by melting point.

Anal. Calcd for $C_{10}H_{14}N_6O_4$: C, 42.55; H, 5.00; N, 29.78. Found: C, 42.36; H, 5.12; N, 29.72.

Recrystallization from H_2O gave a sample of mp 238–240 °C [lit.[3] 252–254 °C (hydrate); lit.[6] 250–252 °C]. Further recrystallization did not increase the melting point.

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Registry No.—**1**, 26929-65-7; **2**, 489-59-8; **3**, 51989-21-0; **4a**, 10407-64-4; **4b**, 10414-81-0; **5**, 60966-26-9; N^6-octanoyladenine, 52854-12-3; N^2-palmitoylguanine, 21047-87-0.

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Communications

Nitrogen-15–Carbon-13 Spin–Spin Coupling Constants of *cis*- and *trans*-1-Alkyl-2-aryl-3-benzoylaziridines

Summary: The ^{15}N–^{13}C spin–spin coupling constants are reported for *cis*- and *trans*-1-cyclohexyl-2-phenyl-3-benzoylaziridines. The one-bond coupling constants are in good agreement with the predictions of Wasylishen, based on INDO-MO calculations. Here the ^1J-(^{15}N,^{13}C) values are in good agreement with the supposition that endocyclic N–C bonds have high p character.

Sir: We wish to report here the ^nJ(^{15}N–^{13}C) values (where $n \leq 2$) for *cis*- and *trans*-1-cyclohexyl-2-phenyl-3-benzoylaziridines (**1** and **2**). The ^1J(^{15}N,^{13}C) values appear in good agreement with recent INDO–FPT calculations on ethylene imine itself, which thereby allows the N(s)–C(s) bond order to be accurately approximated.[1] Our ^1J(^{15}N,^{13}C) values are in good agreement with the supposition that endocyclic N–C bonds have high p characters. The magnitude of ^2J(^{15}N,^{13}C) and ^2J(^{15}N,H) values are related to nitrogen lone pair proximity wherein the syn orientation imparts a positive increment to the absolute value of the coupling constant.[2]

The stereoelectronic properties of small-ring compounds have remained topics of widespread interest.[3] Many chemical reactions and physical properties of cyclopropanes can be explained by the "bent bonds" of the ring, which have a high degree of p character.[4,5] The exocyclic bonds have a correspondingly higher degree of s character as revealed by enhancement of C–H bond acidity[6] and the fact that ^1J(^{13}C,H) values increase in magnitude as ring size decreases, indicative of higher percent s character in the C–H bonds.[7] For small ring heterocycles, hybridization values of endocyclic bonds are less well established.[6] Even though the first linear relationship between s character and ^1J(^{15}N,^{13}C) couplings was established by Binsch et al.[8] and supported by Schulman,[9] latter work has seriously questioned its validity.[10,11] Hence, the Fermi contact mechanism upon which ^1J(^{15}N–^{13}C) coupling is based appears inadequate in this instance.[12]

In other work, Schulman and Newton showed other coupling mechanisms than the Fermi contact mechanism were of importance in small ring compounds.[12] Marshall and coworkers have presented strong evidence that the observed coupling constant represents the sum of coupling through all paths.[13] This should be particularly important in three-ring molecules such as aziridines, where the coupling between nitrogen and adjacent carbon is the sum of one-bond and two-bond paths, both of which may be sizable.

To the best of our knowledge, the only data available for small ring nitrogen compounds comes from the work reported by Jennings[14] on (*Z*)-*cis*- and (*E*)-*trans*-oxaziridines (**3** and **4**) (Figure 1). Our data on the N-15 isotopically enriched aziridines **1** and **2** are also presented in Figure 1.[15,16] Of great importance in our work was the assessment of signs for the ^1J(^{15}N,^{13}C) and ^2J(^{15}N,^{13}C) couplings (Figure 1), which appears consistent with contemporary work in this field.[17-19] For the oxaziridines, the ring oxygen in **3** and **4** increases ^1J(^{15}N,^{13}C) couplings based on the data in Figure 1,[20] relative to the aziridines.

