Synthesis of C-substituted *t*-BuNH-8,9-R,R′-*nido*-7,8,9-$C_3B_8H_9$ (R,R′ = H,H; MeH; Me,Me; Ph,H and Ph,Ph) tricarbollide compounds and their tautomeric conversions. Effect of substituents on tautomeric equilibria between neutral and zwitterionic forms†

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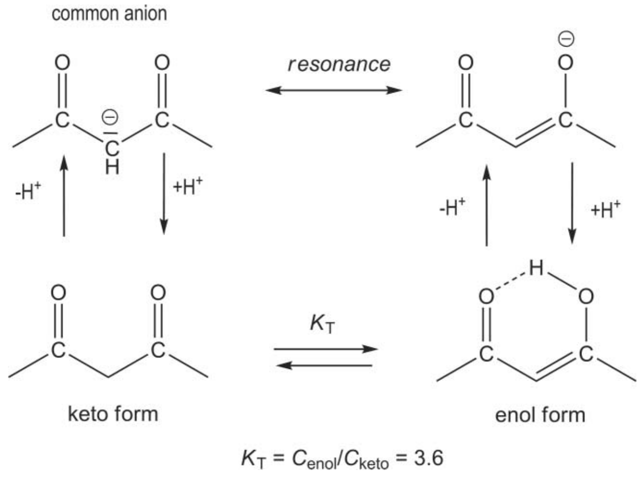
Treatment of C-substituted *nido* dicarbadecaboranes 5,6-R′,R-5,6-$C_2B_8H_{10}$ (**1**) (where R′,R = H,H (**1a**); H,Me, (**1b**); Me,Me, (**1c**); H,Ph, (**1d**) and Ph,Ph, (**1e**) with 1,8-bis-(dimethylamino)naphthalene (proton sponge = PS) and *t*-BuNC in CH_2Cl_2, followed by acidification, generated a series of pure neutral compounds 7-*t*-BuNH-8,9-R,R′-*nido*-7,8,9-$C_3B_8H_9$ (**N2**) (where R,R′ = H,H (**N2a**); H,Me (**N2b**); Me,Me (**N2c**); H,Ph (**N2d**), and Ph,Ph (**N2e**)), each of which exhibits tautomerism. Dissolution of the substituted compounds (**N2b–N2e**) in protic solvents (PRS), such as MeCN and Me_2CO, leads to tautomeric equilibrium with the zwitterionic tautomers 7-*t*-BuNH$_2$-8,9-R,R′-*nido*-7,8,9-$C_3B_8H_8$ (**Z2**) (where R,R′= H,H (**Z2a**); H,Me (**Z2b**); Me,Me (**Z2c**); H,Ph (**Z2d**) and Ph,Ph (**Z2e**)), while the unsubstituted compound **N2a** exhibits absolute tautomerism – a complete conversion into the zwitterionic tautomer **Z2a**. The tautomeric behaviour of individual compounds is therefore strongly affected by the nature of the substituent, as assessed *via* NMR spectroscopy in terms of tautomerisation constants $K_T = C_{Z2}/C_{N2}$ (where C_{Z2} and C_{N2} are equilibrium concentrations of **Z2** and **N2** forms in a given solvent). Individual tautomers were characterised by ^{11}B and ^{1}H NMR spectroscopy and the structure of the monomethylated **N2b** tautomer was determined by an X-ray diffraction study.

Introduction

Tautomerism, which is an equilibrium between two or more alternative structures of a single species, has been observed for many compounds in organic chemistry. This phenomenon is typical for compounds that contain a functionality that is able to donate a proton, and another, which is able to accept it, within the same molecule and in close enough proximity to one another. The tautomerisation equilibrium is in all such cases transmitted *via* a common anion. As far as we are aware, the most pronounced textbook example of tautomerism is the equilibrium between the keto and enol forms of acetylacetone, as shown in Scheme 1.[1] The tautomerisation constant, defined as $K_T = C_{enol}/C_{keto}$, is in this case 3.6 for neat acetylacetone. As a consequence of tautomeric equilibria no pure tautomers of acetylacetone can be isolated. On the other hand, quite common in organic chemistry is the case that a compound occurs in only one tautomeric form. For example, malonamide, $NH_2CO–CH_2–CONH_2$, is known as a keto form only,[2] while hexafluoroacetylacetone occurs only as the enol form, $F_3CCO–CH=C(OH)CF_3$.[3] As far as we are aware, a third case when both tautomeric forms can be isolated in pure state, so called absolute tautomerism has been reported for the first time by our group in a preliminary communication.[4]



Scheme 1 Equilibrium between keto and enol forms in acetylacetone.

