

Energetic Materials |Hot Paper|

Furazans with Azo Linkages: Stable CHNO Energetic Materials with High Densities, Highly Energetic Performance, and Low Impact and Friction Sensitivities

Yanyang Qu,* Qun Zeng, Jun Wang, Qing Ma, Hongzhen Li, Haibo Li,* and Guangcheng Yang^[a]

Abstract: Various highly energetic azofurazan derivatives were synthesized by simple and efficient chemical routes. These nitrogen-rich materials were fully characterized by FTIR spectroscopy, elemental analysis, multinuclear NMR spectroscopy, and high-resolution mass spectrometry. Four of them were further confirmed structurally by single-crystal X-ray diffraction. These compounds exhibit high densities, ranging from 1.62 g cm⁻³ up to a remarkably high 2.12 g cm⁻³ for nitramine-substituted azofurazan DDAzF (**2**), which is the highest yet reported for an azofurazan-based CHNO energetic compound and is a consequence of the formation of strong intermolecular hydrogen-bonding networks. From the heats of formation, calculated with Gaussi-

an 09, and the experimentally determined densities, the energetic performances (detonation pressure and velocities) of the materials were ascertained with EXPLO5 v6.02. The results suggest that azofurazan derivatives exhibit excellent detonation properties (detonation pressures of 21.8– 46.1 GPa and detonation velocities of $6602-10114 \text{ m s}^{-1}$) and relatively low impact and friction sensitivities (6.0–80 J and 80–360 N, respectively). In particular, they have low electrostatic spark sensitivities (0.13–1.05 J). These properties, together with their high nitrogen contents, make them potential candidates as mechanically insensitive energetic materials with high-explosive performance.

Introduction

Chem. Eur. J. 2016, 22, 1-7

Traditional high energy density materials (HEDMs) used for civilian and military applications developed over the last two centuries and still widely used include 2,4,6-trinitrotolune (TNT), cyclo-1,3,5-trimethylene-2,4,6-trinitamine (RDX), 1,3,5,7tetranitrotetraazacyclooctane (HMX), and pentaerythritol tetranitrate (PETN). However, there is ongoing research and interest in the synthesis of HEDMs that are environmentally benign and combine high performance with low sensitivity, a task which poses particular challenges to the synthetic organic chemist. The desirable characteristics of new HEDMs include high density, positive heats of formation (HOF), a positive oxygen balance (OB), high detonation velocity and pressure, high thermal stability, simple synthesis, low sensitivity toward external forces such as impact and friction, and environmental friendliness.^[1] The traditional strategy for designing new HEDMs involves incorporating both fuel and oxidizer properties into a single molecule. The oxidizer part provides the

[a] Dr. Y. Qu, Dr. Q. Zeng, Prof. J. Wang, Dr. Q. Ma, Prof. H. Li, Prof. H. Li, Prof. G. Yang Institute of Chemical Materials, CAEP
P. O. Box 919-311 Mianyang Sichun, 621900 (P. R. China)
E-mail: quyy131226@caep.cn lihb99@caep.cn
Supporting information and ORCID(s) from the author(s) for this article is

available on the WWW under http://dx.doi.org/10.1002/chem.201601901.

oxygen needed for oxidation of the fuel portion to enhance combustion and therefore supports the release of large amounts of energy. Recently, the development of nitrogen-rich energetic materials has been recognized as one of the most effective strategies for the design and synthesis of HEDMs.^[2] In addition, the importance of ring strain and the presence of N-N, C-N, and N-O bonds for the effectiveness of HEDMs has been recognized. However, excessive introduction of functional groups into a limited backbone leads to increased sensitivity to mechanical stimulation. Therefore, seeking a balance between high performance and stability is the main challenge in the design of advanced HEDMs. The field of chemistry related to HEDMs must expand the boundaries of the energy capacity of the compounds, which requires new classes of functionalized compounds,^[3] advanced theoretical prediction techniques,^[4] and new synthetic strategies.^[5]

Unlike the traditionally designed energetic materials, in which the fuel and oxidizing characteristics are the sole factors determining their performance, nitrogen-rich compounds have some unique properties such as high heats of formation, significant gas release in the form of environmentally benign nitrogen, and commonly include moieties such as five-membered azole and six-membered azine rings. Improvements in the OB have been achieved with the development of the oxadiazoles. Of these, 1,2,5-oxadiazole (furazan I, Figure 1) is an appropriate choice as the core structure of new HEDMs due to its high heat of formation (185 kJ mol⁻¹) and release of envi-

