cis-1,3,4,6-Tetranitrooctahydroimidazo-[4,5-d]imidazole (BCHMX), its properties and initiation reactivity

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ABSTRACT

Using the ^{15}N NMR chemical shifts of nitrogen atoms in nitramino groups of cis-1,3,4,6-tetranitrooctahydroimidazo-[4,5-d]imidazole (bicyclo-HMX or BCHMX) and additional 10 nitramines, we have assessed its reactivity in detonation, under the influence of impact, and by action of electric spark. It is stated that the thermal stability of BCHMX is higher than that of 1,3,5-trinitro-1,3,5-triazinane (RDX). The longest N—N bond in the BCHMX molecule (1.412(4) Å) is the cause for its higher impact reactivity, which is at the level of that of penterythritol tetranitrate (PETN). In the experimentally determined detonation velocity, BCMX can be slightly better performing than RDX. From the standpoint of friction sensitivity, BCHMX is similar to 1,3,5,7-tetranitro-1,3,5,7-tetrazocane (HMX). Attention was also focused on the solubility-temperature dependence of BCHMX in acetone, acetonitrile, ethyl acetate, dimethyl sulfoxide, tetrahydrofurane, and nitromethane. X-ray crystallographic study of BCHMX ($C_4H_6N_8O_8$, $M_r = 294.17$), has been carried out at the temperature of 150 K with the following results: $a = 8.5430(8)$, $b = 6.9480(6)$, $c = 8.7780(8)$ Å, $\alpha = 90.0(7)°$, $\beta = 102.452(11)°$, $\gamma = 90.0(9)°$, $V = 508.777(8)$ Å^3, $Z = 2$, $D_x = 1.920$ g cm^{-3}, λ(Mo Ka) = 0.71073 Å, $\mu = 0.169$ cm^{-1}, $F(000) = 856$, final $R = 0.0414$ for 1254 independent observed reflections. In the BCHMX crystal there were found more short contacts in the molecular crystal of BCHMX data of Gilardi creating extensive supramolecular architecture.

1. Introduction

At present time, polycyclic nitramines increasingly gain importance as perspective and highly energetic materials. Main features are their high density and high performance with no significant increase in sensitivity to mechanical stimuli. cis-1,3,4,6-Tetranitrooctahydroimidazo-[4,5-d]imidazole (a.k.a. bicyclo-HMX or BCHMX) is one of attractive compounds predicted to possess higher density than 1,3,5,7-tetranitro-1,3,5,7-tetrazocan (HMX) [1]. This compound has drawn the attention of organic chemists since it was theoretically designed and its superior physical and explosive properties were predicted [2]. During the 1980s a very intense effort was dedicated to find undemanding and economically feasible chemical procedure to obtain this energetic material in larger amounts. Despite extensive work done, only small quantities of BCHMX were prepared by 5-stage process involving expensive reagents and offering very low yields [3–5]. In respect of experimentally determined characteristics of BCHMX, only informative room temperature crystallographic study has been published

[1]. So far, other important data have not been practically estimated. That is why we present some properties of BCHMX in this paper.

2. Experimental

2.1. BCHMX

cis-1,3,4,6-Tetranitrooctahydroimidazo-[4,5-d]imidazole was obtained at our institute. An unpublished novel 2-stage method for BCHMX synthesis which offers fair yields and product of >98% purity was used (checked by HPLC). It was purified by 2× crystallization from acetone, its visible m.p. was of 268 °C under decomposition (determined on a Boëtius micro-heating table equipment); this melting might be in fact a process of dissolving thermally unharmed BCHMX in products of its thermal decomposition.

2.2. X-ray crystallographic study

This study should be taken as a complement to the informative study of Gilardi et al. [1]; the main difference in our procedure from mentioned paper rests in using lower temperature during

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the measurements and in alternative monochromatized radiation. The crystal for study was grown from acetone/methanol solution (50/50 volume parts). The details of the crystal structure determination and refinement for the compound studied are given bellow. The suitable single crystal of BCHMX was mounted on glass fibre with an perfluorinated silicone oil and measured on four-circle diffractometer KappaCCD with CCD area detector by monochromatized Mo Ka radiation ($\lambda = 0.71073$ Å) at 150(1) K and the φ and ω scan mode. Data reductions were performed with DENZO-SMN [6]. Structures were solved by direct methods (Sir92) [7] and refined by full matrix least-square based on F [2] (SHELXL97) [8]. All hydrogen atoms were positioned geometrically and refined on their parent carbon atoms, with C—H = 0.93 Å and $U_{iso}(H)$ = $1.2U_{eq}(C)$.

The numerical absorption corrections from crystal shape by Gaussian integration were applied [9]. Crystallographic data for BCHMX: $C_4H_6N_8O_8$, M = 294.17, monoclinic, $P2_1$, a = 8.5430(8), b = 6.9480(6), c = 8.7780(8) Å, β = 102.452(11), Z = 2, V = 508.78 (8) Å^3, D_c = 1.920 g cm^{-3}, μ = 0.183 mm^{-1}, T_{min} = 0.937, T_{max} = 0.971; 4259 reflections measured (θ_{max} = 27.5°), 1254 independent (R_{int} = 0.070), 1169 with $I > 2\sigma(I)$, 182 parameters, S = 1.097, $R1$(obs. data) = 0.0369, $wR2$(all data) = 0.0916; max., min. residual electron density = 0.192, −0.248 eÅ^{-3}.

Crystallographic data for structural analysis has been deposited with the Cambridge Crystallographic Data Centre [10].