This unique phenomenon was established in the C-amino substituted tricarbollide (11-vertex *nido*-tricarbaborane) series in which a compound adopts only one of two different tautomeric structures, either 7-R,R′NH-7,8,9-$C_3B_8H_{10}$ (**Z**) (zwitterionic) or 7-R,R′N-7,8,9-$C_3B_8H_{11}$ (**N**) (neutral) (where R,R′ = hydrogen or alkyls). Each tautomer can be interconverted using solvents of different proton-transfer capability. We have also established that the solvent induced **Z** → **N** and **N** → **Z** conversions proceed *via* common [7-R,R′N-7,8,9-$C_3B_8H_{10}$]$^-$ anions and are essentially

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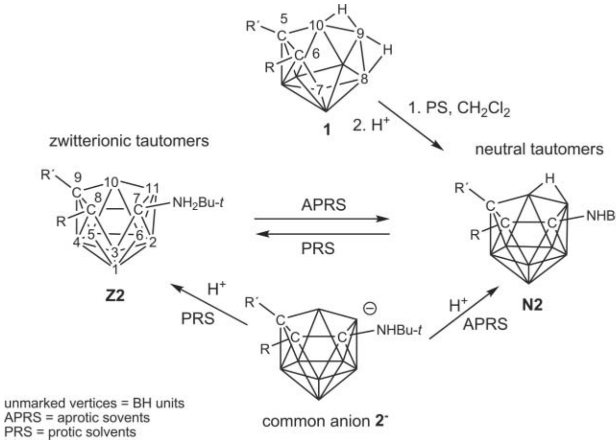
independent of R,R′ alkyls attached to the nitrogen atom.[4] On the other hand, some compounds of the same cluster constitution, but substituted on boron, such as 10-Me-7-*t*-BuNMe-7,8,9-$C_3B_8H_{10}$ and 10,11-Me_2-7-*t*-BuNMe-7,8,9-$C_3B_8H_9$, have so far been isolated only in the **N** form.[5] This means that substituents on boron rather than on carbon vertices of the carborane cluster may significantly affect the formation of individual tautomers. In this work, which initiates more detailed studies of the effects of cluster substitution on tautomeric behaviour, we would like to report on the synthesis of the mutually tautomeric derivatives 7-*t*-BuNH-8,9-R,R′-*nido*-7,8,9-$C_3B_8H_9$ and 7-*t*-BuNH_2-8,9-R,R′-*nido*-7,8,9-$C_3B_8H_8$ that contain H, Me and Ph substituents on cluster carbon atoms, in close proximity to proton donating centres. Presented will also be scope and limitation of their room-temperature tautomeric interconversions along with crystallographic and NMR (^{11}B and ^{1}H) characterisation of individual tautomeric pairs.

Results and discussion

Syntheses and tautomeric conversions

As shown in Scheme 2, treatment of the C-substituted *nido* dicarbadecaboranes 5,6-R′,R-5,6-$C_2B_8H_{10}$ (**1**) (where R′,R = H,H (**1a**); H,Me, (**1b**); Me,Me, (**1c**); H,Ph, (**1d**) and Ph,Ph, (**1e**)[6] with proton sponge (PS = 1,8-bis-(dimethylamino)naphthalene) (*in situ* generation of anion $\mathbf{1}^-$) and *t*-BuNC in CH_2Cl_2, followed by acidification and evaporation of the CH_2Cl_2 layer, generated a series of pure neutral compounds 7-*t*-BuNH-8,9-R,R′-*nido*-7,8,9-$C_3B_8H_9$ (**N2**) (where R,R′ = H,H (**N2a**); H,Me (**N2b**); Me,Me (**N2c**); H,Ph (**N2d**), and Ph,Ph (**N2e**)), each of which exhibits tautomerism. Dissolution of these **N2** compounds in protic solvents (PRS), such as MeCN or Me_2CO, leads in turn either to complete (only in the case of the unsubstituted **N2a**) or equilibrium (in the case of all other substituted derivatives **N2b–N2e**, see also Table 1 below) conversion into the zwitterionic tautomers 7-*t*-BuNH_2-8,9-R,R′-*nido*-7,8,9-$C_3B_8H_8$ (**Z2**) (where R,R′ = H,H (**Z2a**); H,Me (**Z2b**); Me,Me (**Z2c**); H,Ph (**Z2d**) and Ph,Ph (**Z2e**)).



