



Ammonium Nitrate Phase State Stabilization with Small Amounts of Some Organic Compounds

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Abstract: The investigation considers phase stabilization of ammonium nitrate for considerable extension of its application area including new generation of gas-generating compositions for airbag inflators. It was shown that alloys of ammonium nitrate with small amounts (2-10%) of some organic compounds can have no phase transitions or at least have only one instead of three ones in initial ammonium nitrate. The mostly effective as stabilizers are the compounds that have rather close crystallographic parameters. A strong donor-acceptor interaction between nitrate-anion and organic molecules are found. Using quantum-chemical calculations, X-ray analysis, X-ray phase analysis, UV- and IR-spectroscopy it was found a new ammonium nitrate phase state in its alloy with some organic additives. This state is stable in temperature range between -50 and +100 °C.

Keywords: ammonium nitrate, phase transitions, phase stabilization, intermolecular interactions

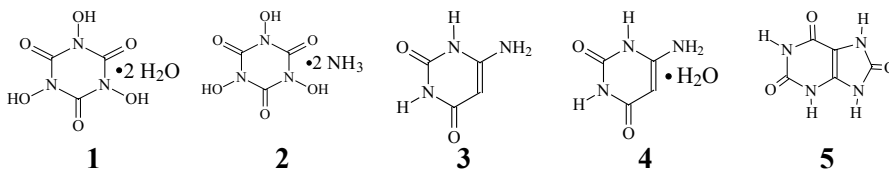
Introduction

There are many known methods to affect phase state and phase transitions in crystalline compounds by introducing of small amount of compounds-stabilizers. Last years the nature and mechanism of such kind of influence is under wide studying. The nature of the influence of otherwise isomorphic ions introducing is more or less clear. This introducing has to influence on the inter-ionic interaction

and consequently on the phase state. E.g. it's possible to stabilize ammonium nitrate (AN) in the phase III by isomorphic potassium nitrate introducing into AN crystalline lattice. However AN stabilized by this method is not applicable in some cases because of the presence of potassium (5-15% of KNO_3 or so). Last year a new group of stabilizers (with no metal) has been found [1, 2]. Due to crystallographic likeness with AN these compounds can entry into the AN lattice, but their influence on the AN phase state is too different in comparison with the influence of ions being introduced. Crystallographic likeness means the most full overlap of the AN interfacial distances and stabilizer's interfacial distances. In this case roentgen-phase analysis shows that X-ray photographs of alloy AN + stabilizer has to be almost alike AN X-ray photograph while lines of the stabilizer has not been observed on the alloy X-ray photograph. Thus, an organic compound "dissolves" in the lattice of the phase IV of AN. Additional intermolecular interactions between built-in atomic planes of stabilizer and atomic planes of AN must appear. The nature of these interactions in modified crystalline lattice is rather complicated: it may include ions changes, new hydrogen bonds formation, and other kinds of chemical interaction. X-ray investigation itself is not enough for studying nature and mechanism of influence of such stabilizers on AN phase state, investigation of UV and IR spectra is necessary too.

This paper is the continuation of our earlier investigations [1-4], here we are representing the results of AN lattice modification with organic compounds containing plane unsaturated N-heterocycles substituted by carbonyl, amine (or imine) groups. Nitrate-anion is plane, quantum-chemical calculations shows that it contains twice degenerate bonding orbital of π -type and not-bonding coplanar orbital of n-type, the lowest orbital is of π -type too. So, accordingly electronic structure of AN, at possible emergence of intermolecular electronic interactions between the nitrate anion and stabilizer molecule the nitrate anion may serve simultaneously as donor of electrons as well as their acceptor.

The following compounds were selected as stabilizers (modifiers) of AN phase state: 1,3,5-trihydroxyisocyanuric acid dihydrate (**1**), diammonium salt of 1,3,5-trihydroxyisocyanuric acid (**2**), 4-aminouracil (**3**), its hydrate (**4**), trioxypurine (**5**).



These compounds were selected because on the one hand they are rather effective acceptors of electrons (due to $>C=O$ group), on the other hand they are good donors of electrons (due to $N-H$ group), so crystalline lattice of the stabilizer may become a model object for studying expectable intermolecular interactions, which may be reliably fixed with X-ray method and with quantum-chemical calculations (these method are not applicable for composites). And the second important reason to select these compounds – their crystallographic likeness with ammonium nitrate crystalline structure.

