NINE-VERTEX POLYHEDRAL MONOAZABORANE CHEMISTRY: SYNTHESIS AND NMR CHARACTERIZATION OF *exo*-6-LIGAND-*arachno*-4-AZANONABORANES(11), 6-L-4-NB_8H_{11}*

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Reactions between *arachno*-4-NB_8H_{13} and Lewis bases L in dichloromethane or without solvent generate the previously unreported series of *arachno* compounds *exo*-6-L-*arachno*-4-NB_8H_{11}, where L = pyridine (py), quinoline (quin), isoquinoline (i-quin), urotropine (uro), and MeCN. These are characterized by mass spectrometry together with ^{11}B and ^{1}H NMR spectroscopy. The NMR results permit complete assignment of all resonances and thence permit comparison with the structurally similar compounds *exo*-6-L-*arachno*-4-EB_8H_{10} (for E = CH_2 or S).

We have a continuing and developing interest in the synthesis, NMR properties, structural characterization, and reactions of the nine-vertex Group 14, 15, and 16 polyhedral heteroboranes[1–13], with special emphasis so far on the *arachno* nine-vertex monocarbaborane[3,4], monoazaborane[5–8] and monothiaborane[9–12] families. Of these, we have previously reported on the *arachno*-4-CB_8H_{14} (refs[3,4]), 6-L-*arachno*-4-CB_8H_{12} (ref.[13]), *arachno*-4-NB_8H_{13} (refs[5–8]), *arachno*-4-SB_8H_{12} (refs[9,11]), and 6-L-*arachno*-4-SB_8H_{10} (ref.[12]) systems. One of the key compounds for the further development of nine-vertex *arachno* heteroborane chemistry is the parent unsubstituted *arachno*-4-azanonaborane(13), 4-NB_8H_{13} (compound *Ia* of the EB_8H_{12} type *A* for E = NH).

This essential basic azaborane was first isolated almost two decades ago, and was also at that time structurally characterized[5]. However, apart from alternative preparative routes[5–7], any further non-metallic chemistry has so far been unexamined. We

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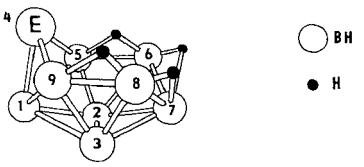
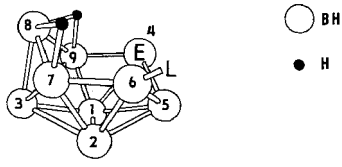
have now therefore developed this area somewhat by the exploration of the reactions of compound *Ia* with Lewis bases. This has led to the isolation of a previously unreported family of compounds of general constitution *exo*-6-L-*arachno*-4-NB_8H_{11} (compounds *IIa – IIe*, of general structure *B*), which we now describe in this paper.



A



B

I	E
a	NH
b	S
c	CH_2

II	E	L
a	NH	py
b	NH	quin
c	NH	i-quin
d	NH	uro
e	NH	MeCN

EXPERIMENTAL

General

Unless otherwise stated, all reactions were carried out under nitrogen though some subsequent operations, e.g., analytical thin layer chromatography (TLC), preparative TLC, and column chromatography, were carried out in air. The parent azaborane *Ia* was prepared by a literature method[7]. Hexane, dichloromethane and benzene were distilled from calcium hydride, and acetonitrile from P_4O_{10}, prior to use. Other compounds were of reagent or analytical grade and were used as purchased. All evaporations of solvents were carried out using standard rotary evaporation techniques and vacuum filtrations were performed using standard Schlenk apparatus. Preparative TLC was carried out using silica gel (Fluka GF 254) as the stationary phase on plates of dimensions 200 × 200 × 1 mm, made on glass formers from aqueous slurries followed by drying in air at 80 °C. The purity of individual chromatographic fractions was checked by analytical TLC on Silufol (Kavalier, silica gel on aluminium foil; detection by diiodine vapor, followed by 2% aqueous $AgNO_3$ spray).