Scheme 2 Formation and tautomeric conversions between neutral 7-*t*-BuNH-8,9-R,R′-7,8,9-$C_3B_8H_9$ (**N2**) and zwitterionic 7-*t*-BuNH_2-8,9-R,R′-7,8,9-$C_3B_8H_8$ (**Z2**) compounds *via* common anions [7-*t*-BuNH-8,9-R^2R^1-7,8,9-$C_3B_8H_8$]$^-$ ($\mathbf{2}^-$). For numbering of the ten- and eleven-vertex *nido* cages see structures **1** and **Z2**, respectively.

Table 1 Tautomerisation constants *K* (% of conversion to the **Z2** form) for 8,9-R,R′-substituted compounds of type **2** in common NMR solvents at 296 K

Compound[a]	CD_3CN	$(CD_3)_2CO$	$CDCl_3$	CD_2Cl_2
2a	∞ (100)	0 (0)	0 (0)	0 (0)
2b	5.62 (85)	2.91 (75)	0.55 (35)	0 (0)
2c	2.02 (67)	1.39 (58)	0 (0)	0 (0)
2d	19.00 (95)	15.00 (93)	0 (0)	0 (0)
2e	25.00 (96)	17.00 (94)	0 (0)	0 (0)

[a] For compounds with K_T = 0 and infinity, pure (absolute) **N2** or **Z2** tautomers can be isolated.

It should be noted that crystallisation from aqueous EtOH also strongly enhances the formation of **Z2** tautomers.

As seen in Fig. 1, a simple ^{11}B NMR experiment at 296 K can be designed to clearly demonstrate and understand the tautomeric interconversion for the simplest (unsubstituted) tautomeric pair 7-*t*-BuNH-7,8,9-$C_3B_8H_{11}$ (**N2a**) and 7-*t*-BuNH_2-7,8,9-$C_3B_8H_{10}$ (**Z2a**). Upper part (a) of Fig. 1 shows the typical ^{11}B NMR patterns of **N2a** in $CDCl_3$. But when the $CDCl_3$ was removed from the NMR tube by the stream of nitrogen and the residue re-dissolved in CD_3CN, a completely different spectrum, attributed to the zwitterionic tautomer **Z2a**,[5] as shown in the bottom part (b) of Fig. 1, was obtained. Moreover, replacement of CD_3CN by $CDCl_3$ in the same sample recovers again the original spectrum of **N2a**. These experiments clearly show that a *quantitative* conversion between **Z2a** and **N2a** tautomers can be achieved *via* a simple switch between solvents of different proton-transfer properties. Both tautomeric forms **Z2a** and **N2a** can also be easily isolated in the solid state as pure chemical individuals and therefore we call

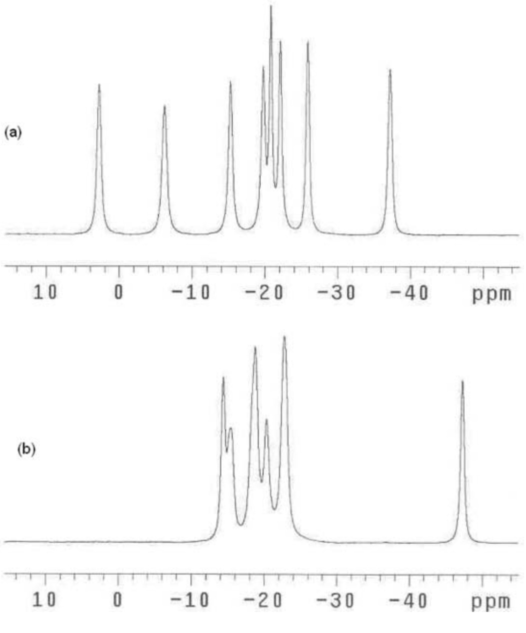


Fig. 1 Absolute tautomerism exemplified by entirely different $^{11}B\{^1H\}$NMR spectra of the same compound "7-*t*-BuNH_2-7,8,9-$C_3B_8H_{10}$" (**2a**) at 296 K in (a) $CDCl_3$ and (b) CD_3CN. Spectrum (a) corresponds to the neutral tautomer 7-*t*-BuNH-7,8,9-$C_3B_8H_{11}$ (**N2a**) and spectrum (b) to the zwitterionic tautomer 7-*t*-BuNH_2-7,8,9-$C_3B_8H_{10}$ (**Z2a**). Both spectra are interconvertible by exchange of these two solvents.

this unique phenomenon absolute tautomerism (AT)[4] – the same compound can be isolated in two different structural forms.