Experimental Methods

Small additives of organic compounds have been introduced into AN mainly by fusion at temperature close to AN melting point.

The following instrumental methods and apparatus were used:

- X-ray diffraction experiments – with diffractometer KM-4 («KUMA-Diffraction», graphite monochromator, $\lambda(Mo-K\alpha) = 0.71073 \text{ \AA}$, 293 K, $\omega/2\theta$ -scanning),
- X-ray phase analysis – with diffractometer DRON-2 with controlling computer. Phase identification at conversions in the temperature diapason from -90 till $+100 \text{ }^\circ\text{C}$ has been accomplished by roentgenograms analysis with preliminary calculation (basing on atoms coordinates, gotten from X-ray investigation of monocrystals) of theoretical roentgenograms of polycrystals of all phases.
- DTA analysis – with derivatograph MOM (Hungary), heating rate $0.6 \text{ }^\circ\text{C/minute}$.
- UV investigations (200-900 nm) – with spectrophotometer Specord M40.
- IR investigations ($4000-700 \text{ cm}^{-1}$) - with spectrophotometer Specord IR75.

Analysis of X-ray Investigations and Quantum-Chemical Calculations

The X-ray data of a part of stabilizers that are under investigation in this paper are already described in [5]. As for the structure of 4-aminouracil there is intermolecular interaction $N-H \cdots O=C$. It forms endless chains of interacting molecules in the crystal. In structure of anhydrous 4-aminouracil all molecules are unified with three-dimensional net of donor-acceptor interactions, this compound

may be called conditionally as “polymers”. The geometry of interacting molecules shows that each molecule serves as a donor of proton and non-fractionalized electron couple of imine nitrogen, as well as an acceptor of electrons due to carbonyl group with low-lying vacant orbital (Figure 1).

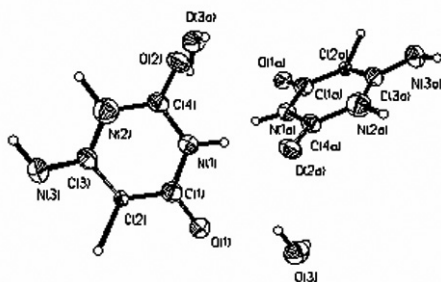


Figure 1. The structure of the molecule monohydrate of 4-aminouracil (the left structure), and of the same molecule after conversion in space group P2(1)/n (the right one).

Using ab-initio calculations of one 4-aminouracil molecule and one couple of interacting molecules, selected in real crystalline lattice, one can obtain full energies of molecules in B3LYP/LANL2DZ approximation [6]. The differences (Δ) of these energies is the energy of interaction of two molecules, being selected from total chain of interacting molecules. The value of Δ , calculated basing on atoms coordinates gotten from X-ray analysis without optimization is -18.1 kcal/mol, while after full geometry optimization it is equal -10 kcal/mol. So, intermolecular orbital interaction energy in conjunction with hydrogen bond energy is rather considerable and can compete against AN ionic lattice energy. For mutual comparison of acceptor capability of molecules-stabilizers ab-initio calculations (using GAUSSIAN-03) of three molecules (1,3,5-trihydroxyisocyanuric acid, 4-aminouracil and trioxypurin) have been accomplished for the main (singlet) state. All systems have been calculated at full geometry optimization in B3LYP/LANL2DZ approximation.

Study of Highest Occupied Molecular Orbitals (HOMO) of these three compounds lets consider them as weakly binding orbitals of π -type. Analysis of energies and symmetry of lower free molecular orbitals of the same molecules shows that all of them are of π -type where carbonyl bonds and multiple C-N bonds introduce the main input. Lowest Unoccupied Molecular Orbitals (LUMO) are symmetrically non-binding, but weakly binding accordingly orbital energy values. Table 1 illustrates values HOMO, LUMO and their difference for three compounds under investigation. The order of HOMO and Δ values

corresponds to acceptor capacity of the compound to nitrate ion: trioxypurine has the higher acceptor capacity, then comes 4-nitriuracil, and then – 1,3,5-trihydroxyisocyanuric acid.

