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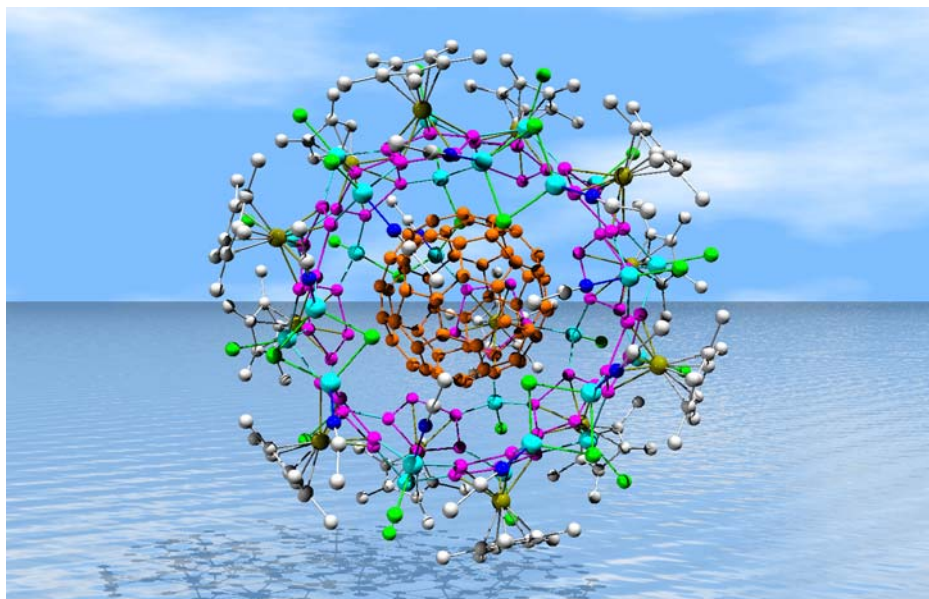
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Can the hexamethylhydrazinium dication [Me₃N–NMe₃]²⁺ be prepared?†‡

Yun Zhang and Christopher A. Reed*

The long sought hexamethylhydrazinium(2+) dication, Me₃N–NMe₃²⁺, calculationally unstable towards "coulombic explosion" because of formal positive charges on adjacent N atoms, can be synthesized and isolated as a CHB₁₁Cl₁₁⁻ carborane salt.
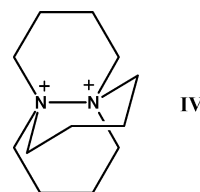
This paper concerns the stability of the hexamethylhydrazinium(2+) ion **I**.

H₃C–N⁺(CH₃)₂–N⁺(CH₃)₂–CH₃
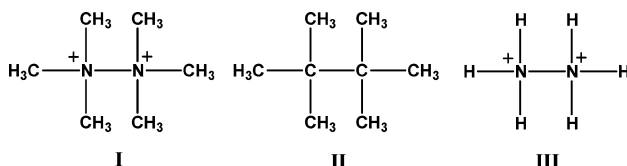
Is the N–N bond in **I** stable like the isoelectronic C–C bond in the ethane core of **II** or do the contiguous positive charges render it unstable to a "coulombic explosion"? How might it be prepared?

Intriguing calculations on this subject were published by Radom and co-workers in the late 1980s.[1] The all-proton analogue of **I**, namely the hydrazinium(2+) ion **III**, is thermodynamically unstable with respect to homolytic N–N bond dissociation ($\Delta H = -66$ kJ mol⁻¹) but is believed to be kinetically stable due to a high activation barrier towards homolytic fission (168 kJ mol⁻¹). This value is more than adequate for stability at room temperature. In fact, many stable salts of **III** are known[2] but due to extensive H-bonding of the N⁺–H groups with counterions or solvent, the full buildup of positive charge on the dication must be significantly compromised. Thus, the calculated metastability of the H₃N–NH₃²⁺ dication has not been fully tested. In the hexamethylated analogue, the dipositive charge is screened from the surrounding environment by methyl groups and arguably presents a better test of the stability of the N–N bond with respect to coulombic dissociation.

Hexaalkyl dications analogous to **I** have been characterized in tricyclic propellane-like structures by Alder and co-workers.[3] For example, compound **IV** is stable at room temperature in acetonitrile solution and has been characterized by X-ray crystallography as a bis-triflate salt.

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The extent to which the tricyclic scaffolding holds the N–N bond intact and contributes entropically to its stability is difficult to gauge but clearly a structural comparison to the untethered nitrogen centers in **I** would be informative.

