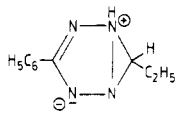
consequently the homoallylic participation[2,8] is probable. A review of the relation between bond lengths and bond order for bonds between sp^2-hybridized carbon and nitrogen atoms was found in the literature[9] (see Table III). A localized single bond has a bond order of 1.0 and a localized double bond a bond order of 2.0.

The dimensions of 1,2,4,5-tetrazine[10] are as follows: C-N, 1.33 Å; N-N, 1.32 Å; C-N-N, 115°; N-C-N, 127°. Comparison with the bond angles and distances in **3** (see Table I) reveals that both the N(1)-N(2) (1.32 Å) and the N(4)-N(5) (1.27 Å) distances are larger than that in the localized double bond (1.23 Å) and smaller than that in the single bond (1.41 Å). Especially, the N(1)-N(2) distance is of the same magnitude as in 1,2,4,5-tetrazine (1.32 Å). Also the N(2)-C(3) (1.33 Å) and the N(4)-C(3) (1.39 Å) bond lengths are between those of the single and double bond lengths. These intermediate bond lengths are in agreement with the delocalization of the π electrons over these ring atoms. It is striking that especially the N(1)-N(2) bond is so aromatic.

On the basis of our model of homoaromaticity (see Figure 1), we would have expected that the N(1)-N(5) distance would have been shorter than the 2.29 Å actually found. It indicates that the contribution of the mesomeric structures **8** and **9** is small. It remains unanswered as to



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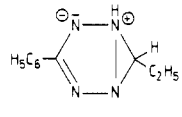

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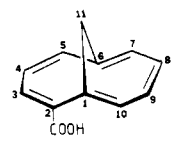
whether this is necessarily in conflict with the homoaromatic character, although the concept of homoaromaticity seems in our opinion to be the only explanation of the results of the ^1H and ^{13}C NMR[2,15] data measured in solution.

In some homoaromatic systems a similar distance has been observed by X-ray crystal analysis. For example in 1,6-methano[10]annulene-2-carboxylic acid (**5**) the 1,6-



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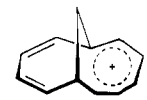

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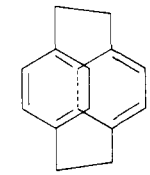

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distance is 2.26 Å, and in bicyclo[5.4.1]dodecapentaenylium ion (**6**) the 1,6-distance is 2.30 Å;[12] yet in these compounds a considerable 1,6-overlap was established.[13] It is regrettable, however, that there are not more crystal structural data available for comparison.

As the tetrazine part of **3** is boat shaped, the tetrazole ring of the homotetrazole is not planar but is puckered. There are some examples of "bent aromaticity" in the literature. An example is the [2.2]paracyclophane system (**7**).[14] In this strained molecule the benzene rings are boat shaped. Although the gradients amount to 13°, the benzene rings have preserved their normal aromatic properties. Also in the above-mentioned annulenes (**5** and **6**) the carbon atoms forming the 10-π-electron system are puckered.[11,12] From these examples it is clear that electron delocalization can occur in a not perfectly planar system.

In conclusion we want to stress the point that the crystal structure determination of **3** is not in conflict with our previous proposal of homoaromaticity, based on ^1H NMR data, but on the other hand is also not a dramatic affirmation of this phenomenon.

Editor's Note. This paper and the following paper by Hoskin, Wooden, and Olofson were reviewed together; both authors were invited to comment on the other paper.

Registry No. 3, 76630-76-7.

Supplementary Material Available: Final atomic parameters, thermal parameters, and bond distance (3 pages). Ordering information is given on any current masthead page.

