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Research paper

Ammonium Dodecahydrododecaborate $(NH_4)_2[B_{12}H_{12}]$: Hydrogen and Boron Rich Fuel for Jet Propulsion Engines

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Abstract: There is dire need for the exploration of boron (B) substitution in jet propulsion engines for improving their combustion characteristics. In this regard, ammonium dodecahydrododecaborate $(NH_4)_2[B_{12}H_{12}]$ has been synthesized, characterized and evaluated for its propulsion characteristics. This hydrogen and boron-rich entity was found to be a potential candidate for future applications in propulsion technology.

Keywords: jet propulsion, boranes, boron, combustion, specific impulse

Supporting Information

Chemical, thermal and spectroscopic analysis of ammonium dodecahydrododecaborate (ADDB) have been provided in supporting information (SI). CEA details have also been provided in SI.

Abbreviations

ADDB	Ammonium dodecahydrododecaborate, $(NH_4)_2[B_{12}H_{12}]$
CEA	Chemical equilibrium analysis
JP-10	Jet Propellant-10 (mixture of endo-tetrahydrodicyclopentadiene, exo-tetrahydrodicyclopentadiene and adamantane)
HTPB	Hydroxyl-terminated polybutadiene
I_{sp}	Specific impulse
TEDDB	Triethylammonium dodecahydrododecaborate, $((C_2H_5)_3NH)_2[B_{12}H_{12}]$

1 Introduction

Hydrogen is a prominent fuel for air-breathing propulsion systems due to it possessing a wide flammability range, a low ignition delay and the highest gravimetric energy density (~140 MJ/kg) [1]. However, issues related to its low density, high flammability and handling aspects limit its application in ground and space systems [2]. Because of this, aviation systems are operated on hydrocarbon-based fuels with limited energy output. On the other hand, high energy-density fuels such as boron (B), aluminum (Al), magnesium (Mg), *etc.* are being extensively researched worldwide as they are essential requirements for aviation, defence and space programmes [3]. The application of energetic metals is one of the ways being attempted to realize higher density and energy output in ramjet, scramjet and turbo jet system [4]. The incorporation of metals also provides additional advantages, such as low air-to-fuel mass flow ratios, excellent thermal characteristics, better storage properties, *etc*. In these respects, B has emerged to be a promising candidate due to it possessing a high energy (58.8 MJ/kg) and delivering about 40 to 50% more energy than hydrocarbons [5]. Moreover, the higher density of B, three times that of conventional liquid fuels, overcomes the constraint of volume in air-breathing propulsion systems. With this background, B-based slurries and gel based propellant systems have attracted researchers aiming to improve the overall performance. The theoretical performance of air-breathing propulsion systems comprising B as an additive was recorded to be the highest among the other metals [4]. B-rich fuel has been reported to exhibit an impressive average theoretical specific impulse of 2190 s [6]. Xio *et al.* [7] highlighted the dual application of a B-containing gel propellant for ramjets as ideal power units for missiles and other aircraft. In spite of the energetic potential, the application of B in propellants is limited due to its incomplete combustion, the formation of an oxide layer during storage and difficulty in obtaining

different particle sizes. Combustion improvisation was attempted through the decoration of B with Mg and Al, ligatures of B, fluorinated compounds, metal halides and oxides. Overall, the objective was to provide the initial energy for promoting the melting and vaporization of the boron oxide layer and improving B ignition. However, the preparative methods for such additives involve wet chemistry, milling, sintering, blending, *etc.*, and pose the inherent limitations of contamination, in-homogeneity and diversified distribution of particle size [8]. On the other hand, the application of boranes was also explored to realize the energetic advantage of B particles through the early ignition of salts as well as achieving its complete combustion.

