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Unveiling the energetic potential of azahomocubane (AHC): a new class of potential propellants, explosives and oxidizers†‡

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Cage compounds are potential kinetic rocks and thermodynamic powerhouses. Their strain energy plays a crucial role. Hence, adamantane, cubane, homocubanes, and bishomocubane skeletons have become prominent recently. However, research on the design and development of azahomocubane-based energetic materials has yet to be explored. The aim of the present work is to illustrate the potential of azahomocubanes as next-generation propellants, explosives and oxidizers. The energetic potential of any new materials was determined using B3LYP/6-31+G**, G2, and MP2/6-311++G** levels at the Gaussian 03 suite of programs. The new azahomocubanes possess a density range of 1.33 g cm^{-3} to 2.14 g cm^{-3}. Most of the azahomocubanes have significantly elevated high-positive heats of formation (ΔH_f° (s) = 289.82 kJ mol^{-1} to 728.41 kJ mol^{-1}). Compounds **AHC-12−19** have superior potentials as solid propellants in rocket propulsion. Additionally, this study reveals that compounds **AHC-20** and **AHC-21** could be highly effective primary explosives (**AHC-20**, P = 44.46 GPa, D = 9706 m s^{-1}; **AHC-21**, P = 45.64 GPa, D = 9708 m s^{-1}) exceeding the performance of RDX, HMX and comparable to that of ONC and CL-20. Our finding suggests that azahomocubanes have great potential in the field of energetic materials.

Introduction

Homocubanes derived by the introduction of one methylene group (–CH$_2$–) into the cubane core are homologues of cubane.[1] Cubane became the most prevalent cage skeleton, which gained the scientific community's interest because of its potential applications in high energy density material (HEDM) and medicinal applications.[2] In contrast, the synthesis, handling, and storage of cubane derivatives are problematic attributed to involving a multiple-step synthesis approach and production cost, and only a few data are available on such materials. The characteristic chemistry of these molecules, by their characteristic strain energy, has been extensively exploited recently.[3,4] Strain with appropriate explosophoric groups, such as nitro (–NO$_2$), nitrato (–ONO$_2$), azido (–N$_3$), and nitramine (–NHNO$_2$), *etc.* yield novel potential high energy density materials.[5] In the present era, computational-based design and prediction of emergent properties of new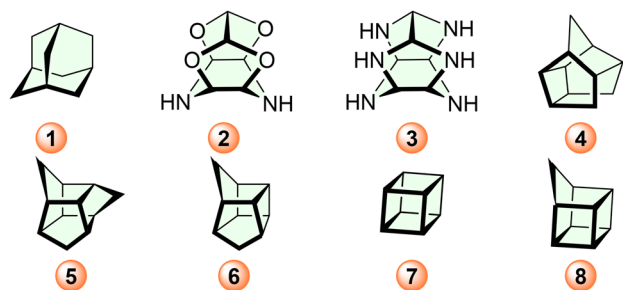 materials are prominent because these computational tools provide us with prospective properties before their actual synthesis, allowing us to design a new material cost-effectively.[6] Recent reports on the synthesis and development of polycyclic cage compounds based on energetic material show that these materials have the potential to become future-generation fuel/propellants in solid rock propulsion.[7] Very few reports also suggest that poly nitro-stained cage compounds possess superior explosive properties, which enhance their applications in civil, military, and space applications.[7,8] Cage skeletons **1–7** based novel compounds are demonstrating prominence in their various applications. However, the homocubane core **8** despite its first synthesis in 1968, has not yet received comparable recognition in the scientific community (Schemes 1 and 2).

A homocubane was synthesized by Dunn *et al.*[9] and Paquette *et al.*[10] Subsequently, various research groups reported notable homocubanes derivatives.[1,2,10,11] In contrast, an azahomocubane (AHC) is a relatively new compound synthesized by Eaton *et al.* by acid-catalyzed rearrangement of cubyl azides, giving 1-substituted 9-azahomocubanes.[12] This transformation inspired Williams and co-workers to synthesize and characterize novel azahomocubane derivatives using dimethyl 1,4-cubanedicarboxylate **10**.[13] Subsequently, a new derivative of AHC, 1-azahomocubane, was reported.[14] These recent reports demonstrate the feasibility of introducing nitrogen atoms into the homocubane skeleton. Based on the position of nitrogen, nine theoretical isomers are possible (Fig. 1).