2.3. NMR chemical shifts

The ^{1}H, ^{13}C, and ^{15}N NMR spectra were recorded on a Bruker Avance 500 spectrometer at 500.13 MHz for ^{1}H, 125.76 MHz for ^{13}C, and 50.68 MHz for ^{15}N in DMSO-d_6. The ^{1}H and ^{13}C chemical shifts are given on the δ scale (ppm) and are referenced to the central signal of the solvent (δ = 2.55 (^{1}H) and 39.60 (^{13}C)). The ^{15}N chemical shifts were referred to external pure nitromethane in a co-axial capillary (δ = 0.0). Positive chemical shifts denote shifts to higher frequencies with respect to a standard. Following shifts were determined: ^{1}H chemical shifts: δ_H = 7.42 (CH), 6.31 and 5.58 (prochiral methylene group, $^2J(^1H, ^1H)$ = 11.0 Hz); ^{13}C chemical shifts: δ_C = 77.9 (CH, $^1J(^{13}C, ^1H)$ = 176.2 Hz) and 65.2 (CH$_2$, $^1J(^{13}C, ^1H)$ = 174.5 and 158.9 Hz). Its ^{15}N chemical shifts are presented in Table 1 together with the shifts of structurally related nitramines.

2.4. Thermal stability

We used a DTA 550 Ex apparatus [11] for thermal analyses of explosives. The measurements were carried out at atmospheric pressure, the tested sample being in direct contact with the air. The sample tested (0.05 g) was placed in a test tube made of Simax glass, 5 mm in diameter and 50 mm long. The reference standard was 0.05 g aluminium oxide. We used linear rate of temperature increase of 5 °C min^{-1}. The results are presented by Fig. 1; here exothermic effects of thermal decomposition overlap endothermic peaks of melting in the case of BCHMX and HMX. Onsets of thermal decomposition of the all substances from this Figure are presented in Table 2.

2.5. The ignition temperature

This temperature was determined [12,15] by heating of 100 mg sample of the given substance (BCHMX, RDX, HMX and PETN) at a heating rate of 5 °C min^{-1} until the point of autoignition of the sample was reached. The corresponding results are presented in Table 2.

Table 1
A survey of impact and electric-spark sensitivities and ^{15}N NMR chemical shifts and corrected [32] heats of explosion of the group of nitramines and PETN

Chemical name	Code designation	Impact sensitivity		Electric-spark sensitivity		^{15}N NMR chemical shifts (ppm)			Corrected heat [32] of explosion Q_{el} (MJ kg^{-1})
		E_{dr} (J)	Ref.	E_{ES} (mJ)	Ref.	δ_N nitro group	δ_A aza–nitrogen	Ref.	
N,N′-Dinitroethane-1,2-diamine	EDNA	8.33	17	392.0 ± 51.7	14	−26.34	−205.47	21	4.874
2,5-Dinitro-2,5-diazahexane	DMEDNA	21.04	f			−27.83	−209.55	21	3.732
2,4,6-Trinitro-2,4,6-triazaheptane	ORDX	Inactive	f	243.3 ± 14.4	14	−28.49[b]	−202.29[b]	21	4.870
						−32.02[c]	−189.90[c]		
1,3-Dinitroimidazolidine	CPX	17.96	18	403.3 ± 14.4	14	−31.21	−209.01	21	4.708
1,3-Dinitro-1,3-diazetidine	TETROGEN	9.97	19	494.0[a]	14	−27.83	−203.62	21	5.236
1,3,5-Trinitro-1,3,5-triazinane	RDX	5.58	17	216.4 ± 15.6	14	−32.90	−198.10	21	5.481
1,3,5-Trinitro-1,3,5-triazepane	HOMO	4.55	f	431.3 ± 19.3	14	−33.04[d]	−201.28[d]	21	5.005
						−34.38[e]	−196.32[e]		
β-1,3,5,7-Tetranitro-1,3,5,7-tetrazocane	β-HMX	6.37	17	236.4 ± 10.1	14	−34.70	−199.10	21	5.530
α-1,3,5,7-Tetranitro-1,3,5,7-tetrazocane	α-HMX	1.93	f						5.530
cis-1,3,4,6-Tetranitrooctahydroimidazo-[4,5-d]imidazole	BCHMX	2.98	f	148.7 ± 73.1	f	−35.2	−190.1	f	5.758[f]
1,3,5,7,9-Pentanitro-1,3,5,7,9-pentazecane	DECAGEN	4.90	19	276.5[a]	14	−33.25	−197.38	21	5.620
Pentaerythritol tetranitrate	PETN	2.90	17	29.3 ± 5.6	20				5.729

[a] The values predicted in Ref. [20].
[b] The chemical shifts for positions 2,6 in the ORDX molecule.
[c] The chemical shifts for position 4 in the ORDX molecule.
[d] The chemical shifts for positions 1,5 in the HOMO molecule.
[e] The chemical shifts for position 3 in the HOMO molecule.
[f] Result of this paper.

Table 2
A survey of the main properties of BCHMX in comparison with those for RDX, HMX and PETN

Property	BCHMX	RDX	β-HMX	PETN
Melting point (°C)	268 decompn.	204	275 decompn.	141
Max. theoretical density (g cm^{-3})	1.86[a]	1.82[b]	1.96[b]	1.76[b]
Calculated [22] max. heat of explosion (MJ kg^{-1})	6.518	6.246	6.225	6.364
Corrected [32] heat of explosion (MJ kg^{-1})	5.758	5.481	5.530	5.729
Calculated [22] detonation velocity (m s^{-1})	9050	8855	9169	8723
Max. experimental detonation velocity (m s^{-1})/for charge density (g cm^{-3})	8650/1.79	8750[c]/1.76[b]	9100[c]/1.90[b]	8400[c]/1.70[b]
Calculated [22] detonation pressure (GPa)	37	35	39	33
Calculated [22] volume of gaseous products of detonation (dm^3 kg^{-1})	724	757	757	709
Onset of thermal decomposition from DTA (°C)	227	198	274	187
Ignition temperature (°C)	214–224	204 decompn.	275	192
Impact sensitivity (J)	2.98	5.58[d]	6.37[d]	2.90[d]
Electric-spark sensitivity (mJ)	148.7	216.4	236.4	29.3
Friction sensitivity (N)	88	152	95	44

[a] The value taken from paper [1].

[b] The value taken from monograph [34].