Ammonia borane appeared as a hydrogen source for propulsion and fuel cells [9]. However, its application is limited in conventional HTPB-based composite propellants due to compatibility issues with isocyanates which are used to cross-link the prepolymer. The United States and Soviet Union believed pentaborane (B_5H_9) and decaborane ($B_{10}H_{14}$) were the most powerful rocket fuels and invested heavily in the research and development of these materials [10]. Meanwhile, the dodecahydro-closo-dodecaborate anion ($[B_{12}H_{12}]^{2-}$) took a central place in boranes due to its regular icosahedron structure as the incarnation of highest simplicity and symmetry. As a result, this anion is found to be extremely rich in B and hydrogen and also has the inherent ability of B to form self-bonded complex molecular networks. Hence, researchers have focused attention on this anion for the realization of various salts essentially required in the fields of fuel cells, propulsion and pharmaceuticals [10], particularly in the propulsion field where it is required to be as energetic as B. The existing salts of $[B_{12}H_{12}]^{2-}$ comprise bulky carbonaceous cations [11], which are usually avoided in jet propulsion due to unwanted combustion characteristics. Hence, there is a dire need to explore combustion friendly salts of $[B_{12}H_{12}]^{2-}$ for application in jet propulsion. With this in mind, the present study proceeded to fill a gap in propulsion technology. In the field of energetic materials, nitrogen rich derivatives have special considerations due to delivery of:

– low molecular weight gaseous products,
– higher kinetic energy,
– more thrust in the rocket, and
– huge amounts of eco-friendly nitrogen gas in the burning process.

Hence, we intended to synthesize nitrogen- as well as hydrogen-rich boranes and to evaluate their potential from the applications point of view. In the present study, the ammonium cation has been selected because it exhibits a higher volumetric hydrogen density (130.18 g H_2/L) [12] and faster combustion kinetics.

2 Test Methods and Materials

2.1 Test methods

Elemental analysis was carried on a VarioMICRO instrument (Elementar Analysensysteme GmbH, Germany).

Differential Scanning Calorimetry (DSC), and Thermo-Gravimetric (TGA) analysis of ADDB were performed on a PerkinElmer thermal analyzer (STA 6000) under a nitrogen atmosphere at 10 C/min heating rate.

Fourier transform infrared spectra (FTIR) were recorded on a Nicolet iS50 FTIR Spectrometer from Thermo Fisher Scientific.

The theoretical rocket performance, assuming equilibrium composition during expansion from an infinite area combustor, was computed using the NASA-GLENN Chemical Equilibrium Program (CEA2) [13].

Combustion of ammonium dodecahydrododecaborate (ADDB) and triethylammonium dodecahydrododecaborate (TEDDB) was carried out using the T-Jump method and the phenomenon was captured using a high-speed camera. Combustion phenomena were captured at 50 frames per second using a Sony camera. Embedded pellets of ADDB and TEDDB in Ni-Cr wire were made of 6×6 mm size and ignited through the supply of a DC current of about 1.5 to 2 A.

2.2 Synthesis of ADDB

A simplified synthesis route for ADDB has been established using aqueous ammonia, and TEDDB, delivering 90% yield. The route is completely different from that reported in [14]. Initially, TEDDB was synthesized in-house according to the literature procedure [11] exhibiting a purity greater than 98%. The dropwise addition of ammonia solution (30% w/v) to TEDDB was performed over 30 min with constant stirring. The reaction was carried out in solid-liquid form. It was noticed that the addition of ammonia solution provided sufficient slurry form to ensure mixing of the reagents. The complete solubility of TEDDB was noticed during addition of the ammonia solution which provided a liquid-liquid reaction regime. Post addition, the reaction mixture was stirred for a further 30 min under constant agitation and ambient conditions, and offered a better yield of ADDB. The synthesis was carried out in a reaction vessel made from polypropylene. The agitator was also coated with polypropylene to avoid etching due to dodecaborates. The precipitated product from the reaction mixture was filtered off and recrystallized from acetone (7% w/v) through the evaporative crystallization method.

3 Results and Discussion

3.1 Characterization details

The crystallized reaction product was characterized by thermal and spectroscopic methods. The results of this characterization are provided in the Supporting Information (SI). The thermal profile revealed decomposition of ADDB at 310 °C, in line with literature data provided by Ivanov *et al.* [15]. It was observed that a positive mass deviation occurred due to the formation of boric oxide; the formation of which adds weight in the DTA. Similar observations were also reported by various researchers [16]. On the other hand, strong peaks at:

– 3231 cm^{-1} (NH_4^+),
– 2468 cm^{-1} (B–H),
– 1401 cm^{-1} (N–H), and
– 1070 cm^{-1} (B–B),