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[b]Department of Applied Chemistry, China Agricultural University, 100193 Beijing, China
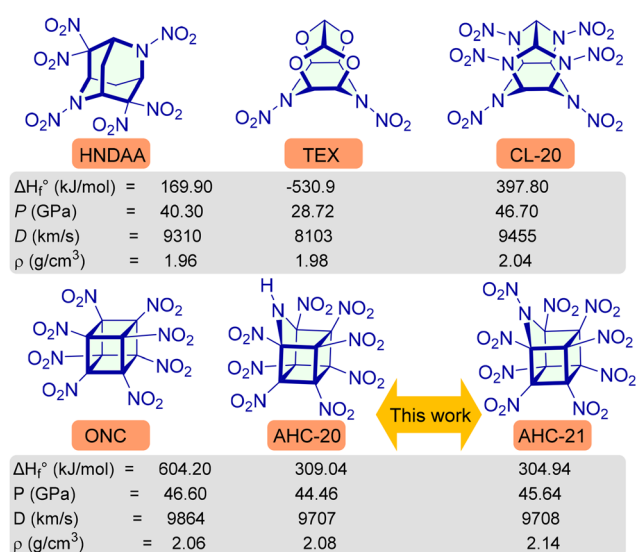† Dedicated to Professor Eaton for his pioneer work in cubane chemistry.
‡ Electronic supplementary information (ESI) available. See DOI: https://doi.org/10.1039/d4dt03457k

Adamantane (**1**). 2,6,8,12-Tetraoxa-4,10-diazatetracyclo[5.5.0.0^{5,9}.0^{3,11}]-dodecane (**2**). 2,4,6,8,10,12-Hexaazatetracyclo[5.5.0.0^{3,11}.0^{5,9}]dodecane (**3**). Pentacyclo-(5.4.0.0^{2,6}.0^{3,10}.0^{5,9})-undecane (**4**). Pentacyclo [6.3.0.0^{2,6}.0^{3,10}.0^{5,9}] undecane (**5**). Pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decane (**6**). Cubane (**7**). Pentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]-nonane (**8**).

Scheme 1 Typical polycyclic cage skeletons.

Scheme 2 Highly dense top-performance energetic cage compounds.[7,8]

Fig. 1 Schlegel diagrams of various isomers of azahomocubane **AHC-9a–9i**.

were calculated at the MP2/6-311++G** level at Gaussian 03 (Revision D.01) suite of programs.[16] The heats of formation for all ten compounds were obtained using an atomization approach using the G2 [17] *ab initio* method and the isodesmic method (Fig. S2, Tables S1 and S2‡). Furthermore, solid-state heats of formation of the new materials were calculated using gas-phase enthalpy and enthalpy of sublimation using eqn (S11) and (S12).‡

The densities of the title compounds were calculated using a newly developed modified Pulitzer method.[18] Subsequently, based on their solid phase enthalpies of formation $\left(\Delta H_{\mathrm{f}}^{\circ}\left(\mathrm{s}\right)\right)$ and calculated densities (Table 1), the corresponding propulsive (Isp and C*) and detonation performances (P and D) were evaluated using EXPLO5 V7.01 software.[19]

Additionally, the stability parameters of the new compounds, such as impact sensitivity (h_{50}) (eqn (S13)‡), kinetic energy ($\Delta E_{\mathrm{HOMO-LUMO}}$), and electrostatic potential (ESP) were predicted at the B3LYP/6-311++G (d,p) level of theory with the help of Multiwfn[20] and VMD software[21]

Results and discussion

A proposed synthetic strategy for compounds **AHC-12–21** is described in Scheme 3. Initially, 9-azahomocubane, **9i**, can be prepared from compound **10** efficiently. Subsequently, using a multi-steps strategy, various explosophoric groups can be introduced. Azahomocubane (**9i**-AHC) with secondary amine (R$_2$NH) enables us to introduce various functionalities by nucleophilic substitution/displacement of an N-proton. Based on the feasibility of the synthesis, we have designed ten deriva-

