NEW ENERGETIC MATERIALS
OF N-HETEROCYCLIC GROUP

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Potential candidates for highly efficient and, at the same time, insensitive energetic materials have been analysed. The group analysed comprises N-heterocyclic compounds, pyridines, pyrazines, pyrimidines, tetrazines, triazoles, pyrazoles and compounds containing a furazane or furoxane unit. Density, heat of formation, and melting point have been chosen for the comparison parameters.

Introduction

Research activities in the area of individual energetic materials (EM) led to successful syntheses of dozens of new substances in 1980s and 1990s. The best-known examples are 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitate (HNIW), octanitrocubane (ONC), 1,3,3-trinitroazetidine (TNAZ), amonium dinitramide (ADN), hydrazinium nitroform (HNF), dinitroazofuroxane (DNAF). Potential applications of the substances, first of all, are for use as high explosive

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charges and propellants. The aim of the present research was, in particular, to increase the performance, i.e. the content of the energy that can be liberated from the substances with simultaneous maintaining sufficient physical and chemical stabilities. At the same time, it was necessary to take into account another requirement — reduction of sensitivity to external stimuli. However, these two requirements, i.e. (i) the increase in performance on the one hand and (ii) the lowering of sensitivity to external stimuli on the other, are considerably antagonistic. In general, an increase of performance of energetic materials is accompanied by an increase in their sensitivity (be it the sensitivity to impact, friction, spark, or detonation transfer). So far the solutions to this problems have not been able without a certain compromise: the percentage of more sensitive effective components in the final explosive mixture had to be reduced to such a level as to reach an acceptable sensitivity to external stimuli. Progressive trends involve the search for such substances whose characteristic of performance and sensitivity are not so sharply antagonistic: 5-nitro-1,2,4-triazol-3-one (NTO) and 2,2-dinitro-1,1-ethenediamine (FOX-7) can be stated as examples. NTO has been known since 1907 as a component of low-sensitivity effective component of explosive systems, but was investigated as late as 1980s. FOX-7 is a substance that has been know for about 5 years and is an object of intensive investigation at present. The expert literature gives a variety of compounds whose performance characteristics are being examined and rigorously compared with their stabilities to external stimuli [1,2,3].

Selection of Substances

The present work predominantly deals with evaluation of properties of the following groups of compounds:

pyridines, pyrazines, pyrimidines, tetrazines, triazoles, pyrazoles, and compounds including a furazane or furoxane grouping.

The following physical quantities have been chosen for each substance:

1) Density
This is one of the most important quantities affecting the performance of an explosive: e.g. the important characteristics of detonation — the detonation pressure P — is a quadratic function of density (see Eq. (1)) [4].

$$P = 1.558\rho^2\Phi \tag{1}$$

where ρ means density, Φ and is a quantity including the other parameters of the substance.

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2) Heat of formation

The meaning of the quantity of heat of formation of a substance ($H_{f,expl}$) can best be seen from the molar equation for heat of explosion Q_{expl} of an explosive

$$Q_{expl} = nH_{f,H_2O} + mH_{f,CO_2} + H_{f,expl} \qquad (2)$$

where n, m are numbers of mols of water and carbon dioxide formed in the explosion of 1 mol explosive. The heat of explosion represents one of the factors that are directly responsible for the performance of explosive, and Eq. (2) shows the effect of positive value of the heat of formation upon its magnitude.

3) Melting point

This characteristic parameter has its significance in the primary estimate of thermal stability of a substance, because first the transformation of solid phase into liquid is accompanied by a change in density (and hence a change in volume), and next potential chemical reactions of the charge components are easier in the liquid phase.

The evaluated substances inclusive of the available data for the above-chosen characteristics are presented in Table I.