These are not the final page numbers! 77

Wiley Online Library





Figure 1. Calculated gas-phase heats of formation for oxadiazole and azole compounds. $^{\rm (6)}$

ronmentally benign gaseous nitrogen as one of the main decomposition products. In addition, several azo-based HEDMs have been investigated in recent years,^[7] and the presence of an azo (-N=N-) moiety generally imparts a high endothermic heat of formation to a compound. Thus, the decomposition energy is largely derived from this source rather than from the fuel-oxidizer reaction. We expected that linking furazans substituted in the 3,3'-positions with energetic functional groups via azo linkages could be a promising new strategy for tailoring new energetic compounds that display physical and energetic properties such as higher detonation parameters and lower sensitivity toward impact and friction. To the best of our knowledge, herein we report the first synthesis of a series of azofurazan-based energetic materials with groups that enhance the energetic characteristics of the molecule [e.g., NH_2 , CN, triazole, tetrazolium, and 1,2,4-oxadiazole (II)].

Results and Discussion

Scheme 1 shows an overview of the synthetic steps to form the various azofurazans. The furazan moiety has been found to be a vital constituent of HEDMs, and its presence greatly contributes to the overall energetic performance. Modeling studies show that when a nitro group is replaced by a furazan group in energetic compounds, the density, heat of formation, and detonation velocity are increased by about $0.06-0.08 \,\mathrm{g\,cm^{-3}}$, 200 kJ mol⁻¹, and 300 m s⁻¹, respectively.^[8] Energetic materials based on triazoles and tetrazoles show the desirable properties of high N content and thermal stability (due to aromaticity). These properties, together with the high heats of formation of oxadiazole heterocycles suggested that linking these moieties to the furazan backbone could be an appropriate strategy to improve the energetic performance of novel HEDMs. Malononitrile was chosen as a useful precursor for the preparation of the azofurazan energetic materials containing the core furazan



Scheme 1. Structures and synthetic routes of azofurazan compounds. a) NaNO₂, NH₂OH·HCl, 0 °C; 100 °C, 72%; b) PbO₂, AcOH, 0 °C, 55%; c) Semicarbazide, TFA, 120 °C, 46%; d) BrCN, KHCO₃, 30 °C, 97%; e) Ac₂O, 120 °C, 89%; f) Trifluoroacetic anhydride, 120 °C, 66%; g) KMnO₄, conc. HCl and CH₃CN, 20 °C, 62%; h) AcOH, Ac₂O and HNO₃, 0 °C, 78%; i) KMnO₄, 20% HCl, 20 °C, 68–90%; j) 1,3-diaminourea (DAU), H₂O, 100 °C, 67%; k) (EtO)₃CH, BF₃·Et₂O, 120 °C, 86%; l) N₂H₄, CH₃CN, 30 °C, 96%; m) NaNO₂, 2 % HCl, 30 °C, 92%; n) Ac₂O, 120 °C, 60%.

Chem. Eur. J. **2016**, 22, 1–7

www.chemeurj.org

2

© 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



scaffold. 4-Amino-N-hydroxyfurazan-3-carboximide (AFA), 4amino-1,2,5-oxadiazole-3-carbonitrile (13), and 4-(1H-tetrazol-5yl)-furazan-3-amine (17) were prepared on the basis of literature methods.^[9] The formation of azo-bridged compounds by oxidative coupling between the amino groups of furazan intermediates such as 13 is well known.^[10] For example, treatment of intermediates 13 and 17 with one equivalent of alkaline potassium permanganate (KMnO₄) in 20% HCl at room temperature yielded 3,3'-dicyano-4,4'-azofurazan DCAzF (10) and tetrazole-substituted azofurazan DTAzF (6) in 90 and 70% yields, respectively. Although 10 and 6 have been previously reported, their full physical and detonation properties were not studied.[11] In addition, the oxime precursor AFA can be treated with a wide variety of reactants to form a whole new set of previously unreported azofurazan compounds 1-4, 7, and 8 via intermediates 19-23 (Scheme 1). Thus cyanogen bromide, acetic anhydride, trifluoroacetic anhydride, triethyl orthoformate, and carbohydrazide give intermediate compounds 19, 20, 21, 22, and 23, respectively (Scheme 1). Further treatment of 13 with semicarbazide leads to the formation of 4-(5-amino-1,3,4-oxadiazol-2-yl)-1,2,5-oxadiazol-3-amine (14).

