azines, and azine-N-oxides are shown in Table IV. In all instances, molecular geometries were optimized at the RHF/6-31G* level. With the exception of aniline, all the molecules were constrained to be planar. Aniline is known to possess a pyramidal amino group, although the planar-pyramidal energy difference is small, as shown in Table IV. So, it seems likely that the optimal geometry of the other

amino-group containing molecules may also be non-planar. The group equivalent, however, was derived using the pyramidal geometry. This may cause the H_f of such molecules to be somewhat overestimated.

Table IV. Calculated energies obtained using the indicated theoretical method. Energies were obtained using the RHF/6-31G* optimized planar geometries and 6-31G* basis set throughout, except for the aniline (py.) calculation, in which the amino group was pyramidal.

	RHF	MP2	MP3	MP4(SDTQ)
Benzene	-230.703137	-231.456505	-231.485222	-231.529688
Aniline (py.)	-285.730822	-286.648505	-286.680310	-286.731673
Aniline (pl.)	-285.728227	-286.645308	-286.677003	-286.728158
Pyridine	-246.695820	-247.480360	-247.502442	-247.549709
Pyridine-N-oxide	-321.473768	-322.452900	-322.466279	-322.530149
Pyrazine	-262.683005	-263.500213	-263.515707	-263.565549
Pyrimidine	-262.693488	-263.506478	-263.522476	-263.572534
Pyridazine	-262.650029	-263.469882	-263.485466	-263.536251
s-Triazine	-278.695843	-279.535017	-279.545486	-279.598109
Melamine	-443.860580	-445.174943	-445.197915	-445.267108
s-Tetrazine	-294.592926	-295.477477	-295.480813	-295.537874
1,4-Diamino-2,3,5,6-tetrazine	-404.671096	-405.889518	-405.895167	-405.966694
1,4-Diamino-2,3,5,6-tetrazine-2,5-dioxide	-554.242424	-555.861070	-555.840745	-555.950532
Pyrazine-di-N-oxide	-412.234811	-413.443425	-413.439431	-413.524027
Pyrimidine-di-N-oxide	-412.230887	-413.438271	-413.435156	-413.520431
Pyridazine-di-N-oxide	-412.203017	-413.423889	-413.413820	-413.504075

The resulting group equivalents and calculated heats of formation are shown in Tables V and VI, respectively. Because the MP2 and MP3 calculations are better calibrated and include some accounting for electron correlation, these results are preferred. As shown in Table VI, the difference between these two methods is typically small, but reaches a maximum of 8.3 kcal/mol for TZX; other differences are typically half this size or less. The MP4 heats of formation show several differences from those at MP2 and MP3. In general, the differences, where they exist, are about 2-3 kcal/mol, which is not surprising because these equivalents are less well calibrated than the others. This suggests that the perturbation expansion is converging reasonably and that the accounting for electron correlation at MP2 and MP3 is adequate for our purposes. This behavior is in marked contrast to the results obtained at the RHF level, which show several differences, some as large as 20 kcal/mol from those at MP2 and

Table V. Group increments (a.u.) for obtaining heats of formation using the indicated theoretical method with the 6-31G* basis set.

	RHF	MP2	MP3	MP4
$C_{ar}-H$	38.45546 ^a	38.58138 ^a	38.58611 ^a	38.59354
N_{ar}	54.46976 ^a	54.62523 ^a	54.62378 ^a	54.63555
$C_{ar}-NH_2$	93.48667	93.77475	93.78291	93.79712
$N_{ar} \rightarrow O$	129.22993	129.57947	129.56920	129.59592

^a Reference 14.

MP3.

There is only one new directly pertinent theory-experiment comparison shown in Table VI. For melamine, the MP2 and MP3 H_f 's are somewhat higher than that observed. This difference could be due to the use of a planar geometry in the calculations, but the difference is not large and is a useful check of the $C_{ar} - NH_2$ equivalent, which was determined with only one experimental datum. The H_f 's of diaminotetrazine and TZX have been measured at LANL. The values obtained, however, are for a polycrystalline sample, not a gaseous molecule, as the calculations give. The difference between these numbers is the heat of sublimation. For these two molecules, the difference between the calculated and observed H_f values gives numbers that are sensible for this quantity for molecules of this size.

