Molecular structures of free quinuclidine and its adducts with metal trihydrides, MH_3 ($\text{M} = \text{B}, \text{Al}$ or Ga), studied by gas-phase electron diffraction, X-ray diffraction and quantum chemical calculations†

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The structure of quinuclidine, $\text{HC}(\text{CH}_2\text{CH}_2)_3\text{N}$, has been re-investigated by quantum chemical calculations and by gas-phase electron diffraction (GED). The GED data, together with published rotational constants, have been analysed using the SARACEN method to determine the most reliable structure (r_{hl}) for the gaseous molecule. The structures of two adducts of quinuclidine with group 13 trihydride molecules, MH_3 ($\text{M} = \text{B}, \text{Al}$), have also been determined by GED and quantum chemical calculations. The effect of the coordination of these hydrides to the quinuclidine nitrogen atom has been investigated, and the structural changes and energetics of adduct formation are discussed. We also present the crystal structure of quinuclidine borane.

Introduction

Quinuclidine (1-azabicyclo[2.2.2]octane), $\text{HC}(\text{CH}_2\text{CH}_2)_3\text{N}$, **1**, is an interesting and valuable compound noted for its ability to stabilise group 13 trihydrides, particularly for use in chemical vapour deposition (CVD) techniques, such as metal organic molecular beam epitaxy (MOMBE) or chemical beam epitaxy (CBE).^{1–3} For example, decomposition of the vapour of quinuclidine gallane, $\text{HC}(\text{CH}_2\text{CH}_2)_3\text{N-GaH}_3$,⁴ can be used to produce GaAs films efficiently at temperatures much lower than those required for

conventional alkylgallium precursors,^{5,6} demonstrating the importance of these adducts. The particular stability of the quinuclidine adducts to dissociation into the free base and MH_3 fragments seems to offer their most important advantage. Furthermore, these same adducts of quinuclidine (in particular with alane and gallane) have found their way into the arsenal of synthetically useful compounds, since they allow relatively stereoselective reduction of ketones and oxiranes to the corresponding alcohols; the selectivity can be tuned by varying the metal centre.⁷ The relative stability of the quinuclidine–gallane adduct under ambient conditions, compared with other amine–gallane adducts,^{1,3,8,9} significantly increases the usefulness of the compound.

In the context of vapour deposition techniques, in which these thermally robust compounds may be applied, it is particularly important to have a thorough understanding of the structures of both the quinuclidine adducts and quinuclidine itself in the gas phase. A gas-phase electron diffraction (GED) study of quinuclidine was published more than 25 years ago,¹⁰ but various assumptions were made to enable the refinements to proceed: all C–C distances were assumed to be equal, as were the C–H distances. The planes describing the H–C–H angles of the methylene groups were assumed to be the perpendicular bisectors of the X–C–C ($\text{X} = \text{C}, \text{N}$) valence angles, and the H–C–N and C–C–H angles were constrained to values previously obtained for triethylenediamine and bicyclo[2.2.2]octane. Furthermore, the necessary vibrational amplitudes and shrinkage corrections for quinuclidine were taken from force fields calculated for those two aforementioned compounds. Finally, a twisted C_3 -symmetry model was found to give the best fit to the experimental data, although the difference from the fit of a C_{3v} model was small.

The possibility of obtaining a set of amplitudes of vibration calculated from a scaled force field, based on *ab initio* or density functional theoretical (DFT) calculations, and the use of a full set of independent parameters, made possible by the SARACEN method,¹¹ are the main reasons for carrying out a new GED analysis of quinuclidine. The publication of rotational constants

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† Electronic supplementary information (ESI) available: Table S1: experimental parameters for the GED analyses of **1–3**. Table S2: interatomic distances (r_a in Å), amplitudes of vibration (u_{hl} in Å) and curvilinear corrections (k_{hl} in Å) from the SARACEN refinement of **1**. Table S3: least-squares correlation matrix ($\times 100$) from the GED refinement of **1**. Table S4: Cartesian coordinates (in Å) for the GED-refined structure of **1**. Table S5: interatomic distances (r_a in Å), amplitudes of vibration (u_{hl} in Å) and curvilinear corrections (k_{hl} in Å) from the SARACEN refinement of **2**. Table S6: interatomic distances (r_a in Å), amplitudes of vibration (u_{hl} in Å) and curvilinear corrections (k_{hl} in Å) from the SARACEN refinement of **3**. Table S7: least-squares correlation matrix ($\times 100$) from the GED refinement of **2**. Table S8: Cartesian coordinates for the GED-refined structure of **3**. Table S9: least-squares correlation matrix ($\times 100$) from the GED refinement of **3**. Table S10: Cartesian coordinates for the GED refined structure of **3**. Table S11: atomic coordinates and equivalent isotropic thermal parameters ($\text{\AA}^2$) for non-hydrogen atoms in **2**. Table S12: atomic coordinates and isotropic thermal parameters ($\text{\AA}^2$) for the hydrogen atoms in **2**. Table S13: anisotropic thermal parameters ($\text{\AA}^2$) for **2**. Fig. S1: experimental and difference (experimental – theoretical) molecular-scattering intensity curves for **1**. Fig. S2: experimental and difference (experimental – theoretical) molecular-scattering intensity curves for **2**. Fig. S3: experimental and difference (experimental – theoretical) molecular-scattering intensity curves for **3**. See DOI: 10.1039/b701476g

for five isotopomers of quinuclidine¹² allows the introduction of these data as restraints in the GED refinement, thereby enabling us to secure a far more reliable geometry for **1**.

The structures of two adducts of quinuclidine, $\text{HC}(\text{CH}_2\text{CH}_2)_3\text{N}\cdot\text{BH}_3$, **2**, and $\text{HC}(\text{CH}_2\text{CH}_2)_3\text{N}\cdot\text{AlH}_3$, **3**, have also been determined using GED and quantum chemical calculations. An attempt was made to extend this study to $\text{HC}(\text{CH}_2\text{CH}_2)_3\text{N}\cdot\text{GaH}_3$, **4**, but it dissociated at the temperatures required for the GED experiment. Additional experimental support comes from the crystal structures determined previously for **3** and **4**,^{4,13} and here we present the crystal structure of the borane adduct, **2**. High-level quantum chemical calculations have allowed the structural changes in the acid and base fragments induced through complexation and the energetics of this process to be investigated, and these are compared with the corresponding properties of other amine complexes of group 13 trihydrides.^{1,3,8,9}

Experimental

Preparation of samples

Quinuclidine, **1**, (from Aldrich, stated purity 97%) was purified by sublimation *in vacuo*, and its purity checked by measuring the ¹H NMR spectrum of a toluene-*d*₈ solution. Quinuclidine hydrochloride (also from Aldrich, stated purity 97%) was purified by recrystallisation from anhydrous ethanol.