Physical Measurements

Low resolution mass spectra were obtained using a JEOL HP-5985 instrument (70 eV EI, ionisation). Proton (^1H) and boron (^{11}B) NMR spectroscopy was performed at 9.4 Tesla on a Bruker AM 400

instrument. The [^{11}B-^{11}B]-COSY and ^{1}H-{^{11}B(selective)} NMR experiments were essentially as described in other recent papers from our laboratories[14,15]. Chemical shifts are given in ppm to high-frequency (low field) of Ξ = 32.083971 MHz (nominally $F_3B \cdot OEt_2$ in $CDCl_3$) for ^{11}B (quoted ±0.5 ppm) and Ξ = 100 MHz ($SiMe_4$) for ^{1}H (quoted ±0.05 ppm), Ξ being defined as in ref.[16]. Solvent resonances were used as internal secondary standards. Coupling constants $^{1}J(^{11}B\text{-}^{1}H)$ are taken from resolution-enhanced ^{11}B spectra with digital resolution 8 Hz and are given in Hz.

General Synthesis of the Compounds *arachno*-6-L-*arachno*-4-NB_8H_{11} (*IIa* – *IIe*) from *arachno*-4-NB_8H_{13} (*Ia*)

A typical experiment is described. Variations for individual compounds are in Table I. A mixture of compound *Ia* (114 mg; 1 mmol) and excess Lewis base was dissolved in dichloromethane or benzene (30 cm^3) and the solution was heated at reflux for 12 – 24 h (dihydrogen evolution). The volatile components were then evaporated and the solid residue subjected to preparative TLC on silica gel using solvent mixtures as in Table I as the liquid phase. The main fractions of R_F (anal.) as in Table I were collected, evaporated to dryness and then crystallized from a concentrated solution in dichloromethane that was overlayered with a twofold amount of hexane. This yielded crystals which were identified as the compounds *exo*-6-L-*arachno*-4-NB_8H_{11} (*IIa* – *IIe*) by NMR spectroscopy and mass spectrometry as described below. Analytical products were obtained by repeated crystallization.

RESULTS AND DISCUSSION

Syntheses

We have recently reported[12,13] on the formation of compounds with the nine-vertex *exo*-6-L-*arachno*-4-EB_8H_{10} constitution *B*, for E = both CH_2 and S. Of these, the thiaboranes were obtained from the reactions between *arachno*-4-SB_8H_{12} (*Ib*) and a variety

TABLE I
Products from reactions between *arachno*-4-NB_8H_{13} (*Ia*) and Lewis bases

Reaction conditions				Products				
Base	ratio[a]	solvent	time, h	product	yield, %	colour	R_F	*m*/*z*(max)[b]
py	2	C_6H_6	24	*IIa*	72	yellow	0.16[c]	192
quin	2	CH_2Cl_2	12	*IIb*	82	yellow	0.20[d]	242
i-quin	2	CH_2Cl_2	12	*IIc*	81	yellow	0.24[d]	242
uro	2	C_6H_6	24	*IId*	45	white	0.23[e]	253
MeCN[f]	excess	MeCN	24	*IIe*	56	white	0.38[g]	154

[a] Molar ratio base/NB_8H_{13}. [b] M^+ under EI mode, with additional fragmentation to $[L^+]$ and $[LBH_3]^+$. [c] 50% hexane in CH_2Cl_2. [d] 33% hexane in CH_2Cl_2. [e] 17% MeCN in CH_2Cl_2. [f] Carried out in the presence of one molar equivalent of I_2. [g] CH_2Cl_2.

of Lewis bases L (ref.[12]). This simple reaction suggested to us that the isostructural analogue, *arachno*-4-NB_8H_{13} (*Ia*), might behave similarly, and this has proved to be so. Thus, the reactions between *Ia* (reaction scale 1 mmol) and the Lewis bases pyridine (py), quinoline (quin), isoquinoline (i-quin), urotropine (uro), and MeCN in dichloromethane or benzene (or without solvent for MeCN) at reflux temperatures over a period of 12 – 24 h gave the series of isostructural compounds *exo*-6-L-*arachno*-4-NB_8H_{11}, where L = pyridine (*IIa*), quinoline (*IIb*), isoquinoline (*IIc*), urotropine (*IId*), and MeCN (*IIe*), in yields of 45 – 82%. For precise quantities and conditions, see Table I. These were isolatable by preparative TLC, and crystallized from a CH_2Cl_2–hexane mixture. Their molecular formulae were confirmed by mass spectrometry and NMR spectroscopy as described below.