Scheme 2 shows that the **N2** and **Z2** tautomers differ in the positioning of one hydrogen atom. This resides either in the bridging position between the B10 and B11 vertices (**N2** tautomers) or on the exohedral nitrogen atom (**Z2** tautomers). From the viewpoint of cluster-boron chemistry such a difference is rather significant: compounds **N2**, in which the bridging H-atom constitutes a part of the cluster, are 7-*t*-BuNH-derivatives of the neutral tricarbaborane *nido*-7,8,9-$C_3B_8H_{12}$, whilst compounds **Z2** are zwitterionic derivatives of the [*nido*-7,8,9-$C_3B_8H_{11}]^-$ anion.[7]

Table 1 demonstrates that the ratio between individual tautomeric forms (defined by $K_T = C_{Z2}/C_{N2}$, where C_{Z2} and C_{N2} are equilibrium concentrations of **Z2** and **N2** forms in a given solvent[1]) is strongly dependent both on the nature of solvent and type of substitution on cluster carbons. Protic solvents (PRS), such as CD_3CN or $(CD_3)_2CO$, induce the formation of the zwitterionic (**Z2**) tautomers, while aprotic solvents (APRS), such as $CDCl_3$ and CD_2Cl_2, induce a complete formation of the neutral (**N2**) tautomers in the series of compounds outlined above. Similar trends of tautomeric conversions were observed also for the Me and Ph substituted compounds, except that their **N2** → **Z2** conversions in CD_3CN are incomplete. This is shown in Table 1 by the K_T constants (defined as $K_T = C_{Z2}/C_{N2}$, where C_{Z2} and C_{N2} are equilibrium concentrations of the **Z2** and **N2** forms in a given solvent)[4] of individual compounds in selected NMR solvents, as determined by room-temperature ^{11}B NMR spectra. It is seen that the K_T values for the C-substituted derivatives of **2a** are strongly solvent-dependent. For instance, while in CD_2Cl_2 (or CH_2Cl_2) the monomethylated compound **2b** occurs only in the neutral **N2b** form ($K_T = 0$), in $CDCl_3$, acetone-d_6, and CD_3CN **Z2b** ≪ **N2b** equilibria are observed ($K_T = 0.55$, 2.91, and 5.62, respectively). The dimethylated compound **2c** adopts the neutral structure **N2c** both in CD_2Cl_2 and $CDCl_3$, while in CD_3CN and $(CD_3)_2CO$ we observe **Z2c**/**N2c** equilibria ($K_T = 2.02$ and 1.39, respectively). Similar trends, but different in magnitudes, are observed for the phenyl analogues **2d** and **2e**. The K_T constants can be thus used as a measure of proton transfer efficiency, which establishes the expected order of solvents of decreasing proton-transfer affinity: MeCN > Me_2CO > $CHCl_3$ > CH_2Cl_2.

As a result, pure tautomers **N2** were isolated for all compounds of type **2**, while pure zwitterionic tautomers **Z2** were isolated only for the unsubstituted compound **Z2a** which exhibits absolute tautomerism. The **N2** → **Z2** conversions of the C-substituted compounds are incomplete due to steric and electronic effects of the Me and Ph substituent(s) residing on the cage carbon atom(s). These findings are also in agreement with higher stability of the **N2** tautomers, as predicted by RMP2(fc)/6-31G* calculations.[4] Nevertheless, these calculations reflect gas-phase results and would not be expected to exactly reproduce experimental findings from solutions.

As demonstrated in Fig. 2 for CD_3CN–$CDCl_3$ mixtures, the addition of CD_3CN to a $CDCl_3$ solution of **N2** leads expectedly to a classical equilibrium between the **Z2** and N2 tautomers. It is seen that by adding CD_3CN to a $CDCl_3$ solution of **N2** tautomer the concentration of the **Z2** tautomer grows in an approx. linear manner and that the growth is dependent of the nature of substituents on the cage-carbon vertices. It can be also inferred from Fig. 2 that the tendency for the formation of the zwitterionic tautomers **Z2** decreases in the series H ≫ Ph > Me and also with the number of substituents on the cluster carbon vertices.