The challenge of isolating acyclic dications with adjacent positive charges has been more easily met with the heavier elements.[2] Thus, the phosphorus analogue of the hexamethylhydrazinium(+2) ion, namely Me₃P–PMe₃²⁺ **V**, has recently been reported.[4] It joins examples of acyclic disulfonium ions, R₂S–SR₂²⁺ **VI**.[2]
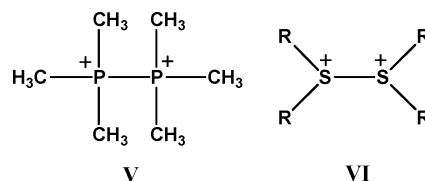
Dications **V** and **VI** are accessible *via* alkylation reactions with methyl triflate. However, methyl triflate only *mono*alkylates acyclic hydrazines, forming monocations **VII**.
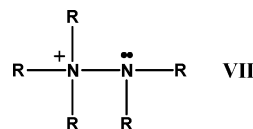
The proximity of the positive charge on the R₃N⁺ moiety to the N atom on the NR₂ moiety apparently supresses the nucleophilicity of its lone pair.

The synthetic challenge of doubly methylating tetramethylhydrazine to produce dication **I** requires an electrophilic methylating agent much stronger than methyl triflate. These have recently become available in methyl carborane reagents, CH₃(CHB₁₁R₅X₆) (R = Me, Cl; X = Cl, Br),[5] which are capable of methylating a number of weakly basic molecules that are inert to methyl triflate (*e.g.* benzene,[5] phosphazenes[6] and phosphabenzenes[7]). They join carborane acids and trialkylsilyl carboranes as more potent sources of H⁺ and R₃Si⁺ electrophiles than their respective triflate counterparts[8] and are used in the present work to diprotonate and disilylate tetramethylhydrazine *en route* to dimethylation.

Tetramethylhydrazine, **1**, has a single ¹H NMR resonance at 2.25 ppm. Upon treatment with methyl triflate in dichloromethane solution, monomethylation to produce the monocation **2⁺** is indicated by the loss of symmetry which produces ¹H resonances

at 3.03 ppm (9H) and 2.44 (6H) ppm. Even in neat boiling methyl triflate there is no evidence for further reaction to produce the desired dimethylated dication 3^{2+}.
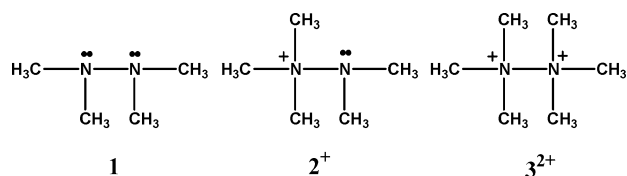
Treatment of **1** with two equivalents of the stronger methylating agent $CH_3(CHB_{11}Me_5Br_6)^5$ in dichloromethane at $< -40 °C$ also failed to produce any evidence for the dimethylated product. By ^1H NMR, only the monoalkylated product $2^+(CHB_{11}Me_5Br_6)^-$ was formed. Three factors may contribute to the failure to doubly alkylate. Firstly, the low temperature that must be used in this reaction will slow the rate of the second alkylation. Low temperature is necessary to prevent reaction of the methyl carborane reagent with the dichloromethane solvent; above $-40 °C$ we observe the formation of protonated tetramethylhydrazine products. Secondly, the monomethylated product precipitates out of solution and may therefore become inaccessible to double alkylation because of insolubility. Thirdly, the methylating power of the $CH_3(CHB_{11}Me_5Br_6)$ reagent may simply be insufficient.

A stronger methylating agent would be available with a less basic carborane anion such as $CHB_{11}Cl_{11}^-$. However, synthesizing $CH_3(CHB_{11}Cl_{11})$ is problematic. At dry ice temperatures it reacts with dichloromethane to create an undesirable protic environment and even reacts with hexane to produce CH_4 and the methyl-*cyclo*-pentyl carbocation.[9] This led us to a strategy of producing $CH_3(CHB_{11}Cl_{11})$ *in situ via* silylated **1**.

