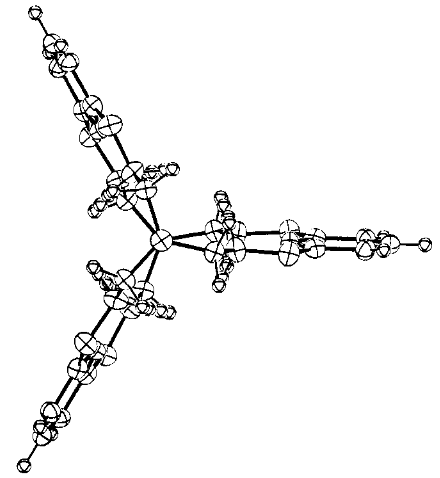

Figure 1. ORTEP[7] drawing of **3** projected down the N-N axis, illustrating nonhydrogen atoms by 40% probability thermal ellipsoids and hydrogen atoms by spheres of arbitrary radius.

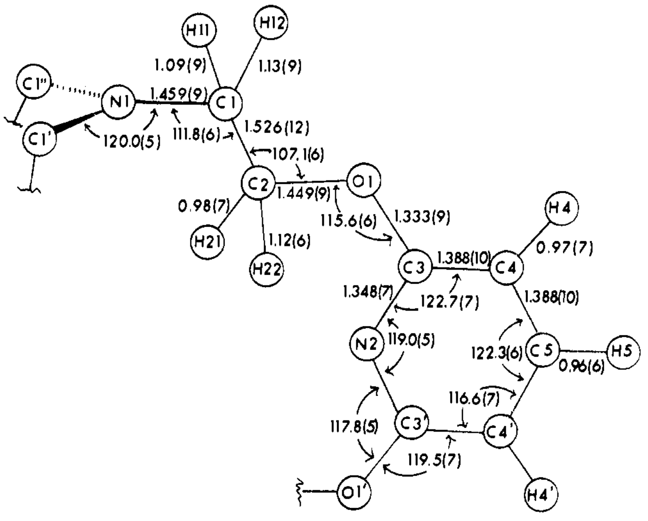

Figure 2. Bond distances and angles of cryptand **3**.

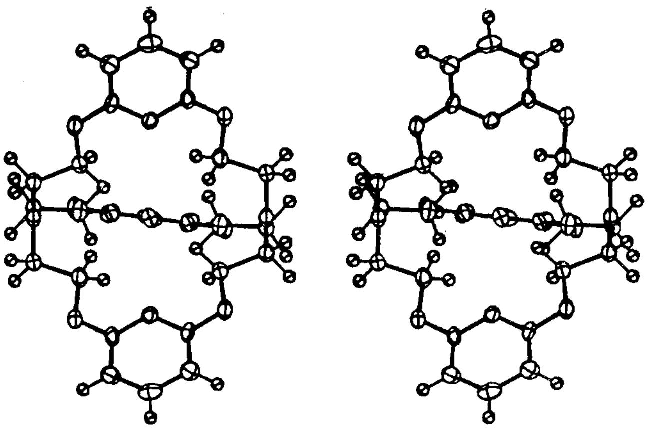

Figure 3. Stereoscopic representation of **3** viewed approximately down a twofold axis.

hybridized, rather than the anticipated sp^3 configuration, the generally accepted in-in and out-out pictorial representation need *not* adequately represent these macropolycyclic structures. Skeletal rigidity of the bridges or intramolecular hinderence imposed by substituents on the bridges apparently may determine the bridgehead nitrogen configurations. Crystallographic details, as well as the synthesis and reactions of similar cryptands, will be the subject of a later paper.

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Supplementary Material Available: Table of the positional and thermal parameters (1 page). Ordering information is given on any current masthead page.