Table 1. Energies LUMO, HOMO and their difference, calculated by experimental and optimized geometry in B3LYP/LANL2DZ approximation

Molecule	Geometry type	LUMO, Atomic units	HOMO, Atomic units	abs[HOMO-LUMO], eV
1,3,5-trihydroxyisocyanuric acid	experimental	-0.05435	-0.31299	7.04
	optimized	-0.05434	-0.31302	7.04
trioxypurine	experimental	-0.05824	-0.23836	4.90
	optimized	-0.06125	-0.23671	4.77
4-aminouracil	experimental	–	–	-
	optimized	-0.03297	-0.23845	5.59

X-ray Phase Investigations and Differential Thermal Analysis

It was shown that if there is a lattice parameters likeness of partners (stabilizer and AN) it is possible to introduce a considerable fraction of stabilizer into AN-stabilizer alloy with no appearance of stabilizer presence on X-ray photograph. The compound that has been introduced into the alloy is distributed in the form of very small clusters among separated AN crystalline blocks, which have almost the same atomic interfacial distances as the similar distances in the stabilizer structure. Figure 2 illustrates comparative X-ray photographs of AN crystalline lattice, crystalline lattices of stabilizers and of alloys. The most characteristic reflexes on individual AN X-ray photograph (Figure 2, curve “a”, they correspond to phase IV of AN), which have to be overlapped at stabilizer introducing are the following: interfacial distances with $d = 4.906$ and $d = 3.091$ Å (the second one is more important because it determines the distance between atomic planes in pile of plane-parallel anions). Curve “b” shows X-ray photograph of crystals of diammonium salt of 1,3,5-trihydroxyisocyanuric acid. There is a strong reflex with $d = 3.100$ Å. Curve “c” shows X-ray photograph of the alloy diammonium salt of 1,3,5-trihydroxyisocyanuric acid (44.7%) + AN (55.3%). This X-ray photograph is an advantageous case of almost full coincidence of

X-ray photographs of both ingredients being neat. Curve “d” shows X-ray photograph of crystals of 4-aminouracil. Here one can see the coincidence of interfacial distances (4.676, 3.151 and 3.077 Å) with adequate close distances on the X-ray photograph of AN. However here there is a very strong reflex with $d = 3.531$ Å, that is absent on AN (phase IV) X-ray photograph. This reflex is absent on X-ray photograph of the alloy AN (83.8%) + 16.2% 4-aminouracil (curve “e”). Thus, 4-aminouracil in amount 16.2% is completely distributed in the lattice of phase IV of AN. The X-ray photograph of trioxypurine (curve “f”) is the most illustrative. The strongest reflex with $d = 6.511$ Å, characteristic for this compound, is completely absent on the X-ray photograph of neat AN, while it appears on the X-ray photograph of alloy AN + trioxypurine only if the content of trioxypurine reaches 30% or so (curve “g”). Moreover here it is rather weak. Thus the ability of trioxypurine to be distributed in AN crystalline lattice is the higher among other compounds that have been investigated. It corresponds with its acceptor capacity that was calculated.

It is widely known that there are five polymorphous modifications and four phase transitions in individual AN: $V \leftrightarrow IV$ at -17 °C, $IV \leftrightarrow III$ at $+32.3$ °C, $III \leftrightarrow II$ at $+84.2$ °C, and $II \leftrightarrow I$ at $+125.2$ °C. These phase transitions are serious obstacles for wide AN application in energetic compositions. The phase transition $IV \leftrightarrow III$ is the most destructive. Studying the kinetics of this transition in isothermal regime using X-ray analysis has been shown that it undergoes through full destruction of phase IV. Figure 3 demonstrates experimental kinetic data of initial phase IV loss and final phase III growth at 33 °C (curves IV, III). During definite time interval the sum of partial amounts of initial and final phases is considerably lower than 1, that may prove the formation of an intermediate phase state X (curve X, $[X]=1-[IV]-[III]$). X-ray analysis does not see this phase because the material representing this phase is not concentrated in clusters of definite dimension, but is distributed among all the sample, and may be it is situated at the separation boundary of initial and final phases.