The PM3 semi-empirical molecular orbital method (16) was also used to calculate H_f 's. Comparison of the results obtained at this level with those at MP2 and MP3 show several large differences. One especially pertinent example is the relative H_f 's of diaminotetrazine and TZX. According to the *ab initio* calculations, oxidation of the former to give the latter lowers the H_f by more than 30 kcal/mol. PM3 on the other hand, shows a small increase. This difference results in a significantly higher heat of detonation for TZX and an overestimate of its detonation performance.

Predicted H_f 's of the di-N-oxides of pyrazine, pyrimidine, and pyridazine show an increase in the heat of formation with decreasing distance between the N-oxides. The additional energy available in the pyridazine isomer is approximately 12.5 ± 3 kcal/mol. This increase is less than that found in the parent compound of about 23 kcal/mol. So the adjacent lone-pairs are more destabilizing than the adjacent N-oxides. Also, the destabilization found from the *ab initio* calculations is much less than that found with the PM3 method.

Crystal Structures: Electrostatic interactions are important in molecular crystal structures (17). Atomic charges determined by fitting the electrostatic potential are frequently used for calculating this quantity. The CHELPG procedure was used in this investigation (18). Alternatively, Hirshfeld (19) atom-centered multipole expansions (ACME's) can be used that are obtained from

Table VI. Calculated and observed standard gaseous H_f 's (kcal/mol).

	RHF	MP2	MP3	MP4	PM3	Obs. ^a
Benzene	18.6 ^b	19.9 ^b	19.7 ^b	19.8 ^c	23.5	19.8 ± .2
Aniline ^c (py.)	20.8	20.8	20.8	20.8	21.4	20.8 ± .6
Pyridine	32.3 ^b	32.5 ^b	32.6 ^b	33.6 ^c	30.4	33.6 ± .2
Pyridine-N-oxide ^c	21.0	21.0	21.0	21.0	27.3	21.0 ^d
Pyrazine	49.2 ^b	47.5 ^b	47.9 ^b	50.0	39.4	46.9 ± .3
Pyrimidine	42.6 ^b	43.6 ^b	43.6 ^b	45.6	38.0	46.8 ± .3
Pyridazine	69.9 ^b	66.6 ^b	66.9 ^b	68.4	56.0	66.5 ± .2
s-Triazine	50.1 ^b	53.2 ^b	52.8 ^b	55.9	46.3	54.2 ± .2
Melamine	5.5	15.7	13.9	19.4	28.8	12.4 ± 1.
s-Tetrazine	123.6 ^b	116.8 ^b	117.0 ^b	120.1	94.7	(117.0 ^b)
1,4-Diamino-2,3,5,6-tetrazine	113.8	101.0	104.0	106.5	87.4	(71.2) ^e
1,4-Diamino-2,3,5,6-tetrazine-2,5-dioxide	81.8	61.4	69.7	66.9	93.4	(39.2) ^e
Pyrazine-di-N-oxide	29.4	25.7	27.2	26.3	39.5	
Pyrimidine-di-N-oxide	31.9	29.0	29.9	28.6	30.3	
Pyridazine-di-N-oxide	49.4	38.0	43.3	38.9	70.1	

^a Unless noted otherwise, values from J.B. Pedley, R.D. Naylor, S.P. Kirby *Thermochemical Data of Organic Compounds*, 2nd Ed., Chapman:New York, 1986.

^b Reference 14.

^c Uniquely determined by the available data.

^d L. Shaofeng, G. Pilcher, *J. Chem. Thermody.*, **1988**, *20*, 463.

^e Value is for the polycrystalline material. Determination by M. Stinecpher, LANL.

direct integration of the electron density (20). Figure 4 shows a comparison of the electrostatic potential surrounding TZX obtained using atomic charges from the CHELPG procedure and ACME's truncated at quadrupoles ($l=2$) and octapoles ($l=3$).

The ability of the charge models to reproduce the potential is measured by the root-mean square (RMS) and relative root-mean square (RRMS) errors. These quantities were evaluated on a rectilinear mesh that enveloped the molecules. The mesh points were spaced .25 Å apart and the closest approach of the boundary of the mesh to an atom of the molecule was 5 Å. At each point of the mesh, the potential was evaluated using either the model charge distributions or rigorous formula as implemented in GAUSSIAN92 (21). The errors in the fit were binned according to the value of the potential. Three bins were used corresponding to values of the potential less than -4.18 kJ/mol, between -4.18 and 4.18 kJ/mol, and larger than 4.18 kJ/mol. This procedure was followed to allow the fits of positive and negative regions to be examined

Figure 4. Electrostatic potential of TZX from potential derived charges (PDC) and ACME's truncated at quadrupoles ($l=2$) and octopoles ($l=3$). Results from RHF/3-21G//RHF/3-21G calculations are shown. Positive values (line), negative values (dash), and zero (chain-dot) are shown at 10 kcal/mol/e intervals.

separately.