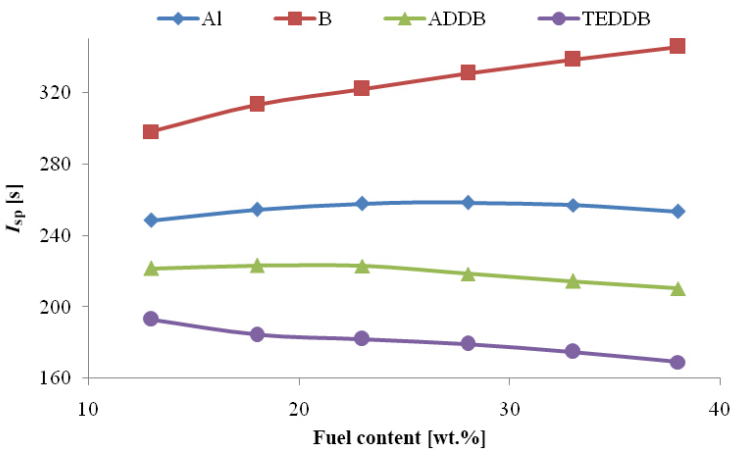
in FTIR analysis confirmed the functional groups of ADDB, supporting the formation of ADDB using the new synthesis route.

In view of the possible applications, ADDB was characterized for friction and impact sensitivity using OZM Research BAM friction (STANAG-4487) and BAM fall hammer (STANAG-4489) instruments, which revealed that ADDB is highly insensitive towards friction (>360 N) and impact (>30 J). The heat of combustion of ADDB was found to be 54.81 MJ/kg (measured in a bomb calorimeter Parr 6200), which is very close to the heat of combustion of B [17]. The heat of formation of ADDB was computed to be –668.47 kJ/mol from the heat of combustion. Thus, these characteristics are found to be much desired and impressive for applications in jet propulsion.

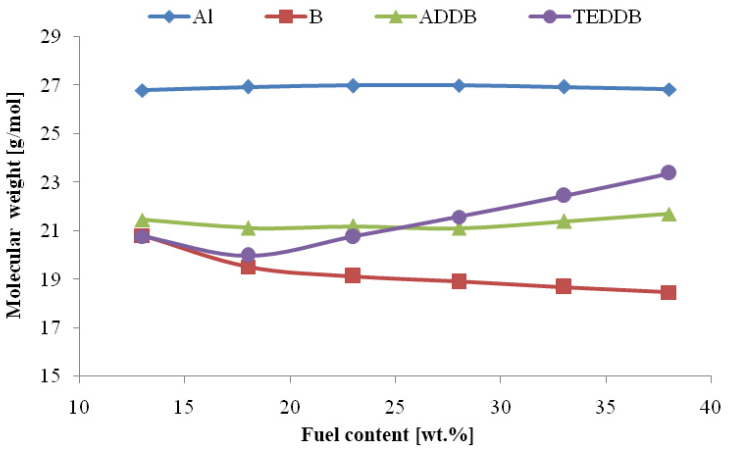
3.2 Propulsion characteristics evaluation

Thermo-chemical evaluations of ADDB in solid and liquid propellant systems were carried out using the Chemical Equilibrium Program CEA2 [13]. For the solid propellant composition, hydroxyl-terminated polybutadiene (HTPB) content was held constant at 12%, as per conventional compositions, while ADDB and ammonium perchlorate (NH_4ClO_4) were balanced accordingly. On the other hand, for the liquid propulsion composition, this was based on JP-10, about 40%, 10% ADDB and with the remainder being air. Calculation details are provided in SI. Figure 1 shows the outcome of CEA for solid propellant compositions for various solid fuels. The specific impulse (I_{sp}) of the compositions was found to be higher for B as a fuel for all compositions compared to the others (Figure 1(a)). However, B actually delivers a lower I_{sp} than expected due to incomplete and delayed combustion [18]. This suggests further exploration of B substituted and/or

derived materials in jet fuel. On the other hand, ADDB has shown comparable propulsion characteristics. The advantage of lower molecular weight gases from ADDB compositions compared to Al-based compositions (Figure 1(b)) makes it a more favorable candidate for application in jet propulsion. Moreover, the higher nitrogen content in the combustion products offers dual benefits in terms of energy output and environmentally benign aspects over other compositions. Figure 1 also highlights the preference for ADDB over Al- and TEDDB-based compositions.