The reaction of **10** with semicarbazide produced azofurazan DIAzF (**11**) as the main product in 72% yield. Oxidation of **18** with one equivalent of KMnO₄ in 20% HCl at room temperature afforded DFAzF (**1**) in 76% yield as a yellow solid. In addition, DNAzF (**12**) was also prepared from DHAzF (**8**) in two steps via *N*-amino imine intermediate **24** in 56% yield. An analogous method gave the corresponding azo-bridged furazans **3–11** in moderate to good yields (Scheme 1). Nitration of **1** with a mixture of nitric acid and acetic anhydride at 10°C gave DDAzF (**2**) in 89% yield (Scheme 1).

Suitable crystals of azofurazans 3, 8, 9, and 21 were grown by slow evaporation of the solvent of solutions in methanol/ acetone, acetonitrile, dimethyl sulfoxide, and ethyl acetate, respectively, at room temperature. Their structures are shown in Figure 2. Data collection and refinement parameters are given in Table S2 (see Supporting Information). The structures of the newly prepared energetic compounds are supported by FTIR spectroscopy, ¹H and ¹³C NMR spectroscopy, high-resolution mass spectrometry, and elemental analysis (see the Supporting Information). ¹⁵N NMR spectra were recorded only for DF₃AzF (4), DHAzF (8), and DXAzF (9) in [D₆]DMSO solutions. Chemical shifts are given in Figure 3 with respect to nitromethane as external standard. Azofurazan 8 shows five signals because of its symmetrical structure, and the signal for the azo nitrogen signals occurs at 60 ppm. The furazan nitrogen signals are observed downfield relative to the signals for N4 and N5 of the isoxazole ring. However, the signals from the furazan nitrogen atoms in DF₃AzF (4) are observed between about -10 and 10 ppm, which may be due to the impact of the CF₃ groups.

The heat of formation $\Delta H_{f,solid}$ is an important parameter that must be considered when designing energetic materials. All enthalpy calculations were performed with the Gaussian 09 software package. By using the isodesmic-reaction approach (see Supporting Information), the heats of formation of the species can be easily extracted. With the exception of the negative heat of formation of DF₃AzF (4), all of the other synthe-



Figure 2. Single-crystal X-ray structures of a) DMAzF (3), b) DHAzF (8), c) DXAzF (9), and d) 21.

sized compounds exhibit positive heats of formation that are considerably higher than those of RDX and HMX (Table 1). The heats of formation of the azofurazans range from 684.1 kJ mol⁻¹ for DIAzF (11) to 1224.3 kJ mol⁻¹ for DTAzF (6), and most of them have values in the range 700–800 kJ mol⁻¹.

Density is an important property contributing to the detonation performance of energetic materials. The densities of the new azofurazans were measured with a gas pycnometer at ambient temperature and were found to be between 1.68 g cm⁻³ for DOAzF (**7**) and 2.12 g cm⁻³ for DDAzF (**2**). (We attempted



Figure 3. ¹⁵N NMR spectra of DXAzF (9), DHAzF (8), and DF₃AzF (4).

to crystallize compound **2** using different solvents, but failed to obtain a single-crystal structure.) The densities of most materials are comparable to those of currently used explosives RDX (1.82 g cm⁻³) and HMX (1.91 g cm⁻³). The remarkably high density of DDAzF (**2**) arises from the presence of the nitramino groups, and it is among the highest for CHNO explosives, such as 5,5'-bis(trinitromethyl)-3,3'-bis(1,2,4-oxadiazole), having densities higher than 2.00 g cm⁻³.