The results are shown in Table VII. It is found that ACME's at successively higher levels provide reductions in the RMS and RRMS errors. In the cases examined, the use of quadrupoles results in lower RMS and RRMS errors than obtained with PDC's. Further improvements are obtained upon the inclusion of octapole terms. Only relatively small differences in the RMS and RRMS errors are found in positive and negative regions. The use of the multipoles provides the greatest improvement for diaminotetrazine. It has many lone-pairs of electrons and consequently an atomic charge model does not reproduce the surrounding potential very well.

The effect of improvements in the fit of the electrostatic potential in the calculation of the corresponding crystal structure of these molecules was studied next. To accomplish this, we have modified D.E. Williams PCK/83 program to calculate multipole-multipole interactions including terms up to quadrupoles (22). The program uses Equation 44 of Nijboer and DeWette (23) to compute the electrostatic lattice sums; numerical tests using only real-space sums have supported the use of these formulas, but a formal derivation is lacking. Several sets of calculations were performed, which are summarized in Table VIII. Use of Williams original potential function parameters (17) supplemented by either PDC's or ACME's led only to small, but noticeable, differences in the calculated crystal structures. In addition, the calculated energies, which are poor estimates of the heat of sublimation, were also noticeably different, but the difference was not large. More serious from the standpoint of HE performance, however, was the difference between the observed and calculated densities. This quantity was significantly underestimated. Hydrogen-bonding was believed to be important in these crystal structures. This leads to unusually short hydrogen-heavy atom distances. To simulate this effect, the preexponential parameter of hydrogen atoms covalently bonded to nitrogen or oxygen were reduced by 30%. When the calculations were repeated with this parameter set, the crystal densities were

Table VII. Error analysis of electrostatic potential fit with different models. PDC refers to the use of potential derived charges. ME n indicates the multipole expansion was carried out to n=0, charges; 1, dipoles; 2, quadrupoles; 3, octapoles. RMS (kJ/mol) and RRMS computed as described in the text. Range refers to potential values (kJ/mol) for which the error analyses were performed.

Diaminotetrazine									
Range:	-185.0	→	-4.18,	-4.18	→	4.18,	4.18	→	161.0
	Npts		RMS	RRMS	Npts		RMS		RRMS
PDC	33730		7.80e+00	3.54e-01	21772		2.14e+00	43230	4.86e+00 2.69e-01
ME 0	33730		1.85e+01	8.24e-01	21772		6.21e+00	43230	1.41e+01 7.27e-01
ME 1	33730		4.55e+00	2.51e-01	21772		2.02e+00	43230	3.98e+00 2.39e-01
ME 2	33730		2.23e+00	1.33e-01	21772		1.17e+00	43230	2.38e+00 1.50e-01
ME 3	33730		8.76e-01	6.83e-02	21772		6.75e-01	43230	1.34e+00 8.43e-02
TZX									
Range:	-194.0	→	-4.18,	-4.18	→	4.18,	4.18	→	296.0
	Npts		RMS	RRMS	Npts		RMS		RRMS
PDC	43912		3.35e+00	1.41e-01	15384		1.40e+00	54956	2.54e+00 1.13e-01
ME 0	43912		1.34e+01	4.90e-01	15384		4.67e+00	54956	1.23e+01 4.61e-01
ME 1	43912		4.47e+00	1.60e-01	15384		2.10e+00	54956	3.54e+00 1.71e-01
ME 2	43912		1.24e+00	6.64e-02	15384		7.60e-01	54956	2.28e+00 8.82e-02
ME 3	43912		1.06e+00	7.66e-02	15384		6.31e-01	54956	1.43e+00 6.55e-02

reproduced much more accurately, as shown in Table VIII. These calculations show that molecular modeling can be used to predict the crystal densities of azine-N-oxides. More experimental work is required to produce greater variations in molecular and crystal structures as a further test of the method.