(a)



(b)

Figure 1. CEA of various fuels for specific impulse (a) and molecular weight of the combustion products from the solid propellants (b)

The performance of ADDB in liquid propellants was also evaluated by consideration of JP-10 as a fuel. Figure 2 highlights that ADDB based JP-10 compositions provide the lowest molecular weight combustion products without compromising the flame temperature. The outcome is tabulated and provide in SI (see Table S1). This resulted in delivering a higher I_{sp} as this is proportional to the square root of the flame temperature divided by the molecular weight of the combustion products. Thus, these characteristics of ADDB are highly desirable as well as appropriate for propulsion technology in view of improving the performance characteristics.

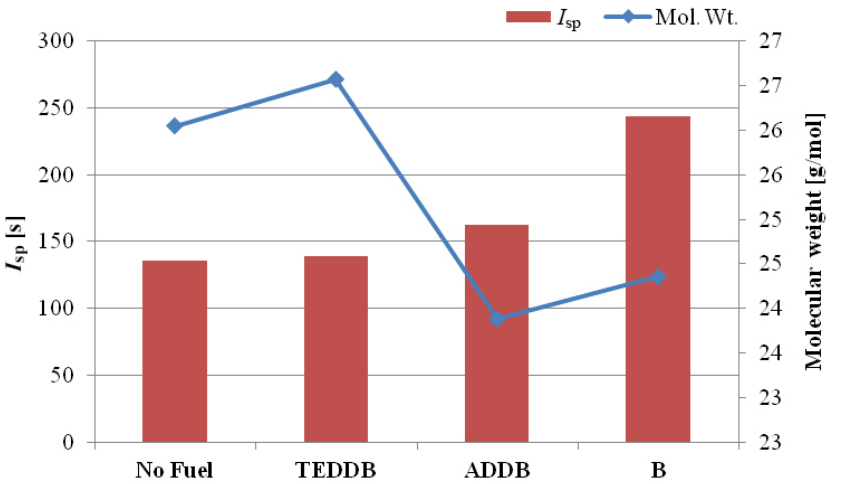


Figure 2. CEA analysis of various fuels in JP-10

3.3 Combustion profile mapping and analysis

In propulsion technology, an appropriate combustion pattern and desired outcome have paramount importance. The performance characteristics of propulsion are solely dependent on combustion phenomena. Combustion frames were captured at fixed intervals and analyzed for their nature. Figure 3(a) shows that TEDDB combustion starts with the formation of a vapour cloud around it. Thus, the inward direction of combustion of TEDDB results in incomplete combustion at the core and leads to a large residue being formed. The residue was observed for TEDDB due to its carbon content, which formed soot after combustion. This effect provides a signature during combustion. These are not desirable characteristics of combustion in propulsion technology.