In contrast to the reactions involving the thiaborane compound *Ib*, some weaker Lewis bases, such as SMe_2 and PPh_3, did not give the corresponding azaborane derivatives under similar conditions. Moreover, the reaction with MeCN had to be promoted by the addition of an equivalent amount of I_2, otherwise no derivative *IIe* is formed. In general, the relative reactivity of the *arachno*-4-EB_8H_{12} compounds of schematic structure *A* [where E = CH_2 (*Ic*), NH (*Ia*), and S (*Ib*)] toward Lewis bases generally decreases along the heteroatomic sequence S > N >> C (the carbon analogue does not react at all).

$$\underset{Ia}{NB_8H_{13}} + L \xrightarrow{\text{fast}} \underset{III}{[LH]^+[NB_8H_{12}]^-} \xrightarrow{\text{slow}} \underset{IIa - IIe}{LNB_8H_{11}} + H_2 \qquad (1)$$

The reaction between *Ia* and Lewis bases is not inconsistent with a simple scheme as in (*1*) that, as in the case of the thiaborane compound[12] *Ib*, would involve an anionic intermediate, here formulated as [*arachno*-4-$NB_8H_{12}]^-$ (compound *III*). Some insight into the reaction between compound *Ia* and the Lewis bases L may be provided by the results of a reaction in an NMR tube between compound *Ia* and pyridine, carried out in $CDCl_3$. In this experiment a species provisionaly identified as the previously uncharacterized [*arachno*-4-$NB_8H_{12}]^-$ anion *III* was detected as a predominant product by ^{11}B NMR spectroscopy in the initial stages of the reaction (ca 15 min). Further attack by the $[LH]^+$ cation on *III*, or a direct nucleophilic reaction between L and the neutral *Ia*, could then therefore be responsible for the formation of the azaborane compounds of type *B*. We find that anion *III* can also be generated in situ by the deprotonation of *Ia* with "proton sponge" (*N,N,N′,N′*-tetramethylnaphthalene diamine, tmnd) in $CDCl_3$ in an NMR tube.

The mass spectra of the ligand derivatives *IIa – IIe* (Table I) exhibited the expected molecular ion peaks and showed principal fragmentations with characteristic $[L]^+$ and $[LBH_3]^+$ molecular ions.

NMR Spectroscopy

All compounds were examined by NMR spectroscopy in order to confirm bulk purity, and in order to measure and assign the observed resonances and to confirm the molecular formulation. ^{11}B and ^{1}H NMR spectroscopy, making use of the [^{11}B-^{11}B]-COSY (ref.[17]) (for characteristic cross-peaks see Table II) and ^{1}H-{^{11}B(selective)} techniques[18], resulted in the complete assignment of all the ^{1}H and ^{11}B resonances for compounds *IIa – IIe*. The measured data for the series of new nine-vertex *arachno* azaboranes are in Table II, and illustrative aspects of the ^{11}B and ^{1}H shielding behaviour are presented graphically in Fig. 1.

The NMR data for all the compounds *IIa – IIe* are entirely consistent with the general constitution *B*, and also with the results of mass spectrometry. Intercomparison of the ^{11}B shielding patterns (lower part of Fig. 1) reveals a very similar shielding behaviour for all the compounds. Although there are significant differences for the ligand-substituted B(6) site, the long-range substituent effects are very small, and there are only trivial differences in chemical shift for the other positions. The individual {$\delta(^{11}B)$,$\delta(^{1}H)$} data points for all the compounds *IIa – IIe* (Fig. 1, uppermost diagram) all fall close to a single $\delta(^{11}B)$:$\delta(^{1}H)$ correlation line, except of course for the more highly shielded ^{1}H(*endo*-6) position, as found also for the isostructural carborane and thiaborane analogs *exo*-6-L-*arachno*-4-EB_8H_{10} (refs[12,13]), As expected, intercomparison