Conclusions

A model for predicting the performance of explosives in the cylinder test has been presented. When accurate heats of formation and crystal densities are available, the largest errors in the predicted wall velocity at 19 mm is about 3%. TATB is worse, but it is predicted that larger diameter cylinders will reduce the error. TZX is treated accurately in the model. Models for obtaining heats of formation and crystal densities have also been investigated. These can be used to estimate these quantities more accurately than before for proposed azine-N-oxides.

Acknowledgment

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Table VIII. Energy optimized lattice parameters ($\text{\AA}$ and degrees) and energy contributions (kJ/mol) of molecular crystal structures for differing parameter sets. Percent errors in parenthesis. PDC and ACME's refer to the use of the indicated charge model with William's original parameters. P(N,O) and A(N,O) refer to the use of the analogous charge model with a reduced pre-exponential factor for hydrogen on nitrogen or oxygen. E(e) is the electrostatic (PDC or ACME), E(d) the dispersion (R^{-6}), and E(r) the repulsion ($A\exp(-CR_{ij})$) components of the total energy (E(t)). ρ is the rotation angle (degrees) between optimized and original asymmetric unit. T($\text{\AA}$) is the translation of the optimized asymmetric unit relative to that observed. D is crystal density (g/cc).

1,4-Diamino-2,3,5,6-tetrazine-2,5-dioxide					
Space Group P2 ₁ /a (#14), cell choice #3, Z=2. ^a					
	Obs. ^a	PDC	P(N,O)	ACME's	A(N,O)
a	6.77	6.72 (-0.7)	6.63 (-2.1)	6.81 (0.6)	6.73 (-0.6)
b	7.35	7.55 (2.7)	7.47 (1.6)	7.55 (2.7)	7.46 (1.5)
c	5.25	5.38 (2.5)	5.25 (-0.0)	5.38 (2.5)	5.26 (0.2)
β	100.5	97.8 (-2.7)	98.2 (-2.3)	98.9 (-1.6)	99.3 (-1.1)
D	1.86	1.77 (-4.8)	1.86 (0.0)	1.75 (-6.0)	1.84 (-1.5)
ρ		5.3	4.7	4.8	4.0
E(e)		-88.78	-97.60	-85.52	-93.92
E(d)		-118.83	-134.93	-115.20	-130.87
E(r)		75.93	87.46	72.28	83.07
E(t)		-131.68	-145.07	-128.44	-141.72
1,4-Diamino-2,3,5,6-tetrazine					
Space Group Amam (#63). Z=4. ^b					
	Obs. ^b	PDC	P(N,O)	ACME's	A(N,O)
a	6.26	6.17 (-1.4)	6.14 (-1.9)	6.24 (-0.3)	6.20 (-1.0)
b	7.84	8.89 (13.4)	8.60 (9.7)	8.45 (7.8)	8.10 (3.3)
c	9.42	8.94 (-5.1)	8.77 (-6.9)	9.46 (0.4)	9.35 (-0.7)
D	1.61	1.52 (-5.6)	1.61 (0.0)	1.49 (-7.4)	1.59 (-1.5)
T		0.03	0.04	0.28	0.40
E(e)		-49.61	-56.88	-62.30	-78.73
E(d)		-90.29	-104.32	-88.03	-105.16
E(r)		53.02	63.14	57.98	75.91
E(t)		-86.88	-98.06	-92.35	-107.98

^a Ryan, R. R., et al., Los Alamos National Laboratory, private communication.

^b Krieger, C.; Fischer, H.; and Neugebauer, F. A., *Acta Cryst.* **1987**, C43, 1320.