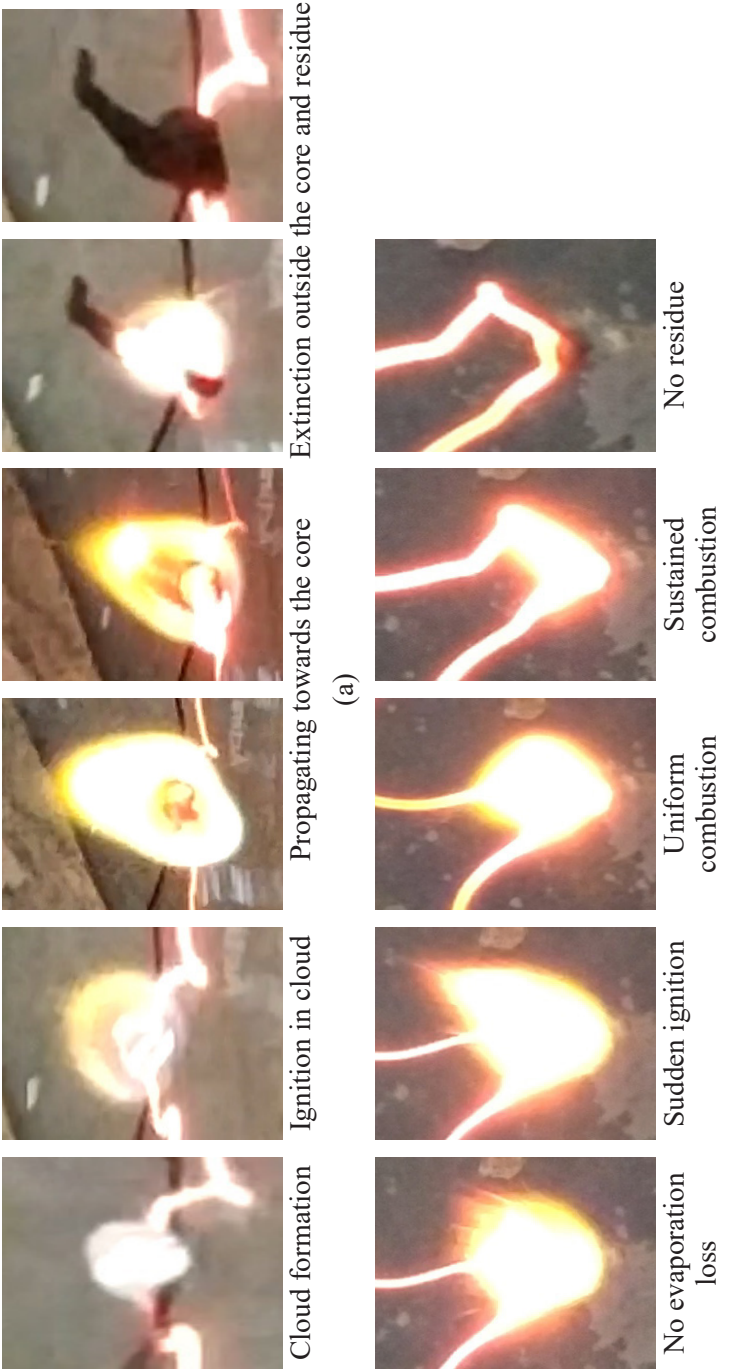


Figure 3. Combustion steps of TEDDB (a) and ADDB (b)

On the other hand, ADDB combustion was found to be instantaneous and uniform (Figure 3(b)). Moreover, it also resulted in a residue-free combustion mechanism, which indicated the early and complete combustion of B. Uniform and sustained combustion of ADDB was observed which led to highly promising sequential decomposition reactions:

$$(NH_4)_2B_{12}H_{12} \rightarrow 2BN + 0.5B_{20}H_{16} + 6H_2 \rightarrow 2BN + 10B + 10H_2$$

and formation of boron nitride (BN) as highlighted by Sun *et al.* [19]. Moreover, the formation of BN would improve the combustion kinetics, possibly through seeding or an alloy catalytic affect. Thus, the impressive characteristics of ADDB were revealed in the present study and indicted its potential and much needed application in present and future propulsion technology.

4 Conclusions

- ADDB offers huge benefits, such as higher hydrogen content, specific impulse, lower molecular weight combustion products, a favorable combustion sequence, a comparable combustion temperature, tailor-made particle size and easy synthesis. This will definitely overcome some of the issues regarding the application of B in propellants. With this, ADDB appears to be one of the promising candidates for future jet propulsion systems.

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References

[1] Møller, K.T.; Jensen, T.R.; Akiba, E.; Li, H.-w. Hydrogen – A Sustainable Energy Carrier. *Prog. Nat. Sci.: Mater. Int.* **2017**, *27*(1): 34-40.

[2] Choubey, G.; Yuvarajan, D.; Huang, W.; Yan, L.; Babazadeh, H.; Pandey, K.M. Hydrogen Fuel in Scramjet Engines – A Brief Review. *Int. J. Hydrogen Energy* **2020**, *45*(33): 16799-16815.

[3] Agrawal, J.P. Recent Trends in High-Energy Materials. *Prog. Energy Combust. Sci.* **1998**, *24*(1): 1-30.

[4] Goroshin, S.; Higgins, A.; Kamel, M. Powdered Metals as Fuel for Hypersonic Ramjets. *37th Joint Propulsion Conference and Exhibit*, Salt Lake City, US, **2001**.