Computational method

The Density Functional Theory (DFT) based geometric optimization and frequency analyses of the new materials were determined using B3LYP/6-31+G** level, and single energy points
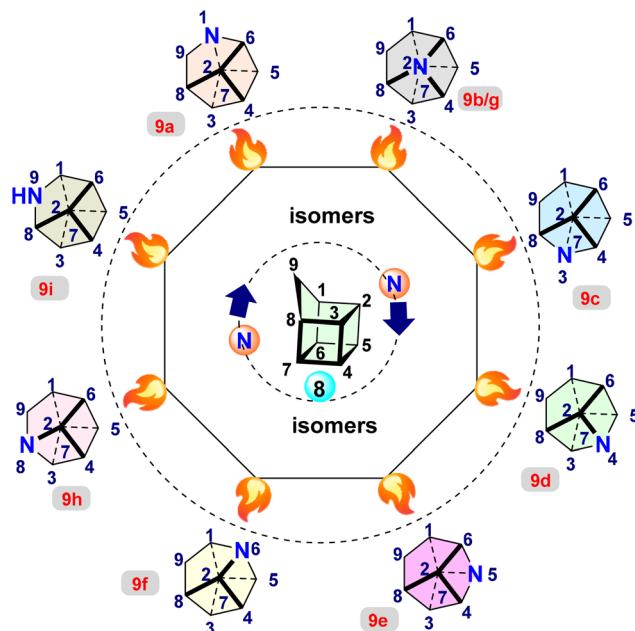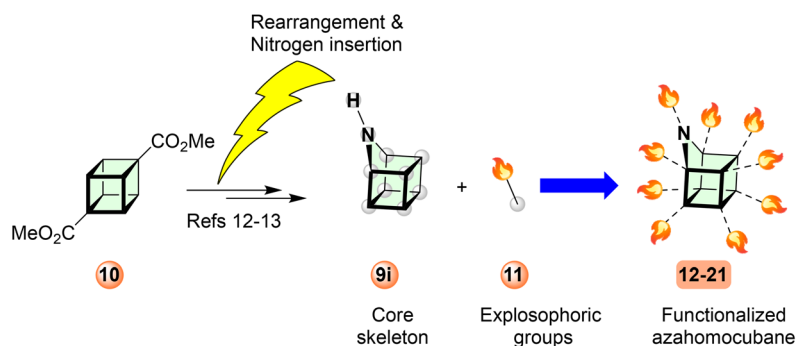
Recent studies suggest that a secondary amine (**9i**, 9-azahomocubane) bearing isomer was the most stable skeleton compared to the other isomers with a tertiary amine.[15] In contrast, 9-azahomocubane (**9i**, 9-AHC), rarely explored in the field of energetic materials, is a promising scaffold from the stereochemical perspective because it is effectively functionalized through the secondary amine moiety and the most stable skeleton over the other isomers, which allows the design of various novel energetic materials identified as an optimal cage skeleton for the present work (Scheme 3).

Scheme 3 Design of new azahomocubanes (**AHC-12–21**).