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Ring-Chain Tautomerism in 1,3-Dimethylimidazolidine on the NMR Time Scale[1]

Sir:

Intramolecular organic rate processes studied at equilibrium by NMR spectroscopy have included bond rotations, atomic inversions, pentacoordinate pseudorotations, sigmatropic shifts, and proton transfers.[2] We report here the first example of a new reaction class that can be studied by this method, ring-chain tautomerism. This process is well known in heterocyclic chemistry[3] but has not previously been subject to study by the DNMR method.

At room temperature 1,3-dimethylimidazolidine (**1**, 1,3-dimethyl-1,3-diazolidine or 1,3-dimethyltetrahydroimidazole) in CF_3CO_2H gives the ^1H spectrum illustrated at the bottom of Figure 1. At first glance, the spectrum appears to be unremarkable, with the NCH_2N resonance at δ 5.2, the NCH_2CH_2N at 4.3, and the NCH_3 at 3.4. In addition, however, there are two puzzling small resonances from δ 7.7 to 8.5, one that is very broad and one that is relatively sharp. The spectrum is identical in CF_3CO_2D, except for the absence of the broad peak at δ 7.7–8.4, which hence can be assigned to the ^+NH protons. Consequently, the sharper peak at δ 8.4–8.5 cannot be from ^+NH protons. Integration of the ^+NH peak shows that the diazolidine is ~50% protonated under these conditions. The equilibrium between unprotonated (**1**) and monoprotonated (**1**-H^+) forms must be fast on the NMR time scale, since separate resonances are not observed and the H-N-C-H couplings are absent.

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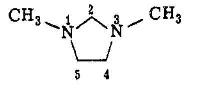


The rather low-field location of the δ 8.4 peak suggested to us an aldehyde-like structure (**2**), which can be readily obtained from the diazolidine by ring-chain tautomerism (eq 1).[4] The anisotropy of the C=N double bond should deshield the

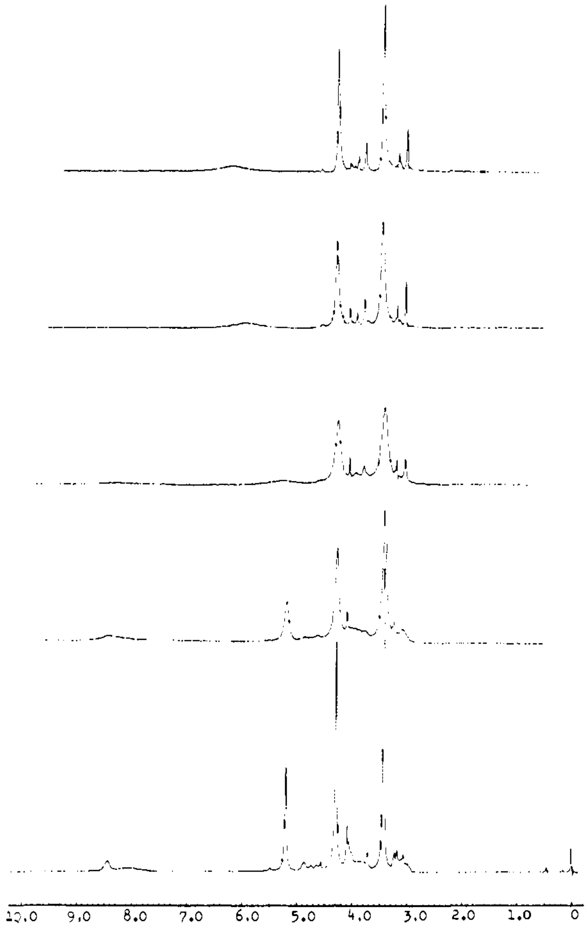
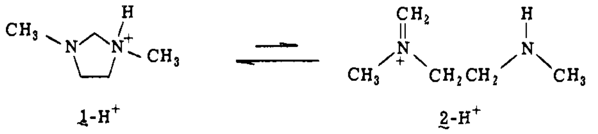


Figure 1. The 60-MHz ^{1}H spectrum of 1,3-dimethyltetrahydroimidazole (**1**) in CF_3CO_2H as a function of temperature (bottom to top: 40, 60, 80, 100, and 120 °C).