Literature Cited

1. Fickett, W.; Davis, W.C. *Detonation*; UC Press; Berkeley, CA, 1979.
2. Mader, C.L. *Numerical Modeling of Detonation*; UC Press; Berkeley, CA, 1979.
3. a) Kury, J.W.; Hornig, H.C.; Lee, E.L.; McDonnell, J.L.; Ornellas, D.L.; Finger, M.; Strange, F.M.; Wilkins, M.L. In *Proceedings of the Fourth Symposium (International) on Detonation*, White Oak, MD, 1965, p. 3-12.
b) Lee, E.; Breithaupt, D.; McMillan, C.; Parker, N.; Kury, J.; Tarver, C.; Quirk, W.; Walton, J. *Proceedings of the Eighth Symposium (International) on Detonation*, Albuquerque, NM, p. 613-624.
4. *LLNL Explosives Handbook*; B.M. Dobratz, Ed.; UCRL-52997.
5. Souers, P.C.; Kury, J.W. *Propellants, Explosives, Pyrotechnics*, **1993**, *18*, 175-183.
6. Finger, M.; Lee, E.; Helm, F.H.; Hayes, B.; Hornig, H.; McGuire, R.; Kahara, M.; Guidry, M. *Proceedings of the Sixth Symposium (International) on Detonation*, Coronado, CA, 1976, p. 710-722.
7. Cowperthwaite, M.; Zwisler, W.H. Ref. 6, p. 162-172.
8. a) Ree, F.H. *J. Chem. Phys.*, **1984**, *81*, 1251-63. b) Ree, F.H. *ibid.* **1986**, *84*, 5845-56.
9. Kerley, G.I.; Christian-Frear, T.L. SAND93-2131, Sandia National Laboratory, Albuquerque, NM 87185, 1993.
10. Kerley, G.I. *Proceedings of the Eighth Symposium (International) on Detonation*, Albuquerque, NM, 1985, p. 540-547.
11. Stine, J.R. In *Structure and Properties of Energetic Materials*, Liebenberg, D.H.; Armstrong, R.W.; Gilman, J.J., Eds.; MRS Symposium Proceedings 296; Boston, MA, 1992; p. 3-12.
12. McGuire, R.R.; Ornellas, D.L.; Helm, F.H.; Coon, C.L.; Finger, M. *Proceedings of the Seventh Symposium (International) on Detonation*, Annapolis, Md., June, 1981, p. 940-951.
13. Suzuki, I.; Nakadate, M.; Sueyoshi, W. *Tetrahedron Lett.*, **1968**, 1855-8.
14. Ullman, E.F.; Singh, P. *J. Am. Chem. Soc.*, **1972**, *94*, 5077-78.
15. Wiberg, K.B.; Nakaji, D.; Breneman, C.M. *J. Am. Chem. Soc.*, **1989**, *111*, 4182-90.
16. Stewart, J.J.P. *J. Comp. Chem.*, **1989**, *10*, 221-264.
17. a) Williams, D.E.; Cox, S.R. *Acta Cryst.*, **1984**, *B40*, 404-417. b) Cox, S.R.; Hsu, L.-Y.; Williams, *Acta Cryst.*, **1981**, *A37*, 293-301.
18. Breneman, C.M.; Wiberg, K.B. *J. Comp. Chem.*, **1990**, *11*, 361-373.
19. Hirshfeld, F.L. *Theor. Chim. Acta*, **1977**, *44*, 129-138.
20. Ritchie, J.P. *J. Am. Chem. Soc.*, **1985**, *107*, 1829-37.
21. GAUSSIAN92, Rev. A, Frisch, M.J.; Trucks, G.W.; Head-Gordon, M.; Gill, P.M.W.; Wong, M.W.; Foresman, J.B.; Johnson, B.G.; Schlegel, H.B.; Robb, M.A.; Replogle, E.S.; Gomperts, R.; Andres, J.L.; Raghavachari, K.; Binkley, J.S.; Gonzales, C.; Martin, R.L.; Fox, D.J.; DeFrees, D.J.; Baker, J.; Stewart, J.J.P.; Pople, J.A., Gaussian, Inc., Pittsburgh, PA, 1992.

- The authors thank Dr. R. Martin for his assistance in implementing the program at Los Alamos.
22. Ritchie, J.P.; Kober, E.M.; Copenhaver, A.S. *Proceedings of the Tenth Symposium (International) on Detonation*, Boston, MA, July, 1993, in print.
 23. Nijboer, B.R.A.; DeWette, F.W. *Physica*, **1957**, *29*, 309-321.