[5] Liu, L.-L.; He, G.-Q.; Wang, Y.-H.; Hu, S.-Q. Ignition and Combustion Performance

of the Primary Condensed-phase Combustion Products from Boron-based Fuel-rich Propellants. *Cent. Eur. J. Energ. Mater.* **2017**, *14*(2): 448-460.

[6] Haddad, A.; Natan, B.; Arieli, R. The Performance of a Boron-loaded Gel-fuel Ramjet. In: *Progress in Propulsion Physics.* Vol. 2, European Conference for AeroSpace Sciences (EUCASS), **2011**, pp. 499-518.

[7] Xiao, Y.-L.; Xia, Z.; Huang, L.Y.; Ma, L.K.; Yang, D.L. Numerical Simulation of the Flowfield in a Boron-Based Slurry Fuel Ramjet. *Combust. Explos. Shock Waves* **2019**, *55*(3): 361-371.

[8] Ojha, P.K.; Karmakar, S. Combustion Characteristics of Jet A-1 Droplet Loaded with Aluminum/Magnesium-Decorated Boron Particles. *Int. J. Energ. Mater. Chem. Propul.* **2020**, *19*(3): 253-274.

[9] Lee, J.G.; Weismiller, M.; Connell, T.L.; Risha, G.A.; Yetter, R.A.; Gilbert, P.D.; Son, S.F. Ammonia Borane-based Propellants. *44th AIAA/ASME/SAE/ASEE Joint Propulsion Conference and Exhibit*, Hartford, US, **2008**.

[10] Sivaev, I.B.; Bregadze, V.I.; Sjöberg, S. Chemistry of Closo-dodecaborate Anion $[B_{12}H_{12}]^{2-}$: A Review. *Collect. Czech. Chem. Commun.* **2002**, *67*(6): 679-727.

[11] Geis, V.; Guttsche, K.; Knapp, C.; Scherer, H., Uzun, R. Synthesis and Characterization of Synthetically Useful Salts of the Weakly-coordinating Dianion $[B_{12}Cl_{12}]^{2-}$. *Dalton Trans.* **2009**, *15*: 2687-2694.

[12] Kiruthika, S.; Fjellvåg, H.; Ravindran, P. Amphoteric Behavior of Hydrogen (H^{+1} and H^{-1}) in Complex Hydrides from van der Waals Interaction – Including *Ab Initio* Calculations. *J. Mater. Chem. A* **2019**, *7*(11): 6228-6240.

[13] McBride, B.; Gordon, G. *Chemical Equilibrium Program CEA2: NASA Glenn Research Center, Cleveland, OH; 2004.* Report NASA RP-1311, Part I, **1994**.

[14] Yisgedu, T.B.; Huang, Z.; Chen, X.; Lingam, H.K.; King, G.; Hingley, A.; Zhao, J.C. The Structural Characterization of $(NH_4)_2B_{10}H_{10}$ and Thermal Decomposition Studies of $(NH_4)_2B_{10}H_{10}$ and $(NH_4)_2B_{12}H_{12}$. *Int. J. Hydrogen Energy* **2012**, *37*(5): 4267-4273.

[15] Ivanov, S.V.; Miller, S.M.; Anderson, O.P.; Solntsev, K.A.; Strauss, S.H. Synthesis and Stability of Reactive Salts of Dodecafluoro-closo-dodecaborate(2−). *J. Am. Chem. Soc.* **2003**, *125*(16): 4694-4695.

[16] Jain, A.; Joseph, K.; Anthonysamy, S.; Gupta, G.S. Kinetics of Oxidation of Boron Powder. *Thermochim. Acta* **2011**, *514*(1-2): 67-73.

[17] Clark, J.D. *Ignition!: An Informal History of Liquid Rocket Propellants*. Rutgers University Press, New Brunswick, **1972**; ISBN 0-8135-0725-1.

[18] Kadosh, H.; Natan, B. Internal Ballistics of a Boron-Containing Solid Fuel Ramjet. *Combust. Sci. Technol.* **2020**, *93*(15): 2672-2691.

[19] Sun, W.Q.; Wolverton, C.; Akbarzadeh, A.R.; Ozolins, V. First-principles Prediction of High-capacity, Thermodynamically Reversible Hydrogen Storage Reactions based on $(NH_4)_2B_{12}H_{12}$. *Phys. Rev. B* **2011**, *83*(6) paper 064112.

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