(8) Warner, P.; Harris, D. L.; Bradley, C. H.; Winstein, S. *Tetrahedron Lett.* **1970**, 4013.
(9) Burke-Laing, M.; Laing, M. *Acta Crystallogr., Sect. B.* **1976**, *B32*, 3216.
(10) Neunhoeffer, H.; Wiley, P. F. In "Chemistry of 1,2,3-Triazines and 1,2,4-Triazines, Tetrazines and Pentazines"; Wiley: New York, 1978.
(11) Dobler, M.; Dunitz, J. D. *Helv. Chim. Acta* **1965**, *48*, 1429.
(12) Destro, R.; Pilati, T.; Simonetta, M. *J. Am. Chem. Soc.* **1976**, *98*, 1999.
(13) Dewey, N. J., Deger, H.; Fröhlich, W.; Dick, B.; Klingensmith, K. A.; Hohlneicher, G.; Vogel, E.; Michl, J. *J. Am. Chem. Soc.* **1980**, *102*, 6412.
(14) Cram, D. J.; Cram, J. M. *Acc. Chem. Res.* **1971**, *4*, 204.

Homoaromaticity and the 1,1,4-Trimethyl-1,4-dihydro-1,2,4,5-tetrazinium Cation: Evidence from a Crystal Structure Determination

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Received January 6, 1981 (Revised Manuscript Received January 6, 1982)

Because the ^1H and ^{13}C NMR spectra of the title cation (**2**) are most easily rationalized by including a strong "ring current" effect, **2** has previously been assigned a homoaromatic structure. The fluorosulfate salt of **2** has now been prepared, and crystals suitable for a single crystal X-ray structure determination have been obtained: $C_5H_{11}FN_4O_3S$, orthorhombic, space group $P2_12_12_1$, cell dimensions a = 9.376 (2) Å, b = 16.716 (5) Å, c = 6.181 (7) Å, V = 969 (2) Å^3, Z = 4, final R = 0.060. The quaternary nitrogen (N1) is tetrahedral which causes the ring to assume a boat shape. There is evidence for substantial delocalization of the N4 electron pair (hybridization between trigonal and tetrahedral; N1 is 0.51 Å above the N2-C3-N5-C6 plane while N4 is only 0.26 Å above the same plane).

In 1972, the methylation of the dihydrotetrazine (**1**) to give the novel trimethyldihydrotetrazinium fluoroborate (**2a**, Chart I) was reported by this laboratory.[1] Because the ^1H NMR absorption of the methyls attached to the

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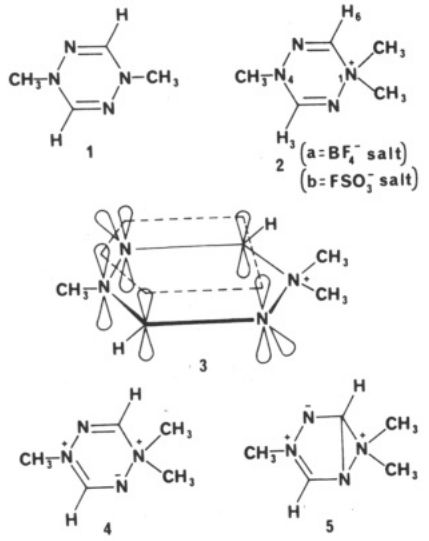
Chart I



positively charged N_1 occurred at higher field (δ 3.35) than the peak for the methyl bonded to the formally neutral N_4 (δ 3.50), the cation **2** tentatively was assigned the unusual homoaromatic structure **3**. Introduction of a plus charge normally has a much stronger deshielding effect at adjacent positions than at more distant sites, and symmetry considerations make N_4Me a good model for most of the other structure features included in the variation of chemical shift for $^{+}N_1Me_2$. Thus, the operation of a "special effect" was indicated, and to play this role, the ring current induced in the 6-π-electron system of **3** was proposed by Kohn and Olofson.[1] For **3**, as in other benzene analogues, the methyl protons in the ring plane should be greatly deshielded while the N_1-methyls, being out of the plane, should be affected to a lesser extent. Because electron density effects are much more important than anisotropy factors (e.g., ring current) in ^{13}C NMR spectra, structure **3** also demands that the ^{13}C resonance for the $N^{+}_1Me_2$ be at lower field (found δ 54.0) than the value for N_4Me (found δ 42.5), a rare reversal of the proton order.[2]

