Improved synthesis and thermochemical properties of amino- and hydrazino-1,2,4,5-tetrazines

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SUPPLEMENTARY INFORMATION
Calorimetric measurements. The main method for determining the enthalpies of formation of high energy compounds is combustion calorimetry. The measurements were carried out on a precision automatic combustion calorimeter with an isothermal shell (designed by the Laboratory of Thermodynamics of energetic compounds, Federal Research Center of the Institute of Chemical Physics of the Russian Academy of Sciences), designed specifically for the study of energetic materials [16].

The basic design features of the calorimeter used in the work: 1) a small thermal equivalent (~ 500 cal/deg) with a large bomb volume (200 cm³); 2) simple installation of the bomb in the calorimeter – it is enough to remove the covers of the shell and the calorimetric vessel, put in the bomb and close the covers; 3) continuously thermostatted shell; 4) a liquid sealed calorimetric vessel permanently fixed in a shell is made in the form of a glass with double walls (a constant amount of a calorimetric liquid ensures the constancy of the thermal equivalent); 5) low measurement error. The calorimeter makes it possible to measure the thermal effect of the combustion reaction of substances with an expanded uncertainty of 0.01±0.02%. The calorimeter was calibrated with standard K-1 benzoic acid manufactured by the D. I. Mendeleev Institute for Metrology (VNIIM). The energy of combustion of benzoic acid under standard conditions was 6322.6 ± 0.2 cal/g. The absence of a systematic error in the calorimetric measurements was controlled by the combustion of secondary reference substances – succinic and hippuric acids, the combustion energies of which on this calorimeter were 3020.3 ± 0.6 cal/g (0.02%) and 5631.4 ± 3.4 cal/g (0.06%), respectively. Samples of the investigated substances were burned in a platinum crucible. Weighed on a Bunge microanalytical balance with an error of 2×10⁻⁶ g. A weighed sample of the substance was placed into a calorimetric bomb and filled with oxygen. The initial oxygen pressure during combustion of all substances is about 30 atm (3 MPa). Before the experiment, 1 ml of distilled water was injected into the bomb to create a saturated vapor pressure and dissolve nitrogen oxides formed during combustion.

The samples were ignited with a cotton thread, which, in turn, was ignited by incandescence of a platinum wire (diameter 0.3 mm) at a dosed current pulse supplied from a special device. The energy of combustion of a cotton thread was measured in a series of seven experiments and amounted to 3968.9 ± 1.6 cal/g. When determining the combustion energy, corrections for the heat effects of nitric acid formation, heat exchange of a calorimetric vessel with an isothermal shell, and the combustion energy of an auxiliary substance and a cotton thread were taken into account. A detailed procedure for preparing samples and conducting a combustion experiment was described earlier [17].