Appendix A. Sample BKW input deck for X-0535.

```

0      1      1      1      1      0      0      0      0      0
X-0535  TZX/FPC-461  95/5
6      18      19
0.500000000000e+00 0.160000000000e+00 0.400000000000e+03 0.10909778444e+02
c      h      n      o      cl      f
0.143100000000e+01 0.272100000000e+01 0.395600000000e+01 0.131900000000e+01
0.55875376900e-01 0.83813065351e-01
0.178700000000e+01 0.100000000000e+03 0.257000000000e+05
0.300000000000e+04 0.300000000000e+00
h2o  co2  n2  h2  o2  co  nh3  h  no  oh  ch4
hcl  ccl4  cl2  hf  cf4  f2  cof2  sol  c
0.13185912061e+01 0.100000000000e-01 0.19778868091e+01 0.41906532675e-01
0.100000000000e-01 0.100000000000e-01 0.100000000000e-01 0.100000000000e-01
0.100000000000e-01 0.100000000000e-01 0.100000000000e-01 0.100000000000e-01
0.100000000000e-01 0.100000000000e-01 0.100000000000e-01 0.100000000000e-01
0.16906532675e-01 0.100000000000e-01 0.14003419599e+01
0.42588420868e+02 0.14808050357e-01-0.26391810479e-05 0.19204529633e-09
0.000000000000e+00 0.13428283691e+04-0.571070000000e+05 0.250000000000e+03
0.47481121063e+02 0.19544629380e-01-0.37212960251e-05 0.27703001004e-09
0.000000000000e+00 0.74628094482e+03-0.939680000000e+05 0.600000000000e+03
0.43923400879e+02 0.12225010432e-01-0.23790050818e-05 0.17983220468e-09
0.000000000000e+00 0.11391613770e+04 0.000000000000e+00 0.380000000000e+03
0.29703470230e+02 0.11438289657e-01-0.22012220597e-05 0.16777609857e-09
0.000000000000e+00 0.11758961182e+04 0.000000000000e+00 0.800000000000e+02
0.47030899048e+02 0.12871470302e-01-0.25002170787e-05 0.19015700126e-09
0.000000000000e+00 0.10353764648e+04 0.000000000000e+00 0.350000000000e+03
0.45330818176e+02 0.12381610461e-01-0.24164030492e-05 0.18281809400e-09
0.000000000000e+00 0.11215882568e+04-0.272010000000e+05 0.390000000000e+03
0.42018161774e+02 0.19116619602e-01-0.31643301099e-05 0.21978009690e-09
0.000000000000e+00 0.12069611816e+04-0.936800000000e+04 0.476000000000e+03
0.26391099930e+02 0.81213722005e-02-0.16907399640e-05 0.13168230395e-09
0.000000000000e+00 0.79463159180e+03 0.516190000000e+05 0.760000000000e+02
0.48414981842e+02 0.12693859637e-01-0.24946000394e-05 0.18932129475e-09
0.000000000000e+00 0.12092497559e+04 0.214770000000e+05 0.386000000000e+03
0.42417919159e+02 0.11568469927e-01-0.22266590349e-05 0.16891550658e-09
0.000000000000e+00 0.11835175781e+04 0.356000000000e+04 0.413000000000e+03
0.38756858826e+02 0.23640129715e-01-0.37079569211e-05 0.24707139112e-09
0.000000000000e+00 0.10424278564e+04-0.160000000000e+05 0.528000000000e+03
0.42936641693e+02 0.11874400079e-01-0.22864060156e-05 0.17278070641e-09
0.000000000000e+00 0.11737486572e+04-0.220000000000e+05 0.637000000000e+03
0.67947479248e+02 0.39482139051e-01-0.79941555668e-05 0.61362437354e-09
0.000000000000e+00 0.82403247070e+03-0.255000000000e+05 0.200000000000e+04
0.51320999146e+02 0.14395629987e-01-0.29638829346e-05 0.23498719637e-09
0.000000000000e+00 0.99022290039e+03 0.000000000000e+00 0.956000000000e+03
0.40000709534e+02 0.11445820332e-01-0.22104300115e-05 0.16817050530e-09
0.000000000000e+00 0.11790649414e+04-0.642000000000e+05 0.389000000000e+03
0.55680858612e+02 0.35636339337e-01-0.68981721597e-05 0.51695342451e-09