The quinuclidine adducts $\text{HC}(\text{CH}_2\text{CH}_2)_3\text{N}\cdot\text{BH}_3$, **2**, $\text{HC}(\text{CH}_2\text{CH}_2)_3\text{N}\cdot\text{AlH}_3$, **3**, and $\text{HC}(\text{CH}_2\text{CH}_2)_3\text{N}\cdot\text{GaH}_3$, **4**, were all prepared by essentially the same method involving the reaction of quinuclidine hydrochloride with LiMH_4 (M = B, Al, or Ga), both freshly recrystallised, in dry Et₂O solution. The procedure was generally similar to that described elsewhere⁴ for the preparation of trimethylamine–gallane, $\text{Me}_3\text{N}\cdot\text{GaH}_3$. It involved adding the hydrochloride powder gradually to an ethereal solution of LiMH_4 at 0 °C over a period of *ca.* 30 min. For **3** and **4**, the stirred reaction mixture was then allowed to warm up to room temperature over a further 5 h. For **2**, the stirred reaction mixture was heated under reflux (to *ca.* 50 °C) for 20 h. After filtering the solution at room temperature, the ether was removed under vacuum in each case, and the white powder remaining (including some LiCl) was heated *in vacuo* to 60–70 °C to give a sublimate of **2**, **3**, or **4**. The purity of each product was assessed by reference to its IR or Raman spectrum and to the ¹H NMR spectrum of a toluene-*d*₈ solution.

Gas-phase electron diffraction

Electron scattering intensities for **1–3** were recorded on Kodak Electron Image films using the Edinburgh GED apparatus,¹⁴ operating at *ca.* 40 kV. For **1** the patterns were converted into digital format using a computer-controlled PDS microdensitometer employing a 200 μm pixel size at the Institute of Astronomy, Cambridge.¹⁵ For **2** and **3**, as is now standard procedure in Edinburgh, the patterns were digitised using an Epson Expression 1680 Pro flatbed scanner with a scanning program described elsewhere.¹⁶ The data reduction and analysis were performed using the *ed@ed* program¹⁷ employing the scattering factors of Ross *et al.*¹⁸ Table S1 (see electronic supplementary information, ESI†) gives the sample and nozzle temperatures, nozzle-to-film distances, weighting functions

used for the off-diagonal weight matrix, correlation parameters, scale factors, *k*, and electron wavelengths, *λ*.

Quantum chemical calculations

Calculations for all compounds were performed using the Gaussian 03 suite of programs.¹⁹ Graded series of calculations were performed to gauge the effects of basis sets and levels of theory on the optimised structures. It is worth noting at the start that this series does not include the corresponding indium adduct since the 6–311+G* basis set is currently not available for this element. The use of a smaller Gaussian-type basis set or one based on an effective core potential would not allow a rigorous comparison of the geometry and other properties of the indium compound with those of the other adducts, so that including it would not therefore be very informative.

For **1–4**, calculations were performed using standard techniques (i) at the RHF level of theory using first 3–21G* and secondly 6–31G* basis sets on all atoms, (ii) at the B3LYP level using 6–31G* on all atoms, (iii) at the B3LYP level with 6–311+G* on all atoms, and (iv) at the MP2(full) level using the 6–311+G* basis set on all atoms; all basis sets were used as implemented in Gaussian 03. Vibrational frequencies were calculated at RHF and B3LYP levels to ascertain that the resulting structures represented energy minima. For **1** MP2 frequency calculations were also performed. The force fields obtained from the B3LYP/6–311+G* calculations (MP2/6–311+G* for **1**) were used to calculate the amplitudes of vibration, *u*, for use in the GED refinements. In addition, perpendicular amplitudes of vibration, *k*_{h1}, were calculated using the program SHRINK,^{20,21} which draws on the calculated force field to represent the curvilinear motions of the atoms in the molecule. These *k* values allowed the *r*_{h1} structure to be refined rather than the *r*_{h0} (*≡ r*_a) structure, which would be obtained using *k* values determined assuming rectilinear motions of the atoms. For more detailed definitions of *r*_{h0} and *r*_{h1}, see ref. 20. In the case of **1**, the MP2 and B3LYP calculations disagreed about whether the minimum-energy structure had C₃ or C_{3v} symmetry. Potential-energy surface scans were performed at both levels, as well as at the more sophisticated CISD level.

Calculations were also performed to determine the energies involved in the interactions between the quinuclidine fragments and the metal hydrides. For each of **2–4**, first the optimised geometry of the adduct was calculated (MP2/6–311+G*). The single-point energies of the quinuclidine and metal hydride fragments were then recalculated in the absence of one another; the basis-set superposition error (BSSE) was estimated by counterpoise correction. This allowed the fragmentation energies for **2–4** to be calculated. In order to calculate the dissociation energies, it was necessary to allow the fragments to relax in the absence of their acid/base partners. Borane, alane and gallane optimised in D_{3h} symmetry, giving results in good agreement with those of earlier calculations.²² Again the BSSE was calculated. Together, the fragmentation and dissociation energies allow the relaxation energies of each adduct to be determined.

X-Ray diffraction

Crystals of **2** were formed on the cold finger (kept at 0 °C) of the vacuum sublimation apparatus used for purification of the

compound. A single crystal with dimensions approximately $0.18 \times 0.20 \times 0.20$ mm was mounted on a glass fibre using perfluoropolyether oil and cooled rapidly to 150 K in a stream of cold N_2 using an Oxford Cryosystems CRYOSTREAM unit. Diffraction data were measured using an Enraf-Nonius KappaCCD diffractometer (graphite-monochromated MoK α radiation, $\lambda = 0.71073$ Å). Intensity data were processed using the DENZO-SMN package.²³

Results and discussion

Calculated molecular geometries

For **1**, geometry optimisations were performed with the molecule in both C_{3v} and C_3 symmetries and torsional potential-energy scans were performed at the MP2, B3LYP and CISD levels to investigate the effect on the overall energy of **1** of twisting the cage. As shown in Fig. 1, the B3LYP calculations find that the lowest energy structure has C_{3v} symmetry ($\phi_{C-N-C-C} = 0^\circ$), whereas the MP2 and CISD calculations show minima with twist angles of approximately 8 and 4° , respectively. Although at the MP2 level a geometry can be optimised with no twist, frequency calculations (MP2/6-311+G*) show this stationary point to be a maximum on the potential-energy surface.