The impact sensitivities (IS) and friction sensitivities (FS) of the compounds were determined with a standard BAM Fall Hammer and a BAM Friction Apparatus, respectively. The electrical spark sensitivity tests (ESD, electrostatic discharge), which provide a measure of the electrostatic hazards associated with the handling of explosive materials, used approximately 20 mg samples; the capacitance was 30000 pF with an electrode gap of 0.5 mm. For all of the compounds, the impact sensitivities range from those of the relatively insensitive azofurazans DCAzF (10), DHAzF (8), and both DMnAzF (5) and DNAzF (12), with IS values of 7.5, 12.5, and 40 J, respectively (Table 1), to the very insensitive compounds DFAzF (1), DMAzF (3), DF₃AzF (4), DIAzF (11), and DOAzF (7) with IS \geq 80 J. DDAzF (2) is overall the most mechanically sensitive compound, with an impact sensitivity of 6.0 J, friction sensitivity of 40 N, and electrical spark sensitivity of 0.51 J. Tetrazole-substituted azofurazan DTAzF (6) has the highest impact sensitivity (IS = 4.7 J), is also quite friction sensitive (FS = 96 N), and has an electrical spark sensitivity of 0.13 J. Overall, most of the compounds exhibit improved sensitivity parameters compared to the common explosive RDX (IS = 7.4 J, FS = 120 N, ESD = 0.2 J).

The phase transitions and thermal stabilities of all compounds were determined by differential scanning calorimetry (DSC) at a scan rate of 10°C min⁻¹ (Table 1; see Supporting Information for further details and scans). DHAzF (8) and DMAzF (3) are the only compounds that melt prior to decomposition, at 142 and 131 °C, respectively. Both DFAzF (1) and DTAzF (6) have sharp exothermic peaks, which indicate rapid decomposition. Compound DFAzF (1), with an onset decomposition temperature of 246.85 °C, exhibits an exothermic peak at 267.29 °C, which is 10°C higher than that of DTAzF (6). However, DNAzF (12) has a wider exothermicity temperature range with an onset decomposition temperature of 179.29°C and an exothermic peak maximum at 308.59 °C. Tetrazole- and cyano-substituted azofurazans DTAzF (6) and DF₃AzF (4) decomposed at 258 °C and 240 °C, respectively. Surprisingly, nitramino compound DDAzF (2), which was shown to be a powerful energetic material with high detonation velocity, detonation pressure, and heat of formation, decomposes at 317 °C. With the exception of the triazole-substituted analogues DMnAzF (5) and DNAzF (12) (T_{dsc} = 350 and 309 °C, respectively), other deriva-

Table 1. Physical properties and detonation parameters.									
	$T_{dsc} [^{o}C]^{[a]}$	$ ho~[{ m g/cm^3}]^{ m [b]}$	$\triangle_{\rm f} H_{\rm m} [\rm kJ/mol]^{[c]}$	OB [%] ^[d]	<i>v</i> _{Det} [m/s] ^[e]	P [GPa] ^[f]	IS [J] ^[g]	FS [N] ^[h]	ESD [J] ^[i]
DFAzF	267	1.85	711.2	-67.45	8445	28.3	\geq 80	\geq 360	0.68
DHAzF	259	1.68/1.79 ^[j]	832.9	-68.85	7685	22.7	12.5	\geq 360	0.51
DMAzF	271	1.75/1.65 ^[j]	696.5	-92.12	7781	22.6	\geq 80	80	0.78
DF₃AzF	240	1.94	-488.6	-58.44	6602	24.3	\geq 80	\geq 360	0.87
DMnAzF	350	1.81	864.3	-97.59	8482	26.4	40	80	0.67
DCAzF	234	1.62 ^[j]	933.9	-74.07	7640	21.8	7.5	\geq 360	0.39
DTAzF	258	1.69/1.75 ^[j]	1224.3	-58.27	8477	28.0	4.7	96	0.13
DIAzF	233	1.83	684.1	-67.45	8323	27.3	\geq 80	\geq 360	1.05
DXAzF	-	1.57 ^[j]	-	-63.45	-	-	\geq 80	120	0.85
DOAzF	241	1.68	769.9	-66.28	7774	22.4	\geq 80	252	0.73
DNAzF	309	1.79	920.8	-82.40	8458	26.2	40	\geq 360	0.65
DDAzF	317	2.12	1038.0	-92.10	10114	46.1	6.0	80	0.51
RDX ^[j]	206	1.82	92.6	-21.6	8977	35.1	7.4	120	0.20
HMX ^(j)	282	1.94	116.1	-21.6	9221	39.2	7.0	120	0.10