In comparison with other stable compounds generally accepted as homoaromatic, **2** remains interesting today in that no formal charge is associated with the π-system. The instability inherent in such a charged species (or in an excited state) generally is needed to bring into operation the amount of "homoaromatic stabilization" required for an experimentally observable effect.[3] The novelty of the structure **3** together with the availability of alternative interpretations of the NMR data[2] combine to make **2** an attractive candidate for a crystal structure determination.

This has now been completed and is reported here for **2b**, easily made by methylation of **1** with FSO_3Me. Anisotropic refinement of nonhydrogen atoms and isotropic refinement of H's converged at $R = 0.060$ and $R_w = 0.058$. ORTEP drawings of the cation **2** with significant bond distances and angles are presented in Figure 1 and a stereoscopic view of the unit cell showing the molecular packing is depicted in Figure 2.

From Figure 1, it is seen that the cation exists as a flattened boat with its prow, N1, somewhat higher than its stern, N4: 0.51 vs. 0.26 Å above the plane of the other four ring atoms. The planes through N2–N1–C6 and through C3–N4–N5 have dihedral angles of 36.7° and 21.6°, respectively, vs. the N2–C3–N5–C6 plane (for additional data see the supplementary material). Although the C7 and C8 methyls are not equivalent in the crystal, they are NMR equivalent in solution, even at very low temperature,[1] an indication that the inversion barrier from one boat to its mirror image is very low. The primary responsibility for the boatlike shape of the cation can almost certainly be attributed to the tetrahedral hybridization of N1 and the repulsion between the two methyls, C7 and C8, which prevent the N2–N1–C6 angle from opening out from the found tetrahedral 109.8° to the larger value required to flatten the ring. The other end of the molecule makes a valiant effort to overcome the constraints put on the ring by N1. The C3–N4–N5 angle opens out to a near sp^2 value of 117.4°, and, as has already been

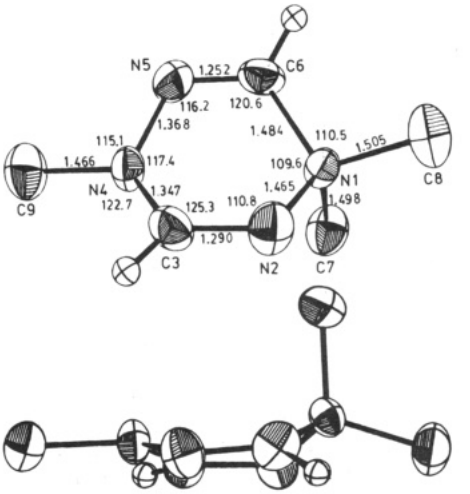


Figure 1. Bond distances (in angstroms; esd 0.004–0.008) and angles (in degrees; esd 0.3–0.5) for the 1,1,4-trimethyl-1,4-dihydro-1,2,4,5-tetrazinium cation. Unlisted angles are as follows (excluding data for H's): N2–N1–C7, 110.2 (5)°; N2–N1–C8, 107.3 (4)°; C6–N1–C7, 109.4 (5)°; C7–N1–C8, 109.8 (5)°. Methyl H's are left out for clarity.