Table 1 Comparison of physicochemical properties of compounds **AHC-12–21**

Compound	Formula[a]	FW[b] [g mol⁻¹]	N + O[c] [%]	OB^{CO_2}[d] (%)	ΔH_{fs}[e] [kJ mol⁻¹]	ρ[f] [g cm⁻³]	P[g] [GPa]	D[h] [m s⁻¹]	h_{50}[i] [cm]
AHC-12	C_8H_9N	119.16	11.76	−275.25	390.22	1.33	12.52	5670.94	27.07
AHC-13	$C_8H_8N_2O_2$	164.16	36.55	−175.44	402.36	1.53	15.88	6297.39	21.96
AHC-14	$C_8H_9N_3O_2$	179.18	41.31	−165.20	454.36	1.53	15.66	6593.09	44.66
AHC-15	$C_9H_{10}N_2O_2$	178.19	33.68	−188.57	356.02	1.47	14.67	6155.14	42.50
AHC-16	$C_9H_{10}N_2O_3$	194.19	39.15	−164.79	289.82	1.51	15.57	6278.67	45.26
AHC-17	$C_9H_{10}N_4$	174.21	32.16	−211.25	728.41	1.40	14.41	6259.27	41.02
AHC-18	$C_9H_8N_4O_6$	268.19	56.68	−95.46	345.45	1.71	21.40	7254.70	56.70
AHC-19	$C_{10}H_{10}N_4O_6$	282.21	53.86	−107.72	322.45	1.66	19.20	7009.23	51.22
AHC-20	$C_8HN_9O_{16}$	479.14	79.74	25.04	309.04	2.08	44.46	9706.85	6.96
AHC-21	$C_8N_{10}O_{18}$	524.14	81.66	30.53	304.94	2.14	45.64	9708.21	6.98
Cubane	C_8H_8	104.15	0.0	−307.69	602.64	1.29	12.70	5990.00	24.14
TNT	$C_7H_5N_3O_6$	227.13	60.76	−73.96	−59.30	1.65	18.56	6839.96	46.79
RDX	$C_3H_6N_6O_6$	222.12	81.06	−21.61	70.30	1.80	34.01	8858.00	26.14
HMX	$C_4H_8N_8O_8$	296.16	81.06	−21.61	74.80	1.91	38.44	9285.00	27.58
CL-20	$C_6H_6N_{12}O_{12}$	438.18	82.17	−10.95	397.80	2.04	46.70	9455.00	9.25
ONC	$C_8N_8O_{16}$	464.13	79.29	0.0	604.20	2.06	46.60	9864.00	2.86

[a] Molecular formula. [b] Formula weight. [c] N + O contents in %. [d] CO_2 based oxygen balance. [e] Calculated solid-phase standard enthalpy of formation. [f] Density calculated using the correlation of $\rho = 1.0330\,(M/V) + 0.001836\,(\sigma_{tot}^2\nu) - (\nu/6)$.[18.] [g] Detonation pressure calculated using EXPLO5 V 7.01. [h] Detonation velocity calculated using EXPLO5 V 7.01. [i] h_{50} [cm] is the height from where 50% probability of the dropped materials resulted in an explosion calculated using equation S13. Then their corresponding impact energies h_{50}[J] were calculated using a correlation h_{50}[J] = mgh, where, m = 2.5 kg hammer weight, g = 9.81 m/s, and h = h_{50} [cm] values.

tives of 9-AHC by introducing the most promising explosophoric groups, as listed in Fig. 2.

Interestingly, derivatives **AHC-14** and **AHC-20** have vast potentials to generate energetic salts **AHC-22–23**, and that could be the future generation green solid propellants, explosives, and oxidizers (Scheme 4).
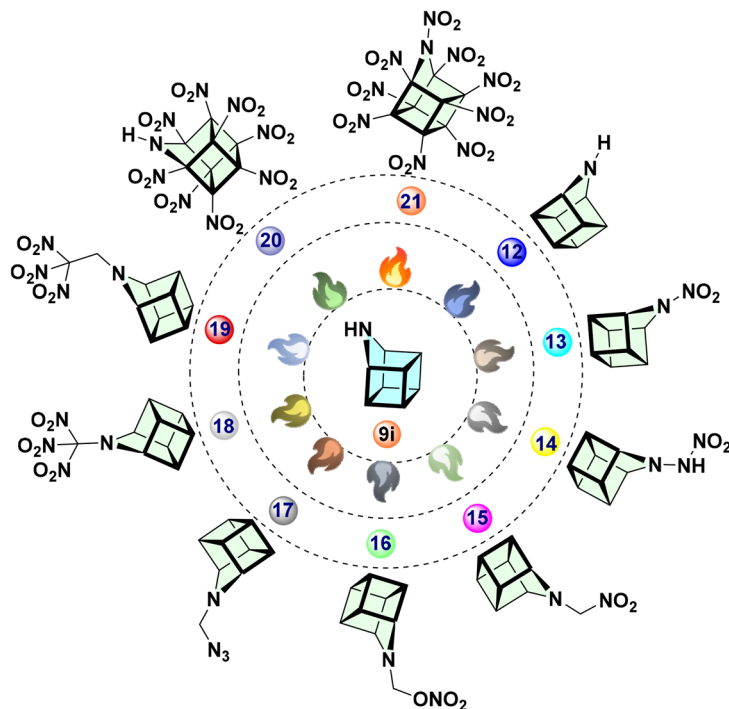
The computationally based design and studies of new high energy density materials (HEDMs) reveals the potential of new materials as an explosive and propellent in military and space industry applications. Thus, the efficiency of potential explosives can be measured in terms of their detonation performance (P and D), an oxidizer can be identified based on the combination of available oxygen for combustion, which is typically quantified in terms of oxygen balance (OB%) and specific impulse (Isp). High specific impulse (Isp) and density specific impulse (Isp) of a material, suggest their potential use as a propellant. In the present study, we evaluated all materials as solid materials, and their explosive and propulsive performances were calculated with different propellant formulations