[a] Decomposition temperature under nitrogen gas (DSC, 10 °C min⁻¹). [b] Density measured with a gas pycnometer (25 °C). [c] Heat of formation. [d] Oxygen balance (OB) is the index of the deficiency or excess of oxygen in a compound required to convert all carbon to carbon dioxide and all hydrogen into water; for a compound with the molecular formula of $C_aH_bN_cO_{dr}$ OB/% = 1600[(d-2a-b/2)/M]. [e] Detonation velocity (calculated with EXPLO5 v6.02). [f] Detonation pressure (calculated with EXPLO5 v6.02). [g] Impact sensitivity measured with a 5.0 kg hammer. [h] Friction sensitivity. [j] Electrical spark sensitivity. [j] Crystal density. [j] From ref. [7a].

www.chemeurj.org

@ 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

tives are less thermally stable with decomposition temperatures below 300 °C (T_{dsc} =234 °C-271 °C).

The experimental densities of these compounds range from 1.22 g cm⁻³ to 2.12 g cm⁻³ and are comparable to those of currently used energetic materials such as RDX (1.82 g cm⁻³) and (HMX, 1.91 g cm⁻³). The remarkably high density of compound **2** (2.12 g cm⁻³ at 25 °C, measured with a gas pycnometer) is noteworthy, and is the highest value yet reported for an azofurazan-based CHNO energetic material. Other reported examples include 4,4'-bis(nitramino)azofurazan (150 K, 1.957 g cm⁻³) and 4,4'-bis(nitramino)azoxyfurazan (173 K, 2.020 g cm⁻³).^[12] The higher density of **2** may be attributed to the nitramino group being involved in multiple intermolecular hydrogenbonding interactions and the conjugate planar structure.

In addition to the heat of formation and the impact and friction sensitivities, the electrical spark sensitivities and the detonation properties also play a major role in the design and development of new energetic materials. The ESDs from this work are listed in Table 1 and are compared with those of RDX and HMX. Most of them are greater than 0.2 J and thus much higher than those of RDX and HMX, except for DTAzF (6). These properties indicate that the azo-linked furazan structure plays a more important role in increasing the stability and decreasing the sensitivity of the molecule than the fuel and oxidizing systems. With heats of formation and experimental densities in hand, the detonation pressures P and velocities v_{Det} were calculated by using EXPLO5 v6.02 (Table 1). The calculated detonation pressures and velocities of the azofurazan derivatives lie between 21.8 GPa for DCAzF (10) and 46.1 GPa for DDAzF (2), and between 6602 ms⁻¹ for DF₃AzF (4) and 10114 ms⁻¹ for nitramine (2). In contrast, RDX and HMX have detonation pressures of 35.2 and 39.6 GPa and detonation velocities of 8748 and 9059 ms⁻¹, respectively. The significantly improved detonation pressures and velocities of azofurazan 2, coupled with the rather high thermal stabilities of the energetic materials, especially of the triazole-substituted derivatives 5 and 12, suggest that these newly developed nitrogen- and oxygen-rich azofurazan materials may be attractive candidates for energetic applications.

Conclusion

A series of novel azofurazan derivatives were prepared starting from the parent compound 4-amino-*N'*-hydroxy-furazan-3-carboximide. Their energetic properties were obtained on the basis of experimentally determined densities and enthalpies of formation determined with Gaussian 09. These compounds exhibit good thermal stabilities and, with the exception of **4**, large positive heats of formation, considerably in excess of those of the common energetic materials RDX and HMX. The experimentally derived densities are high and lie between 1.62 g cm^{-3} for cyano-substituted **10** and 2.12 g cm^{-3} for nitramine **2**. The remarkably high density of **2** is the highest yet reported for an azofurazan-based CHNO energetic compound and is a consequence of the formation of strong intermolecular hydrogen-bonding networks between the amino hydrogen and the nitro oxygen atoms. The new compounds exhibit excellent detonation properties, with calculated detonation pressures of P=21.8-46.1 GPa and detonation velocities of $v_{Det}=$ 6602-10114 ms⁻¹. These azofurazans have acceptable impact and friction sensitivities in the ranges of 4.7-80 J and 80-360 N, respectively. The electrostatic spark sensitivities are also improved over those of RDX and HMX, and range from 0.13 to 1.05 J. In conclusion, the acceptable impact and friction sensitivities of these novel azofurazan derivatives, coupled with their high thermal stability, make them potential candidates for future applications as high-performance CHNO energetic materials.