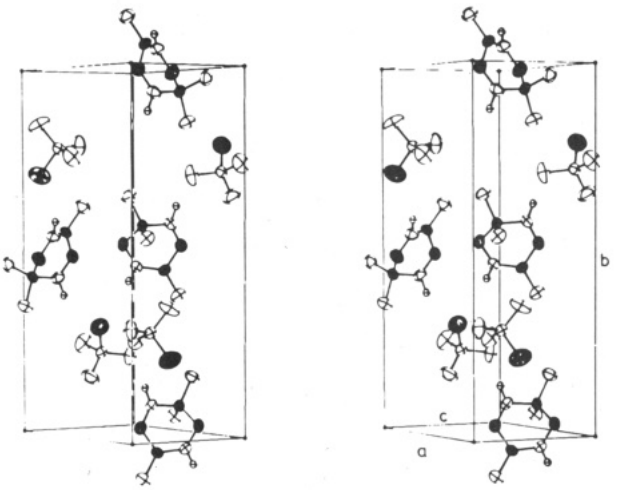


Figure 2. Stereoscopic view of unit cell showing molecular packing (F and N atoms shaded, methyl H's omitted for clarity). Thermal ellipsoids for nonhydrogen atoms represent 50% probability. The SO_3F^- bond distances and angles are as follows: S1–O2, 1.44 (4) Å; S1–O3, 1.419 (5) Å; S1–O4, 1.436 (5) Å; S1–F5, 1.557 (4) Å; O2–S1–O3 112.9 (3)°; O2–S1–O4, 114.7 (3)°; O2–S1–F5, 103.0 (3)°; O3–S1–O4, 112.5 (4)°; O3–S1–F5, 106.5 (3); O4–S1–F5, 106.2 (3)°.

(1) Kohn, H.; Olofson, R. A. *J. Org. Chem.* **1972**, *37*, 3504.
(2) See footnote 19 and the text in ref 1. The insulating CH_2 of cyclohexadienyl anion mixes in to stabilize the HOMO: Hoffmann, R.; Olofson, R. A. *J. Am. Chem. Soc.* **1966**, *88*, 943.
(3) Paquette, L. A. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 106 (review). Also see text and notes 21 and 22 in ref 1.

noted, N4 is only 0.26 Å above the N2–C3–N5–C6 plane. Also, C9 is 0.26 Å above the N2–C3–N5–C6 plane while the value predicted from a Dreiding model for C9 attached to tetrahedral N4 is 0.15 Å *below* the same plane. If N4 were completely trigonal, C9 would be slightly further above the ring plane than the found 0.26 Å (a quantitative estimate requires a decision on how to apportion the distortion from trigonal N4 between C3, N5, and C9). The delocalization guaranteed by substantial trigonal character at N4 is reflected in the lengthened double bond distance, C3=N2, vs. the comparison model C6=N5 distance (1.29 vs. 1.25 Å). This difference is one measure of the importance of canonical structure **4**. The fact that the difference is not even larger[4] hints at, but does not promise, a contribution to the resonance hybrid from structure **5**, the key to measuring the "homoaromaticity" of **2**.

Today NMR rationalizations such as that cited in the introduction are widely used to "guarantee" homoaromaticity.[5] When such a conclusion is not dramatically confirmed by a direct X-ray structure determination, the basis of the NMR argument would seem due for a critical reappraisal, and the theoretical foundation for such an evaluation is presently being laid.[6] The experimental structure of **2b** has predictive value which could be of aid here. If planarity is a crucial factor, replacement of the N_1-methyls by a trimethylene unit could widen the N2–N1–C6 angle and thus flatten the ring. If greater delocalization is achieved by overlapping one lobe of the p orbitals at N2 and C6 and the N2–C6 distance is critical (found 2.41 Å for **2b**), the introduction of bulkier substituents at N1 could pucker the ring further, push the bottom p lobes together, and shrink the N2–C6 distance. Only the latter situation pertains in other "accepted" homoaromatic systems.

We have examined the paper of Stam, Counotte-Potman, and van der Plas[7] which accompanies this publication. In both laboratories, NMR data promised that stable, crystalline compounds under investigation were homoaromatic and thus among the rare candidate systems where the direct structural effects of homoaromaticity could be determined from successful X-ray structure analysis. In our 1972 NMR rationalization,[1] fortuitous structural features permitted the molecule to serve as its own model in the NMR tests used to define homoaromaticity (vide supra). In the 1981 Dutch publications,[5] several models and a more extended argument allowed the authors to reach the same conclusion.