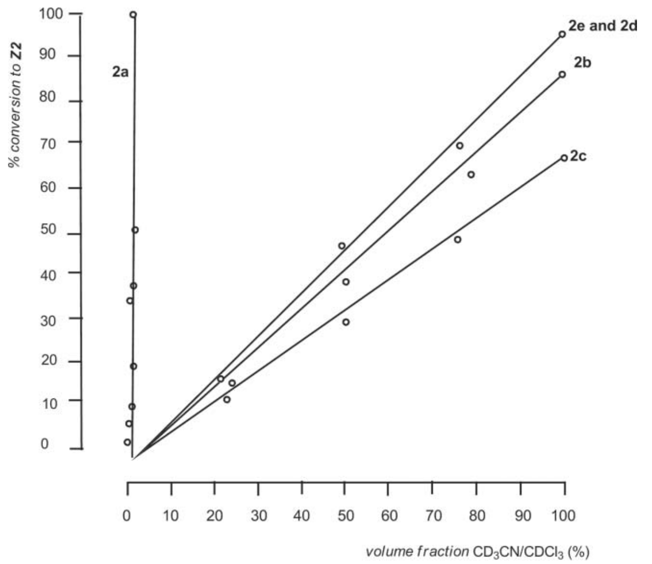


Fig. 2 Tautomeric equilibria between **Z2** and **N2** forms in CD_3CN–$CDCl_3$ solvent mixtures at 296 K.

It is reasonable to suggest that the tautomeric conversions outlined above are achieved *via* a simple proton transfer between the two proton donating and proton accepting centers, the N atom and the open-face B10–B11 bond (see Scheme 2).[4] The tautomeric conversions are thus supposed to proceed *via* common [7-*t*-BuNH-8,9-R,R′-7,8,9-$C_3B_8H_8]^-$ ($\mathbf{2}^-$) anions, the protonation of which at the N center leads to **Z2** tautomers, while the protonation of the open-face B10–B11 bond results in the corresponding **N2** tautomers. The proton transfer from the bridging μ-H10,11 position to the N atom is strongly affected by the nature of substituents (Me and Ph) residing in close proximity of the amine nitrogen. Both size and electronic effects of these substituents may play a dominating role in the transfer of the tautomerising hydrogen. Table 1 clearly shows that the tendency for the formation of **Z** tautomers decreases in the following order of substituents:

$$8,9\text{-}H_2 \gg 8,9\text{-}Ph_2 > 8\text{-}Ph > 8\text{-}Me > 8,9\text{-}Me_2$$

Intercomparison of ^{11}B NMR chemical shifts of individual boron vertices for the whole series of **N2** and **Z2** tautomeric pairs is given in Fig. 3 and 4. For C-substituted compounds, the values for **Z2** were extrapolated by subtracting the spectra of **N2** from the mixed spectra. The figure shows sharp, dramatic differences between individual pairs on one hand and gross similarities within each series (**N** or **Z**) on the other. Similar considerations are also valid for the corresponding ^{1}H NMR shifts.

Individual tautomers of the **N2** and **Z2** series can be also isolated in the solid state, as documented by X-ray diffraction analyses of the zwitterionic 7-*t*-BuN(Me)H-*nido*-7,8,9-$C_3B_8H_{10}$.$COMe_2$ (**Z2**configuration)[5] and **N2b** (see Fig. 5). The figure clearly shows that the two structures differ mainly in the open-face B10–B11 bond distances. This is for **N2b**, 0.112 Å shorter than that in **Z2** because of the presence of the bridging μ-$H_{10,11}$ hydrogen atom. The C7–N1 distance in **N2b** (1.486 Å) is only 0.023 Å shorter than the equivalent C–N vector in the zwitterionic