[c] Detonation velocity under confined conditions—this velocity for BCHMX is obtained under unconfined conditions (see in paragraph 2.9 of this paper).

[d] The value taken from paper [17].

2.6. Impact sensitivity data

For the impact sensitivity determination the standard impact tester (Julius Peters [15]) was used with exchangeable anvil, the amount of tested substance being 40 mm^3 [12]; 1 and 2 kg weight drop hammers were used [12,15]. Using the up-and-down statistical method, the obtained sensitivity was expressed as the drop energy, E_{dr} [12,15], its values are presented in Tables 1 and 2 together with relevant values for structurally related nitramines.

2.7. Friction sensitivity data

Friction is electromechanically generated between a small, stationary, cylindrically shaped porcelain pistil having a rough spherical end surface and a rough porcelain plate bearing a sample [15]. The normal force between the porcelain pistil and the plate, at which 50% of initiation occurs, is reported as the friction sensitivity, expressed as sliding frictional force, $F_{x,y}$ [15]. Result in comparison with friction sensitivities of RDX, HMX and pentaerythritol tetranitrate (PETN) is presented in Table 2. A graphic comparison of friction sensitivities of these compounds is presented by Fig. 2.

2.8. Electric-spark sensitivity data

These data were obtained by means of an apparatus developed at Institute of Energetic Materials and designated as ESZ KTTV [13,14].
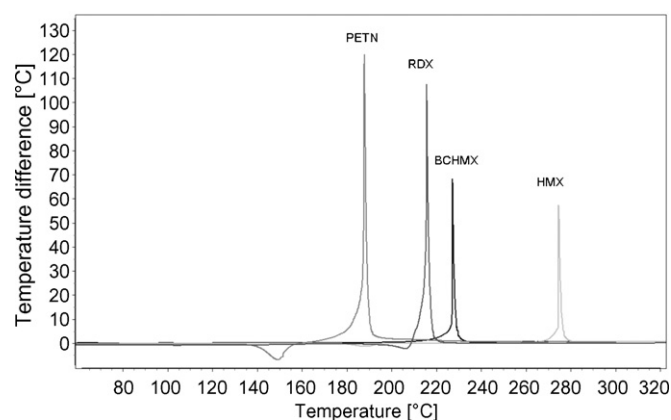
The instrument is designed for a small-scale sensitivity testing of energetic materials [13,14]. A high voltage power supply (operating voltage 4–10 kV) and a set of capacitors of overall capacity in the range from 100 pF to 350 nF produces an electrostatic discharge of total energy from 10 mJ to 16 J. A sample of 1 mm height is fitted into an isolation tube mounted on the lower cylindrical metal electrode. The upper electrode is equipped with manual vertically adjustable positioner. The micro container itself is placed in a separate test box with ventilation. The time behavior of voltage and current at the spark gap is registered with a scope and than evaluated using a microcomputer to give the effective energy transmitted to the sample. The resulted sensitivity to the electric spark is expressed in Tables 1 and 2 as the spark energy, E_{ES}, in mJ. For a comparison also the E_{ES} values of other structurally related nitramines and also PETN are presented in this Table.

2.9. Detonation velocity measured

A sample of BCHMX was for this kind of measurement phlegmatized by coagulative method using 10% of wt. solution of Viton B in acetone; Viton B is a terpolymer of hexafluoropropylene, vinylidene fluoride and tetrafluoroethylene. The nitramine was mixed with this solution and then precipitation was made by hexane in the sense of published method [16]. Thus, a fine product was prepared with content of 3% of Viton B (impact sensitivity was of 4.32 J). Phlegmatized BCHMX was pressed by pressure of 390 GPa in vacuum into cylinders with diameter 16 mm and height 16 mm. These cylinders were put together with nitrocellulose-based glue to form 3 charges, each weighing approximately 40 g. For actual mea-
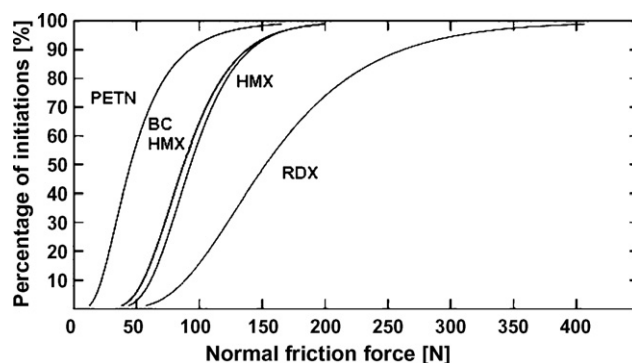
Fig. 1. Differential thermal analysis records of BCHMX, PETN, RDX and HMX; here exothermic effects of thermal decomposition overlap endothermic peaks of melting in the case of BCHMX and HMX.

Fig. 2. A comparison of friction sensitivities of BCHMX, PETN, RDX and HMX.

Table 3
Solubility of BCHMX in organic solvents (grams of BCHMX per 100 ml of solvent)

Solvent/temperature	20 °C	40 °C	60 °C	80 °C	100 °C	120 °C
Acetone	25.0	28.9	27.2	–	–	–
Dimethylsulfoxide	94.6	102.5	116.3	133.3	140.9	158.6
Acetonitrile	10.5	13.7	17.6	22.7	–	–
Tetrahydrofurane	4.6	4.7	5.0	–	–	–
Nitromethane	3.1	4.2	5.9	8.2	12.8	–
Ethyl acetate	10.5	10.5	10.5	10.5	–	–

surement in accordance with method [12] ionisation sensors with copper wire thickness of 0.3 mm were used and inserted in charge at 100 mm distance from each other (registration by means of electronic stopwatch). Charges were set off using booster composed of 4.0 g pentolite (i.e. PETN phlegmatized by TNT) and 3.5 g A-IX-2 explosive (phlegmatized hexogen with aluminium). The detonation velocity of BCHMX with 3% of wt. Viton B at density 1.79 g cm^{-3} was 8650 m s^{-1} (see also Table 2).