Fig. 1 Plots of potential-energy scans for the C(2)–N–C(4)–C(3) torsion in **1** at B3LYP (■), MP2 (●) and CISD (▲) levels.

For **2–4**, the lowest energy structure had C_3 symmetry when calculated using both MP2 and B3LYP methods. The molecular structures and atomic numbering of **1–4** are shown in Fig. 2 and selected parameters from the B3LYP and MP2 calculations are presented in Table 1. In general, improving the level of theory had little effect on the geometric parameters, as is to be expected for this type of regular organic and rigid cage structure. The high confidence in these values is reflected in the fact that well-founded restraints could be introduced in the GED analysis (see below).

Vibrational spectra

Several vibrational studies have been performed for quinuclidine,^{24–26} although no complete assignment of the vibrational spectra has been published. Brüesch and Günthard provide

Fig. 2 Molecular structures and atomic numbering of quinuclidine, **1**, and the MH_3 adducts **2** ($M = B$), **3** ($M = Al$), and **4** ($M = Ga$). The quinuclidine hydrogen atoms are numbered in relation to the carbon atoms to which they are bonded, e.g. H(2) and H'(2).

a general view of the vibrational behaviour of quinuclidine,²⁴ starting from their own normal-coordinate calculations, which are based on a rather crude assumption of the molecular geometry of the compound obtained from an X-ray powder analysis. Nevertheless, the authors provide a detailed assignment of the vibrational spectra, particularly in the high wavenumber region. In presenting an analysis of the low-energy part of both the infrared and Raman spectra ($\nu < 1000$ cm^{-1}), McDivitt and Humphrey cast doubt on some of Brüesch and Günthard's assignments in that part of the spectrum.²⁵ Finally, the Raman data presented by Santos and Mello confirm the Brüesch and Günthard Raman spectra.²⁶

Based on our superior geometric and force-field data, we were able to confirm McDivitt and Humphrey's original doubts²⁵ and to scrutinise the original assignments of the vibrational spectra. Finally, we combined the three spectra and compared this set of frequencies with the calculated values from both B3LYP/6-311+G* (C_{3v} symmetry) and B3LYP/6-311+G* (C_3 symmetry) calculations and scaled the theoretical spectrum accordingly. Since a complete experimental vibrational spectrum was unavailable in the end, we limited the scaling of the force field to the νCH modes (0.90 for B3LYP, 0.94 for MP2) and the CH_2 scissoring modes (0.94 for B3LYP, 0.96 for MP2). It was deemed unnecessary to scale the remaining modes. The resulting fit had an absolute root-mean-square difference of 24 cm^{-1} (root-mean-square % difference = 1.3%) for MP2 and 13 cm^{-1} (root-mean-square % difference = 0.6%) for B3LYP. Using the scaled frequencies from the MP2 calculations, we obtained a force field more than suitable for the calculation of the amplitudes of vibration. Table 2 lists the scaled theoretical frequencies with the corresponding symmetry species, IR intensities, and the experimental frequencies.

GED models

For **1**, a C_3 -symmetric model was written using 15 parameters to define the structure. These are listed in Table 3. Four distance parameters were used, namely the average of the N–C(2), C(2)–C(3) and C(3)–C(4) distances (p_1), the difference between N–C and the average C–C distance (p_2), the difference between the two C–C distances (p_3), and the mean C–H distance (p_4). Six angles, labelled C(2)–N–C(4) (p_5), H(2)–C(2)–N (p_6), H'(2)–C(2)–N (p_7), H(3)–C(3)–C(4) (p_7) and H(4)–C(4)–C(3) (p_8), and three dihedral angles,

Table 1 Molecular geometries (distances in Å and angles and torsions in degrees) calculated for **1–4** using the MP2 and B3LYP methods. The 6-311+G* basis set was used for all atoms^a

Parameter	1		2		3		4	
	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2
<i>r</i> N–C(2)	1.472	1.469	1.501	1.493	1.498	1.493	1.493	1.486
<i>r</i> C(2)–C(3)	1.561	1.553	1.549	1.542	1.552	1.543	1.553	1.547
<i>r</i> C(3)–C(4)	1.541	1.535	1.538	1.534	1.538	1.533	1.539	1.539
<i>r</i> C(2)–H(2)	1.094	1.096	1.090	1.092	1.091	1.094	1.091	1.094
<i>r</i> C(2)–H'(2)	1.094	1.095	1.090	1.093	1.091	1.094	1.091	1.094
<i>r</i> C(3)–H(3)	1.095	1.096	1.094	1.096	1.094	1.096	1.094	1.096
<i>r</i> C(3)–H'(3)	1.095	1.097	1.094	1.095	1.094	1.095	1.094	1.096
<i>r</i> C(4)–H(4)	1.095	1.096	1.093	1.095	1.093	1.095	1.093	1.096
<i>r</i> M–N	—	—	1.642	1.630	2.079	2.056	2.168	2.188
<i>r</i> M–H	—	—	1.213	1.217	1.604	1.608	1.585	1.604
$\angle$ C(6)–N–C(2)	109.4	108.7	108.7	108.3	109.0	108.5	109.1	108.9
$\angle$ N–C(2)–C(3)	111.7	111.7	111.3	110.6	111.2	110.6	111.2	110.7
$\angle$ C(2)–C(3)–C(4)	108.0	107.7	108.9	108.2	108.8	108.2	108.7	108.1
$\angle$ C(3)–C(4)–C(5)	108.7	108.4	108.6	108.1	108.8	108.2	108.7	108.3
$\angle$ C(2)–N–C(4)	70.4	69.8	69.7	69.4	70.1	69.6	70.2	70.0
$\angle$ H(2)–C(2)–N	107.8	108.1	106.6	106.8	107.1	107.6	107.0	107.7
$\angle$ H'(2)–C(2)–N	107.8	107.3	106.3	106.2	106.9	106.6	107.2	106.7
$\angle$ H(3)–C(3)–C(4)	110.0	109.7	110.0	110.0	110.0	110.0	110.2	109.9
$\angle$ H'(3)–C(3)–C(4)	110.0	110.5	110.3	110.8	110.2	110.8	110.0	110.7
$\angle$ H(4)–C(4)–C(3)	110.2	110.5	110.3	110.8	110.2	110.7	110.2	110.7
$\angle$ N–M–H	—	—	105.9	105.6	100.4	100.0	99.1	98.2
ϕ H(2)–C(2)–N–C(4)	122.5	130.7	127.1	134.0	124.7	133.3	120.7	132.3
ϕ H'(2)–C(2)–N–C(4)	–122.5	–114.1	–118.9	–111.5	–120.7	–111.6	–124.7	–112.6
ϕ H(3)–C(3)–C(4)–H(4)	58.6	66.4	62.3	69.0	60.6	68.9	56.8	68.0
ϕ H'(3)–C(3)–C(4)–H(4)	–58.6	–51.3	–55.1	–49.1	–56.9	–49.3	–60.6	–50.0
ϕ H(11)–M–N–C(2)	—	—	62.7	66.0	61.2	64.4	59.4	63.5
ϕ C(2)–N–C(4)–C(3)	0.0	–7.9	–3.9	–10.8	–1.9	–10.5	–2.0	–9.5

^a See Fig. 2 for atom numbering.