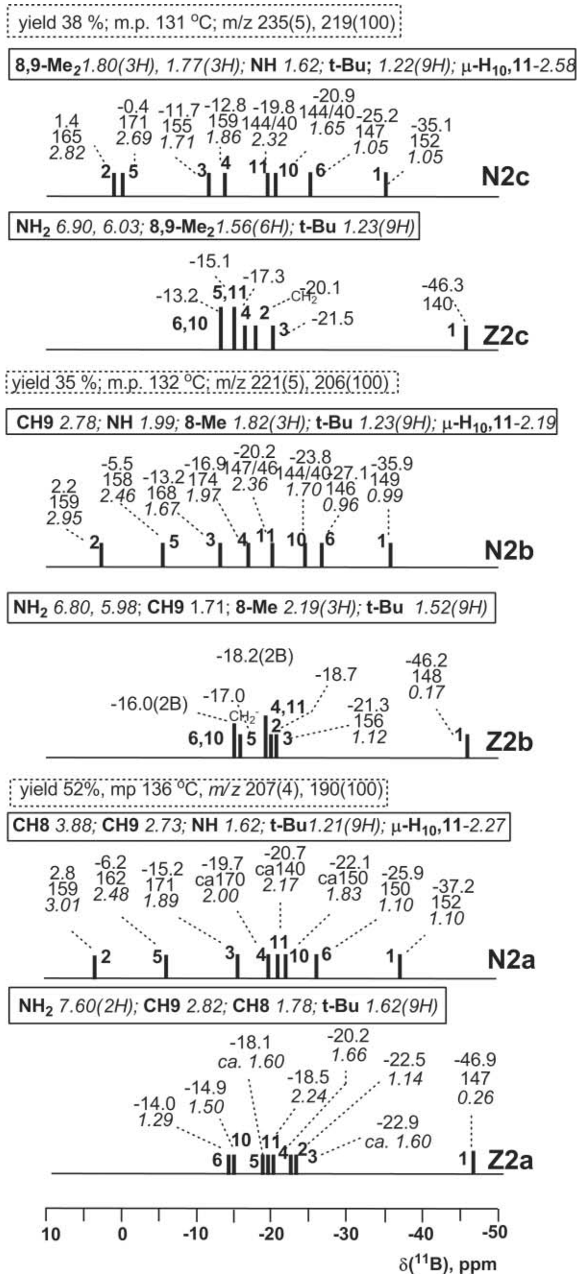


Fig. 3 Graphical representation of experimental data for the H- and Me-substituted derivatives of the **N2** and **Z2** series (NMR data at 296 K in $CDCl_3$ and CD_3CN, respectively). Stick-type intercomparison of ^{11}B NMR chemical shifts and intensities for individual tautomeric pairs. Included are also numerical values for individual BH vertices (ordered as $\delta(^{11}B)$, $^{1}J(BH)$ and $\delta(^{1}H)$ (in italics)). Framed (full line) text includes additional $\delta(^{1}H)$ data (in italics) and other experimental data are in dotted frames. For numbering see Scheme 1. Data for **Z2a** from ref. 5.

7-*t*-BuN(Me)H-*nido*-7,8,9-$C_3B_8H_{10}$.$COMe_2$[5] and is therefore consistent with a single bond. However, the C7–N1–C11 angle in **N2b** (123.86(8)°) shows a considerable distortion from the ideal 109°, which may be attributed to the presence of a free electron pair on N1 rather than to the double-bond character of the C7–N1 bond. On the other hand, the associated C7–N1–H1A (109.4(9)°) and C11–N1–H1A (111.1(9)°) angles are in agreement with a tetragonal arrangement around the N1 atom.

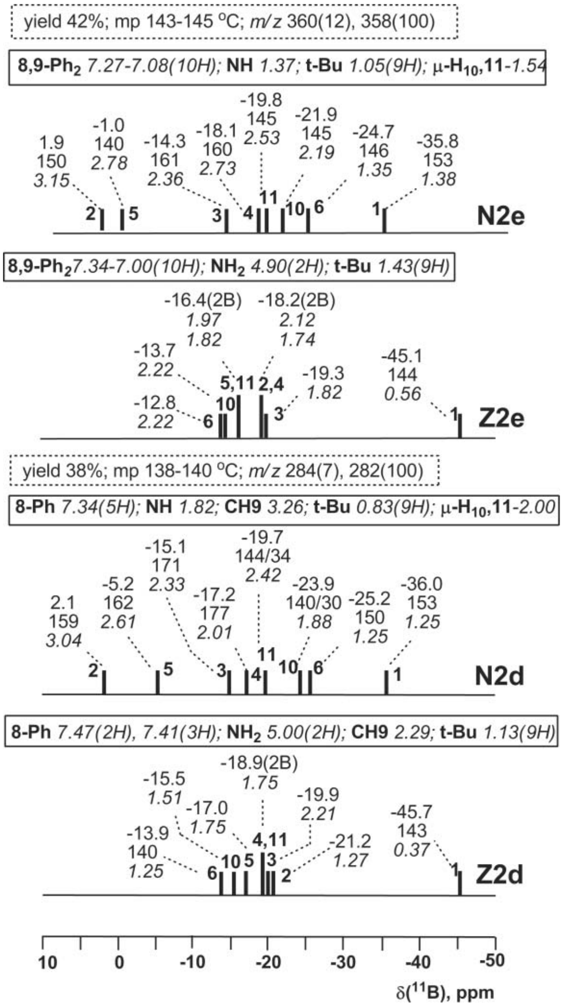


Fig. 4 Graphical presentation of experimental data for the Ph-substituted derivatives of the **N2** and **Z2** series (NMR data at 296 K in $CDCl_3$ and CD_3CN, respectively). For other comments see Fig. 3.