Experimental Section

Safety precautions

Although none of the compounds described has exploded or detonated, manipulations must be done with appropriate standard safety precautions in a hood behind a safety shield with eye protection and leather gloves. Mechanical treatments of these energetic materials involving scratching or scraping must be avoided. All of these azofurazans were very stable on prolonged storage at room temperature.

General methods

Decomposition temperatures were recorded with a differential scanning calorimeter (TA Instruments Q10) at a scan rate of 10° Cmin⁻¹. The ¹H and ¹³C NMR spectra were collected with a Bruker AVANCE 300 NMR spectrometer operating at 300.13 and 75.48 MHz, respectively. A Bruker AVANCE 500 NMR spectrometer operating at 50.69 MHz was used to collect ¹⁵N spectra. [D₆]DMSO was employed as the solvent and locking solvent. Chemical shifts are given relative to Me₄Si for ¹H and ¹³C spectra and MeNO₂ for ¹⁵N spectra. Elemental analyses (C, H, N) was performed on a CE-440 Elemental Analyzer. Impact and friction sensitivity measurements were done with a standard BAM Fall Hammer and a BAM Friction Apparatus. The FTIR spectra of the solid samples were recorded by using KBr pellets with a Bio-Rad Model 3000 FTS spectrometer. Densities were determined at room temperature by employing a Micromertics AccuPyc 1340 gas pycnometer.

Theoretical study

All calculations were performed with Gaussian 09. Geometric optimization of the structures was carried out by using the DFT/M06-2X functional with the 6-311⁺G(d) basis set. The optimized structures were conformed to be true local energy minima on the potential-energy surface by frequency analyses at the same level. According to the isodesmic-reaction approach, the gas-phase enthalpies of formation were computed. The enthalpies of reaction were obtained by combining the M06-2X/6-311 + G(d) energy difference for the reactions, the scaled zero-point energies, and other thermal factors. Thus, the gas-phase enthalpy of the species under study can be extracted.

Solid-state heats of formation of the resulting compounds can be determined by subtracting the heats of sublimation from the gasphase heats of formation [Eq. (1)]:

$$\Delta H_{\rm f,solid} = \Delta H_{\rm f,gas} - \Delta H_{\rm sub} \tag{1}$$

Chem. Eur. J. 2016, 22, 1-7 ww

www.chemeurj.org

© 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

These are not the final page numbers! **77**



Politzer and co-workers found that the enthalpy of sublimation of energetic compounds correlates well with the molecular surface area and electrostatic interaction index $v\sigma_{tot}^2$ according to Equation (2):^[13]

$$\Delta H_{\rm sub} = aA2 + b(\nu \sigma_{\rm tot}^2)0.5 + c \tag{2}$$

where *A* is the surface area of the 0.001 bohr⁻³ isosurface for the electronic density of the molecule, *v* the degree of balance between the positive and negative potentials on the isosurface, and σ_{tot}^2 is a measure of the variability of the electrostatic potential on the molecular surface. The coefficients *a*, *b*, and *c* were determined to be $a=2.670\times10^{-4}$ kcalmol⁻¹ A⁻⁴, b=1.650 kcalmol⁻¹, and c=2.966 kcalmol⁻¹ from a calculation of the values of ΔH_{sub} by Byrd and co-workers.^[14a] The descriptors *A*, *v*, and σ_{tot}^2 were obtained according to the computational procedures described by Bulat and co-workers.^[14b]

Therefore, the expression for the solid-state enthalpy of formation becomes Equation (3):

$$\Delta H_{\rm f,solid} = \Delta H_{\rm f,gas} - aA2 + b(v\sigma_{\rm tot}^2)0.5 + c \tag{3}$$

Acknowledgements

The authors gratefully acknowledge the support of the National Natural Science Foundation of China (No. 11402240) and the CAEP Foundation (No. 2014B0302038). We are also grateful for the support of the comprehensive training platform in the specialized laboratory, College of Chemistry, Sichuan University. We acknowledge the considerable assistance of Jinpeng Shen, Yuntao Yang, Shaojun Yu, and Yinshuang Sun for carrying out the IS, FS, and thermal performance tests. We are also indebted to Dr. Jie Sun for considerable assistance with the crystal structure determinations.