Theoretic modeling of phase transition $IV \leftrightarrow III$ process in monocrystals shows that it is not possible to make this transition with small ions moving, a full destruction of the initial structure is needed and then the construction of the new one. That’s why one calls sometimes this phase transition at $+32.3$ °C “catastrophic point”. Modification of AN crystals with compounds described in this paper allows to obtain a completely new phase state of AN. There are no phase transitions $V \leftrightarrow IV$ and $IV \leftrightarrow III$ in these samples, however the phase transition $IV \leftrightarrow II$ intervenes. It reminds the fact that phase transition $IV \leftrightarrow II$ is characteristic for samples of absolutely dried individual AN [7]. Kinetics of phase transition in alloy 90% AN + 10% trioxypurine at 53 and 54 °C showed that

the sum of initial and final phases are close to 1 on any depth of transformation. That the transition of phase IV into II undergoes directly from crystal to crystal practically without intermediate X-ray-amorphous phase formation. So, AN modification with compounds under investigation in this paper does not allow to solve the task to obtain product with no phase transitions at temperature from -50 till +100 °C. This product is stabilized only for the application from -50 till +50°C. Numerous abrupt cyclic temperature changes between -50 and +100°C (temperatures shocks) of obtained AN samples containing modifiers at different humidity values showed that the phase state of samples remains the same, that is with IV-II phase transition.

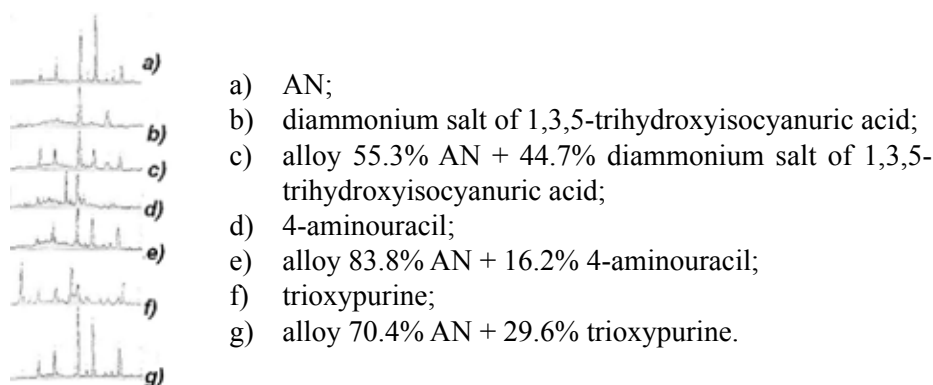


Figure 2. X-ray photographs of polycrystalline samples (λ CuK $_{\alpha}$, $2\theta = 10-50^{\circ}$).

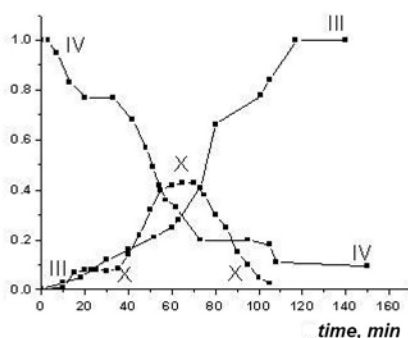
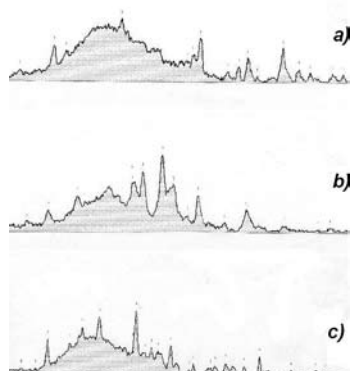


Figure 3. Direct phase transition IV \rightarrow III in AN (33 °C).

Anyway after many efforts we have found the definite conditions of processing these samples allowing to obtain product without phase transitions even after numerous temperature shocks in temperature range between -50 and +90 °C.