Treatment of tetramethylhydrazine **1** with 1 equivalent of $Et_3Si(CHB_{11}Cl_{11})$ in *o*-dichlorobenzene solution cleanly produced the expected monosilylated cation 4^+. The product was precipitated with hexane and characterized by ^1H NMR spectroscopy in liquid SO_2 at $-40 °C$. Two signals from the methyl groups appear at 4.42 (6H) and 4.03 (6H) indicating broken symmetry. Ethyl groups (15H) appear in the 2.2–2.4 range along with the 1H from the carborane at 4.62 ppm. When a second equivalent of $Et_3Si(CHB_{11}Cl_{11})$ was used, ^1H NMR spectroscopy indicated that disilylation had occurred to produce the disilylated dication 5^{2+}.
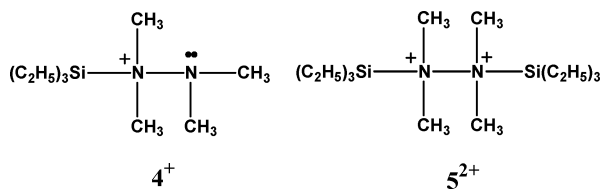

In liquid SO_2 solution, 5^{2+} was characterized by a single methyl group signal at 4.32 ppm (12H), ethyl group signals in the range 2.2–2.4 ppm (30H) and the carborane at 4.62 ppm (1H × 2).

When the disilylated dication 5^{2+} was treated with 2–3 equivalents of methyl triflate in *o*-dichlorobenzene, followed soon after by hexane, a white precipitate was formed. This product was sufficiently soluble in d_2-dichloromethane at $-40 °C$ for characterization by ^1H NMR spectroscopy. The conditions are a trade off between solubility and the low temperature required to maintain stability. The simplicity of the NMR spectrum indicates that the desired hexamethylhydrazinium dication 3^{2+} is formed. A

single methyl signal is seen at 2.91 ppm (18H) and the only other signal is that from the carborane anion at 3.29 ppm (1H × 2). The chemical shift is reasonable for formulation as 3^{2+}. The 2.91 ppm value is close to that for the Me_3N^+ group in monomethylated 2^+ (3.03 ppm) and downfield of the average of the methylated and unmethylated groups (2.74 ppm). Caution must be exercised in making comparisons to chemical shifts of the methyl groups in the disilylated cation 5^{2+} because data on this cation were gathered in SO_2 rather than dichloromethane. In our experience, peaks in SO_2 are frequently downfield shifted by at least 1 ppm relative to CD_2Cl_2, as illustrated by the carborane anion resonance at 3.29 ppm in dichloromethane *versus* 4.62 ppm in SO_2. Thus, the 2.91 ppm methyl group signal for 3^{2+} in dichloromethane is considered to correlate well with that at 4.32 ppm for 5^{2+} in SO_2.

We conclude that the target hexamethylhydrazinium dication 3^{2+} has been prepared and is stable at room temperature in the solid state as a $1:2$ $CHB_{11}Cl_{11}^-$ salt. Although it is soluble enough in dichloromethane at $-40 °C$ to obtain an ^1H NMR spectrum, low solubility and limited thermally stability in solution have thwarted attempts to obtain single crystals for X-ray analysis. Hexaalkylhydrazinium dications are strong Brønsted acids and decompose *via* α-H^+ dissociation followed by N–N bond cleavage to ammonium and iminium salts.[10] Consistent with this, the decomposition of **3** in dichloromethane produces an acidic solution from which crystallographically disordered mixtures of 3^{2+} and protonated hydrazines (probably $Me_3NNMe_2H^{2+}$) can be isolated. In lieu of good structural data on a pure 3^{2+} salt, we have investigated the purposeful protonation of **1** to characterize the $[HMe_2N–NMe_2H]^{2+}$ dication.

Just as treatment of the disilylated cation 5^{2+} with methyl triflate produces dimethylated 3^{2+}, so addition of 2–3 equivalents of triflic acid to 5^{2+} produces the diprotonated 6^{2+}.
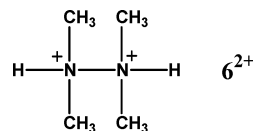
The salt $6^{2+}(CHB_{11}Cl_{11}^-)_2$ was quickly precipitated out of *o*-dichlorobenzene solution with hexane and characterized by ^1H NMR spectroscopy and by X-ray crystallography.

In CD_2Cl_2 at $-40 °C$, the ^1H NMR signal from the methyl groups in **6** appears as a singlet at 2.86 ppm. This is similar to (and distinguishable from) that in the all-methylated dication 3^{2+} at 2.91 ppm. The chemical shift difference is understandable in terms of a lower positive charge in 6^{2+} due to N^+-$H \cdots$ anion-H bonding in an ion pair (as seen in the crystal structure below). The N^+-$H \cdots$ anion-H bonding in **6** will be much stronger than the C-$H \cdots$ anion-H bonding in **3**. The acidic NH protons in 6^{2+} appear appropriately downfield at 9.14 ppm (2H) and the protons of the cation integrate correctly *versus* the carborane proton at 3.38 ppm (1H × 2).