Discussion and Conclusion

Comparison of values of Table I for the pyridine derivatives (substances *1 ÷ 12*) shows that an introduction of nitro, amino, and *N*-oxide groups into the basic skeleton usually increases the density as well as the melting point while the heat of formation is lowered. With the pyrazine derivatives (substances *13 ÷ 17*), this trend is similar, the same being true of the pyrimidine derivatives (substances *18 ÷ 20*). In contrast to this, the tetrazines (substances *21 ÷ 24*) possess considerably high heats of formation but, of course, do not contain a nitro group. The nitropyrazoles (substances *25 ÷ 28*) exhibit considerably high densities, melting points and heats of formation, the same being observed with the nitrotriazoles (substances *30 ÷ 32*). In general, the furazane and furoxane derivatives (substances *33 ÷ 42*) reach high values of density and heat of formation, but the melting points are considerably low. Out of this group, benzofuroxanes appear promising, having favourable explosive properties and being relatively simply accessible by syntheses from the respective azidonitroaromates.

It is highly probable that a number of substances exhibit a positive influence of intermolecular forces, particularly hydrogen bonds, upon the magnitudes of both density and melting point. This can be seen in compounds *9, 10, 14, 15, 25, 26, 31, 40 – 42*, in which the proportions of nitrogen and oxygen are relatively low, but the densities and melting points reach to high values. This influence was
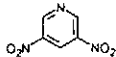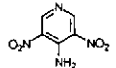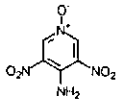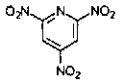
Table I Properties of selected *N*-heterocycles
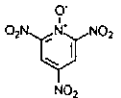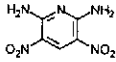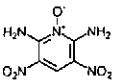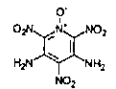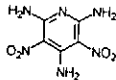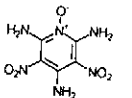
No.	Acronym	Structure formula	Molecular formula	M, g mol^{-1}	Density, g cm^{-3}	ΔH_f, kJ mol^{-1}	M.p., °C
1	3,5DNPy		$C_5H_3N_3O_4$	169	1.65		105
2	4A3,5DNPY		$C_5H_4N_4O_4$	184	1.6	36.11	166
3	2.+1-ox		$C_5H_4N_4O_5$	200	1.83	−190.37	212
4	246TNPY		$C_5H_2N_4O_6$	214	1.84	78.91	162
5	4.+1-ox		$C_5H_2N_4O_7$	230	1.86	98.7	170 (dec.)
6	26A35DNPY		$C_5H_5N_5O_4$	199	1.75	−19.66	
7	6.+1-ox		$C_5H_5N_5O_5$	215	1.878	−132	358
8	35A246TNP-1ox		$C_5H_4N_6O_7$	250	1.9		
9	246A35DNP		$C_5H_6N_6O_4$	214	1.819		353 (dec.)
10	9.+1-ox		$C_5H_6N_6O_5$	230	1.876		308

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Table I – Continued
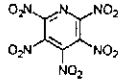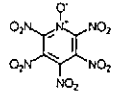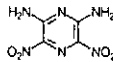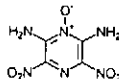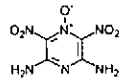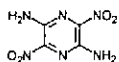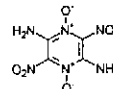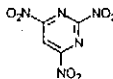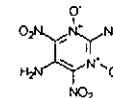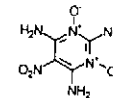
No	Acronym	Structure formula	Molecular formula	M, $g\,mol^{-1}$	Density, $g\,cm^{-3}$	ΔH_f, $kJ\,mol^{-1}$	M.p., °C
11	PeNPY		$C_5N_6O_{10}$	304	1.95		
12	11.+1-ox		$C_5N_6O_{11}$	320	2.07		
13	26A35DNPz		$C_4H_4N_6O_4$	200	1.8	−22.55	
14	13.+1-ox		$C_4H_4N_6O_5$	216	1.91	−37.66	342 (dec.)
15	35A26DNox		$C_4H_4N_6O_5$	216	1.913	−12.97	
16	ANPZ-i		$C_4H_4N_6O_4$	200	1.88		
17	16.+1,4diox		$C_4H_4N_6O_6$	232	/1.92/		
18	246TNPM		$C_4HN_5O_6$	215	1.9		
19	25A46NP2ox		$C_4H_4N_6O_6$	232	1.92		
20	46A25NP2ox		$C_4H_4N_6O_6$	2.32	1.92		