2.10. Detonation characteristics calculated [22]

Detonation velocities, D, maximum heat of explosion, Q_{max}, detonation pressure, P, for published density [1] of 1.861 g cm^{-3} and heat of formation [23] of 49.3 kcal mol^{-1} were calculated by means of Kamlet and Jacobs method [22]. By this method values were obtained which are presented in Table 2. In Table 1 the heats of explosion, Q_{real}, are presented which were calculated for monocrystals by means of the semi-empirical relationships devised by Pepekin et al. [32]. These values should correspond to the experimentally determined heats of explosion in the calorimetric bomb [32,33].

2.11. Solubility determination

The modified method of Sitzman and Foti [18] was used. A volume of 10, 20, or 50 ml of solvent was used. A volume of solvent (measured by pipette) was stirred at the desired temperature on a magnetic hotplate. Explosive was added to a stirred solvent until no more substance dissolved (the amount of explosive added was pre-weighed) and the mixture was stirred for a 15-min period (to make sure no more explosive dissolves). The suspension was filtered rapidly (a heated fritted ceramics S4 was used for filtration of mixtures above 20 °C) and the undissolved explosive was sucked dry. The undissolved explosive was dried at 60 °C for 4 h and then weighed, in the case of dimethylsulfoxide (DMSO) solvent suction-pump was used (vacuum of 45 mm Hg). The weight of explosive dissolved in the solvent was taken as the difference between the amount of explosive added to the solvent and the amount of undissolved explosive. To check rightness of the result the saturated solution of the explosive was evaporated at 60 °C and the resulting solid weighed (in the case DMSO again suction-pump was used—vacuum of 45 mm Hg). The sum of both undissolved and dissolved part was equal to the grammage of explosive added. By such procedure also fact was proved that no explosive was decomposed at higher temperatures in a solvent. The results are summed up in Table 3. The solubilities were calculated as grams of explosive per 100 ml of solvent. BCHMX is insoluble in toluene (<100 mg), diethyl ether (<20 mg), methanol (<500 mg) and dichlormethane (<80 mg) per 100 ml of solvent.

In the case of DMSO solvent a linear relationship exists between temperature and solubility of BCHMX in the form

$$y = 0.646t + 79.147 \tag{1}$$

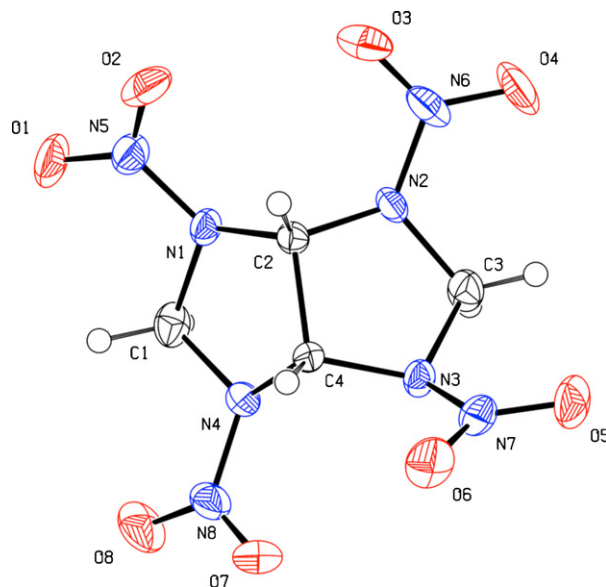with $R^2 = 0.988$, where y is a solubility and t is temperature in °C.

Fig. 3. Drawing of the BCHMX molecule in order to define the atoms numbering that is used.

3. Results and discussion

The numbering scheme for the BCHMX molecule is shown in Fig. 3. Corresponding bond lengths, selected bond and torsion angles and their mutual comparison with the Gilardi's et al. data [1] (the most from them are taken from the Cambridge Crystallographic Data Centre) are given in Supporting Information (Tables 4–6). In our determination seems to be more precise in the point of view that the thermal motion was slowed down. The unit cell distances and angles as well as the cell volume are different.

Table 4
Mutual comparison of Gilardi's et al. [1] and measured bond lengths (Å) (standard uncertainties) in BCHMX molecular crystal

Data of Gilardi et al. [1]		Data measured	
Bond[a]	Bond length (Å)	Bond	Bond length (Å)
O(2A)–N(2A)	1.221(3)	O(1)–N(5)	1.224(4)
O(2B)–N(2A)	1.226(4)	O(2)–N(5)	1.213(4)
O(4A)–N(4A)	1.228(4)	O(3)–N(6)	1.228(4)
O(4B)–N(4A)	1.206(4)	O(4)–N(6)	1.209(4)
O(6A)–N(6A)	1.222(4)	O(5)–N(7)	1.211(4)
O(6B)–N(6A)	1.216(3)	O(6)–N(7)	1.209(4)
O(8A)–N(8A)	1.205(3)	O(7)–N(8)	1.225(4)
O(8B)–N(8A)	1.211(4)	O(8)–N(8)	1.211(4)
N(2)–N(2A)	1.369(3)	N(1)–N(5)	1.352(4)
N(2)–C(1)	1.458(3)	N(1)–C(1)	1.454(4)
N(2)–C(3)	1.445(3)	N(1)–C(2)	1.447(4)
N(4)–N(4A)	1.363(3)	N(2)–N(6)	1.355(4)
N(4)–C(3)	1.454(3)	N(2)–C(2)	1.445(4)
N(4)–C(5)	1.447(3)	N(2)–C(3)	1.464(4)
N(6)–N(6A)	1.357(3)	N(3)–N(7)	1.412(4)
N(6)–C(5)	1.454(3)	N(3)–C(3)	1.460(4)
N(6)–C(7)	1.455(3)	N(3)–C(4)	1.458(4)
N(8)–N(8A)	1.415(3)	N(4)–N(8)	1.365(4)
N(8)–C(1)	1.459(3)	N(4)–C(1)	1.452(4)
N(8)–C(7)	1.464(3)	N(4)–C(4)	1.454(4)
C(1)–C(5)	1.543(3)	C(2)–C(4)	1.538(4)
O(2A)–O(2B)	2.194(4)[b]	O(1)–O(2)	2.164(4)[b]
O(4A)–O(4A)	2.167(4)[b]	O(3)–O(4)	2.175(4)[b]
O(6B)–O(6A)	2.181(4)[b]	O(5)–O(6)	2.161(4)[b]
O(8A)–O(8A)	2.153(4)[b]	O(7)–O(8)	2.184(4)[b]

[a] Atoms indexing according to Gilardi et al. [1].