H(2)–C(2)–N–C(4) (p_9), H(3)–C(3)–C(4)–H(4) (p_{10}) and C(2)–N–C(4)–C(3) (p_{11}), which describes the degree of twist of the quinuclidine cage (0° indicates no twist), complete the set of parameters. Although the three different C–H distances are described by a single parameter (p_4), the calculated amplitudes of vibration and shrinkage corrections were markedly different in the three cases, and so three different amplitudes and perpendicular corrections were included in the refinement. As the calculated C–H distances were so similar (all within 0.001 Å) the use of a single C–H parameter is justified even when rotational constants are included.

The rotational constants relating to an axis perpendicular to the C_3 axis of **1**, determined from the microwave spectra of five different isotopomers,¹² *i.e.* quinuclidine (**1**), ¹⁵N-quinuclidine (**2**), 4-¹³C-quinuclidine (**3**), 3-¹³C-quinuclidine (**4**) and 2-¹³C-quinuclidine (**5**), were combined with the GED data. The microwave B_0 constants were corrected to B_z for the structural refinements using values calculated by SHRINK,^{20,21} based on the MP2/6-311+G* force field. The five corrected rotational constants were presented in the refinements as the absolute value of B_z for the parent isotopomer, B(1), and the four differences from this value for the other isotopomers, *i.e.* B(2)–B(1), B(3)–B(1), B(4)–B(1), B(5)–B(1). These constants are given in Table 4. The vibrational corrections to the microwave constants, which transform B_0 into B_z , are summations of the corrections for each of the 57 normal modes of quinuclidine. For the five relevant isotopomers this sum was small, typically 0.3–1.5 MHz, but contributions from some

modes were of the order of 7–9 MHz. The uncertainties of the vibrational corrections to the microwave constants were taken as 10% of the value of the vibrational correction for quinuclidine (**1**) and 20% of the corrections for the four differences. The weights applied to all data depended on the uncertainties of the observations, in accordance with the SARACEN method.¹¹

Geometric models were written for **2** and **3**, in C_3 symmetry, using 19 independent parameters, as listed in Table 5. These included six distance parameters, which were defined slightly differently for **2** and **3**. This reflects substantial differences in the lengths of the Al–N and B–N bonds and of the Al–H and B–H bonds. For **2** it makes sense to group together the B–H and C–H bonds, and the B–N, N–C and C–C distances and for **3** it is more intuitive to group Al–H, N–C and the two C–C distances and allow Al–N, which is much longer, and C–H, which is much shorter, to refine independently.

All other parameters were common to both **2** and **3** and are listed in Table 5. For both the N–C–H and C–C–H angles, where each molecule has two different values because of the twist of the quinuclidine group, these were considered as the average of the two values and the difference between them (p_{8-11}). The C(2)–N–M–H(11) dihedral angle (p_{18}) describes the position of the M–H bond relative to the N–C bond, where a value of 0° indicates a perfectly eclipsed structure. The C(2)–N–C(4)–C(3) dihedral angle (p_{19}) gives a numerical value to the degree of twist in the quinuclidine cage, where a value of 0° indicates no twist.

Table 2 Experimental (ν_{exp}) and scaled MP2/6–311+G* and B3LYP/6–311+G* (ν_{calc}) vibrational data for quinuclidine, **1**, in C_{3v} symmetry (MP2) and C_{3v} symmetry (B3LYP). See text for details of scaling^a

ν_{exp}	ν_{calc} (MP2)	Symmetry species	ν_{calc} (B3LYP)	Symmetry species
—	109	A	83	A_2
305(m)	299	E	306	E
410(m)	404	E	408	E
545(m)	544	E	552	E
605(w)	611	A	611	A_1
785(m)	782	A	785	A_1
805(s)	814	A	799	A_1
—	829	A	806	A_2
823(s)	843	E	832	E
882(m)	912	E	878	E
975(s)	980	A	971	A_1
—	996	A	973	A_2
990(vs)	1030	E	1001	E
?	1043	A	1018	A_1
1058(s)	1108	E	1067	E
1120(m)	1143	E	1140	E
—	1186	A	1178	A_2
1205(m)	1242	E	1231	E
—	1283	A	1269	A_2
1275(m)	1320	E	1303	E
1325(m)	1349	E	1344	E
1350(m)	1371	A	1356	A_1
?	1373	E	1357	E
?	1393	E	1379	E
?	1396	A	1387	A_1
?	1454	E	1448	E
1445(s)	1466	A	1462	A_1
1458(sh)	1467	E	1464	E
?	1488	A	1481	A_1
?	2875	E	2863	E
?	2876	A	2864	A_1
2866	2889	E	2880	E
2866(m)	2891	A	2885	A_1
—	2909	A	2892	A_2
2888(w,sh)	2921	E	2895	E
2916(m)	2922	A	2900	A_1
—	2943	A	2919	A_2
2937(s)	2947	E	2926	E

^a Wavenumbers, ν , in cm^{-1} ; A_2 modes are IR and Raman inactive in C_{3v} symmetry; vs = very strong, s = strong, m = medium, w = weak, sh = shoulder.