During the fusion of the mixture AN+ organic additive a solid solution having unordinary properties forms. It's nature cannot be considered as any known typed of solid solutions. It is not a solid solution alike AN+ KNO_3 – the difference between sizes of modifier's molecule and nitrate-ion is too high. It differs considerably of interstitial solid solutions where the second compound implants into the space between molecules (atoms, ions) of the main compound. In our case the difference is the following: molecules of the modifier are binding with nitrate ions with strong intermolecular bonds and thereby they form something like the own crystalline lattice in the ammonium nitrate one with no considerable influence on the lattice of AN. This solid solution (that can be called "modified AN") is actually a new phase of AN with it's proper crystalline lattice, that is close to ordinary AN crystalline lattice, but it has considerable differences. Diffractogrammes show it clearly: the ratios between the most intensive peeks change too, new peeks appear, that are not typical nor for AN or the additive, some weak peeks disappear. Actually this modified product (some modifiers work even at small amounts, from 2 to 2.5%) may be considered as a new phase IV' with it's own existence area. Solid solutions formed at introducing some specific substances-modifiers can be crystal chemically transmuted forming finally high disperse X-ray amorphous substances having no phase transitions between -100 and + 100 °C and with melting point higher than AN has. For understanding this very complicate processes at interaction of AN with modifiers and the nature of obtained solid solutions a set of experiments has been carried out. The main investigation object was the mixture AN: 4-aminouracyl (83.4:16.2 mass ratio) because alloys with this organic compound are mostly capable of further crystal chemical transformations. Attempts to obtain the vitriform state at chaotic introduction of the modifier into AN molecule (a small sample of hot melt at 160-170 °C was quickly put into -40 °C and was kept there within 1 hour) failed. The X-ray photograph was almost the same as one of the product cooled in inartificial conditions. It seems intermolecular interactions are rather strong for fast formation of crystal structure. The crystalline lattice of modified AN has been formed at melt cooling and hereby the molecules of the organic addition have built in between AN atomic planes. The final result may be explained as the incorporation of own atomic planes of the modifier between atomic planes of AN. This product maintains the initial phase state (phase IV of AN) and the phase state stabilization expands on the temperature diapason from -50 up to +50 °C. The conditions of the additional processing of the modified product have been selected because the phase transition IV-III must undergo at $t > +32.4$ °C in presence of water steam [8]. So, the selected temperature was +37 °C, humidity – 70%, the time of exposition was between 1 and 7 hours. Then the samples were dried in vacuum during 4-17 hours. X-ray photographs and DTA analysis show

that only 50% or so of the product have the phase transition IV-II at +50 °C, so a half of the product is still in the initial (before the additional processing) state. The X-ray analysis shows a halo presence. It confirms that a half or so of product has undergone into X-ray amorphous disordered state. The additional processing (numerous humidity change from 0 up to 70-80%) transforms all the sample into X-ray amorphous state, with no phase transitions and with melting point higher than both m.p. of AN and it's alloy with the modifier. The obtained product is less hygroscopic than the initial alloy. Calorimetric investigations (DTA and DSC) confirm that there is no re-crystallization of the amorphous phase back into the phase IV of AN, at least in temperature range between -50 and +100 °C and maybe higher. UV and IR spectra of this new state differ considerably from spectra of AN or initial solid alloys (before additional processing). Some X-ray photographs of obtained samples are shown on Figure 4. These X-ray photographs are characteristic for X-ray-amorphous state with particles dimension lower than 100 nm. Physico-chemical properties of these products seems very exceptional and one has to study them more accurately.



- a) 90% AN + 10% diammonium salt of 1,3,5-trihydroxyisocyanuric acid;
- b) 83.8% AN+ 16.2% aminouracil;
- c) 81.1% AN + 18.9% trioxypurine.

Figure 4. Some X-ray photographs (λ $\text{CuK}\alpha$, $2\theta = 10\text{-}50^\circ$) of polycrystalline composites after processing.

Spectral Investigations

Intermolecular interaction in composites AN + diammonium salt of 1,3,5-trihydroxyisocyanuric acid and AN + 4-aminouracil has been investigated with UV and IR spectroscopy. The samples were prepared as emulsions in vaseline oil to avoid the AN interaction with KBr.

It was found that these additives modify considerably the system of hydrogen bonds in alloys with AN. Two compositions with diammonium salt of 1,3,5-trihydroxyisocyanuric acid have been investigated: with 10 and 44.7% of this additive. The first composite represents an X-ray-amorphous state, while the second one does not. IR-spectra shows that in both composites the additive is dispersed in molecular level, e.g. the most intensive adsorption band at 3236 cm^{-1} in the spectrum of initial diammonium salt of 1,3,5-trihydroxyisocyanuric acid is absent in spectra of the both composites (there are bonds at 3400, 3270, 3196, 3116 cm^{-1} for the first composite and one wide bond at 3400 cm^{-1} for the second one). These data is the result of very intensive interaction between modifier molecules and ions of AN. UV-spectrum of the composite AN + 44.7% diammonium salt of 1,3,5-trihydroxyisocyanuric acid (44.7%, with no special treating) is almost equivalent to the spectrum of the individual diammonium salt. However UV-spectra of the composite AN + 10% diammonium salt of 1,3,5-trihydroxyisocyanuric acid (it is an X-ray-amorphous state) two other adsorption bonds (between 240-300 nm) appear. It's possible that their appearance is the result of the emergence of new molecular orbital interaction of $\pi(\text{NO}_3) \rightarrow \pi^*(\text{C}=\text{O})$ type. It requires more detailed exploration.