Table I – Continued

No	Acronym	Structure formula	Molecular formula	M, g mol^{-1}	Density, g cm^{-3}	ΔH_f, kJ mol^{-1}	M.p., °C
21	LAX 112		$C_2H_4N_6O_2$	144	1.86	164	266
22	DHT		$C_2H_6N_8$	142	1.61	536	
23	AAT		$C_4H_4N_{12}$	220	1.84	862	273
24	BTT		$C_2H_6N_{14}$	248		883	264
25	DNPP		$C_4H_2N_6O_4$	198	1.865	272	330
26	LLM 119		$C_4H_4N_8O_4$	228	1.845	510	253
27	LLM 121		$C_4N_8O_8$	288		500	
28	LLM 116		$C_2H_3N_5O_4$	161	1.9		178
29	2,4-DNI		$C_3H_2N_4O_4$	158	1.763	20.5	

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Table I – Continued
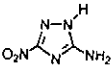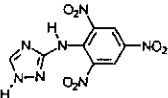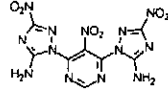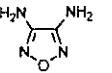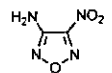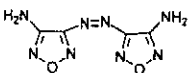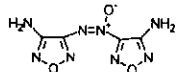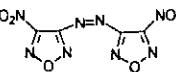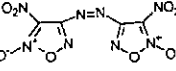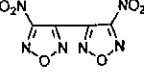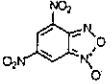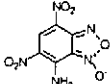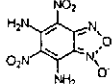
No	Acronym	Structure formula	Molecular formula	M, $g\,mol^{-1}$	Density, $g\,cm^{-3}$	ΔH_f, $kJ\,mol^{-1}$	M.p., °C
30	ANTA		$C_2H_2N_5O_2$	128	1.819	88	238
31	PATO		$C_8H_5N_7O_6$	295	1.94	151.5	
32	DANTNP		$C_8H_5N_{13}O_6$	379	1.865	413	330
33	DAF		$C_2H_4N_4O$	100	1.61	103.7	180
34	ANF		$C_2H_2N_4O_3$	130	1.86	143	125
35	DAAzF		$C_4H_4N_8O_2$	196	1.767	532	325
36	DAAF		$C_4H_4N_8O_3$	212	1.747	444	
37	DNDAF		$C_4N_8O_6$	256	1.75		
38	DNAF		$C_4N_8O_8$	288	2	582	128 (dec.)
39	DNBiF		$C_4N_6O_6$	228	1.92		85

Table I – Continued

No	Acronym	Structure formula	Molecular formula	M, g mol^{-1}	Density, g cm^{-3}	ΔH_f, kJ mol^{-1}	M.p., °C
40	DNBF		$C_6H_2N_4O_6$	226	1.79	192	174
41	ADNBF		$C_6H_3N_5O_6$	241	1.901	153.9	267 (dec.)
42	CL-14		$C_6H_4N_6O_6$	256	1.942	86.3	287 (dec.)

M. p. melting point
ΔH_f enthalpy of formation

The values of physical quantities given in the table were obtained from the ICT thermochemical database (version 3 (2001)) and the literature quoted.

1. 3,5-dinitropyridine
2. 4-amino-3,5-dinitropyridine
3. 4-amino-3,5-dinitropyridine-1-oxide
4. 2,4,6-trinitropyridine
5. 2,4,6-trinitropyridine-1-oxide
6. 2,6-diamino-3,5-dinitropyridine
7. 2,6-diamino-3,5-dinitropyridine-1-oxide
8. 3,5-diamino-2,4,6-trinitropyridine-1-oxide
9. 2,4,6-triamino-3,5-dinitropyridine
10. 2,4,6-triamino-3,5-dinitropyridine-1-oxide
11. pentanitropyridine
12. pentanitropyridine-1-oxide
13. 2,6-diamino-3,5-dinitropyrazine (ANPZ)
14. 2,6-diamino-3,5-dinitropyrazine-1-oxide (LLM-105, ANPZ-O)
15. 3,5-diamino-2,6-dinitropyrazine-1-oxide
16. 2,5-diamino-3,6-dinitropyrazine (ANPZ-i)
17. 2,5-diamino-3,6-dinitropyrazine-1,4-dioxide
18. 2,4,6-trinitropyrimidine
19. 2,5-diamino-4,6-dinitropyrimidine-1,3-dioxide
20. 4,6-diamino-2,5-dinitropyrimidine-1,3-dioxide
21. 3,6-diamino-1,2,4,5-tetrazine-1,4-dioxide (LAX-112, TZX)
22. 3,6-dihydrazino-1,2,4,5-tetrazine (DHT)
23. 3,3'-azobis(6-amino-1,2,4,5-tetrazine) (AAT)
24. 3,6-bis(1H-1,2,3,4-tetrazol-5-ylamino)-1,2,4,5-tetrazine (BTT)
25. 3,6-dinitropyrazolo[4,3-c]pyrazole (DNPP)

