

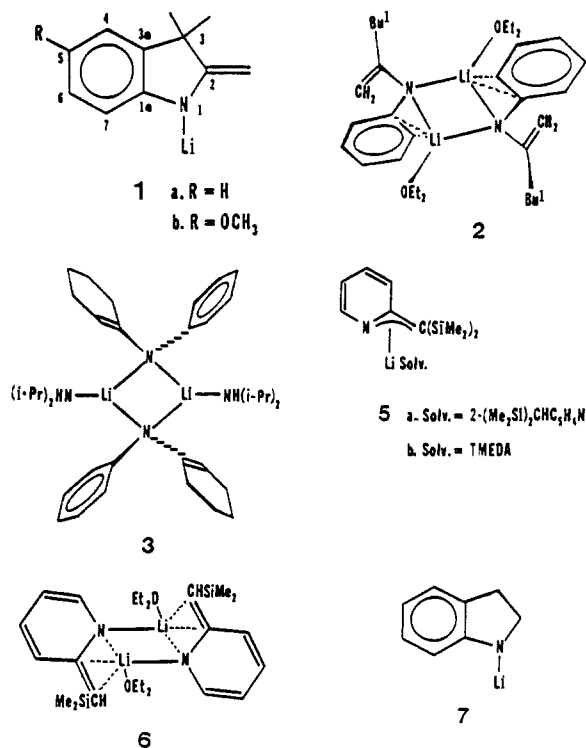
# Structures of Lithium Salts of 2,3,3-Trimethylindolenine and Its 5-Methoxy Derivative in Solution and the Solid State

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**Abstract:** An X-ray crystal structure of lithium 2,3,3-trimethylindolenide etherate shows it to be a disolvated dimer having a  $\eta^3$ -azaallyl-type structure. The structures of the salt in several solvents have been established by studies of  $^{13}\text{C}$  chemical shifts,  $^6\text{Li}$ ,  $^{15}\text{N}$  spin-spin splitting,  $^7\text{Li}$  quadrupole splitting constants, and apparent degrees of aggregation determined by vapor pressure barometry. It is the  $\eta^3$ -azaallyl dimer disolvate in diethyl ether, a tetrasolvated dimer in dioxolane, a mixture of monomer and tetrasolvated dimer in tetrahydrofuran, and a monomer in pyridine. The species are characterized by  $^7\text{Li}$  quadrupole splitting constants of 230, 156, 180–190 (0.27–0.75 M), and 217 kHz, respectively. In diethyl ether with 4 equiv of hexamethylphosphoric triamide, the salt is a mixture of monomeric and triple ion species. Lithium 5-methoxy-2,3,3-trimethylindolenide forms similar species except that, in tetrahydrofuran, the tendency for dimer formation is enhanced, which leads to a higher proportion of C- to N-methylation in its reaction with methyl chloride in that solvent.

In recent years there has been considerable interest in the potential of imine anions, particularly (1-azaallyl)lithium reagents, in organic synthesis.<sup>3</sup> Such reagents offer advantages over the corresponding enolates in that they generally react with electrophiles much faster than they undergo proton transfer with the resulting imines so that monoalkylation, for instance, is not complicated by concomitant dialkylation. Furthermore, certain (1-azaallyl)lithium reagents,<sup>4–6</sup> lithioimino ethers,<sup>7,8</sup> and hydrazones<sup>9</sup> form the basis of one of the most useful classes of chiral auxiliaries employed in organic synthesis. Imine anions are ambident and undergo reactions at both their C- and N-termini.<sup>10</sup> Frequently, reactions are performed on the lithium salts in ether or tertiary amine solvents, and it is probable that in these solvents the salts, like those of aromatic secondary amines,<sup>11</sup> are monomeric or dimeric tight ion pairs, the structures of which determine reactivity and regio- and stereochemistry. In order to extend our studies<sup>12</sup> of the relation of the solution structure of lithium salts involving organic ambident anions to reactivity and regiochemistry to include imine anions, we have chosen the salts **1a** and **b** since they are readily generated from the corresponding imines by treatment with alkyllithium reagents and have fixed (anti) stereochemistry.<sup>13</sup> In this paper, we present the results of structural studies of the salts in several solvents as well as an X-ray crystal structure of the etherate of **1a**. In addition, we report some preliminary results that establish that these salts can undergo both



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(13) In general, C-alkylation can give rise to syn and anti isomeric imines<sup>14–16</sup> and N-alkylation to (E)- and (Z)-enamines.<sup>15,17</sup>

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C- and N-methylation and are, therefore, eminently suitable for a proposed, detailed mechanistic study.