with hydroxylterminated polybutadiene (HTPB, a novel energetic binder), ammonium perchlorate (AP, oxidizer), and aluminium (Al, fuel supplement). Subsequently, their performance was compared with well-known energetic materials as listed in Tables 1 and 2.

Newly designed azahomocubanes **AHC-12–21** possess high calculated densities (ρ = 1.33 g cm⁻³ to 2.14 g cm⁻³), associated with significantly positive solid-phase enthalpy of formation (ΔH_f° (s) = 289.82 kJ mol⁻¹ to 728.41 kJ mol⁻¹), those are comparable to top performing energetic materials as listed in Table 1, which establish them as viable candidatesin the field of energetic materials. Compounds **AHC-20–21** have high positive oxygen balances (**AHC-20**, OB% = 25.04 and **AHC-21**, OB% = 30.53) comparable to well-known oxidizers such as ammonium dinitramide (ADN, OB% = 25.80), ammonium perchlorate (AP, OB% = 27.23), 2,2,2-tetranitroacetimidic acid (TNAA, OB% = 30.12).
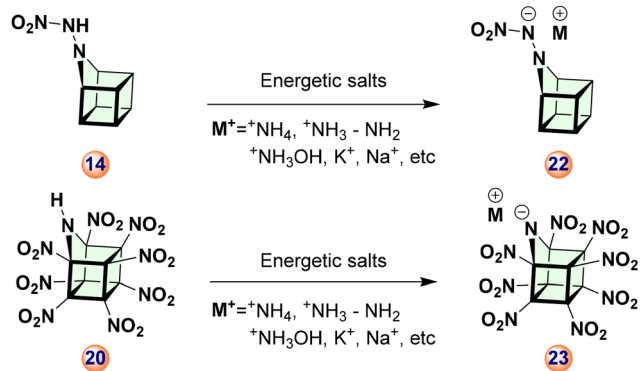
The detonation performance of azahomocubane was calculated using EXPLO5 V7.01 software as listed in Table 1.

9-Azapentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonane (**12**). 9-Nitro-9-azapentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonane (**13**). 9-Azapentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonan-9-yl)nitramide (**14**). N-9-(Nitromethyl)-9-azapentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]-nonane (**15**). 9-Azapentacyclo-[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonan-9-yl)methyl nitrate (**16**). 9-(Azidomethyl)-9-azapenta-cyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonane (**17**). 9-(Trinitromethyl)-9-azapentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonane (**18**). 9-(2,2,2-Trinitroethyl)-9-azapentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]-nonane (**19**).1,2,3,4,5,6,7,8-Octanitro-9-azapentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonane (**20**). 1,2,3,4,5,6,7,8,9-Nonanitro-9-azapentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonane (**21**).

Fig. 2 Azahomocubane (AHC) derivatives studied in the present work.

Scheme 4 Future aspect of current work.

Compounds **AHC-12–19** have an average detonation perform-ance (P = 12.52 GPa to 21.40 GPa; D = 5670 m s^{-1} to 7254 m s^{-1}) and which are comparable to cubane (P = 12.70 GPa; D = 5990 m s^{-1}), and TNT (P = 18.56 GPa; D = 6839 m s^{-1}). On the other hand, compound **AHC-20–21** have detonation properties (**AHC-20**, P = 44.46 GPa, D = 9706 m s^{-1}; **AHC-21**, P =

45.64 GPa, D = 9708 m s^{-1}) which are better than those of top performing primary explosives RDX and HMX and comparable to ONC and CL-20.