Experimental

General

All reactions were carried out with use of standard vacuum or inert-atmosphere techniques as described by Shriver,[8] although some operations, such as column LC (silica gel Aldrich 250-350 mesh), were carried out in air. The starting carboranes of type **1** were prepared according to the literature.[6] Dichloromethane and hexane were dried over CaH_2 and freshly distilled before use. Other chemicals were of reagent or analytical grade and were used as purchased. Analytical TLC was carried out on Silufol (silica gel on aluminium foil; detection by I_2 vapour, followed by 2% aqueous $AgNO_3$ spray). Low-resolution mass spectra were obtained using a Finnigan MAT Magnum ion-trap quadrupole mass spectrometer equipped with a heated inlet option, as developed by Spectronex AG, Basel, Switzerland (70 eV, EI ionisation). ^{1}H and ^{11}B NMR spectroscopy was performed at 9.4 T on a Varian Mercury 400 instrument at 296 K. The $[^{11}B–^{11}B]$-COSY[9] and $^{1}H–\{^{11}B(selective)\}$[10] NMR experiments were made essentially as described earlier.[11]

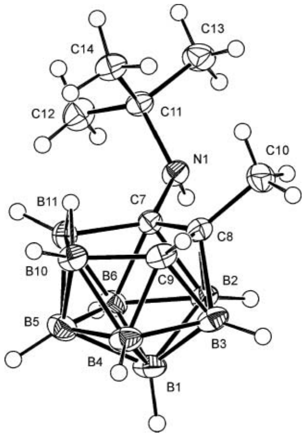


Fig. 5 ORTEP representation of the crystal and molecular structure of the neutral tautomer 7-*t*-BuNH-8-Me-7,8,9-$C_3B_8H_{10}$ (**N2b**). Displacement ellipsoids are drawn on 50% probability level. Selected intracluster bond distances (Å) and angles (°) C7–N1 1.486(1), C7–C8 1.5616(12), C8–C9 1.5234(13), C9–B10 1.6539(16), B10–B11 1.8374(15); C8–C7–B11 107.29(7), C7–C8–C9 115.35(8), C8–C9–B10 110.03(8), C9–B10–B11 102.69(7), B10–B11–C7 104.02(7), C7–N1–C11 123.86(8). Other C–B and B–B bond lengths fall within usual limits.

General synthesis of the neutral tautomers 7-*t*-BuNH-8,9-R,R′-*nido*-7,8,9-$C_3B_8H_9$ (N2) (where R,R′ = H,H (N2a); H,Me (N2b); Me,Me (N2c); H,Ph (N2d), and Ph,Ph (N2e)

A solution of compounds of type **1** (**1a–1e**) (reaction scale *ca.* 5 mmol) in CH_2Cl_2 (30 ml) was treated with PS (1.1 g, 5 mmol) under stirring and cooling at 0 °C and the mixture was then stirred for an additional 2 h at ambient temperature. Upon treatment with 5% aq. HCl (10 ml) under shaking at 0 °C, the organic (bottom) layer was separated, dried with $MgSO_4$ and treated with silica gel (*ca.* 5 g). The mixture was evaporated and mounted onto the top of a silica gel column (2.5 × 30 cm). Elution with CH_2Cl_2 gave the main fractions of R_f (analytical) *ca.* 0.3–0.45, which were evaporated to give 36–55% yields of compounds of type **N2** (**N2a–N2e**) which were identified by NMR spectroscopy (for properties of individual compounds see Fig. 3 and 4).

X-Ray crystallography†

Crystal data for **N2b**: $C_8H_{23}B_8N$, $M = 219.75$, colourless plate, 0.51 × 0.25 × 0.08 mm^3, monoclinic, space group $P2_1/n$ (no. 14), $a = 9.9813$ (2), $b = 11.5093$ (2), $c = 12.7934(2)$ Å, $\beta = 111.6510$ (11)°; $V = 1365.99(4)$ Å^3, $Z = 4$, $D_c = 1.069$ Mg m^{-3}. Diffraction data were recorded with a Nonius Kappa CCD diffractometer (graphite-monochromatised Mo Kα radiation, $\lambda = 0.71073$ Å at 150(2) K; absorption was neglected ($\mu = 0.05$ mm^{-1}). A total of 24 777 was measured ($\theta_{max} = 27.5°$), from which 3120 were unique ($R_{int} = 3.0\%$), and 2746 observed according to the $I > 2\sigma(I)$ criterion.