In IR spectrum of the composite AN with 16.2% 4-aminouracil (X-ray-amorphous state) there are three adsorption bands ($3412, 3250, 3192\text{ cm}^{-1}$ with close intensity), in the area of N-H bonds oscillations. These frequencies values differs from those in individual 4-aminouracil ($3416, 3396, 3176\text{ cm}^{-1}$) and AN (3125 and 3015 cm^{-1}). The fact that the spectrum of the composite is not a simple summation of its components spectra proves that there is any intermolecular interaction between modifiers molecule and ions of AN, that modifies the hydrogen bonds net in alloy. IR spectrum of such an alloy (with no special treating, X-ray-amorphous state is absent) differs from the spectrum of amorphous phase too, but is not an additive sum of components spectra any more. In this spectrum an intensive band of N-H oscillation (3180 cm^{-1}) dominates, on the slope of this band two weak bands appear (3460 and 3344 cm^{-1}). In the UV spectrum of the same composite (X-ray-amorphous state is absent) a rather intensive band appears at 220-230 nm. This band is absent in 4-aminouracil spectrum. It is possible it is a result of new intermolecular orbital interactions. It requires more detailed investigation.

Conclusions

1. Among organic compounds only those having crystallographic structure close to AN crystalline structure are able to influence on phase transitions

- of ammonium nitrate.
2. Due to organic compound could stabilize phase state of AN its molecules has to be acceptors of electrons for creation intermolecular orbital interactions, and/or these molecules have to form easily new hydrogen bonds with ions of AN.
 3. Conditions of additional treatment AN alloys are found, that allow to obtain a new X-ray-amorphous phase stable is the temperature range from -50 till +100°C.
 4. UV and IR spectroscopy shows that X-ray-amorphous state of composites AN + additive is characterized by new intermolecular interactions, different from those in individual components and in virgin composites before treatment.

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References

- [1] Manelis G.B., Golovina N.I., Lempert D.B., Nechiporenko G.N., Dolganova G.P., Nemtsev G.G., Kinetics of the Direct and Reverse IV-III Phase Transition in Ammonium Nitrate Crystal Lattice, *7th Int. Airbag-2004*, Karlsruhe, Germany, **2004**, p. 43/1.
- [2] Lempert D.B., Nechiporenko G.N., Golovina N.I., Shilov G.V., Dolganova G.P., Nemtsev G.G., Ammonium Nitrate Cocrystallites as a Way to Eliminate Phase Transition in Ammonium Nitrate Crystal Lattice, *7th Int. Airbag-2004*, Karlsruhe, Germany, **2004**, p. 44/1.
- [3] Golovina N.I., Nechiporenko G.N., Nemtsev G.G., Dolganova G.P., Roshchupkin V.P., Lempert D.B., Manelis G.B., Phase Stabilization of Ammonium Nitrate, *J. Appl. Chem. (Russ)*, **2007**, *80*(1), p. 25.
- [4] Nechiporenko G.N., Golovina N.I., Manelis G.B., Lempert D., Dolganova G.P., Nemtsev G.G., Phase Stabilization of Ammonium Nitrate, Patent Rus. Fed. 2298540 (**2007**).
- [5] Golovina N.I., Nechiporenko G.N., Zyuzin I.N., Lempert D.B., Nemtsev G.G. *et al.*, Some Aspects of Intermolecular Interactions Between Carboxyl and Imine Groups in Crystals of Hexamerous Heterocycles, *J. Struct. Chem. (Russ)*, in press.
- [6] Licence to Use Agreement: Gaussian, Inc., 340 Quinpiac Street, Building 40, Wallingford, CT 06492.
- [7] Heintz T., Reinhard W., Hermann M., Teipel U., Spherical Ammonium Nitrate

for Gas Generators, *6th Int.Airbag-2002.*, Karlsruhe, Germany, **2002**, pp. 26/1-26/10.

- [8] Hong Bo Wu, Man Nin Chan, Chak K. Chan, Characterization of Polymorphic Transformation of Ammonium nitrate, *Aerosol Science and Technology*, **2007**, *41*, 581-588.