The propulsive performance of azahomocubanes were pre-dicted using EXPLO5 V7.01 software at five different propellent formulations and was examined (i) as a neat compound; (ii) at the ratio of 88 : 12 (azahomocubanes : Al); (iii) at the ratio of 78 : 12 : 10 (azahomocubanes : Al : HTPB); (iv) at the ratio of 20 : 80 (azahomocubanes : AP); and (v) at the ratio of 80 : 20 (azahomocubanes : HTPB) listed in Table 2 and Fig. 3. This indicates that the specific impulse (Isp, s) and density specific impulse (ρIsp, g cm^{-3} s) of compounds **AHC-20** and **AHC-21** are significantly higher than TNT, RDX and AP. On the other hand, most of the compounds possess high characteristic vel-ocity, making them promising candidates for solid rocket pro-pulsion. Interestingly, compounds **AHC-13** and **AHC-14** at the ratio of 88 : 12 (azahomocubanes : Al) exhibit optimal specific impulse (**AHC-13**, Isp = 268 s; **AHC-14**, Isp = 270 s), revealing the best combination of strain (azahomocubanes core) and energy (–N–NO$_2$ and –N–NH–NO$_2$).

As for the kinetic stability, the energy gaps between HOMO and LUMO were estimated and are in the order of CB >

Table 2 Comparison of physicochemical properties of compounds AHC-12–21

Compound	$\Delta E^{a,i}$ [HOMO–LUMO]	Isp^{b,i} [s]	ρIsp^{c,i} [s]	C*^{d,i} [m s^{-1}]	Isp^{e,i} [s]	Isp^{f,i} [s]	Isp^{g,i} [s]	Isp^{h,i} [s]
AHC-12	6.080	167.55	223.52	990.40	178.30	173.79	246.08	158.48
AHC-13	5.825	202.64	311.66	1226.70	267.98	248.30	258.38	185.10
AHC-14	5.446	207.17	318.63	1257.60	270.04	253.04	258.98	188.72
AHC-15	4.733	191.82	283.52	1155.60	242.20	226.34	256.28	177.16
AHC-16	4.869	199.36	301.63	1208.50	223.30	227.87	257.79	182.92
AHC-17	5.372	194.68	273.53	1166.10	203.03	195.66	255.71	179.49
AHC-18	4.326	227.86	390.78	1415.80	240.91	232.06	243.45	201.99
AHC-19	3.432	219.73	365.41	1358.50	236.95	229.91	247.79	196.94
AHC-20	5.183	263.02	548.40	1563.40	266.40	267.44	194.66	232.91
AHC-21	5.331	256.49	549.40	1525.40	261.51	273.27	189.49	237.40
Cubane	7.046	114.30	147.45	667.40	105.44	106.87	231.53	108.99
TNT	4.926	206.49	341.54	1283.5	232.00	225.11	186.98	200.55
RDX	5.991	266.91	480.45	1648.00	276.68	274.08	254.06	234.12
AP	—	156.63	306.15	977.00	232.00	262.11	156.63	227.37

