of coplanarity around zinc is indicated by the sum of the three bond angles, which equals 359.2°. Three coordination is rare for zinc, and [\(\mathrm{H}_2\mathrm{~B}(3\text{-Bu'pz})_2\)]Zn(CðCH_3\) represents the first structurally characterized monomeric organozinc complex that exhibits such coordination.

The reactivity of the complexes [\(\mathrm{H}_2\mathrm{~B}(3\text{-Bu'pz})_2\)]Zn is shown in Scheme 1. Protonic reagents (H_2O and CH_3CO_2H) react specifically at the Zn-C bond to give [\(\mathrm{H}_2\mathrm{~B}(3\text{-Bu'pz})_2\)]Zn(X), (X = OH or OC\(\mathrm{CH}_3\)) and eliminate the alkane. The hydroxy complex [\(\mathrm{H}_2\mathrm{~B}(3\text{-Bu'pz})_2\)]Zn[\(\mu\)-OH]) has been characterized as a cyclic trimer by an X-ray diffraction study (Figure 2), and the molecule possesses approximately C_3 symmetry, with each hydroxogroup bridging to zinc centers. Although the X-ray structure determination did not reveal the location of the hydroxy hydrogen atoms, convincing evidence for their presence is provided by the absorption at 361 cm\(^{-1}\) that is assigned to \(v(\text{OH})\). The molecule possesses approximately 6Li and 15N nuclear magnetic resonance spectroscopic studies of lithiated cyclohexanone phenylene Revisited. Aggregation-State Determination by Single-Frequency 15N Decoupling.

Acknowledgment

Is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research, and we thank Professor Arne Haaland for discussions.

Supplementary Material Available: Tables of spectroscopic data for the new compounds and tables of crystal and intensity collection data, atomic coordinates, and thermal displacement and bond angles, and anisotropic displacement parameters and electron drawings for [\(\mathrm{H}_2\mathrm{~B}(3\text{-Bu'pz})_2\)]Zn(CðCH_3\) and [\(\mathrm{H}_2\mathrm{~B}(3\text{-Bu'pz})_2\)]Zn(\(\mu\)-OH)], (29 pages); tables of observed and calculated structure factors for [\(\mathrm{H}_2\mathrm{~B}(3\text{-Bu'pz})_2\)]Zn(CðCH_3\) and [\(\mathrm{H}_2\mathrm{~B}(3\text{-Bu'pz})_2\)]Zn(\(\mu\)-OH)], (30 pages). Ordering information is given on any current masthead page.


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4Li and 15N NMR spectroscopy has proven to be a powerful probe of the atom connectivities and aggregation states of lithium dialkylamides and lithiated imines in solution.1-4 Multiplicities consistent with monomers, cyclic oligomers, ion triplets, and mixed aggregates (Chart I: I-4) have all been recorded on substrates isotopically enriched in \(^6\)Li and \(^15\)N. The two major limitations of the double-labeling technique are as follows: (1) topologically equivalent cyclic oligomers—cyclic dimers, trimers, and tetramers—cannot be rigorously distinguished; and (2) the \(^15\)N and \(^6\)Li multiplets are not readily correlated when several chemically inequivalent sites are observed. We will demonstrate that \(^{15}\)N resonance correlations resulting from very simple single-frequency decoding distinguishes cyclic dimers from higher oligomers for the lithiated phenylene of cyclohexanone (5).1-3

4Li and 15N NMR spectroscopic studies of \([\text{Li},^15\text{N}]-5\) have been described previously; representative spectra are illustrated in Figure 1A,B.

**Note**

6.3 Hz) and the 1:1:1 \(J_{\text{NN}}\) triplet (\(J_{\text{NN}} = 3-4\) Hz each) and the two 2:1:2:2:1 \(^{15}\)N quintets (\(J_{\text{NN}} = 3-4\) Hz) appear to derive from cyclic aggregate structural units. The 2:1 ratio of aggregate-derived resonances remains constant with changes in the concentration of either 5 or THF (using toluene-\(d_8\) as diluent).6 The two \(^6\)Li triplets and two \(^{15}\)N quintets are consistent with either a mixture of stereoisomeric cyclic dimers 6 and 7 or cis,trans trimers 8 (\(C_8\) = 1-cyclohexenyl). Colligative measurements,13 crystallographic analogies,4 the absence of resonances expected for the all-cis stereoisomeric trimers 9, and ab initio calculations on \((\text{Li}_2\text{Ni}_5\text{S}_2)^+\) all implicate dimers 6 and 7. Nevertheless,

