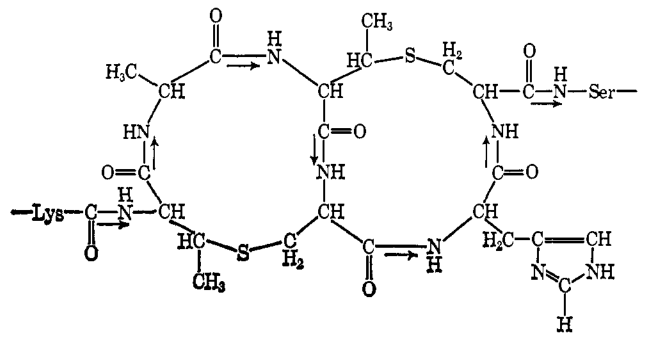
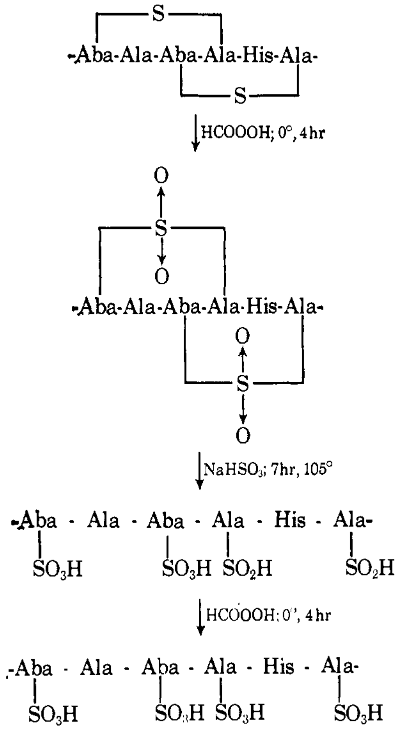


Figure 1. Bicyclic structure of identical ring size formed by sulfide bridges of β-methyllanthionine (arrows parallel to peptide bonds indicate the direction of the peptide chain).

hydrolysate rules out a sulfide bridge between residues 4 and 5. The **thioether linkages** may therefore be assigned unequivocally to residues 2 and 5 and 4 and 7, respectively.



In this way, a novel bicyclic structure of identical ring size has been assigned to nisin. Figure 1 traces the direction of the peptide chain of the bicyclic portion of the molecule as it is seen in the Stuart–Briegleb model. The two sulfur atoms constrain "head" and "tail" of the peptide chain to a center where four atoms are shared.

Thirteen-membered ring structures with one sulfur atom are new to peptide chemistry. Other heterodetic cyclic peptides with sulfur in the ring are of larger size.

Nisin has been found to be membrane active in experiments with lysosomes from which it releases enzymes. It shall be interesting to see whether this activity is associated with the unique ring size or whether it is due to the presence of other structurally unique features.

With the exception of residues 2 and 4, all α-carbon atoms possess the L configuration as determined with the amino acid oxidases and by the susceptibility of the peptides to reaction with amino peptidase and carboxypeptidase A. The configurations of the β-carbon atoms of the methyllanthionine residues are now being determined.

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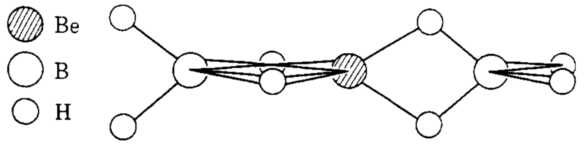
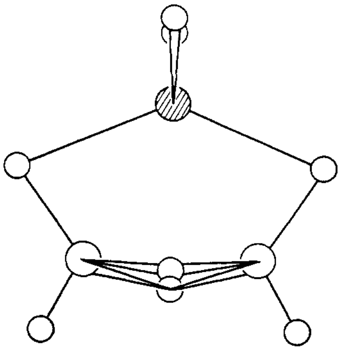
Electric Deflection and Dipole Moment of Beryllium Borohydride

Sir:

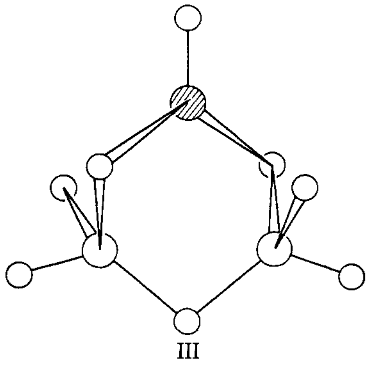
From electron diffraction experiments, several structures for BeB_2H_8 have been proposed, the most recent being the rather surprising models II and III.[1,2] In fact, these latter models must now be questioned since very recent efforts to reproduce the diffraction data have not been successful.[3] Although the nonzero dipole moment reported by one of us[4] would seem to eliminate I and favor II or III, unfortunately the dielec-



I



II



III

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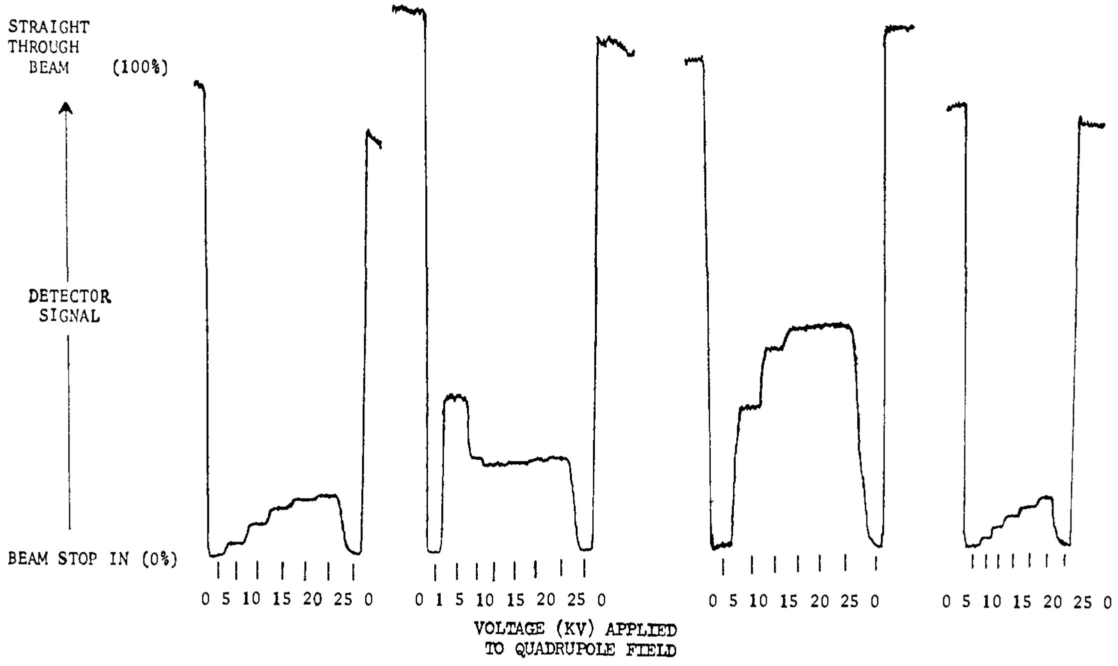
[1] A. Almenningen, G. Gundersen, and A. Haaland, *Acta Chem. Scand.*, 22 859 (1968).

[2] G. Morgan and T. Cook, *J. Amer. Chem. Soc.*, **91**, 774 (1969).

[3] A. Almenningen, A. Haaland, and G. L. Morgan, University of Oslo, private communication; also, G. Gundersen and K. W. Hedberg, Oregon State University, unpublished results.

[4] J. W. Nibler and J. McNabb, *Chem. Commun.*, 134 (1969).



(a) (b) (c) (d)

Figure 1. Refocusing patterns of (a) BeB$_2$H$_8$, (b) fluorobenzene, (c) acetone, (d) OCS.

tric data were of marginal quality because of the low vapor pressure (<8 mm) at temperatures at which BeB$_2$H$_8$ did not decompose. Thus the question of the structure, and even the symmetry, of BeB$_2$H$_8$ is still open.