Keywords: azo compounds · density functional calculations · energetic materials · heterocycles · synthetic methods

- a) M. B. Talawar, R. Sivabalan, T. Mukundan, H. Muthurajan, A. K. Sikder, B. R. Gandhe, A. S. Rao, *J. Hazard. Mater.* **2009**, *161*, 589–607; b) H. W. Qiu, V. Stepanov, A. R. DiStasio, T. M. Chou, W. Y. Lee, *J. Hazard. Mater.* **2011**, *185*, 489–493; c) Y. Bayat, M. Eghdamtalab, V. Zeynali, *J. Energ. Mater.* **2010**, *28*, 273–284; d) Q. Zhang, J. M. Shreeve, *Chem. Rev.* **2014**, *114*, 10527–10574; e) D. Fischer, T. M. Klapötke, J. Tierstorfer, *Angew. Chem. Int. Ed.* **2014**, *53*, 8172–8175; *Angew. Chem.* **2014**, *126*, 8311– 8314; f) A. A. Dippold, T. M. Klapötke, *J. Am. Chem. Soc.* **2013**, *135*, 9931–9938.
- [2] a) J. P. Agrawal, Prog. Energy Combust. Sci. 1998, 24, 1-30; b) D. E. Chavez, M. A. Hiskey, R. D. Gilardi, Angew. Chem. Int. Ed. 2000, 39, 1791 1793; Angew. Chem. 2000, 112, 1861–1863; c) M. H. V. Huynh, M. A. Hiskey, D. E. Chavez, D. L. Naud, R. D. Gilardi, J. Am. Chem. Soc. 2005,

127, 12537–12543; d) M. Smiglak, A. Metlen, R. D. Rogers, Acc. Chem. Res. 2007, 40, 1182–1192; e) R. P. Singh, R. D. Verma, D. T. Meshri, J. M. Shreeve, Angew. Chem. Int. Ed. 2006, 45, 3584–3601; Angew. Chem. 2006, 118, 3664–3682; f) C. B. Jones, R. Haiges, T. Schroer, K. O. Christe, Angew. Chem. Int. Ed. 2006, 45, 4981–4984; Angew. Chem. 2006, 118, 5103–5106; g) R. Wang, Y. Guo, Z. Zeng, B. Twamley, J. M. Shreeve, Chem. Eur. J. 2009, 15, 2625–2634.