The structure was solved by direct methods (SIR92)[12] and refined by full-matrix least squares routine based on F^2 (SHELXL97[13]). Non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically, except those in methyl moieties which were placed in their optimised positions and refined as riding atoms with U_{iso}(H) assigned to a 1.5 multiple to U_{eq} of its bonding atom. The refinement converged ($\Delta/\sigma_{max} = 0.001$, 202 parameters) to $R = 3.8\%$ for the observed, and $wR = 11.0\%$, GOF = 1.04 for all diffractions. The final difference map displayed no peaks of chemical significance ($\Delta\rho_{max} = 0.23$, $\Delta\rho_{min} = -0.18$ e Å^{-3}).

Conclusions

As far as we are aware, the isolation of pure tautomers of the unsubstituted compound **2a** (structures **Z2a** and **N2a**) represents the first example of absolute tautomerism. This phenomenon introduces a new type of structural dualism to the discipline of chemistry, as the same compound can be isolated in two different structural forms, depending of proton transfer properties of the solvent used. We have also demonstrated that the C-substituted Me and Ph derivatives of type **2** can be isolated as pure neutral **N2** tautomers which can be partially converted into their zwitterionic (**Z2**) counterparts, the tautomeric conversion being remarkably dependent of the nature of substitution on the cluster carbon atoms. We are currently studying other chemical consequences of this unique phenomenon of tautomerism in the area of cluster boron chemistry.

Acknowledgements

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Notes and references

1 See, for example: F. A. Carey and R. A. Sundberg, *Advanced Organic Chemistry*, Springer, 5th edn, 2007.
2 N. V. Belova, H. Oberhammer, G. V. Girichev and S. A. Shlykov, *J. Phys. Chem. A*, 2007, **111**, 2248.
3 R. L. Lindvedt and H. F. Holtzclaw, *J. Am. Chem. Soc.*, 1966, **88**, 2713; A. L. Andeassen, D. Zebelman and S. H. Bauer, *J. Am. Chem. Soc.*, 1971, **93**, 1148.
4 M. Bakardjiev, J. Holub, D. Hnyk, I. Císařová, M. G. S. Londesborough, D. S. Perekalin and B. Štíbr, *Angew. Chem., Int. Ed.*, 2005, **44**, 6222–6226.
5 B. Štíbr, J. Holub, I. Císařová, F. Teixidor, C. Viñas, J. Fusek and Z. Plzák, *Inorg. Chem.*, 1996, **35**, 3635.
6 B. Štíbr, F. Teixidor, C. Viñas and J. Fusek, *J. Organomet. Chem.*, 1998, **550**, 125; Z. Janoušek, P. Kaszynski, J. D. Kennedy and B. Štíbr, *Collect. Czech. Chem. Commun.*, 1999, **64**, 986.
7 J. Holub, B. Štíbr, D. Hnyk, J. Fusek, I. Císařová, F. Teixidor, C. Viñas, Z. Plzák and P. V. R. Schleyer, *J. Am. Chem. Soc.*, 1997, **119**, 7750.
8 D. F. Shriver and M. A. Drezdon, *Manipulation of Air Sensitive Compounds*, Wiley, New York, 2nd edn, 1986.
9 See, for example: J. D. Kennedy, in *Multinuclear N. M. R.*, ed. J. Mason, Plenum Press, New York, 1987, p. 221; W. C. Hutton, T. L. Venable and R. N. Grimes, *J. Am. Chem. Soc.*, 1984, 106, 29; J. Schraml and J. M. Bellama, *Two-Dimensional NMR Spectroscopy*, Wiley, New York, 1982, and references therein.
10 X. L. R. Fontaine and J. D. Kennedy, *J. Chem. Soc., Dalton Trans.*, 1987, 1573.
11 B. Štíbr, J. Holub, M. Bakardjiev, D. Hnyk, O. Tok, W. Milius and B. Wrackmeyer, *Eur. J. Inorg. Chem.*, 2002, 2320.
12 A. Altomare, G. Cascarano, C. Giacovazzo and A. Guagliardi, *J. Appl. Crystallogr.*, 1993, **23**, 350.
13 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **64**, 112.