GED refinements

For the GED refinement of **1**, starting values for all parameters were taken from the calculations performed at the MP2/6–311+G* level. All the distance parameters and most of the angle and torsion parameters refined to chemically reasonable values. However, the refinement of the H–C(2)–N and H–C(3)–C(4) angles and the H–C(3)–C(4)–H(4) dihedrals gave values that were unreasonable and so they were restrained using the SARACEN method.¹¹ All heavy-atom amplitudes were refined without restraint; the H...H amplitudes were not refined. The final R_G factor for the refinement was 0.039 ($R_D = 0.026$). This structure for quinuclidine represents the best that can be achieved on the basis of the experimental and theoretical information currently available; all standard deviations are realistic estimates of the errors. Interatomic distances and vibrational amplitude values for the final structure are given in Table S2[†] and the final radial-distribution curve is given in Fig. 3. The molecular-scattering intensity curve is in Fig. S1,[†] the least-squares correlation matrix

Fig. 3 Experimental and difference (experimental – theoretical) radial-distribution curves for **1–3** (a–c, respectively). Before Fourier inversion the data were multiplied by $s \exp(-0.00002s^2)/(Z_C - f_C)(Z_X - f_X)$, where $X = \text{N}$ (for **1**), B (for **2**) and Al (for **3**).

is in Table S3[†] and the Cartesian coordinates for the final structure are in Table S4.[†]

The newly refined structure is similar to that determined by Schei *et al.*¹⁰ The average C–C distance [1.552(2) Å] from the earlier refinement lies almost midway between the two experimental values determined here and the C–N distance [1.469(3) Å] in the original report lies within 0.006 Å of that presented here. Although three studies of the crystalline structure of **1** have been reported, none of these describes the molecular structure of the disordered compound.^{27–29}

Table 3 Experimental geometric parameters (r_{hl}) from the GED study of **1** (distances in Å and angles in degrees)^a

Parameter	GED	Restraint uncertainty ^b	
Independent			
p_1	$r\{[\text{N}-\text{C}(2)/3]+[\text{C}(2)-\text{C}(3)/3]+[\text{C}(3)-\text{C}(4)/3]\}$	1.524(1)	—
p_2	$r\{[\text{N}-\text{C}]-[\text{C}(2)-\text{C}(3)/2]-[\text{C}(3)-\text{C}(4)/2]\}$	−0.091(2)	—
p_3	$r\{[\text{C}(2)-\text{C}(3)]-[\text{C}(3)-\text{C}(4)]\}$	0.016(7)	—
p_4	$r\text{C}-\text{H av}$	1.111(2)	—
p_5	$\angle\text{C}(2)-\text{N}-\text{C}(4)$	70.1(8)	—
p_6	$\angle\text{H}(2)-\text{C}(2)-\text{N}$	107.1(9)	1.0
p_7	$\angle\text{H}'(2)-\text{C}(2)-\text{N}$	107.8(9)	1.0
p_8	$\angle\text{H}(3)-\text{C}(3)-\text{C}(4)$	109.7(9)	1.0
p_9	$\angle\text{H}'(3)-\text{C}(3)-\text{C}(4)$	108.7(9)	1.0
p_{10}	$\angle\text{H}(4)-\text{C}(4)-\text{C}(3)$	110.1(7)	—
p_{11}	$\phi\text{H}(2)-\text{C}(2)-\text{N}-\text{C}(4)$	114.8(9)	—
p_{12}	$\phi\text{H}'(2)-\text{C}(2)-\text{N}-\text{C}(4)$	131.1(9)	—
p_{13}	$\phi\text{H}(3)-\text{C}(3)-\text{C}(4)-\text{H}(4)$	50.5(9)	1.0
p_{14}	$\phi\text{H}'(3)-\text{C}(3)-\text{C}(4)-\text{H}(4)$	66.0(9)	1.0
p_{15}	$\phi\text{C}(2)-\text{N}-\text{C}(4)-\text{C}(3)$	5.0(6)	—
Dependent			
p_{16}	$r\text{N}-\text{C}(2)$	1.463(2)	—
p_{17}	$r\text{C}(2)-\text{C}(3)$	1.562(4)	—
p_{18}	$r\text{C}(3)-\text{C}(4)$	1.547(3)	—

^a For parameter definitions and details of the refinement, see text. Values in parentheses are esd's obtained in the least-squares refinement. ^b SARACEN-restrained parameters were set to values calculated at the MP2/6-311+G* level (see Table 1) with uncertainties as shown.

Table 4 Microwave rotational constants, B in MHz, used in the GED refinements. For isotopomer numbering, see text

Constant	$B_z(\text{exp})$	$B_z(\text{GED})$	$B_z(\text{exp} - \text{GED})$	Uncertainty
B(1)	2415.79	2415.06(90)	0.73	0.98
B(2)–B(1)	−18.39	−18.40	0.01	0.02
B(3)–B(1)	−19.46	−19.47	0.01	0.03
B(4)–B(1)	−8.46	−8.50	0.04	0.04
B(5)–B(1)	−8.35	−8.34	−0.01	0.11

To ensure that the twisted structure of **1** did indeed give the best fit to the experimental data, the C(2)–N–C(4)–C(3) dihedral angle was fixed at some values and the effects on the R factor and the other parameters noted. When the dihedral angle is 0° R_G rises to 0.051 and, although there is little effect on the other refining parameters, this signifies that the C_{3v} -symmetric geometry is not favoured. Similarly, when the dihedral angle is fixed at the value calculated *ab initio* (7.9°; MP2/6-311+G*), the R factor is 0.057.

For the GED refinements of **2** and **3**, the starting values were once again taken from MP2/6-311+G* calculations. For both **2** and **3** 14 parameters were restrained during the refinement process. For all distances under a given peak in the radial-distribution curve, the amplitudes of vibration were grouped and allowed to refine. Again amplitudes of vibration relating to H...H distances were not refined. The final R factors for **2** were $R_G = 0.070$ ($R_D = 0.046$) and for **3** were $R_G = 0.041$ ($R_D = 0.029$). Table S5† and Table S6† contain details of interatomic distances and their amplitudes of vibration for **2** and **3**. The molecular-scattering intensity curves for **2** and **3** are given in Fig. S2† and S3,† respectively, and the least-squares correlation matrices in Table S7† and Table S8.† Table S9† and Table S10† list the

Cartesian coordinates of the structures determined by GED. The radial-distribution curves are shown in Fig. 3.

Crystal structure of quinuclidine–BH₃

Examination of the systematic absences of the diffraction data for **2** and comparison of the intensities of symmetry-related reflections showed the space group to be $P2_13$. The structure was solved using the direct-methods program SIR92,³⁰ which located all non-hydrogen atoms. A subsequent full-matrix least-squares refinement was carried out using the CRYSTALS program suite.³¹ Coordinates and anisotropic thermal parameters of all non-hydrogen atoms were refined. The BH hydrogen atoms were located in a difference Fourier map and their coordinates and isotropic thermal parameters subsequently refined. The quinuclidine hydrogen atoms were positioned geometrically after each cycle of the refinement. A three-term Chebychev polynomial weighting scheme was applied. Refinement converged satisfactorily to give $R = 0.0333$ and $wR = 0.0354$. Fig. 4 shows a thermal ellipsoid plot (ORTEP-3)³² at 40% probability for the heavy atoms. A summary of the crystallographic data is given in Table 6 and full lists of atomic coordinates and isotropic and anisotropic thermal parameters are given in Tables S11–13.†

The molecule is located on a crystallographic threefold axis of rotation. The local geometry approximates to $3m$ (C_{3v}) but there is a twist of the quinuclidine group about its axis, as illustrated by the torsion angle C(2)–N–C(4)–C(3) of 8.6°. The BH₃ group adopts a staggered orientation with respect to the nitrogen substituents resulting in a H(10)–B(9)–N(1)–C(2) torsion angle of 177°.