In comparing the two crystal structures, the reader should note their remarkable similarity. Both molecules are boats with their prows (the four-coordinate atom) twice as high as their sterns although nitrogens occupy these apices in our compound while carbons occupy these sites in the Dutch system. Our molecule is slightly flatter than that of the Dutch (distances of 0.51 and 0.26 Å vs. 0.69 and 0.32 Å from the "boat bottom plane" to the prow and stern atoms, respectively).[8] The increased "boat character" of the Dutch molecule is reflected in a decreased rate of ring inversion from one boat to the other (NMR coalescence temperature of ca. −30 °C for their symmetrical compound with 2 H's at C_6[5]). In both structures, the "stern" substituent makes a slightly pyramidal angle with the stern plane, though less so in the Dutch model where that substituent is a delocalizing phenyl than in our molecule where the site is occupied by methyl.[9]

Experimental Section[10]

1,1,4-Trimethyl-1,4-dihydro-1,2,4,5-tetrazinium Fluorosulfate (2b). FSO_3Me (97%, 1.1 mL, 0.013 mol) in CH_2Cl_2 (25 mL) was added to a stirred solution of **1**[1] (1.52 g, 0.014 mol) in the same solvent (25 mL) slowly enough (10 min) to mitigate the ensuing exothermic reaction. Vacuum evaporation of the solvent after stirring overnight afforded a nearly quantitative yield of solid **2b** which was purified by precipitation with ether from 2:3 $CH_2Cl_2/MeNO_2$, filtered, triturated with ether, and dried in vacuo: yield 2.84 g (92%); off-white solid; mp 105–107 °C dec; NMR (Me_2SO-d_6) δ 3.38 (6 H, s), 3.47 (3 H, s), 7.48 (1 H, s), 8.27 (1 H, s) (in accord with data[1] for **2a**). Crystals suitable for X-ray analysis were grown as large rectangular tablets in 2:3 $CH_2Cl_2/MeNO_2$ over ether in a sealed desiccator.

X-ray Crystallographic Analysis of 2b. The crystal data are as follows: $C_5H_{11}FN_4O_3S$; mol wt 226.23; orthorhombic; a = 9.376 (2) Å, b = 16.716 (5) Å, c = 6.181 (7) Å, V = 969 (2) Å^3, d_c = 1.55 g/cm^3, d_o = 1.5 g/cm^3 (flotation CH_2Cl_2/CCl_4), Z = 4, $F(000)$ = 472; systematic absences, $h00$ for h odd, $0k0$ for k odd, $00l$ for l odd; space group $P2_12_12_1$ (No. 19).

A fragment measuring 0.3 × 0.3 × 0.3 mm^3 was cleaved from a larger crystal and mounted in a random orientation on an Enraf-Nonius CAD-4 four-circle counter diffractometer. Cell dimensions were obtained by least-squares refinement[11] from 50 reflections at moderate 2θ angles. Reflection intensities were measured by using graphite-monochromated incident beam (takeoff angle = 2.8°) Mo Kα radiation (λ = 0.709 26 Å) and were collected by the θ-2θ scan method with a variable scan rate ranging from 20°/min for intense to 2°/min for weak reflections. Right and left backgrounds were each scanned 25% of the total scan time. The variation in intensities of three standard reflections (measured every 4 h) was small and random (maximum fluctuation ±3%). Intensities were corrected for Lorentz and polarization factors. A total of 2400 reflections were collected up to 2θ = 70°. Of these, 1367 had $I > 2\sigma(I)$ and were used for the structure analysis. Refinement was performed by the full-matrix least-squares method. The starting parameters for S1 of the FSO_3^- were obtained from MULTAN E map synthesis. Subsequent difference Fourier maps located all remaining atoms. Anisotropic refinement of all nonhydrogen atoms and isotropic refinement of H's converged with R = 0.060 and R_w = 0.058 and an esd of an observation of unit weight of 0.973. (Convergence was considered complete when all parameter shifts were <0.2 of their esd's.) Here, $R = (\sum||F_o| - |F_c||)/\sum|F_o|$ and $R_w = \sum(|F_o| - |F_c|^2)/|\sum F_o^2|^{1/2}$ (unit weights used throughout). The function minimized was $\sum(|F_o| - |F_c|)^2$. The final difference map was featureless with maxima and minima in the range of ±0.278 e/Å^3.