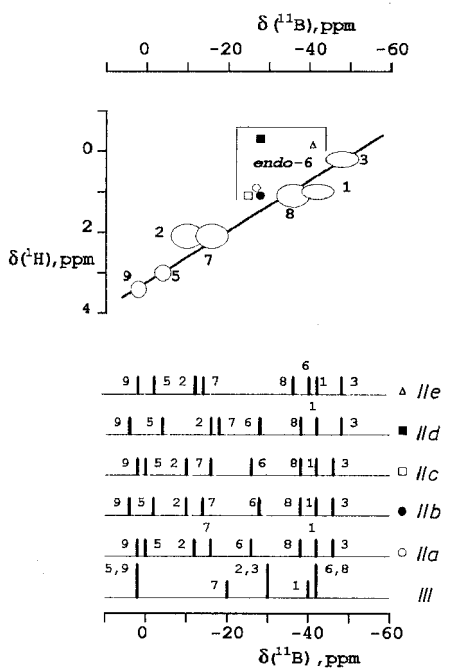


FIG. 1

The upper diagram is a plot of $\delta(^{1}H)$ versus $\delta(^{11}B)$ for the thiaboranes *exo*-6-L-*arachno*-4-NB_8H_{11} [where L = py (*IIa*, ❍), quin (*IIb*, ●), i-quin (*IIc*, ❒), uro (*IId*, ■), and MeCN (*IIe*, Δ)]. The line drawn has a slope $\delta(^{1}H)/\delta(^{11}B)$ ca 1 : 16 and intercept +3.2 ppm in $\delta(^{1}H)$. The lower diagram shows stick representations of the chemical shifts and relative intensities in the ^{11}B spectra of these compounds, together with equivalent data for the anion [*arachno*-4-$NB_8H_{12}]^-$ (*III*)

of the ^{11}B and ^{1}H shielding patterns for equivalent compounds in the three isostructural series that consist of the carbaboranes[13] (E = CH_2), the present azaboranes, and thiaboranes[12] (E = S) of schematic structure *B* reveals a marked similarity between most of the ^{11}B and ^{1}H resonances for corresponding positions. Also the order of shielding by individual ligands L at the substituted site B(6) is practically identical for all three series of compounds.

In connection with this work we also present complete assignments of all the ^{1}H and ^{11}B resonances for the neutral azaborane *arachno*-4-NB_8H_{13} *Ia*, for which previously only tentative ^{11}B assignments have been presented[7,8] together with the hitherto unreported data for the species we tentatively identify as the [*arachno*-4-NB_8H_{12}]$^-$ anion *III* (Table III and Figs 1 and 2). The ^{11}B spectrum of the anion *III* consists of a set of 2 : 1 : 2 : 1 : 2 resonances. This 2 : 2 : 2 : 1 : 1 intensity pattern may imply a fluxionality between structures *IIIa* and *IIIc* or an intermediate static structure *IIIb* (as occurs for the isoelectronic [SB_8B_{11}]$^-$ anion[10]) for the anion *III* (see Scheme 1). Figure 1 (lower diagram) shows that there is a marked ^{11}B shielding parallel between *III* and the *arachno* species *IIa – IIe* when the ^{11}B chemical shifts are averaged across the effective mirror plane. This would be expected with *III* having structure *IIIc* (approximating to *B*, where L = H^-), which may also involved in the dynamic equilibrium as in Scheme 1. Interestingly, however, we have not yet been able to observe either the NH(6) or the μ-H(6,7;7,8) (for *IIIa*)/*endo*-H(6,8) (for *IIIb* and *IIIc*) ^{1}H resonances by ^{1}H NMR spectroscopy, even though the former is very apparent in the spectra of compounds *IIa – IIe*,

