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Explosives at Extreme Conditions: Polymorphism of 2,4-Dinitroanisole

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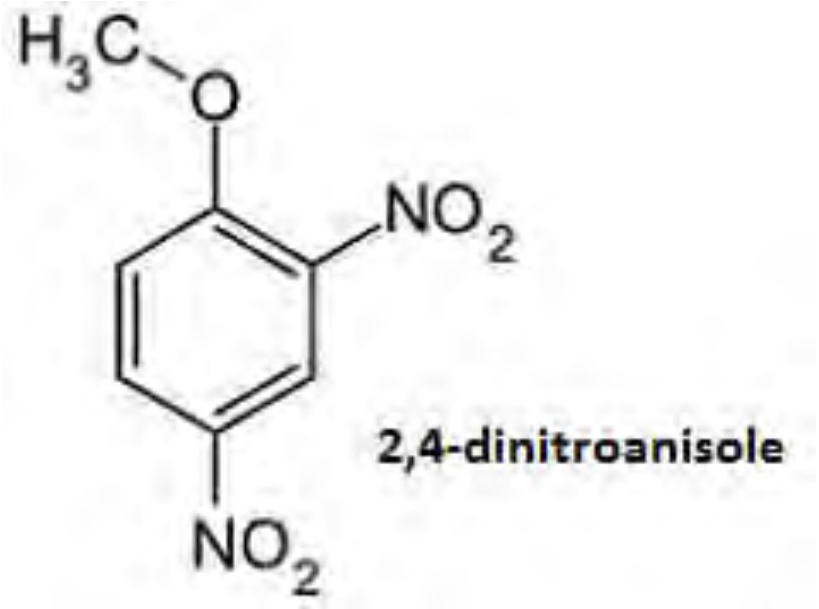
2,4-dinitroanisole (DNAN) is an energetic material, developed as an insensitive replacement for TNT in melt-cast explosive formulations. While DNAN-based formulations demonstrate greatly reduced sensitivity to accidental initiation compared to those using TNT, issues remain with the replacement of TNT with DNAN. For instance, DNAN based formulations have demonstrated catastrophic levels of irreversible growth during heat-cycling, with volume increases of up to 15% reported. [1] In order to investigate the role of polymorphism in the irreversible growth of DNAN, high-pressure and variable-temperature neutron and x-ray diffraction studies have been performed. Two polymorphs of DNAN have been found to exist at ambient temperature and pressure, the thermodynamic form, DNAN-I, and the kinetic form, DNAN-II.[2,3] The phase diagrams of both form-I and -II of DNAN have been explored for the first time. In the case of DNAN-II, two high-pressure phase transitions were found. DNAN-II initially transformed to DNAN-III, which at higher pressures transformed to DNAN-IV. In addition, variable temperature studies demonstrated that the DNAN-II to DNAN-III transition also occurs when DNAN-II is cooled below room temperature. The thermal expansion of the DNAN-II/III lattice was investigated from 150K to 363K, demonstrating that an abrupt change in the thermal behaviour of lattice parameters occurs at the DNAN-II/III transition. From these combined crystallographic studies, the structure of DNAN-III has been solved, showing it is closely related to DNAN-II. In the case of DNAN-I, high-pressure neutron powder diffraction studies demonstrated that it transforms to a new form (DNAN-V) that is distinct from DNAN-II,-III or -IV. Rietveld refinement of the high-pressure DNAN-I data also determined that the material exhibits negative linear compressibility, which is of interest given the use of DNAN as a shock-insensitive energetic material. Comparison of the behaviour of DNAN-I and –II under variable temperature and high-pressure conditions indicates that the kinetic form, DNAN-II, is the denser phase under all conditions studied. This work highlights the importance of crystallographic techniques in order to understand the polymorphism of energetic materials.

[1] *P. Samuels, Irreversible Growth of DNAN Based Formulations, 2012 NDIA IM/EM Presentation, May 2012.,* ***[2]*** *S.C. Nyburg, C.H. Faerman, L. Prasad., Acta. Cryst., 1987, C43, 686.,* ***[3]*** *G. Xue, C. Gong, H. Chen, Z. Kristallogr., 2007, 222, 321.*



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