CCDC reference number 635246.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b701476g

Table 5 Experimental geometric parameters (r_{ht}) from the GED studies of **2** and **3** (distances in Å and angles and torsions in degrees)^a

Parameter	2		3	
	GED	Restraint uncertainty ^b	GED	Restraint uncertainty ^b
Independent				
p_1 $r_{\text{B-H/C-H av}}$	1.158(5)	—	2.033(5)	—
p_2 $r_{\text{Al-N}}$	0.129(9)	0.01	1.523(1)	0.01
p_3 $r_{\text{B-H/C-H dif}}$	—	—	—	—
p_4 $r\{[3*\text{N-C}(2)/10]+[3*\text{C}(2)\text{--C}(3)/10]+[3*\text{C}(3)\text{--C}(4)/10]+[\text{Al-H}/10]\}$	1.547(2)	—	—	—
p_5 $r\{[\text{N-C}(2)/3]+[\text{C}(2)\text{--C}(3)/3]+[\text{C}(3)\text{--C}(4)/3]+[\text{Al-H}]\}$	—	—	—	—
p_6 $r\{[\text{N-C}(2)/3]+[\text{C}(2)\text{--C}(3)/3]+[\text{C}(3)\text{--C}(4)/3]+[\text{N-B}]\}$	−0.101(9)	0.01	−0.073(7)	0.01
p_7 $r\{[\text{N-C}(2)]\text{--}[\text{C}(2)\text{--C}(3)/2]\text{--}[\text{C}(3)\text{--C}(4)/2]\}$	—	—	2.913(6)	0.01
p_8 $r\{[\text{N-C}(2)]\text{--}[\text{C}(2)\text{--C}(3)/2]\text{--}[\text{C}(3)\text{--C}(4)/2]\}$	−0.048(9)	0.01	0.023(9)	0.01
p_9 $r\{[\text{C}(2)\text{--C}(3)]\text{--}[\text{C}(3)\text{--C}(4)]\}$	0.003(9)	0.01	1.111(14)	—
p_{10} $r_{\text{C-H mean}}$	—	—	—	—
p_{11} $\angle\text{C-N-M}$	109.5(5)	—	111.9(3)	—
p_{12} $\angle\text{N-C-H av}$	106.2(9)	1.0	108.0(8)	1.0
p_{13} $\angle\text{N-C-H dif}$	0.6(9)	1.0	1.3(10)	1.0
p_{14} $\angle\text{C-C-H av}$	110.5(9)	1.0	110.0(8)	1.0
p_{15} $\angle\text{C-C-H dif}$	0.8(9)	1.0	0.8(9)	1.0
p_{16} $\angle\text{N-M-H}$	105.8(9)	1.0	100.3(8)	1.0
p_{17} $\angle\text{H(4)-C-C}$	110.3(5)	—	110.4(2)	—
p_{18} $\phi\text{H(2)-C(2)-N-C(4)}$	134.1(19)	2.0	133.0(9)	2.0
p_{19} $\phi\text{H'(2)-C(2)-N-C(4)}$	−110.6(18)	2.0	−110.6(15)	2.0
p_{20} $\phi\text{H(3)-C(3)-C(4)-H(4)}$	49.6(17)	2.0	48.5(14)	2.0
p_{21} $\phi\text{H'(3)-C(3)-C(4)-H(4)}$	−69.5(18)	2.0	−67.9(15)	2.0
p_{22} $\phi\text{C(2)-N-M-H(11)}$	53.7(19)	2.0	55.8(20)	2.0
p_{23} $\phi\text{C(2)-N-C(4)-C(3)}$	−4.5(23)	—	−8.3(6)	—
Dependent				
p_{24} $r_{\text{M-N}}$	1.623(9)	—	2.033(5)	—
p_{25} $r_{\text{N-C}(2)}$	1.489(6)	—	1.482(2)	—
p_{26} $r_{\text{C}(2)\text{--C}(3)}$	1.539(6)	—	1.536(2)	—
p_{27} $r_{\text{C}(3)\text{--C}(4)}$	1.536(6)	—	1.529(2)	—
p_{28} $r_{\text{M-H}}$	1.222(9)	—	1.589(7)	—
p_{29} $\angle\text{N-C(2)-C(3)}$	110.7(8)	—	108.6(9)	—
p_{30} $\angle\text{C(2)-C(3)-C(4)}$	108.7(10)	—	107.5(3)	—
p_{31} $\angle\text{C(3)-C(4)-C(5)}$	108.7(6)	—	108.6(2)	—
p_{32} $\angle\text{C(2)-N-C(6)}$	109.4(5)	—	106.9(3)	—
p_{33} $\angle\text{H-M-H}$	112.8(7)	—	116.9(5)	—

^a For parameter definitions and details of the refinement, see text. Values in parentheses are esd's obtained in the least-squares refinements. ^b SARACEN-restrained parameters were set to values calculated at the MP2/6-311+G* level (see Table 1) with uncertainties as shown.

Fig. 4 A thermal ellipsoid plot of the molecular structure of quinuclidine-BH₃, **2**, determined by X-ray crystallography, showing heavy atoms with a 40% probability. The hydrogen atoms are represented by spheres of a nominal size. Atom numbering as in Fig. 2.

Comparison of gas-phase, crystal and theoretical structures of quinuclidine-MH₃ adducts (M = B, Al, Ga)

Fig. 2 shows the molecular structure and the atomic numbering for an MH₃ adduct. Table 1 contains calculated parameters for molecules **2–4**, Table 5 contains GED parameters for **2** and **3**, and Table 7 lists selected parameters from the crystal structures of the borane, **2**, alane, **3**,¹³ and gallane, **4**,⁴ adducts. Geometric parameters concerning the quinuclidine H atoms have been omitted from Table 7 because the distances, angles and torsion angles involving these atoms vary negligibly with the nature of M. Equally, the coordination of the MH₃ fragment to the quinuclidine affects these parameters only marginally. It is noted that the largest differences always relate to the hydrogen atoms on C(2), C(6) and C(7), as would be expected since they are closest to the metal atom.