[b] Arithmetic mean of these nonbinding interatomic distances according to the published data[1] is of 2.17375 Å, according to the measured data is of 2.171 Å.

Table 5
Mutual comparison of Gilardi's et al. [1] and measured values of torsion angles (°) (standard uncertainties) in the BCHMX molecule

Data of Gilardi et al. [1]		Data measured	
Atoms[a]	Torsion (°)	Atoms	Torsion (°)
C(1) N(2) N(2A) O(2A)	167.68(18)	C(1) N(1) N(5) O(1)	−22.7(4)
C(1) N(2) N(2A) O(2B)	−15.0(3)	C(1) N(1) N(5) O(2)	159.0(3)
C(3) N(2) N(2A) O(2A)	18.9(3)	C(2) N(1) N(5) O(1)	−169.0(3)
C(3) N(2) N(2A) O(2B)	−163.8(2)	C(2) N(1) N(5) O(2)	12.8(4)
C(3) N(4) N(4A) O(4A)	−21.7(3)	N(5) N(1) C(1) N(4)	−146.8(2)
C(3) N(4) N(4A) O(4B)	159.1(3)	C(2) N(1) C(1) N(4)	1.5(3)
C(5) N(4) N(4A) O(4A)	−169.1(2)	N(5) N(1) C(2) N(2)	−110.9(2)
C(5) N(4) N(4A) O(4B)	11.8(3)	N(5) N(1) C(2) C(4)	138.5(2)
C(5) N(6) N(6A) O(6A)	−12.9(3)	C(1) N(1) C(2) N(2)	102.2(3)
C(5) N(6) N(6A) O(6B)	170.6(2)	C(1) N(1) C(2) C(4)	−8.5(3)
C(7) N(6) N(6A) O(6A)	−168.5(2)	C(2) N(2) N(6) O(3)	−14.8(4)
C(7) N(6) N(6A) O(6B)	15.0(3)	C(2) N(2) N(6) O(4)	169.3(3)
C(1) N(8) N(8A) O(8A)	27.2(3)	C(3) N(6) O(3)	−167.8(3)
C(1) N(8) N(8A) O(8B)	−157.4(2)	C(3) N(2) N(6) O(4)	16.3(4)
C(7) N(8) N(8A) O(8A)	157.2(2)	N(6) N(2) C(2) N(1)	95.9(3)

[a] Atoms indexing according to the Gilardi's et al. measurements [1].

The results of the structure determination show the crystal to be an array of molecular units with connectivity and geometry consistent with those expected. A drawing of the two molecules in the unit cell is shown in Fig. 4. The higher density of BCHMX crystal determined by us (1.920 g cm^{-3}) as compared with that given in Ref. [1] (1.861 g cm^{-3}) is due to the application of a lower temperature in our measurement (150 K, while 294 K was adopted in Ref. [1]).

From the standpoint of ^{15}N NMR spectroscopy (in solution) the BCHMX molecule is isochronous (see Table 1), but in the crystal it

Table 6
Mutual comparison of Gilardi's et al. [1] and measured values of valence-bond angles (°) (standard uncertainties) in the BCHMX molecule

Data of Gilardi et al. [1]		Data measured	
Atoms[a]	Torsion (°)	Atoms	Torsion (°)
N(2A)–N(2)–C(1)	118.7(2)	N(5)–N(1)–C(1)	116.6(2)
N(2A)–N(2)–C(3)	118.1(2)	N(5)–N(1)–C(2)	120.5(2)
C(1)–N(2)–C(3)	115.81(18)	C(1)–N(1)–C(2)	114.4(2)
O(2A)–N(2A)–O(2B)	127.4(3)	N(6)–N(2)–C(2)	120.2(2)
O(2A)–N(2A)–N(2)	115.6(3)	N(6)–N(2)–C(3)	120.1(2)
O(2B)–N(2A)–N(2)	116.9(2)	C(2)–N(2)–C(3)	114.5(2)
N(4A)–N(4)–C(3)	117.1(2)	N(7)–N(3)–C(3)	115.8(2)
N(4A)–N(4)–C(5)	120.09(19)	N(7)–N(3)–C(4)	115.1(2)
C(3)–N(4)–C(5)	114.88(19)	C(3)–N(3)–C(4)	109.9(2)
O(4A)–N(4A)–O(4B)	125.9(3)	N(8)–N(4)–C(1)	117.2(2)
O(4A)–N(4A)–N(4)	115.4(2)	N(8)–N(4)–C(4)	118.8(3)
O(4B)–N(4A)–N(4)	118.7(2)	C(1)–N(4)–C(4)	115.6(2)
N(6A)–N(6)–C(5)	119.99(19)	O(1)–N(5)–O(2)	125.2(3)
N(6A)–N(6)–C(7)	121.51(19)	O(1)–N(5)–N(1)	116.2(3)
C(5)–N(6)–C(7)	114.28(19)	O(2)–N(5)–N(1)	118.6(3)
O(6A)–N(6A)–O(6B)	126.9(3)	O(3)–N(6)–O(4)	126.4(3)
O(6A)–N(6A)–N(6)	117.0(2)	O(3)–N(6)–N(2)	116.5(3)
O(6B)–N(6A)–N(6)	116.0(3)	O(4)–N(6)–N(2)	116.9(3)
N(8A)–N(8)–C(1)	115.39(18)	O(5)–N(7)–O(6)	126.5(3)
N(8A)–N(8)–C(7)	116.05(19)	O(5)–N(7)–N(3)	116.5(3)
C(1)–N(8)–C(7)	109.46(19)	O(6)–N(7)–N(3)	116.8(3)
O(8A)–N(8A)–O(8B)	126.1(2)	O(7)–N(8)–O(8)	127.4(3)
O(8A)–N(8A)–N(8)	117.1(2)	O(7)–N(8)–N(4)	116.3(3)
O(8B)–N(8A)–N(8)	116.6(2)	O(8)–N(8)–N(4)	116.2(3)
N(2)–C(1)–N(8)	110.59(15)	N(1)–C(1)–N(4)	101.1(2)
N(2)–C(1)–C(5)	102.58(17)	N(1)–C(2)–N(2)	112.8(2)
N(8)–C(1)–C(5)	106.86(19)	N(1)–C(2)–C(4)	104.9(2)
N(2)–C(3)–N(4)	101.04(19)	N(2)–C(2)–C(4)	102.4(2)
N(4)–C(5)–N(6)	113.14(18)	N(2)–C(3)–N(3)	102.6(2)
N(4)–C(5)–C(1)	104.48(17)	N(3)–C(4)–N(4)	110.4(2)
N(6)–C(5)–C(1)	102.15(18)	N(3)–C(4)–C(2)	106.8(2)
N(6)–C(7)–N(8)	102.91(19)	N(4)–C(4)–C(2)	102.5(2)