To establish at least the polarity of this unusual hydrogen-bridged molecule, we have reexamined the dielectric data and have sought an independent verification of the presence of a dipole moment by an electric deflection experiment. This experiment involves passing a molecular beam through a quadrupole focuser which acts to spread (defocus) a beam of nonpolar molecules while concentrating (refocusing) a beam of polar molecules. Polar molecules are thus focused onto the entrance slit of an ionization chamber of a mass spectrometer detector. The apparatus has been described previously.[5]

An unperturbed beam of BeB$_2$H$_8$ gave the reported mass spectrum[2] and indicated no impurities. After ionization, fragments of mass 39–34 (BeB$_2{}^{11}$H$_8{}^+$ to BeB^{10}B^{11}H$_4{}^+$) were monitored at a resolution of 100 and each gave a refocusing pattern similar to that shown in Figure 1a for mass 37. The 13% refocusing observed at 25 kV indicates that the molecule must be polar, since induced moments at this field will be small ($\sim$0.01 D) and will tend to *defocus* the beam. In the harmonic approximation, vibrational effects will also tend to defocus the beam.

The shape of the refocusing pattern also contains some information, and in this case suggests that the dipole moment is perpendicular to any near-symmetric-top axis. Prolate and near-prolate tops such as fluorobenzene with the dipole moment along the top axis have refocusing curves which reach a maximum at low voltages and then decrease at higher voltages (Figure 1b). This is because these molecules have fast Stark effects for states with $J \approx K, M$. Thus these states refocus at low voltages but at higher voltages they are overfocused and thrown away. Although states with $J \gg K, M$ will refocus at higher voltage, these states are less populated and thus the total refocused beam is smaller at high voltages.

If the dipole moment is perpendicular to the top axis, these fast Stark effects do not occur since the K doublets are no longer connected by dipole moment matrix elements. The Stark effect is then similar to that for linear molecules except that there are many manifolds of J states for $K > 0$. Thus for acetone (Figure 1c) there is no maximum at low voltages and the curve somewhat resembles that for OCS (Figure 1d). The BeB$_2$H$_8$ curves follow this pattern also, a result which is consistent with II or III but not with a linear BeBB skeleton. Model I is, of course, eliminated.

The deflection experiment thus verifies the presence of a dipole moment and alleviates our concern that the very small effects observed in the dielectric experiments might be due to some determinate error such as condensation between the cell electrodes. *If* the spread in our 38 separate determinations is in fact random, the molar polarization of BeB$_2$H$_8$ at 25° is 107 cc/mol with a 90% confidence interval of ± 9 cc/mol. Because of thermal decomposition, a temperature dependence study was not possible; however, using molar refractivities, we estimate the electronic and atomic contributions to the polarization to almost certainly lie in the range 15–25 cc/mol. A value of 20 ± 5 cc/mol yields a dipole moment of 2.06 D with a 90% confidence interval of ± 0.12 D. A microwave study of the rotational spectrum

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(5) E. W. Kaiser, J. S. Muenter, and W. Klemperer, *J. Chem. Phys.*, **48**, 3339 (1968).

would obviously be desirable to confirm this value and to shed further light on the structure.

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Isomerization of Alkylbicyclo[2.2.1]heptanes over Palladium Catalysts

Sir:

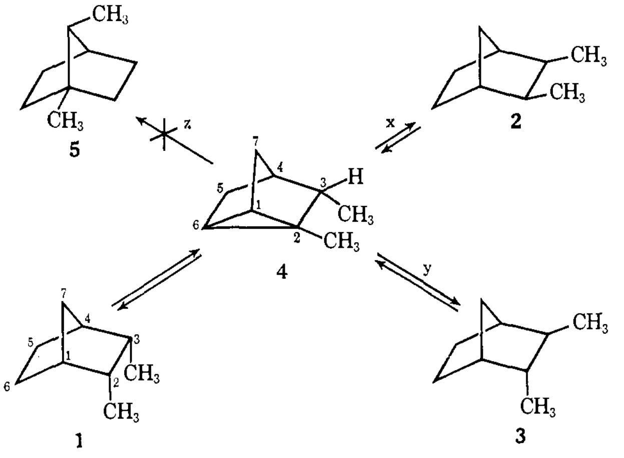
Exchange reactions of cycloalkanes with deuterium catalyzed by transition metals, especially palladium, often show substantial amounts of replacement of hydrogen atoms on both faces of the ring in the initial product distributions.[1,2] In appropriate compounds deuterium–hydrogen exchange is associated with racemization at tertiary carbon centers[2] and with *cis–trans* isomerization.[3] Although the mechanisms of these reactions are still controversial, it is widely accepted that interconversion of adsorbed alkyl and alkene intermediates is a general surface reaction (α,β process) which is limited to *cis* elimination and *cis* addition. The α,β process alone cannot therefore explain the observed distributions for deuterium–hydrogen exchange and isomerization in cycloalkanes of ring size C_4–C_7. Two additional processes have been proposed. Process A: olefinic intermediates desorb, turn over, and readsorb, and the α,β process then continues on the other face of the ring; Schrage and Burwell[4] have suggested that the turnover step may occur while the olefinic intermediates are still attached to the metal surface. Process B: π-bonded olefinic intermediates interconvert with π-allyl complexes during which *trans* addition or elimination of hydrogen (or deuterium) to or from one of the terminal carbon atoms of the allylic system may occur.[5]