^{a} Energy difference between HOMO and LUMO orbitals in eV. ^{b} Isp = specific impulse of neat compound (monopropellant). ^{c} ρIsp = density specific impulse of neat compound (monopropellant). ^{d} Characteristic velocity. ^{e} Isp = specific impulse at 88% compound and 12% Al. ^{f} Isp = specific impulse at 78% compound, 12% Al (fuel additive) and 10% binder (HTPB). ^{g} Isp = specific impulse at 20% compound and 80% AP. ^{h} Isp = specific impulse at 80% compound and 20% HTPB. ^{i} Specific impulse calculated at an isobaric pressure of 70 bar and initial temperature of 3300 K using EXPLO5 V 7.01.
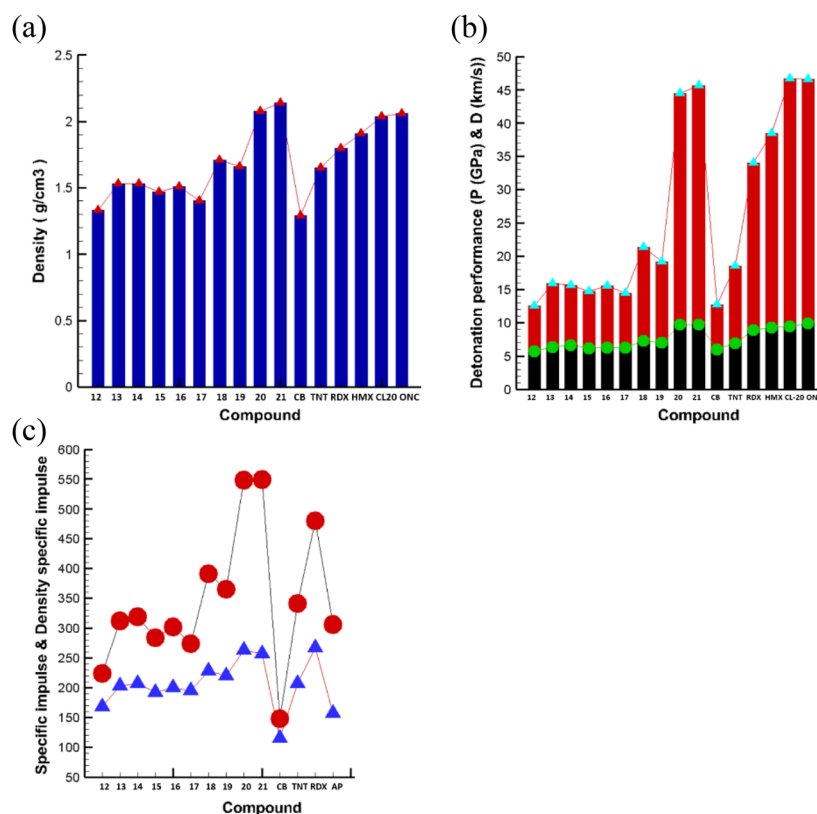

Fig. 3 Comparison of physicochemical properties. (a) Densities (b) Detonation properties. (c) Propulsive properties.

AHC-12 > RDX > **AHC-13** > **AHC-14** > **AHC-17** > **AHC-21** > **AHC-20** > TNT > **AHC-16** > **AHC-15** > **AHC-18** > **AHC-19**, as listed in Table 2. Interestingly, the impact sensitivity of **20** and **21** is significantly higher (h_{50} (cm) = 6.96 and 6.98 respectively) compared to the impact sensitivity of RDX (26.14), HMX

(27.58) and lower than that of ONC (2.86), making them promising primary explosive.