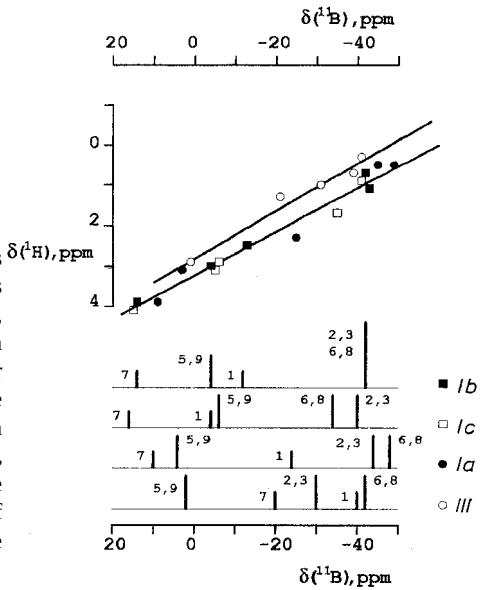


FIG. 2
The upper diagram is a plot of δ(^{1}H) versus δ(^{11}B) for the nine-vertex heteroboranes *arachno*-4-EB_8H_{12} (*A*) [where E = NH (*Ia*, ●), CH_2 (*Ic*, ❒, data from ref.[20]), and S (*Ib*, ■, data from ref.[10])], together with equivalent data for the anion [*arachno*-4-NB_8H_{12}]$^-$ (*III*, ❍). The lines drawn have slopes δ(^{1}H) versus δ(^{11}B) ca 1 : 19 and intercept +3.3 ppm in δ(^{1}H) (for *Ia – Ic*), and 1 : 17 and +3.0 (for *III*), respectively. The lower diagram shows stick representations of the chemical shifts and relative intensities in the ^{11}B spectra of these compounds

and the latter very apparent[10] in the spectrum of the isoelectronic [*arachno*-4-SB_8H_{11}]$^-$ anion. It may be that the Brønsted acidities of the NH(6) and the μ-H(6,7;7,8)/*endo*-H(6,8) sites are very similar, and that there is dynamic exchange between them in solution containing *III* at room temperature, in accord with Scheme 1.

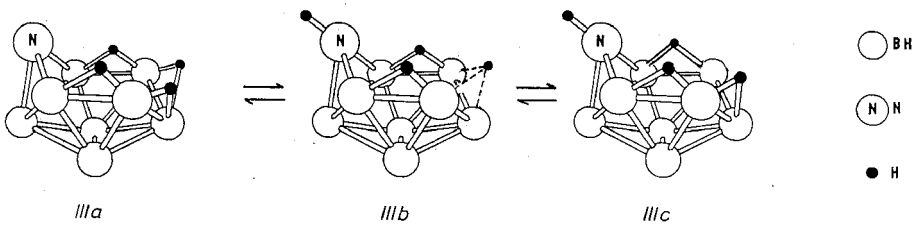
Figure 2 (lower diagram) also demonstrates a graphical intercomparison between individual ^{11}B shifts for compound *Ia* and those for the two other isostructural neutral species of the nine-vertex *arachno* series, 4-CB_8H_{14} (*Ic*; refs[3,4,19]) and 4-SB_8H_{12} (*Ib*;

TABLE II
^{11}B and ^{1}H chemical shifts for the compounds *exo*-6-L-*arachno*-4-NB_8H_{11} (*IIa – IIe*) in $CDCl_3$ at 294 – 297 K. δ(^{11}B)[a], ^1J(^{11}B-^{1}H) in parentheses, δ(^{1}H)[a] in square brackets

Compound	BH(9)	BH(5)	BH(2)	BH(7)	BH(6)[b]	BH(8)[c]	BH(1)	BH(3)	μ-8,9	μ-7,8
IIa	+2.9	–0.8	–11.1	–15.8	–25.4	–37.9	–42.2	–46.4	–	–
	(150)	(144)	(136)	(138)	(124)	(144/71)	(169)	(143)	–	–
	[3.30]	[3.12]	[2.02]	[2.04]	[0.94]	[0.86]	[0.81]	[0.11]	[–0.74]	[–2.98]
IIb	+3.4	–1.7	–9.9	–14.1	–28.0	–37.0	–41.6	–46.4	–	–
	(136)	(141)	(132)	(126)	(98)	(129/66)	(168)	(144)	–	–
	[3.48]	[3.16]	[2.31]	[2.14]	[1.10]	[1.10]	[1.00]	[0.27]	[–0.53]	[–2.72]
IIc	+2.8	–0.8	–10.8	–15.4	–25.3	–37.4	–41.8	–46.5	–	–
	(132)	(143)	(132)	(124)	(83)	(128/61)	(168)	(143)	–	–
	[3.39]	[3.21]	[2.21]	[2.21]	[1.06]	[1.03]	[0.96]	[0.28]	[–0.67]	[–2.83]
IId	+3.3	–3.4	–15.5	–18.6	–27.5	–38.1	–42.9	–47.1	–	–
	(150)	(143)	(139)	(136)	(117)	(144/74)	(169)	(143)	–	–
	[3.24]	[3.02]	[1.79]	[1.79]	[–0.65]	[0.77]	[0.75]	[0.02]	[–0.95]	[–3.35]
IIe	+2.3	–2.0	–11.2	–13.5	–39.2	–36.6	–41.3	–47.9	–	–
	(147)	(147)	(144)	(140)	(116)	(152)	(170)	(144)	–	–
	[3.26]	[3.04]	[2.01]	[2.15]	[–0.05]	[0.98]	[0.96]	[0.08]	[–0.90]	[–3.14]