Editor's Note. This paper and the preceding paper by Stam, Counotte-Potman, and van der Plas were reviewed together; both

(4) This problem is made more difficult by the lack of good data for an unconjugated C=N distance in the literature.

(5) Since this manuscript initially was submitted for publication, papers on homoaromaticity in a similar system based on NMR arguments analogous to those outlined in this introduction but using a more extensive series of comparison models have appeared in this journal: Counotte-Potman, A. D.; van der Plas, H. C.; van Veldhuizen, B. *J. Org. Chem.* **1981**, *46*, 2138, 3805.

(6) Houk, K. N.; Gandour, R. W.; Strozier, R. W.; Rondan, N. G.; Paquette, L. A. *J. Am. Chem. Soc.* **1979**, *101*, 6797. Grutzner, J. B.; Jorgensen, W. L. *Ibid.* **1981**, *103*, 1372. Kaufmann, E.; Mayr, H.; Chandrasekhar, J.; Schleyer, P. v. R. *Ibid.* **1981**, *103*, 1375. Also see ref 3.

(7) Stam, C. H.; Counotte-Potman, A. D.; van der Plas, H. C. *J. Org. Chem.*, preceding paper in this issue.

(8) Added after submission: 6-methyl-2,4-diphenyl-1,4-dihydropyrimidine is an even "flatter boat" with its prow 0.25 Å (C4) and its stern (N1) 0.10 Å above the "boat bottom" plane: Weis, A.; Frolow, F. *J. Chem. Soc., Chem. Commun.* **1982**, 89.

(9) In our opinion, any differences in the conclusions of the two groups arise in part because the Dutch workers assume in their bond order argument that the N–N bonds of 3,6-diphenyl-1,2,4,5-tetrazine are of order 1.5.

(10) For list of apparatus used in physical and spectral measurements see: Olofson, R. A.; Cuomo, J. *J. Org. Chem.* **1980**, *45*, 2538. Programs used for this study were part of the Enraf-Nonius Structure Determination Package as revised in 1977 and implemented on a PDP 11/34 computer.

(11) Subroutine PARAM of XRAY 76: Stewart, J. M. University of Maryland Crystallographic Computer System.

authors were invited to comment on the other paper.

Acknowledgment. We are grateful to Drs. R. Whittle and M. Bernheim for valuable advice. We also thank the National Institutes of Health and McNeil Pharmaceutical for grants supporting part of this research.

Registry No. 1, 35341-96-9; **2b**, 81815-31-8.

Supplementary Material Available: Tables of atomic positional parameters, bond distances and angles, thermal parameters, useful least-squares planes, and general temperature-factor expressions (5 pages). Ordering information is given on any current masthead page.

Stereospecific Transannular Cyclization of Mesocyclic Homoallylic Sulfides. 2. (*Z*)- and (*E*)-Thiacyclonon-4-enes. Synthesis, Carbon-13 Nuclear Magnetic Resonance, and Conformation of Methyl-Substituted *cis*-1-Thioniabicyclo[4.3.0]nonane Salts[1]

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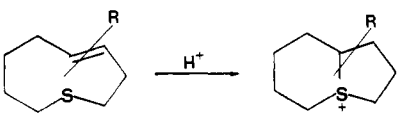
Received December 2, 1981