Additional analysis of stabilities of title compounds were evaluated with the help of electrostatic potential (ESP) measurements as shown in Fig. 4 and Fig. S14–S23.‡
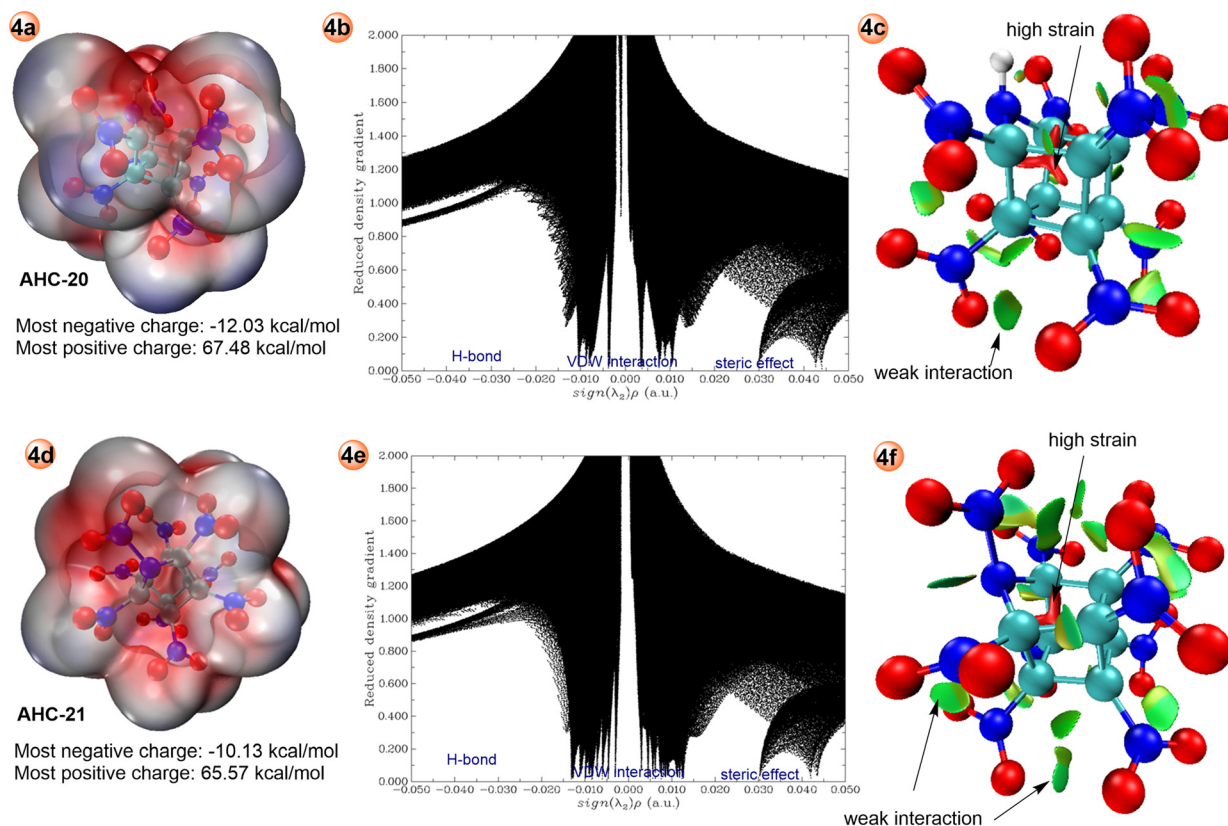
Fig. 4 Computed electrostatic potential (ESP) maps of **AHC-20** (**4a**) and **AHC-21** (**4d**). scatter diagram of **AHC-20** (**4b**) and **AHC-21** (**4e**). Reduced density gradient (RDG) of **AHC-20** (**4c**) and **AHC-21** (**4f**) calculated at B3LYP/6-311++G(d,p) level.

Compounds **20** and **21** have comparable ESP maxima ($+67.48$ kcal mol^{-1} and $+65.57$ kcal mol^{-1}, respectively) and global ESP minima (-12.03 kcal mol^{-1} and -10.13 kcal mol^{-1}, respectively) to CL-20 ($+66.61$ kcal mol^{-1} and -15.74 kcal mol^{-1}). For RDX ($+50.01$ kcal mol^{-1} and -20.81 kcal mol^{-1}), and HMX ($+53.74$ kcal mol^{-1} and -24.80 kcal mol^{-1}) see Fig. S3.‡ Furthermore, using scatter diagram and reduced density gradient (RDG), the high strain in the core structure and weak interaction between the substituents can be explained as shown in the Fig. 4b, 4c, 4d, 4e and Fig. S14–S23.‡

Conclusions

This study identified azahomocubanes as a new class of potential propellants and oxidizers. The densities were predicted to be 2.08 g cm^{-3} to 2.14 g cm^{-3} for compound **AHC-20** and **AHC-21**, respectively, which are significantly higher than those of top energetic materials. In addition, the title compounds exhibit superior detonation performances with good propulsive performances and higher sensitivities than RDX, HMX, and CL-20, which suggests that **AHC-20** and **AHC-21** have a potential comparable to RDX, HMX and CL-20 for civil and military applications. Additionally, these azahomocubanes demonstrate significant potential as solid propellants in the form of their energetic salts **22** and **23**.

Author contributions

S. L. investigation, methodology, conceptualization and manuscript writing. H. G. manuscript writing – review and editing. J. M. S. conceptualization, manuscript writing – review and editing, supervision.

Data availability

All data relevant to the work described here are available in the ESI‡ or from the current literature.

Conflicts of interest

The authors declare no competing financial interests.

Acknowledgements

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