Figure 1. NMR spectra recorded at -93°C of a 0.3 M solution of lithiated imine 5 in toluene-δ, containing 2.0 equiv of THF/lithium: (A) 13N NMR spectrum (30.42 MHz); (B) 6Li NMR spectrum (44.19 MHz) observed via the 2H lock channel as described in the text; (C) 6Li NMR spectrum observed via the 2H lock channel with concomitant irradiation of the downfield (minor) 15N resonance in spectrum A; (D) 6Li NMR spectrum observed via the 2H lock channel with concomitant irradiation of the downfield (minor) 15N resonance in spectrum A.

we were unable to unequivocally exclude trimer 8. The inability to distinguish dimers from higher oligomers has haunted subsequent structural and mechanistic studies of N-lithiated species.4,5

The results of single-frequency irradiations are illustrated in Figure 1C,D. Irradiation of the major 15N quintet centered at 134.6 ppm causes clean collapse of the major 6Li resonance to a singlet. Similarly, irradiation of the minor 15N quintet causes the minor 6Li triplet to collapse to a singlet. The decouplings are consistent with two chemically distinct isomeric dimers 6 and 7,10

Furthermore, if cis,trans trimer 8 had been the predominant aggregate in solution, irradiation of the major 15N resonance would have caused the major and minor 6Li triplets to collapse to a doublet and singlet, respectively. Similarly, irradiation of the minor 15N resonance would have caused collapse of the major 6Li triplet to a doublet without change in the minor 6Li triplet. Thus, the results of the single-frequency decouplings are consistent with stereoisomeric dimers 6 and 7 and inconsistent with a trimer structure.

6Li and 15N resonance correlations, when placed in the context of the stereochemical consequences of aggregation, provide a direct probe of aggregate structure. The exclusion of cyclic trimers in this specific case strengthens the dimer assignments for other solvated lithium amide species as well. As we continue to uncover lithium amide aggregates and mixed aggregates of increasing complexities,11 such 6Li-15N resonance correlations will become essential components of solution structure determinations.

Acknowledgment. We thank Jim Simms of MIT and Brian Andrew of Bruker for several very helpful discussions. We acknowledge the National Science Foundation Instrumentation Program (CHE 7904825 and PCM 8018643), the National Institutes of Health (RR20020), and IBM for support of the Cornell Nuclear Magnetic Resonance Facility. D.B.C. and J.H.G. thank the National Institutes of Health for support of this work.

Registry No. 5, 101773-95-9; 6Li, 14258-72-1.

Enantioselective Total Synthesis of Neooxazolomycin
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Received January 10, 1990

Neooxazolomycin (1) is a structurally novel C34H47N3O9 oxazole polyene lactam–lactone antibiotic isolated from several Streptomyces strains.1,2 The structures and absolute configurations of this compound13 and its β-lactone congener, oxazolomycin (2),14 were described in 1985. Neooxazolomycin (1) is an acid-, base- and light-sensitive molecule that may be regarded as an amide formed between a Z,Z,E oxazole triene acid left half (22) and a highly functionalized lactam–lactone amino diene (37, R1 = H) right half (Chart I). We now report the first enantioselective total synthesis of neooxazolomycin.2

The oxazole triene acid left half of the antibiotic was synthesized from the known3 (Z)-3-bromo-2-methyl-2-propenol (3), converted to the Z aldehyde 5 in 84% yield by a four-step sequence (Scheme I): (1) O-silylation, (2) Pd-catalyzed coupling4 with (trimethylsilyl)acetylene to produce the enyne 4, (3) selective O-

(9) In several other instances wherein N-lithiated species display a concentration-independent pair of 6Li resonances,23 ratios closer to 1:1 further argue against cyclic trimers.

(10) In contrast to the irradiations of the 15N multiplets separated by 55 Hz, irradiation of each of the narrowly spaced (11 Hz) 6Li triplets failed to afford fully selective decoupling.


(2) All new compounds showed NMR, IR, and C,H or mass spectrometric analyses consistent with the assigned structures.


0002-7863/90/1512-4070$02.50/0 © 1990 American Chemical Society