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# Theoretical Prediction of 2,4,6-Trinitro-1,3,5-triazine (TNTA). A New, Powerful, High-Energy Density Material?

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Our recent prediction of nitryl cyanide, $O_2NCN$, as a new high-energy molecule[1] has prompted us to make a theoretical search of its possible derivatives with similar performance (exothermic decomposition) but with possibly increased stability and a higher density in its condensed state. Nitryl cyanide itself has been estimated to possess a rather high heat of formation ($\Delta H°_{f(300)} = 60$ kcal/mol) and exothermic decomposition energy ($\Delta E_r = 150$ kcal/mol) along with a reasonably large barrier ($\Delta E_r^{\ddagger} = 54$ kcal/mol) on a complex unimolecular decomposition pathway.[1]

The formation of molecular complexes (e.g., di-, tri-, oligo-, and polymers) is a conceivable way to increase density and stability and to improve the material properties of propellants and explosives. Taking into account that trimerization leading to aromatic *s*-triazines (e.g., $3ClCN \rightarrow (ClCN)_3$)[2] is a well-known and characteristic reaction for cyanides, it is logical to envision the cyclic trimer of nitryl cyanide, 2,4,6-trinitro-1,3,5-triazine (TNTA), as a potential high-energy molecule. Surprisingly, there seems to be only one obscure reference to this compound in 1907,[3] but with a predictive *ab initio* theory we can assess its energy performance and other important properties.

Extending our theoretical search and investigation of high-energy molecules, new potential rocket propellants, and explosives,[1,4] we have performed an *ab initio* study of TNTA and some reference molecules in order to obtain its structure and spectra and to estimate performance of this intriguing molecule. The geometrical parameters have been optimized at HF/6-31G* and at MBPT(2)/6-31G* levels by use of the ACES II program system.[5] The analytical harmonic vibrational frequencies were obtained at HF/6-31G* for TNTA and at both levels for smaller reference molecules and are available for identification of the molecules.[1,6] Energy comparisons are discussed at MBPT(2)/6-31G*//MBPT(2)/6-31G + ZPE level unless otherwise noted.[7]

The minimum energy $C_3$ structure of TNTA has a planar aromatic six-membered cycle with the $NO_2$ group rotated out of the ring plane by 40°. The out-of-plane rotation of $NO_2$ groups compromises the conjugation of the nitro groups and the aromatic six-electron ring system (maximum for the planar form) and the repulsion of negatively charged oxygens and ring nitrogens (minimum for the 90° rotation). The energy effect of the rotation is small. The $D_{3h}$ forms with $NO_2$ groups planar and perpendicular to the ring plane are 1.8 and 3.1 kcal/mol higher in energy than the $C_3$ minimum. Although neither of the two $D_{3h}$ forms are minima at the HF/6-31G* level, the perpendicular orientation of the $NO_2$ groups is 1.6 kcal/mol more favorable than the planar structure at HF in contrast to MBPT-(2). The ring CN bond length in TNTA (1.331 Å) is shorter, and the NCN bond angle (128.4°) is smaller than the corresponding values in *s*-triazine (1.341 Å and 126.0° at MBPT-(2)/6-31G*[8] and 1.338 Å and 126.2° in an electron diffraction experiment,[9] respectively) (Scheme 1). Although the aromatic ring geometry almost does not change with $NO_2$ group rotation, the external $C-NO_2$ bond is longer in the planar form (1.498 Å) than in the perpendicular form (1.465 Å). A similar effect of CN bond variation induced by $NO_2$ group rotation was observed in nitrobenzene.[10] Trinitrobenzene (TNB) has a somewhat shorter C−N bond than TNTA.[11] The nitro groups influence the benzene and triazine rings in a similar way by shortening the ring bonds and enlarging the bond angles at the carbons bound to $NO_2$ groups.

The most fundamental performance properties of a potentially energetic metastable molecule are the heat of formation ($\Delta H°_f$) and energy release in decomposition to stable species ($\Delta E_r$). The heat of formation of TNTA (46 kcal/mol) can be obtained from the isodesmic reaction (Scheme 2) and experimental $\Delta H°_f$ values of the reference molecules benzene (19.8 kcal/mol),[12] *s*-triazine (53.9 kcal/mol),[13] and TNB (−8.5 kcal/mol).[14] The estimated heat of formation of TNTA in the solid state is 24 kcal/mol lower than its gas phase value.[15]

Once the $\Delta H°_f$ for TNTA was estimated, the 304 kcal/mol energy release in decomposition into $N_2$ and $CO_2$ ($\Delta E_r$), specific decomposition energy (1410 cal/g; $\Delta E_r$ divided by the molecular mass), and specific impulse (269 s in the atmosphere and 294 s in a vacuum)[16] can be easily derived. Our estimates of $\Delta E_r$ and $I_{sp}$ for TNTA demonstrate its performance to be similar to that of RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine), but the estimated density of TNTA (2.1 g/cm$^3$)[17] is higher than in RDX (1.82 g/cm$^3$).[14] Of course, the actual gaseous product distribution and other factors, which are not considered here, could reduce the effective performance of TNTA, but it has sufficient energy and density to be of interest as a potential propellant.

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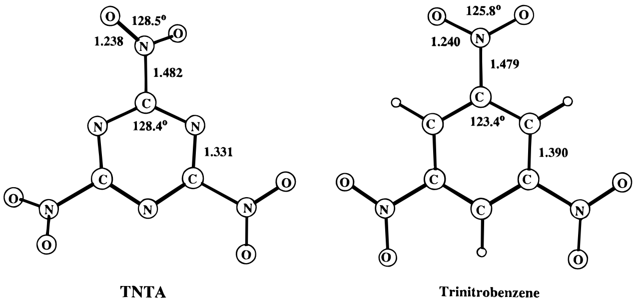
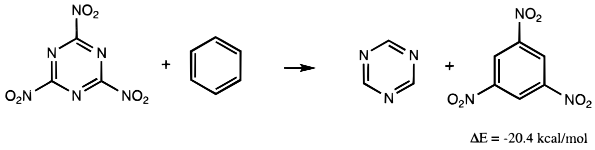
S0002-7863(96)02744-8 CCC: $12.00

**Scheme 1**



**Scheme 2**



As suggested in 1907, one might expect the synthesis of TNTA from industrially available cyanuric chloride (2,4,6-trichlorotriazine) and $AgNO_2$;[2b,3] however, this does not occur.[18] No further information about preparation or characterization of TNTA is available in the literature. Other possible synthetic roots can be based on the intrinsic tendency of cyanides toward trimerization.[2] Comparison of the computed MBPT(2) energies of trimerization in eqs 1 and 2 shows that TNTA should be a more stable species than nonsubstituted *s*-triazine:

$$3O_2NCN \rightarrow (O_2NCN)_3 \qquad \Delta E = -70.2\ \text{kcal/mol} \quad (1)$$

$$3HCN \rightarrow (HCN)_3 \qquad \Delta E = -26.5\ \text{kcal/mol} \;(\text{expt } -43\ \text{kcal/mol})^{19} \quad (2)$$

A higher stability of the six-membered TNTA ring structure compared to that of *s*-triazine can be explained by the $\sigma$ acceptor effect of $NO_2$ groups, which increases the effective electronegativity of carbon atoms and cyclic electron delocalization.

We have designed and characterized theoretically 2,4,6-trinitro-1,3,5-triazine, and we encourage synthesis of it and its derivatives.

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[18] K. Christe, private communication.

[19] Estimated from the heats of formation of HCN (32.3 kcal/mol in ref 12) and *s*-triazine (53.9 kcal/mol in ref 13).