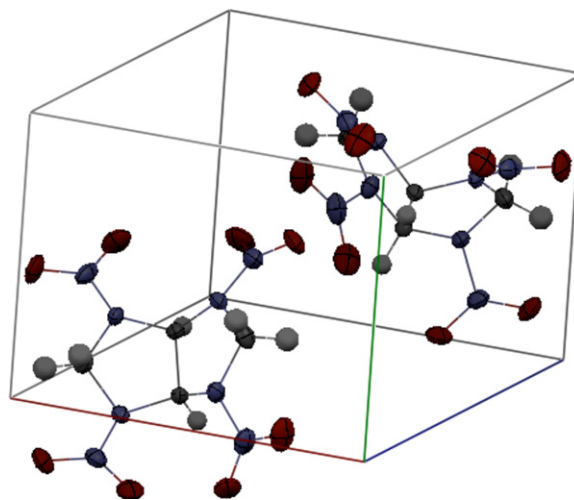[a] Atoms indexing according to the Gilardi's et al. measurements [1].

Fig. 4. Drawing showing the connectivity of two BCHMX molecules in the cell unit.

Table 7
A survey of the longest N—N bonds in molecules of several nitramines

Nitramine	The longest N–N bond		
	Length (Å)	Note	Ref.
TETROGEN	1.355	Obtained by HF/6-31G*optimization	25
RDX	1.398	Axial N–N bond in its molecule in the crystal	26
HMX	1.392	Equatorial N-N bond of δ-polymorph	26
BCHMX	1.412	See Table 1 in this paper	

is distinctly deformed. The dihedral inter-nuclear angle in BCHMX molecule is from 112.8(2)° (N2–C2–N1) to 110.4(2)° (N4–C4–N3). The N—N bonds in its molecule are not equivalent either—the longest of them (N3–N7) corresponds to the smallest mutual distance of oxygen atoms in the respective nitro group (2.161(4) Å for O5...O6). Table 7 gives a comparison of the longest lengths of N—N bonds in several cyclic nitramines. Nonbinding interatomic distances of oxygen atoms in all of the nitro groups in the BCHMX molecule (see Tables 4 and 8) are shorter than those corresponding to the intermolecular contact radii for oxygen in carbonyl or nitro groups (i.e. 1.35–1.63 Å [35]). This fact corresponds with the general finding [24] in the field of polynitro compounds which is a topic of new scientific interest at present [24] (Fig. 4).

Table 8
All short contacts found in the BCHMX molecular crystal

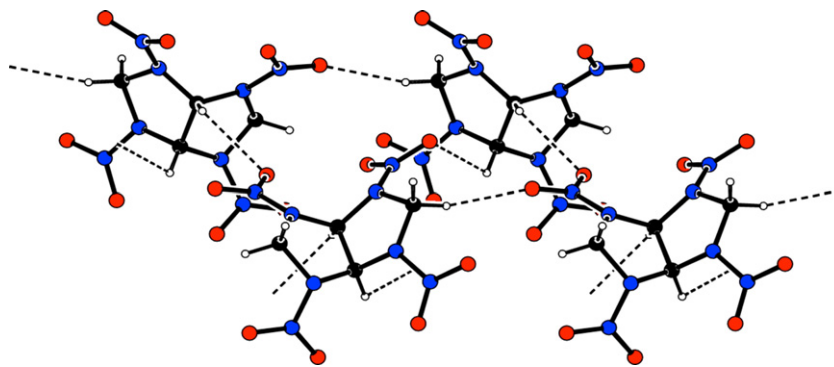| Atom1 Atom2	Symm. op.	Distance (Å)
N3 O7	*x,y,z*	3.068
O3 O2	*x,y,z*	2.833
O6 N2	*x,−1 + y,z*	3.010
O6 N1	*x,−1 + y,z*	2.865
N2 O6	*x,1 + y,z*	3.010
N1 O6	*x,1 + y,z*	2.865
O6 O8	*1 − x,−1/2 + y,−z*	2.984
O7 N4	*1 − x,−1/2 + y,−z*	3.065
O5 O8	*1 − x,−1/2 + y,−z*	3.026
N1 O1	*1 − x,−1/2 + y,1 − z*	3.009
N4 O7	*1 − x,1/2 + y,−z*	3.065
O8 O6	*1 − x,1/2 + y,−z*	2.984
O8 O5	*1 − x,1/2 + y,−z*	3.026
O1 N1	*1 − x,1/2 + y,1 − z*	3.009
N2 O3	*2 − x,−1/2 + y,1 − z*	3.060
O6 O3	*2 − x,−1/2 + y,1 − z*	2.964
O3 N2	*2 − x,1/2 + y,1 − z*	3.060
O3 O6	*2 − x,1/2 + y,1 − z*	2.964

Fig. 5. Drawing showing the non-classical H-bonds in the BCHMX crystal lattice.