[a] Assignment by relative intensities, [^{11}B-^{11}B]-COSY (measured for all compounds; observed cross-peaks: 1-2m-s, 1-3m-s, 2-3m-s, 2-5s, 2-6m-w, 2-7m, 3-8s, 3-9m-w, 5-6m, 6-7s-m; s = strong, m = medium, w = weak), and ^{1}H-{^{11}B(selective)} experiments (for ^{1}H); additional ^{1}H signals of the ligands L: *IIa*, 8.8 to 7.5 m, 5 H (py); *IIb*, 10.91 to 7.46 m, 7 H (quin); *IIc*, 9.91 to 7.77 m, 7 H (i-quin); *IId*, 4.69 to 4.35 m, 12 H (uro); *IIe*, 2.12 s, 3 H (MeCN); additional ^{1}H signals of the cage NH groups: *IIa*, 3.64; *IIb*, 3.56; *IIc*, 3.52; *IId*, 3.50; *IIe*, 3.42. [b] Resonances of the *endo* hydrogen atoms in the ^{1}H spectra. [c] Doublet of triplets in the ^{11}B spectra due to μ-H splitting.

ref.[10]). As expected for this isostructural[8,20] set, it is seen that the general shielding patterns are closely related, the most significant differences being at the B(1) site α to the heteroborane constituent. Although these shielding patterns are obviously related, the changes at the other sites are, interestingly, not small: in particular, the 6,8 sites β to the heteroatom are affected more than the α-5,9 positions, showing that the electronic effects of the heteroatom on the cluster are not localized. Included also in Fig. 2



SCHEME 1

TABLE III
^{11}B and ^{1}H chemical shifts for the compounds *arachno*-4-NB_8H_{13} (*Ia*) and [*arachno*-4-NB_8H_{12}]$^-$ [tmnd]$^+$ *III* in $CDCl_3$ at 294 – 297 K. δ(^{11}B)[a], ^1J(^{11}B-^1H) in parentheses, δ(^1H)[a] in square brackets

Compound	BH(7)	BH(5,9)	BH(1)	BH(2,3)	BH(6,8)	μ-6,7/7,8	μ-5,6/8,9
Ia	+9.2	–6.2	–24.4	–45.01	–47.0	–	–
	(153)	(153)	(174)	(148)	(148)	–	–
	[+3.97]	[+3.01]	[+2.16]	[+0.29]	[+0.76]	[–0.77]	[–2.38]
III	–20.6	+2.0	–43.1	–28.9	–43.2	–	–
	(–)[b]	(144)	(–)[b]	(132)	(–)[b]	–	–
	[+1.25]	[+3.10]	[+0.68]	[+0.87]	[+0.09]	(–)[c]	[–1.25]
	or						
	[+2.83]						

[a] Assignment by relative intensities, [^{11}B-^{11}B]-COSY (observed cross-peaks for *Ia*: 1-2,3s, 1-5,9w, 2,3-5,9s, 2,3-6,8s, 6,8-5,9s, 6,8-7m; observed cross peaks for *III*: 1-2,3s, 1-5,9m, 2,3-5,9s, 2,3-6,8s, 6,8-5,9m, 6,8-7m; s = strong, m = medium, w = weak), and ^1H-{^{11}B(selective)} experiments (for ^1H); δ(^1H) for NH(4) + 2.94 ppm (for *Ia* in C_6D_6)[7]. [b] Value uncertain. [c] ^1H resonances for μ-H(6,7;7,8)/*endo*-H(6,8) and NH(6) not observed (see text).

(lower diagram) are the shielding data for the [*arachno*-4-NB_8H_{12}]$^-$ anion *III*. This now has a considerably perturbed ^{11}B shielding pattern compared to the neutral species of type *A*, emphasizing its greater similarity with the ligand adducts of structure *B*, as demonstrated in Fig. 1, and as discussed above.

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