While the solid-state molecular structure of **2** has C₃ symmetry, the symmetry of the gaseous adducts **3** and **4** is reduced to C_s.

Table 6 Crystal data and refinement details for quinuclidine-BH₃, **2**

Chemical formula	C ₇ H ₁₆ BN
Formula weight	125.02
Temperature/K	150
Wavelength/Å	0.71073
Crystal system	Cubic
Space group	<i>P</i> 2 ₁ 3
<i>a</i> /Å	9.2919(4)
Cell volume/Å ³	802.26(6)
<i>Z</i>	4
Calculated density/Mg m ⁻³	1.035
Absorption coefficient/mm ⁻¹	0.058
<i>F</i> ₀₀₀	280
Crystal size/mm	0.18 × 0.20 × 0.20
Description of crystal	Colourless octahedron
Absorption correction	Semi-empirical from equivalent reflections
Transmission coefficients (min, max)	0.98, 0.99
θ range for data collection/°	5.0 ≤ θ ≤ 27.5
Index ranges	0 ≤ <i>h</i> ≤ 8, 0 ≤ <i>k</i> ≤ 8, 0 ≤ <i>l</i> ≤ 8
Reflections measured	2063
Unique reflections	360
<i>R</i> _{int}	0.042
Observed reflections (<i>I</i> > 3σ(<i>I</i>))	274
Refinement method	Full-matrix least-squares on <i>F</i>
Parameters refined	32
Weighting scheme	Chebyshev three-term polynomial
Goodness of fit	1.1445
<i>R</i>	0.0333
<i>wR</i>	0.0354
Residual electron density (min, max)/e Å ⁻³	−0.10, 0.10

Table 7 Selected bond lengths and angles from the solid-state (XRD) geometries for the quinuclidine-borane, **2** (*M* = B; this work), quinuclidine-alane, **3** (*M* = Al; ref. 13), and quinuclidine-gallane, **4** (*M* = Ga; ref. 4), adducts. Bond lengths are in Å and angles are in degrees^a

	2	3	4		
<i>r</i> N–C(2)	1.501(2)	1.475(7)	1.506(4)	1.507(6)	^b
<i>r</i> C(2)–C(3)	1.529(2)	1.505(9)	1.524(5)	1.514(7)	1.529(5)
<i>r</i> C(3)–C(4)	1.528(2)	1.491(8)	1.531(5)	1.514(7)	1.525(5)
<i>r</i> M–N	1.608(5)	1.991(4)	—	2.063(4)	—
<i>r</i> M–H	1.151(20)	1.38(5)	1.56(3)	1.69(6)	1.55(5)
∠N–C(2)–C(3)	111.1(2)	112.4(4)	111.3(3)	114.4(4)	111.9(3)
∠C(2)–C(3)–C(4)	108.7(2)	110.0(5)	109.3(3)	109.6(4)	108.7(3)
∠C(3)–C(4)–C(5)	108.4(1)	107.7(4)	108.9(3)	108.3(3)	109.1(3)
∠C(2)–N–C(6)	108.1(1)	107.0(3)	108.7(2)	108.3(3)	108.1(3)
∠M–N–C(2)	110.8(1)	112.0(3)	110.1(2)	110.6(3)	110.7(2)
∠H–M–N	104.5(12)	102(2)	101(1)	100(2)	105(2)
∠H–M–H	114.0(10)	102(2)	123(1)	110(2)	117(2)

^a In the crystal structures of **3** and **4**, the symmetry of the molecules is lowered to *C*_s, leading to an increased number of parameters compared with the gas-phase and the crystal structures of **2**. ^b Not given in ref. 4.

symmetry in the crystal environment.^{4,13} A difference in the space group of the crystallographic unit cell is also observed, with **2** crystallising in the cubic *P*2₁3 space group and **3** and **4** in the monoclinic *P*2₁/*m* and *P*2₁/*n* space groups, respectively.

Disregarding the parameters involving the hydrogen atoms of the MH₃ group, which are too ill-determined, the four heavy-atom distances diverge more significantly with the reduction in symmetry of **3** and **4** than do the five angles: the XRD experimental values of these angles correspond generally quite well with the calculated ones for all three adducts. The GED studies of **1–3** give values for the heavy-atom parameters that are also in good

agreement with *ab initio* calculations. In general the calculations performed at the MP2/6–311+G* level of theory compare more favourably with the gas-phase structures than those performed at the B3LYP level using the same basis sets. This is especially true for **1**, where the B3LYP calculations find the lowest energy structure to have *C*_{3v} symmetry, contrary to the findings of both MP2 calculations and the GED experiment.

The differences in the bond lengths between the symmetry-independent sets in **3** and **4** are substantial—the largest amounts to 0.040 Å for the C(3)–C(4) distance in **3**—but the trends remain clear: within each symmetry-independent set, the two C–C bond lengths remain virtually equal, in contrast to the results of the calculations, for which the difference is larger. The C–N distances are the shortest of the heavy-atom distances in the cage found experimentally in the gas phase and in the solid, and according to the calculations. While the MP2 calculations estimate the M–N distances well for **2** and **3** in the gas phase, the M–N bonds in the crystal structures are shorter than calculated by 0.022, 0.065 and 0.125 Å for **3** and **4**, respectively, but this is rather common for adducts, for which crystallisation usually results in a significant shortening of the coordinate link.^{8,9,33,34}

It is interesting to observe that the three heavy-atom distance parameters of the quinuclidine fragment remain fairly constant on going from **2** to **4**. This is particularly true for the calculated distances (largest difference 0.007 Å for MP2/6–311+G* calculations). Similarly small differences are observed for the GED structures of **2** and **3** although there are bigger differences in the crystal values, with the N–C(2) distance in **3** differing by 0.032 Å from that in **4**. The M–N distance increases with the atomic number of *M*, as observed by both calculation and experiment. From calculations, the increase upon changing B in **2** to Al in **3** amounts to about 0.426 Å, while the increase is only 0.132 Å for the transition from Al in **3** to Ga in **4**. The difference is understandable, up to a point, on the basis of the covalent radii of the relevant atoms, *viz.* 0.88, 1.25 and 1.25 Å for B, Al and Ga, respectively.³⁵ The similar sizes of Al and Ga are also reflected in the M–H distances, which are calculated to be virtually identical for **3** and **4**, at least at the MP2 level; B3LYP/6–311+G* gives a difference of 0.02 Å. That some of the XRD experimental values for M–H differ substantially from those calculated while others are very close can be attributed mainly to the poor experimental definition of the H atom positions.^{4,13,36} The bond lengths for **3** and **4** are in keeping with a general pattern. For bonds of relatively low polarity, *e.g.* M–H and M–C, the lengths are indeed usually much the same for *M* = Al and Ga. However, increasing polarity causes the bonds to gallium to become slightly longer than those to aluminium (a feature reflected in ionic radii of 0.535 Å and 0.620 Å for Al³⁺ and Ga³⁺, respectively, admittedly in sixfold coordination).³⁵