Single crystals of $6^{2+}(CHB_{11}Cl_{11}^-) \cdot C_6H_4Cl_2$ were grown from *o*-dichlorobenzene–hexane and the X-ray structure is shown in Fig. 1.‡ The $[HMe_2N–NMe_2H]^{2+}$ cation 6^{2+} is ion-paired with the carborane anions *via* $NH \cdots Cl$ H-bonding. This is a feature common to carborane salts of highly acidic cations such as arenium ions[11] and alkyl carbocations ($CH \cdots Cl = 2.71$–2.85 Å).[9] The shortest $H \cdots Cl$ contact in $6^{2+}(CHB_{11}Cl_{11}^-) \cdot C_6H_4Cl_2$
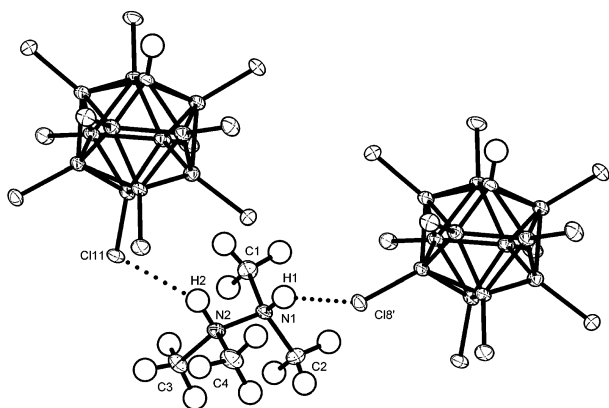
Fig. 1 X-Ray structure of diprotonated tetramethylhydrazine, $6^{2+}(CHB_{11}Cl_{11}^-)_2 \cdot C_6H_4Cl_2$. o-Dichlorobenzene is omitted for clarity. H-bonding is shown with dotted lines. Thermal ellipsoids are shown at the 50% probability level.

(H2′···Cl11) is 2.35 Å ($\angle$NHCl = 150°) reflecting stronger N–H H-bonding relative to C–H. Like neutral hydrazines, 6^{2+} adopts a *gauche* conformation. The N–N bond distance is 1.495(3) Å which is significantly shorter than that of the tricyclic all-alkylated **IV** at 1.532(6) Å but significantly longer than that in the all-protonated **III** (1.41–1.44 Å depending on the counterion).[2,12] This is consistent with a trend of increasing N–N bond length with increasing positive charge inasmuch as increasing the number of alkyl groups relative to H diminishes the ability of the dications to disperse charge *via* H-bonding with their surrounding anions. The DFT calculated N–N bond distance for 6^{2+} at the B3LYP/6-311+G(d,p) level *in vacuo* (1.521 Å) is somewhat longer than that measured experimentally in the presence of anions. Again, this is consistent with the trend of increasing N–N distance with increasing positive charge. The DFT calculated value for 3^{2+} at the same level is 1.594 Å, an increase of *ca.* 0.7 Å. Applying this calculated difference to the expected experimental difference between 3^{2+} and 6^{2+} leads to a predicted bond length in $3^{2+}(CHB_{11}Cl_{11}^-)$ of *ca.* 1.56 Å.

In conclusion, the electrophilic methylating power of the carborane reagent $CH_3(CHB_{11}Cl_{11})$ is sufficient to dimethylate tetramethylhydrazine and produce the long sought hexamethylhydrazinium dication 3^{2+}. It is sufficiently stable as a carborane salt that it can be characterized in solution by ^{1}H NMR spectroscopy at sub-ambient temperatures and isolated as a solid at room temperature. From X-ray data on closely related compounds it is predicted to have a relatively long N–N bond length (*ca.* 1.56 Å) resulting from maximal buildup of positive charge at adjacent hydrazinium N atoms. Thus, the hexamethylhydrazinium dication is, at the very least, metastable towards coulombic dissociation at room temperature, consistent with a high barrier to N–N bond homolysis.

Experimental

Air sensitive solids were handled in a Vacuum Atmospheres Corp. box (O_2, H_2O < 2 ppm) or Schlenk tubes with Teflon stopcocks. High purity solvents were dried over Na–K, P_2O_5, or CaH and distilled prior to use.