Bicyclic bridgehead [4.3.0] sulfonium salts are obtained from nine-membered cyclic homoallylic sulfides (thiacyclonon-4-enes) by the action of acids. Independently of the geometry, *Z* or *E*, of the starting olefin, cis-ring-joined products are obtained which, while formed under kinetic control, also appear to be thermodynamically favored. The reaction is stereospecific: thus the noninterconverting diastereomeric conformers of (*E*)-2,4,5-trimethylthiacyclononene (**2h'** and **2h''**) give rise to endo/exo C_9 CH_3 epimers (**18** and **19**) without crossover. Several methyl-substituted *cis*-1-thioniabicyclo[4.3.0]nonane salts have been prepared in this way (**4–11**, **14–19**) while two more (**12** and **13**) were obtained by alkylation of the ylide from the parent system, **4**. The ^{13}C spectra of the bicyclic salts have been recorded and elucidated with the aid of a number of regiospecific deuteration methods, thus permitting their unambiguous configurational and conformational assignment.

Transannular interactions are commonplace in medium-size rings (eight to ten membered) where the spatial relationship between the 1,5-functionalities gives rise to unusual reaction patterns, unknown to either smaller or larger rings or to acyclic analogues. This matter has been recently reviewed extensively by Leonard,[2] while Musker has reviewed his work on the transannular reactivity of 1,5-dithiacyclooctane.[3]

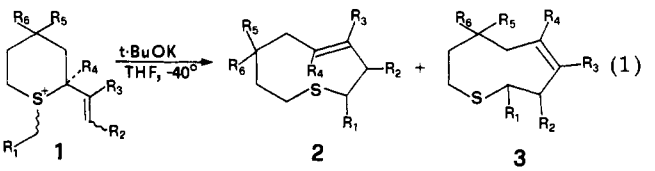
The recently developed ring enlargement by [2,3] sigmatropic rearrangement of sulfonium ylides[4] provides facile access to homoallylic mesocyclic sulfides (thiacycloalk-4-enes) which are expected to be expecially prone to interactions between the S atom and the transannular double bond. Indeed, in a recent report we have given an account of the transannular cyclization of substituted (*Z*)- and (*E*)-thiacyclooct-4-enes to *cis*-1-thioniabicyclo[3.3.0]-octanes promoted by H^+ or Lewis acids, focussing especially on stereochemical aspects.[1] In this paper we report and discuss along similar lines the acid-promoted cyclization of the higher homologues, thiacyclonon-4-enes, to *cis*-1-thioniabicyclo[4.3.0]nonanes.



The ^{13}C NMR spectra of these salts, while unequivocally establishing their configurations, provide considerable insight in to the conformational properties of these bicyclic [4.3.0] bridgehead sulfonium cations.

Results and Discussion

The methyl-substituted thiacyclonon-4-ene precursors have been prepared via ring expansion by [2,3] sigmatropic rearrangement of the appropriately substituted 2-vinylthianium alkylides obtained by in situ deprotonation of the corresponding sulfonium salts (eq 1) as previously reported.[4b,d,5-7]



(1)

all R's = H unless otherwise specified: a, all R's = H; b, $R_1 = CH_3$; c, $R_2 = CH_3$; d, $R_4 = CH_3$; e, $R_5 = CH_3$; f, $R_3 = R_4 = CH_3$; g, $R_5 = R_6 = CH_3$; h, $R_1 = R_3 = R_4 = CH_3$

This synthesis is known to largely afford *E* homoallylic sulfides,[4b,e,5] the *Z* isomers being obtained only in special cases where, because of steric reasons, the transoid transition-state energy is raised substantially.[7] Thus, nine homoallylic sulfides were prepared which have the *E* configuration [**2a–g**, plus the two diastereoisomers of **2h**

(1) Calderoni, C.; Cerè, V.; Pollicino, S.; Sandri, E.; Fava, A. *J. Org. Chem.* **1980**, *45*, 2641. This paper is considered to be part 1 in the series.
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