- [3] For some examples see: a) P. Yin, D. A. Parrish, J. M. Shreeve, J. Am. Chem. Soc. 2015, 137, 4778-4786; b) H. X. Gao, J. M. Shreeve, Angew. Chem. Int. Ed. 2015, 54, 6335-6338; Angew. Chem. 2015, 127, 6433-6436; c) M. A. Kettner, K. Karaghiosoff, T. M. Klapötke, M. Sućeska, S. Wunder, Chem. Eur. J. 2014, 20, 7622-7631.
- [4] a) K. Baum, N. V. Nguyen, R. Gilardi, J. L. Flippen-Anderson, C. George, J. Org. Chem. 1992, 57, 3026–3030; b) K. Baum, S. S. Bigelow, N. V. Nguyen, T. A. Archibald, R. Gilardi, J. L. Flippen-Anderson, C. George, J. Org. Chem. 1992, 57, 235–241.
- [5] Z. X. Chen, H. M. Xiao, Propellants Explos. Pyrotech. 2014, 39, 487-495.
- [6] a) H. Wei, J. H. Zhang, C. L. He, J. M. Shreeve, *Chem. Eur. J.* 2015, *21*, 8607–8612; b) J. H. Zhang, J. M. Shreeve, *J. Am. Chem. Soc.* 2014, *136*, 4437–4445.
- [7] For some examples see: a) T. T. Vo, J. H. Zhang, D. A. Parrish, B. Twamley, J. M. Shreeve, J. Am. Chem. Soc. 2013, 135, 11787-11790; b) V. Thottempudi, H. X. Gao, J. M. Shreeve, J. Am. Chem. Soc. 2011, 133, 6464-6471; c) Y. C. Li, C. Qi, S. H. Li, H. J. Zhang, C. H. Sun, Y. Z. Yu, S. P. Pang, J. Am. Chem. Soc. 2010, 132, 12172-12173; d) T. M. Klapotke, D. G. Piercey, Inorg. Chem. 2011, 50, 2732-2734; e) P. Yin, D. A. Parrish, J. M. Shreeve, Chem. Eur. J. 2014, 20, 6707-6712; f) L. H. Zhen, L. J. Shan, H. Ming, Z. X. Qing, Chin. J. Org. Chem. 2009, 29, 798-801; g) L. Qing, H. J. Xuan, G. Y. Yuan, C. Y. Li, Chin. J. Energ. Mater. 2008, 16, 53-55; h) L. H. Zhen, H. Ming, H. Y. Gang, D. H. Shan, L. J. Shan, Chin. J. Energ. Mater. 2005, 13, 192-195.
- [8] a) A. B. Sheremeteev, T. S. Pivina, in the proceedings of the 27th International Annual Conference of ICT, Karlsruhe, Germany, 1996, pp. 1–13;
 b) A. B. Sheremeteev, V. O. Kulagina, in the proceedings of the 22th International Pyrotechnics Seminar, Colorado, USA, 1996, pp. 377–388.
- [9] a) V. G. Andrianov, A. V. Eremeev, *Khimiya* **1994**, 693–696; b) J. H. Come, J. Green, C. Marhefka, S. L. Harbeson, L. Pham, *PCT Int. Appl.* **2005**, WO2005019190; c) O. M. Suleimenov, T. K. Ha, *Chem. Phys. Lett.* **1998**, 290, 451–460; d) H. Martinez, Z. Zheng, W. R. Dolbier, Jr., *J. Fluorine Chem.* **2012**, *143*, 112–122; e) L. Hui, Y. Q. Qian, W. B. Zhou, G. Z. Xue, L. Yin, *Chin. J. Energ. Mater.* **2013**, *21*, 821–824.
- [10] a) Q. Zhang, J. M. Shreeve, Angew. Chem. Int. Ed. 2013, 52, 8792–8794; Angew. Chem. 2013, 125, 8954–8956; b) X. Xiao, G. Z. Xue, L. Qing, X. Cheng, W. Wei, S. H. Peng, B. F. Qiang, Chin. J. Energ. Mater. 2013, 21, 173–179; c) Y. X. Tang, H. W. Yang, B. Wu, X. H. Jun, C. X. Lu, G. B. Cheng, Angew. Chem. Int. Ed. 2013, 52, 4875–4877; Angew. Chem. 2013, 125, 4975–4977.
- [11] a) P. W. Leonard, D. E. Chavez, P. F. Pagoria, D. L. Parrish, *Propellants Explos. Pyrotech.* 2011, *36*, 233–239; b) F. Y. Jie, W. B. Zhou, Z. Y. Shui, J. S. Yuan, H. Huan, *Chin. J. Energ. Mater.* 2009, *17*, 385–388.
- [12] J. H. Zhang, J. M. Shreeve, J. Phys. Chem. C 2015, 119, 12887-12895.
- [13] a) P. Politzer, Y. Ma, P. Lane, M. C. Concha, Int. J. Quantum Chem. 2005, 105, 341–347; b) P. Politzer, J. S. Murray, M. E. Grice, M. Desalvo, E. Miller, Mol. Phys. 1997, 91, 923–928.
- [14] a) E. F. C. Byrd, B. M. Rice, *J. Phys. Chem. A* 2006, *110*, 1005–1013; b) F. A. Bulat, A. Toro-Labbé, T. Brinck, J. S. Murray, P. Politzer, *J. Mol. Model.* 2010, *16*, 1679–1691.

Received: April 22, 2016 Published online on ■■ ■, 0000



FULL PAPER

Mechanically insensitive energetic materials: Various azofurazans (see figure; Y = N or C) were prepared from the parent compound 4-amino-*N'*-hydroxyfurazan-3-carboximiide and their energetic properties were determined. These compounds exhibit high densities, excellent detonation properties, and relatively low impact and friction sensitivities. These properties, together with their high nitrogen contents, make them potential candidates as mechanically insensitive high explosives.



Energetic Materials

Y. Qu,* Q. Zeng, J. Wang, Q. Ma, H. Li, H. Li,* G. Yang



Furazans with Azo Linkages: Stable CHNO Energetic Materials with High Densities, Highly Energetic Performance, and Low Impact and Friction Sensitivities