In an effort to distinguish between processes A and B isomerization reactions of di-*endo*-, di-*exo*-, and *exo*,-*endo*-2,3-dimethylbicyclo[2.2.1]heptane (**1–3**) were investigated. Experiments were carried out using a flow system using a large excess of hydrogen and a 2% palladium on silica catalyst.[6] Some results for **1** are given in Table I.

Table I. Isomerization of 1

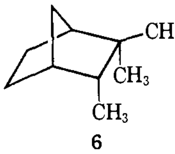
Temp, °C	**1**, %	**2**, %	**3**, %	3/2
116	72	9	9	1.0
126	55	25	20	0.8
135	19	41	40	1.0
146	2	8	90	11.3
162	3	9	88	9.8

Up to high conversions **2** and **3** are formed from **1** in equal amounts. At the higher temperatures, where equilibrium is approached, **3** largely predominates. In separate experiments it was found that the order of reactivity is **1** > **2** > **3** since comparable reactivity was shown at *ca.* 120, 140, and 180° for the three compounds, respectively. These results cannot be explained by mechanism B, a detailed consideration of which shows that only sequential formation of **2** from **3** is allowed. Process A is also unsatisfactory since it requires the appropriate olefinic intermediates from **2** and **3** to form, turn over, readsorb, and hydrogenate off at nearly equal rates.



An intermediate which can explain the results and also the isomerizations described below is a nortricyclene derivative, such as **4** (2,3-dimethylnortricyclene), which can be formed reversibly from **1** by *trans* elimination–addition of hydrogen at C_2 and C_6. Cleavage of C_1–C_2 by process x and of C_2–C_6 by y with concurrent hydrogen addition gives **2** and **3**, respectively. Cleavage of C_1–C_6 by process z should give 1,7-dimethylnorbornane (**5**), a product not observed at these temperatures (but see below). At this stage details of the mechanism of formation and the nature of the bonding to the surface of intermediates such as **4** are unknown.

A mixture containing 74% of 2-*endo*-3,3-trimethylnorbornane (**6**) and 26% of 2-*exo*-3,3-trimethylnorbornane (**7**) was treated under similar conditions. These structures preclude *endo–exo* isomerization by process B, but again isomerization occurred (see Table II). At higher temperatures 1,7,7-trimethylnorbornane



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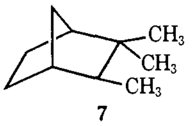

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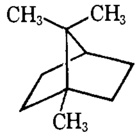

8

(**8**) was also formed, together with some products resulting from fragmentation. The formation of **8** is obviously inexplicable in terms of either process A or B but could arise *via* a reaction similar to z from a nortricyclene intermediate similar to **4**. Table III gives results for the isomerization of pure **8** under similar reaction conditions, showing that the above reactions are

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(1) J. R. Anderson and C. Kemball, *Proc. Roy. Soc., Ser. A*, **223**, 361 (1954).

(2) R. L. Burwell, Jr., B. K. S. Shim, and H. C. Rowlinson, *J. Amer. Chem. Soc.*, **79**, 5142 (1957).

(3) F. G. Gault, J. J. Rooney, and C. Kemball, *J. Catal.*, **1**, 255 (1962).

(4) K. Schrage and R. L. Burwell, Jr., *J. Amer. Chem. Soc.*, **88**, 4555 (1966).

(5) J. J. Rooney, *J. Catal.*, **2**, 53 (1963).

(6) Silica (Whatman chromatographic silica, 60–80 mesh) alone did not catalyze isomerization. Separate experiments employing palladium films in a static system showed the metal was responsible for reaction.