Coordination of an MH₃ molecule to the quinuclidine skeleton distorts the former from the planar *D*_{3h} symmetry of the free molecule to a pyramidal *C*_{3v} shape. Since the parameters associated with the hydrogen atoms of the hydrides are poorly determined in the crystal structures, the following discussion will be based solely on the calculated values and those for **2** and **3** obtained by GED. The extent of the distortion is expressed most conveniently by the N–M–H angle, which is about 100° for **3** and **4** and 106° for **2**, compared with 90° in the absence of any distortion. The same trend is reflected in the angles between the hydrogen atoms in the MH₃ fragment, which are about 117° for the adducts with

the heavier atoms, **3** and **4**, and only 113° for **2**. The extent of pyramidalisation correlates with the length of the M–N bond, which is at its shortest for the borane adduct **2**. The N–M–H and H–M–H angles reflect the degree to which charge is transferred to the MH₃ unit from the base molecule, and hence the strength of the coordinate link as a covalent bond.^{33,34,37} With the formation of the M–N bond, electron density flows out of the base and increases the net negative charge on the MH₃ unit, causing the M–H bonds to become longer. The calculated M–H bond lengths (MP2/6–311+G*) in the free hydrides are 1.191 Å (M = B), 1.575 Å (M = Al) and 1.573 Å (M = Ga); in the adducts these are extended by 0.026, 0.033 and 0.029 Å, respectively.

By contrast, coordination of the MH₃ molecule to quinuclidine has a relatively small impact on the geometric parameters of the latter, but several changes are noteworthy. Both by calculation and GED experiment, the C(3)–C(4) distances remain virtually identical to those in the parent molecule, the C(2)–C(3) distances become shorter by about 0.01 Å, and the N–C(2) distances are elongated by about 0.02 Å, the exact values depending on the method and basis set. On the other hand, the valence angles change little, the maximum difference being about 2°, although many differences are smaller.

When quinuclidine is linked to an MH₃ group, the quinuclidine cage is calculated to be more twisted than in the isolated molecule, **1**. The twist is most pronounced in **2**, where ϕ C(2)–N–C(4)–C(3) was calculated to be –10.8° (MP2/6–311+G*) and for **3** and **4** the equivalent values were –10.5° and –9.5°, respectively. The values calculated at the B3LYP/6–311+G* level were smaller in all cases: –3.9°, –1.9° and –2.0° for **2**, **3** and **4**, respectively, although we found this level of calculation to be unreliable for **1**. For the GED-refined structures ϕ C(2)–N–C(4)–C(3) was found to be –4.5(23)° for **2** and –8.3(6)° for **3**.

Calculations (MP2/6–311+G*) were performed where ϕ C(2)–N–C(4)–C(3) and its two symmetrically equivalent dihedral angles were fixed at 0° for each of **2–4**. For **2** the constrained structure was 2.9 kJ mol^{–1} higher in energy than the global minimum structure and for **3** and **4** the increases in energy were 2.5 and 1.6 kJ mol^{–1}, respectively. As is the case for **1**, the experimental data seem to support the case for these molecules possessing twisted quinuclidine cages.

The energetics of quinuclidine–MH₃ adduct formation

To assess the strength of the interaction between a group 13 trihydride MH₃ and a neutral base L, such as quinuclidine, it is necessary to consider not just the dissociation energy, E_{diss} , but also the fragmentation energy, E_{frag} , of the gaseous adduct. With respect to reaction (1), E_{diss} is the energy change associated with the formation of the separated acid and base molecules, each with the geometries of their relaxed ground states.

E_{frag} , on the other hand, is the energy change associated with the formation of the separated acid and base molecules while still unrelaxed and retaining the geometries prescribed by the adduct. The counterpoise-corrected E_{diss} values we have calculated for the quinuclidine adducts are 165, 140, and 109 kJ mol^{–1} for the borane **2**, the alane **3**, and the gallane **4**, respectively; corresponding E_{frag} values are 229, 182, and 125 kJ mol^{–1}. The total relaxation

energies are therefore 64 kJ mol^{–1} for the quinuclidine and borane, 42 kJ mol^{–1} for the quinuclidine and alane, and 16 kJ mol^{–1} for the quinuclidine and gallane. These energies naturally invite comparison with those calculated for related adducts involving other nitrogen bases. For example, the following $E_{\text{diss}}/E_{\text{frag}}$ values (in kJ mol^{–1} and without ZPE corrections) have been estimated for some gallane complexes: H₃N·GaH₃ 113/127,³⁸ Me₂(H)N·GaH₃ 101/144,^{9,39} and Me₃N·GaH₃ 102/144.^{9,39} Admittedly different methods of calculation have been used [DFT/BP/SVP for ref. 38 and MP2/6–311++G(d,p) for ref. 9 and ref. 39] and so no great weight can be given to comparisons of the absolute values, but the implied relaxation energies of 14, 43, and 42 kJ mol^{–1} suggest that the value of 16 kJ mol^{–1} for quinuclidine–gallane, **4**, is relatively small. Hence quinuclidine gains its strength as a base in these circumstances not from any electronic or steric advantage, but from the relative rigidity of its cage-like structure. This causes the dissociation energy of a complex such as **4** to be higher than it would be for a similar adduct involving an equivalent base but with an open structure. Significantly, too, it also leads to a less favourable entropy term in the dissociation of the quinuclidine complex, since degrees of freedom gained by the release of a base such as Me₃N (involving inversion, for example) do not exist with the rigid quinuclidine molecule.

Conclusions

A definitive molecular structure of the gaseous quinuclidine molecule has been determined from its GED pattern on the basis of (i) the refinement of all independent parameters, and (ii) the inclusion of rotational constants as additional observations. Quantum chemical calculations at the MP2 level of theory generate comparable results, which correspond well with those obtained from the GED experiment, although calculations at the B3LYP level identify a different minimum. A computational, electron diffraction and crystal-phase analysis of the structures and energetics of the adducts of quinuclidine with three group 13 trihydrides, MH₃ (M = B, Al or Ga), indicates that the cage fragment is fairly insensitive to the effects of adduct formation. Significant changes in the hydride fragment have been discussed in terms of the properties of M and the strength and nature of the M–N interaction.

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