Table 9
Mutual comparison of data of Gilardi's et al. [1] and measured values of non-classical H-bonds lengths in the molecular crystal of BCHMX

Donor–H...Acceptor	Equivalent position code	Distances (Å)			Angles (°)	
		D–H	H...A	D...A	D–H...A	A...H...A* A'...H...A''
Data of Gilardi et al. [1]						
C(1)–H(1A)...O(8A)	Intra	0.98	2.25	2.661(3)	104	
C(3)–H(3B)...O(6B)	$-1+x,y,z$	0.97	2.43	3.357(3)	160	
C(5)–H(5A)...O(6A)	$1-x,-1/2+y,1-z$	0.98	2.53	3.017(3)	110	
C(7)–H(7A)...O(8B)	Intra	0.97	2.25	2.671(4)	105	
Data measured						
C(1)–(H1A)...O(4)	$-1+x,y,z$	0.97	2.38	3.307(4)	159	
C(2)–H(2)...O(3)	$2-x,-1/2+y,1-z$	0.98	2.51	2.987(4)	110	
C(3)–(H3A)...O(5)	Intra	0.97	2.23	2.655(4)	105	
C(4)–H(4)...O(6)	Intra	0.98	2.23	2.648(4)	104	
C(4)–H(4)...O(1)	$1-x,-1/2+y,1-z$	0.98	2.57	3.039(4)		109' 145'

Analogously to the paper [1] atypically short distances were found between oxygen atoms of nitro groups of one molecule and hydrogen atoms of adjacent molecules in the BCHMX crystal (see Fig. 5 and Table 9); these distances fall in the interval 2.655(4) to 3.307(4) Å for C–H...O separations. The extra contact C(2)–H(2)...O(3) with (i) $2-x,-1/2+y,1-z$ and separation 2.987(4) Å was found at a lower temperature. Intermolecular interaction distances between N–H...O–N of adjacent molecules in the molecular crystals of 2,3,4,6-tetranitroaniline, for example, lay in the 2.39–2.41 Å interval [27]. There were also found in the BCHMX molecular crystal more short contacts in the new structure making extensive supramolecular architecture (see Table 8).

3.1. Initiation reactivity [28]

Generally, this reactivity depends on [28,29] (a) steric conditions and (b) electron configuration in the ground state of the reaction centre of the molecule. Both the electron configuration and steric situation in the reaction centre of the molecule can be advantageously characterized from the standpoint of organic chemistry on the basis of the NMR chemical shifts of key atoms of the reaction centre of molecule [28,29]. This approach is documented by Figs. 6, 7 and 9.

Primary fission of the *sec*-nitramines during initiation lies in the N–N bond homolysis [21,26,28–31]. Nitramino groups, particularly those of non-isochronous molecules of nitramines, are not equivalent from the point of view of their chemical reactivity [21,28,29]. This is clearly documented by Fig. 6, which was constructed using the data of Ref. [21] with added data of BCHMX. This figure represents a relationship between the real heats of explosion, Q_{real}, and the ^{15}N NMR chemical shifts of nitrogen atoms in primarily reacting nitro groups; in order to be more illustrative, the diagram also presents structural formulae of some non-isochronous molecules

(for a more detailed discussion, see Refs. [21,28,29]). The detonation reactivity and performance of BCHMX, judged in the sense of Fig. 6, corresponds to its molecular structure and, hence, to the expectations, too (see also Table 2).

Fig. 7 presents a relationship between logarithm of drop energies, E_{dr} and ^{15}N NMR chemical shifts, δ_A, of aza (amino) nitrogen atoms of the most reactive nitramino groups. This figure shows that the impact reactivity of polynitramines is connected with primary homolysis of N–NO$_2$ bonds in their molecules [28,29]. The primary rupture of the longest N–N bond in the nitramine molecule by action of impact is also documented by the approximate relationship between the E_{dr} values and the lengths of the longest
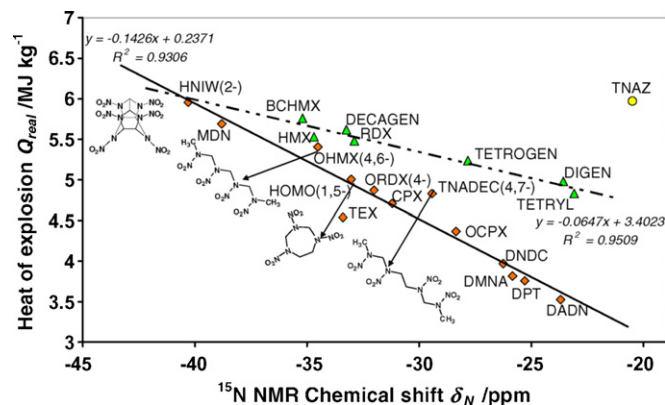