26. 1,4-diamino-3,6-dinitropyrazolo[4,3-c]pyrazole (LLM-119)
27. 1,3,4,6-tetranitro-pyrazolo[4,3-c]pyrazole (LLM-121)
28. 4-amino-3,5-dinitropyrazole (LLM-116)
29. 2,4-dinitroimidazole (2,4-DNI)
30. 3-nitro-5-amino-1,2,4-triazole (ANTA)
31. 3-picrylamino-1,2,4-triazole (PATO)
32. 4,6-bis(5-amino-3-nitro-1,2,4-triazolyl)-5-nitropyrimidine (DANTNP)
33. 3,4-diaminofurazane (DAF)
34. 3-amino-4-nitrofurazane (ANF)
35. 4,4'-diamino-3,3'-azofurazane (DAAzF)
36. 4,4'-diamino-3,3'-azoxyfurazane (DAAF)
37. 4,4'-dinitroazofurazane (DNDAF)
38. 4,4'-dinitroazofuroxane (DNAF)
39. 4,4'-dinitro-3,3'-bifurazane (DNBiF)
40. 4,6-dinitrobenzofuroxane (DNBF)
41. 7-amino-4,6-dinitrobenzofuroxane (ADNBF)
42. 5,7-diamino-4,6-dinitrobenzofuroxane (CL-14)

also confirmed by crystallographic measurements in a series of bifuroxanes [5]. In addition, in their case it was found that in the absence of H-bonds the neighbouring molecules in the crystal lattice are mutually perpendicular and, therefore, the density does not reach such high values.

Substances containing no hydrogen in their molecules (i.e. the composition CNO) can reach to high density values, but their melting points — and sometimes also stabilities — are low. This is manifested in compounds *11, 12, 27, 38,* and *39.* In addition, these types of compounds are considerably sensitive if they contain enough energy.

It is extremely difficult to find substances fulfilling the requirements of high values of density, melting point and the energy content that can be liberated on the one hand, and low sensitivity on the other. As model structures (which, however, do not reach the parameters of the present effective explosives) for guiding future research activities it is possible to take into account substances *7, 10, 14, 21, 25, 32, 41* and *42,* which (with considerable probability) contain hydrogen bonds, predominantly have positive heats of formation and higher melting points. It is obvious that most of these structures contain all the functional groups followed (nitro, amino, *N*-oxide) or at least two of them.

References

[1] Doherty R.M., Simpson R.L. : *A Comparative Evaluation of Several Insensitive Explosives,* 28th Int. Annual Conf. ICT Proc., Karlsruhe, Germany, 1997.

[2] Agrawal J.P.: Prog. Energ. Combust. Sci. **24,** 1 (1998).

Jalový Z., Vávra P./Sci. Pap. Univ. Pardubice Ser. A 9 (2003) 187–196

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[3] Fried L.E., Manaa M.R., Pagoria P.F., Simpson R.L.: Annu. Rev. Mater. Res. **31**, 291 (2001).

[4] Kamlet M.J., Jacobs, S.J.: J. Chem. Phys. **48**, 23 (1968).

[5] Bearl R.W., Incarvito C.D., Rhatigan B.J., Rheingold A.L., Brill T.B.: Propel. Explos. Pyrotech. **25**, 277 (2000).