[(Et₃Si)₂Me₄N₂][CHB₁₁Cl₁₁]₂ 5

Freshly prepared $Et_3Si(CHB_{11}Cl_{11})$[11] (196 mg, 0.308 mmol) was dissolved in ~1 mL of dry o-dichlorobenzene in a 5 mL vial equipped with a stir bar. Two equivalents of tetramethylhydrazine (17.5 μL, 0.154 mmol) were added and the reaction mixture allowed to stir for 1 min before dry n-hexane (~3 mL) was used to precipitate the product from the solution. The resulting white powder was filtered off, washed with dry n-hexane (~2 mL) and dried under vacuum (184 mg, 88%). The solid product was re-dissolved in SO_2 at −40 °C for NMR spectroscopic analysis. ^{1}H NMR (500 MHz, δ, SO_2, CD_2Cl_2 as external reference, 25 °C) Fig. S2a:‡ 2.35 (m, 30H, SiEt₃), 4.32 (s, 12H, NCH₃), 4.62 (s, 2H, CH).

[Me₆N₂][CHB₁₁Cl₁₁]₂ 3

Freshly prepared **5** (146 mg, 0.107 mmol) was dissolved in ~1 mL of dry ODCB in a 5 mL vial equipped with a stir bar. One drop of MeOTf (~3 equivalents) was added and the solution allowed to stir for 1 min before dry n-hexane (~3 mL) was used to precipitate the product from the solution. The resulting white powder was filtered off, washed with dry n-hexane (~2 mL) and dried under vacuum (92 mg, 74%). The solid product was re-dissolved in CD_2Cl_2 at *ca.* −40 °C for NMR spectroscopic data. ^{1}H NMR (500 MHz, δ, CD_2Cl_2, −40 °C) Fig. S3:‡ 2.91 (s, 18H, NCH₃), 3.29 (s, 2H, CH). ^{13}C NMR (500 MHz, δ, CD_2Cl_2, −40 °C): 45.24 (NCH₃), 48.37 (CH).

[H₂Me₄N₂][CHB₁₁Cl₁₁]₂ 6

This was prepared in the same manner as **3** replacing methyl triflate with triflic acid. ^{1}H NMR (500 MHz, δ, CD_2Cl_2, 25 °C) Fig. S4:‡ 3.38 (s, 2H, CH), 3.86 (s, 12H, NCH₃), 9.14 (bs, 2H, NH). ^{13}C NMR (500 MHz, δ, CD_2Cl_2, 25 °C): 40.90 (NCH₃), 47.87 (CH).

Notes and references

1 (*a*) P. M. W. Gill and L. Radom, *J. Am. Chem. Soc.*, 1989, **111**, 4613–4622; (*b*) J. Bouma and L. Radom, *J. Am. Chem. Soc.*, 1985, **107**, 345–348.
2 V. G. Nenajdenko, N. E. Shevchenko, E. S. Balenkova and I. V. Alabugin, *Chem. Rev.*, 2003, **103**, 229–282.
3 (*a*) R. W. Alder, A. G. Orpen and J. M. White, *J. Chem. Soc., Chem. Commun.*, 1985, 949–951; (*b*) R. W. Alder, R. B. Sessions, A. J. Bennet and R. E. Moss, *J. Chem. Soc., Perkin Trans. 1*, 1982, 603–609.
4 J. J. Weigand, S. D. Reigel, N. Burford and A. Decken, *J. Am. Chem. Soc.*, 2007, **129**, 7969–7976.
5 T. Kato, E. Stoyanov, J. Geier, H. Grutzmacher and C. A. Reed, *J. Am. Chem. Soc.*, 2004, **126**, 12451–12457.
6 Y. Zhang, K. Huynh, I. Manners and C. A. Reed, *Chem. Commun.*, 2008, 494–496.
7 Y. Zhang, F. S. Tham, J. F. Nixon, C. Taylor, J. C. Green and C. A. Reed, *Angew. Chem., Int. Ed.*, 2008, **47**, 3801–3804.
8 C. A. Reed, *Chem. Commun.*, 2005, 1669–1677.
9 T. Kato and C. A. Reed, *Angew. Chem., Int. Ed.*, 2004, **43**, 2908–2911.
10 R. W. Alder, R. B. Sessions, J. O. Gmünder and C. A. Grob, *J. Chem. Soc., Perkin Trans. 2*, 1984, 411–417.
11 C. A. Reed, K.-C. Kim, E. S. Stoyanov, D. Stasko, F. S. Tham, L. J. Mueller and P. D. W. Boyd, *J. Am. Chem. Soc.*, 2003, **125**, 1796–1804.
12 T. M. Klapoetke, P. S. White and I. C. Tornieporth-Oetting, *Polyhedron*, 1996, **I15I**, 2579–2582.