```

```

0.0000000000e+00 0.20372969055e+03-0.21800000000e+06 0.13300000000e+04
0.46372489929e+02 0.13958250172e-01-0.28047579690e-05 0.21583379528e-09
0.00000000000e+00 0.95607006836e+03 0.00000000000e+00 0.38700000000e+03
0.56752330780e+02 0.26767069474e-01-0.51359011195e-05 0.38333131114e-09
0.00000000000e+00 0.56443182373e+03-0.15000000000e+06 0.13300000000e+04
-0.24615189433e+00 0.71798549034e-02-0.12975500567e-05 0.93499950837e-10
0.00000000000e+00-0.25820437622e+03 0.00000000000e+00 0.00000000000e+00

0.44444444776e+00 0.83093583584e+00-0.13938181400e+01 0.67256969213e+00
-0.11353725940e+00 0.64915586263e-02-0.22670534253e+00 0.12051656842e+00
0.83159998059e-01-0.17558999360e+00 0.15531000495e+00 0.12010000229e+02
0.00000000000e+00 0.20000000000e+01 0.00000000000e+00 0.10000000000e+01
0.00000000000e+00 0.00000000000e+00 0.10000000000e+01 0.00000000000e+00
0.00000000000e+00 0.20000000000e+01 0.00000000000e+00 0.00000000000e+00
0.00000000000e+00 0.00000000000e+00 0.20000000000e+01 0.00000000000e+00
0.00000000000e+00 0.00000000000e+00 0.00000000000e+00 0.20000000000e+01
0.00000000000e+00 0.00000000000e+00 0.00000000000e+00 0.00000000000e+00
0.00000000000e+00 0.00000000000e+00 0.00000000000e+00 0.20000000000e+01
0.00000000000e+00 0.00000000000e+00 0.10000000000e+01 0.00000000000e+00

```

Appendix B. Sample SIN input deck for RDX.

```

      3 127 124 1 1 0 0 1 1 0 0 0
Cylinder Test
0.20000000000E+01 0.50000000000E+04 0.20000000000E+03 99999.0000000E+00
RDX
 100 1 1 0
0.12700000000E-01 0.25400000000E-02 0.20000000000E+01 0.18000000000E+01
0.10000000000E-05 0.30000000000E+03 0.00000000000E+00 0.00000000000E+00
0.24230000000E+00 0.18830000000E+01 0.10000000000E-01 0.00000000000E+00
0.00000000000E+00-0.90418722204E+01-0.71318525243E+02-0.12520497936E+03
-0.92042417760E+02-0.22189382573E+02 0.67500000000E+00 0.40000000000E+00
0.54229934924E+00 0.50000000000E-04 0.00000000000E+00 0.00000000000E+00
0.30000000000E+03 0.10000000000E-05 0.00000000000E+00 0.00000000000E+00
0.00000000000E+00 0.00000000000E+00 0.00000000000E+00 4.15944771549E-01
-0.34939402446E+01-0.25521450345E+01 0.25510714285E+00 0.11234997249E-01
-0.96121668096E-02-0.16050449713E+01 0.51908426867E+00 0.65757361251E-01
0.40261694558E-02 0.94796916331E-04 0.74073902496E+01-0.49641482820E+00
0.39721126724E-01 0.30458400580E-01-0.10680694321E-01 0.50000000000E+00
0.10000000000E+00
copper
 25 0 0 0
0.10160000000E-01 0.20320000000E-02 0.20000000000E+01 0.89029999999E+01
0.10000000000E-05 0.30000000000E+03 0.00000000000E+00 0.00000000000E+00
0.39580000000E+00 0.14970000000E+01 0.00000000000E+00 0.00000000000E+00
0.00000000000E+00-0.31983419917E+04-0.55743953279E+04-0.36248840041E+04
-0.10433967951E+04-0.11206726387E+03 0.20000000000E+01 0.93000000000E-01
0.11232168932E+00 0.17670000000E-04 0.00000000000E+00 0.00000000000E+00
0.30000000000E+03 0.10000000000E-05 0.00450000000E+00 0.46600000000E+00
0.05000000000E+00 0.00000000000E+00 0.00000000000E+00 0.00000000000E+00
0.10000000000E+01 0.00000000000E+00 0.00000000000E+00 0.00000000000E+00
air
 0002
+5.0000 +000+0.02 +000+0.000001 +000+0.000001 +001
+1.0 -006+3.0 +002+0.0 +000+0.0 +000
+0.254 +000+1.5 +000+0.0001 +000+0.0 +000
+0.0 +000+8.17773414663+002+6.10099511390+002+9.09042692454+001
-2.20373162776+001-4.87356368431+000+0.0 +000+0.0276 +000
+5.2882072 -002+1.1666 -005
+3.0 +002+1.0 -006+0.0 +0.0
+0.0 +1.0 -006
+1.0

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