(1)

CH_2=N protons, just as the C=O double bond deshields aldehyde (CH=O) protons. We corroborated these assignments by the preparation of 1,3-dimethyl-1,3-diazolidine-*2,2-d*$_2$, whose ^{1}H spectrum lacked not only the NCH_2N resonance of **1**-H$^+$ at δ 5.2 but also the CH_2=N resonance of **2**-H$^+$ at 8.4. Taken in CF_3CO_2D, the spectrum of the *2,2-d*$_2$ variant exhibits only the two sharp singlets at δ 3.4 and 4.3. Some of the small peaks in the δ 3.0-5.0 region are from the remaining protons in **2**, but specific assignments could not be made. In addition, there are some impurities. Integration of the δ 5.2 and 8.4 peaks indicates that the ring form (**1**) is present at equilibrium to the extent of 82 ± 2%.[5] Our evidence does not prove conclusively that the less abundant species is **2**, but this form is consistent with all evidence to date.

The temperature dependence of the ^{1}H spectrum (Figure 1) demonstrates a dynamic interconversion of the ring (**1**-H$^+$) and chain (**2**-H$^+$) forms,[5] as best seen from the dramatic alterations of the NCH_2N resonance at δ 5.2. This peak begins to broaden above 40 °C and all but disappears by 80 °C. The CH_2=N peak at δ 8.4 also broadens and disappears, and the pair of peaks is replaced above 120 °C by an average singlet at about δ 6.3 (the fast exchange extreme was not fully attained). That the NCH_2N protons of the ring form and the CH_2=N protons of the chain form were indeed undergoing mutual exchange was confirmed by Forsén-Hoffman-type double resonance experiments[6] in the range 40-80 °C, whereby irradiation of either peak brought about considerable reduction in the intensity of the other peak. The NCH_2CH_2N and NCH_3 resonances also undergo alterations due to exchange, but less obviously. In both the undeuterated and the deuterated (*2,2-d*$_2$) forms, these peaks simply broaden at 60 °C and resharpen above 100 °C (Figure 1). The changes are less dramatic than for the NCH_2N resonances because the chemical shift differences between the ring and chain resonances are much smaller. All the temperature effects are fully reversible.

The coalescence temperature for ring-chain tautomerism in protonated 1,3-dimethyl-1,3-diazolidine (**1**) is ~90 °C, and the free energy of activation ($\Delta G^{\ddagger}$) at this temperature is 16.9 ± 0.3 kcal mol^{-1}. This reaction is an example of the normally disfavored 5-endo-trigonal ring closure (**2** → **1**).[7] Its relatively rapid rate may result from the strongly electrophilic nature of the iminium carbon in **2**-H$^+$ or from a variety of other possibilities. The DNMR method promises to be an extremely useful approach to studying this heterocyclic phenomenon. Our current work explores the effect of ring size and heteroatom identity on ring-chain tautomerism.

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Racemization of Isovaline by γ-Radiation. Cosmological Implications

Sir:

Isovaline (α-amino-α-methylbutyric acid) is of considerable cosmological interest since (1) it is one of the 12 nonprotein amino acids isolated and identified from the Murchison carbonaceous chondrite[1] and (2) it has no α hydrogen at its asymmetric center and has been shown[2] to be incapable of racemization by the mechanisms accounting for the racemization of ordinary α-amino acids. It had previously been suggested[3] that the enantiomeric composition of the Murchison isovaline should represent that prevailing at the time of its original synthesis in the meteorite, thus giving a clue as to the primordial enantiomeric composition of the other amino acids in the meteorite regardless of their present composition. Recently we reported[4-6] that ionizing radiation could cause "radioracemization" of α-amino acids both in the solid state and in solution, along with their well-known radiolysis.[7] We now have found that such radiation is capable of racemizing isovaline as well.

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