The ^1J(^{15}N,^{13}C) values for **1** and **2** are in good agreement

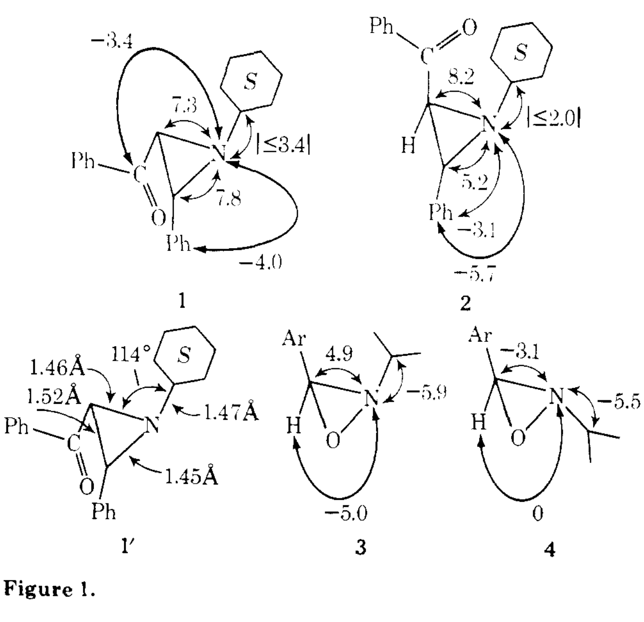

Figure 1.

with Wasylishen's predictions, based on INDO-MO calculations.[1] These calculations correlate $^1J(^{15}N,^{13}C)$ with $P^2s(n)$-$s(c)$, where $Ps(n)s(c)$ is the bond order between the valence-shell s orbitals of nitrogen and carbon. These density matrix elements may then be related to the hybridization of the ring carbon-nitrogen bond.[11,21,22] The excellent agreement provides a strong indication that the s character of these ring bonds is very low (~20%), indicative of ~sp^4 hybridization. The exocyclic N-C bonds showed small coupling constants, indicative of a hybridization similar to that of methylamine[1] [$^1J(^{15}N,^{13}C) = -3.74$ Hz], and, hence, indicative of substantial p character in the N-C bond. [It is noteworthy from the crystallographic data (1) that the C-N-C_6H_{11} bond angle of 114° (interorbital angle, ~112°) and the exocyclic C-N bond length of 1.47 Å are not indicative of high s character.[23]] It is possible, however, that the lone pair at nitrogen maintains high s character, thus permitting greater p character in all bonding orbitals at nitrogen.[6,24,25]

Jennings et al. regarded the direction of the lone pair at nitrogen as an important factor affecting the magnitude of $^2J(^{15}N,H)$ and $^2J(^{15}N,^{13}C)$, as well as other coupling constants.[14] Thus, $^2J(^{15}N,H)$ was shown to be greater in magnitude where the lone pair was roughly parallel to the C-H bond in question. It is known from other extensive work[2] that the cyclohexyl group in 1 and 2 prefers the conformation shown in Figure 1. The $^2J(^{15}N,H)$ coupling constant is only observed in 2 but indeed in the situation where C-H was syn to the lone pair. In 2 $^2J(^{15}N,^{13}C)$ was observable (−3.1 Hz) only when the C-C bond was syn to the lone pair, but not to COPh, where the C-C bond was anti to the lone pair.[17,26]

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An Unusually Facile Ring Opening of 5-Alkoxyoxazoles. Application to the Synthesis of Dimethoxy-α-methyldopa

Summary: In the presence of *n*-BuLi, 5-alkoxyoxazoles undergo an unusually facile ring-opening reaction leading directly to lithiated isocyanoacetic acid derivatives, which in turn are versatile intermediates for the preparation of a variety of heterocyclic systems and amino acid derivatives.

Sir: As a part of our continuing efforts to exploit the latent functionality of heterocyclic systems, we have recently investigated the preparation of a number of highly substituted oxazoles such as **3** shown in Scheme I.[1] Within this context, it initially appeared that a convenient route to these materials would involve the lithiation and subsequent alkylation of the parent alkoxyoxazoles **1**,[2] and we were further encouraged by the fact that a variety of closely related species have been successfully lithiated and trapped with electrophilic agents.[3] Unexpectedly, however, the lithiation of oxazoles **1** took an entirely different course. Thus, for example, oxazole **1a** reacted rapidly with *n*-BuLi (1.05 equiv, THF, −78 °C, 5 min), but after quenching with D_2O the only detectable product was ethyl α-deuterio-α-isocyanopropionate (**5b**).[4] Similarly, reaction with a variety of alkyl iodides and bromides gave the corresponding alkylated derivatives **5c** to **5j** (Table I),[5] and in analogous fashion, alkoxyoxazole **1b** gave the lithio derivative **4** (cf. Scheme I, R = H).

Scheme I