Fig. 6. Relationship between real heats of explosion, Q_{real}, and ^{15}N NMR chemical shifts of nitrogen atoms in the primary outgoing nitro groups during initiation and growth of nitramines detonation (in parenthesis given are the positions in molecule)—constructed by means of data from paper [21] and data of BCHMX from Table 1.
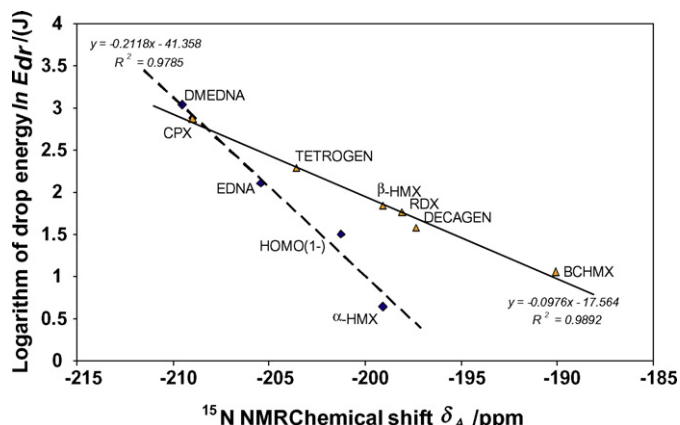
Fig. 7. Relationship between logarithm of impact sensitivity of nitramines, expressed as drop energy (E_{dr}), and ^{15}N NMR chemical shifts of aza-nitrogen atoms in their primary split nitramino groups during instrumentation of impact (in parenthesis given is the position in molecule).
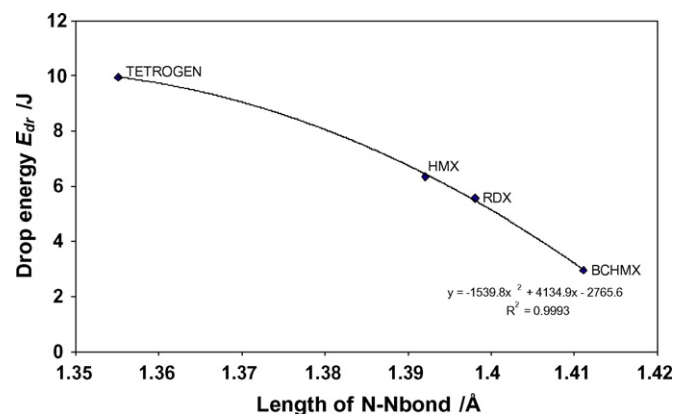

Fig. 8. Approximative relationship between impact sensitivity of the four nitramines, expressed as drop energy (E_{dr}), and the longest length of N—N bond in their molecules (from Table 7).

N—N bonds in molecules of this type (see Fig. 8). Both the figures confirm and rationalize the higher impact reactivity of BCHMX as compared with those of other nitramines studied, except for α-HMX.
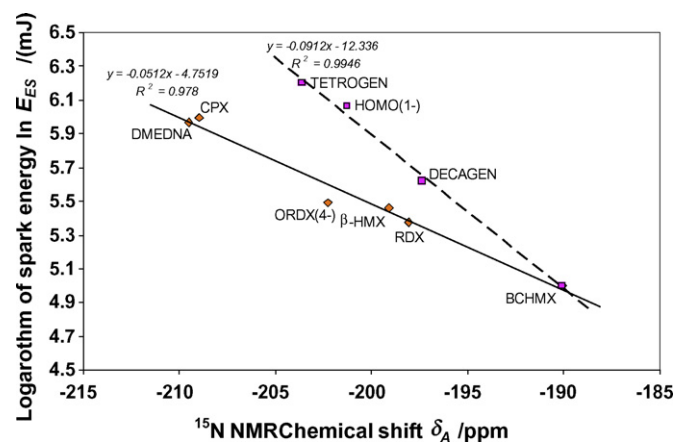
Fig. 9. Relationship between logarithm of electric-spark sensitivity of nitramines, expressed as spark energy (E_{ES}), and ^{15}N NMR chemical shifts of aza-nitrogen atoms in their primary split nitramino groups during instrumentation of spark (in parenthesis given is the position in molecule).

The electric-spark sensitivity of nitramines was previously dealt with in Ref. [14]. This article presents a relationship between this sensitivity and the ^{15}N NMR chemical shifts of nitrogen atoms in the most reactive nitro groups [14]. Addition of data of BCHMX and a new analysis using the ^{15}N NMR chemical shifts of the aza-atoms carrying the most reactive nitro groups resulted in finding a more unambiguous semi-logarithmic relationship presented in Fig. 9. This relationship also confirms and explains the higher sensitivity of BCHMX to electric spark as compared with the sensitivities of other nitramines studied in this work.

On grounds of the facts presented so far, it can be stated that BCHMX is a typical secondary nitramine with enhanced impact sensitivity (at the level of that of PETN), which corresponds to the rigid structure of its molecule and the length of the longest N—N bond in it. Its position amongst explosives can be seen from the comparison of its main properties with properties of technologically attractive high explosives in Table 2.

4. Conclusions

From the standpoint of the ^{15}N NMR spectroscopy (in solution), the *cis*-1,3,4,6-tetranitrooctahydroimidazo-[4,5-*d*]imidazole (bicyclo-HMX or BCHMX) molecule is isochronous. However, the crystallographic study performed at 150 K shows that the N—N bonds in its molecule in molecular crystal are not mutually equivalent—the longest of them (1.412 Å) is associated with the shortest mutual distance of oxygen atoms in the corresponding nitro group (2.161 Å). Nonbinding interatomic distances of oxygen atoms in all the nitro groups in the BCHMX molecule are shorter than those corresponding to the intermolecular contact (van der Waals) radii for oxygen. In the BCHMX molecular crystal there were also found other more short contacts in the new structure creating extensive supramolecular architecture. According to the above-mentioned study the dihedral inter-nuclear angle in its molecule has the magnitude of 112.8–110.4°. The characteristics of initiation reactivity of BCHMX, determined in this work, fully correspond to its molecular structure. Its impact sensitivity is at the level of impact sensitivity of PETN. The bearer of the higher impact and electric-spark sensitivities of BCHMX, as compared with those sensitivities of RDX and HMX, is the longest N—N bond in its molecule. The thermal stability of BCHMX is higher than that of RDX. With regard to the energy content, BCHMX is approximately equivalent to PETN. Judged according to detonation velocity, *D*, BCHMX does not reach the level of HMX, but under confined conditions it could attain the maximum *D* values for RDX and exceed the maximum *D* values for PETN. The solubility of BCHMX in ethyl acetate is temperature-independent, that in acetone and tetrahydrofurane depends slightly on temperature. The best solvent for BCHMX is dimethyl sulfoxide.

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