Two X-ray crystal structures of simple (1-azaallyl)lithium compounds have been reported. Dietrich, Mahdi, and Knorr<sup>18</sup> found that the etherate of lithium *N*-(2,2-dimethyl-1-methylenepropyl)anilide is a dimer,  $[\text{CH}_2=\text{C}(t\text{-Bu})\text{NPhLi}(\text{OEt}_2)_2]$  (**2**), the most interesting feature of which is that although it is N-lithiated, there is evidence of incipient  $\pi$ -bonding to the 1,2-bond of the aromatic ring. A somewhat similar interaction between lithium and the double bond on a benzene ring has been observed<sup>19</sup> in the crystal structure of the "loose" dimer of the tetramethylethylenediamine solvate of lithium *N*-1-naphthylanilide. In contrast, Collum, Clardy, and co-workers<sup>16a</sup> have established that a diisopropylamine solvate of lithiated *N*-phenyl-1-cyclohexenylamine, **3**, which is also an N-lithiated dimer, exhibits no evidence of  $\pi$ -interactions with either the aromatic ring or the

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cyclohexene double bond. It is a normal  $\text{Li}_2\text{A}_2\text{S}_2$  dimer similar to those found for *N*-alkylanilides in diethyl ether.<sup>11,20</sup> In addition to these simple systems, 1-lithio-3,6-diethoxy-2,5-dimethyl-1,2-dihydropyrazine has been found to crystallize from THF as a trisolvated dimer.<sup>21</sup> The 2-lithiocyclohexanone phenylimine solvate, **3**, has been studied<sup>16</sup> by  $^{13}\text{C}$  NMR in toluene- $d_8$  and by cryoscopy in benzene and appears to retain the  $\text{Li}_2\text{A}_2\text{S}_2$  ( $\text{S} =$  diisopropylamine) structure even in the presence of 10 equiv of  $\text{S}$ . The dimer appears to exhibit *E/Z* isomerism similar to that observed for lithium *N*-alkylanilide  $\text{Li}_2\text{A}_2\text{S}_2$  species. Other studies<sup>13,15,22-25</sup> have been directed toward stereochemical aspects of imine anions, particularly the configurations of the partial double bonds of the 1-azaallyl anion. In these stereochemical studies, the questions of aggregation or solvation of the lithium salts were not addressed.

### Experimental Section

**Materials.** Diethyl ether, tetrahydrofuran, pyridine, and hexamethylphosphoric triamide were purified immediately prior to use.<sup>11</sup> 2,3,3-Trimethylindolenine (Aldrich Chemical Co.) was fractionally distilled from  $\text{CaH}_2$  under nitrogen prior to use:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.22 (s, 6 H), 2.18 (s, 3 H), 7.02–7.44 (m, 4 H). 2-Methylene-1,3,3-trimethylindolenine (Eastman Kodak Co.) was distilled under nitrogen:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.31 (s, 6 H), 2.97 (s, 3 H), 3.82 (s, 2 H), 6.49–7.09 (m, 4 H).

**$^{15}\text{N}$ -2,3,3-Trimethylindolenine.**  $^{15}\text{N}$ Isatin was prepared from  $^{15}\text{N}$ aniline (33%)<sup>26</sup> and was subsequently converted to the indolenine by the method of Wenkert.<sup>27</sup>

**5-Methoxy-2,3,3-trimethylindolenine.** The reaction of (4-methoxyphenyl)hydrazine with 2-methylbutanone in acetic acid afforded the indolenine<sup>28</sup> as a white solid, mp 56–57 °C:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.20 (s, 6 H), 2.13 (s, 3 H), 3.83 (s, 3 H), 6.84 (d,  $J = 8.2$  Hz, 1 H), 6.85 (s, 1 H), 7.4 (d,  $J = 8.2$  Hz, 1 H).

**2-Methylene-5-methoxy-1,3,3-trimethylindolenine.** This compound<sup>29</sup> was obtained as an oil, which turned purple in air, by *N*-methylation of the indolenine using the method of Heaney and Ley:<sup>30</sup>  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.18 (s, 6 H), 2.80 (s, 3 H), 3.56 (s, 2 H), 3.57 (s, 3 H), 6.22 (d,  $J = 8.2$  Hz, 1 H), 6.49 (dd,  $J = 2.5, 8.3$  Hz, 1 H), 6.59 (d,  $J = 2.25$  Hz, 1 H).

**3,3-Dimethyl-2-ethylindolenine.** A 1.55 M solution (8.1 mL, 0.0126 mol) of *n*-butyllithium in hexane was added dropwise to a cooled solution of 2,3,3-trimethylindolenine (2.0 g, 0.0126 mol) in anhydrous diethyl ether (20 mL) under nitrogen, and the resulting solution was stirred for 2 h at room temperature. Methyl iodide (2.7 g, 0.019 mol) was added, and stirring was continued overnight. The resulting mixture was treated with ether (100 mL) and 10% NaOH (20 mL). The ether layer was separated, washed successively with 10% NaOH (20 mL) and water (20 mL), and dried ( $\text{MgSO}_4$ ). Removal of the ether gave a yellow oil, which crystallized on the addition of petroleum ether (bp 60–90 °C). Repeated crystallization from petroleum ether afforded 3,3-dimethyl-2-ethylindolenine (0.9 g, 41%) as white needles, mp 52–53 °C [lit.<sup>31</sup> mp 52–53 °C]:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.14 (s, 6 H), 1.28 (t,  $J = 7.1$  Hz, 3 H), 2.46 (q,  $J = 7.1$  Hz, 2 H), 7.15 (m, 3 H), 7.46 (m, 1 H).

**3,3-Dimethyl-2-ethyl-5-methoxyindolenine.** (4-Methoxyphenyl)hydrazine (2.4 g, 0.017 mol) and 2-methyl-3-pentanone (2.6 g, 0.026 mol) in glacial acetic acid (20 mL) were refluxed for 2 h. The solution was cooled, diluted with  $\text{H}_2\text{O}$  (100 mL), made alkaline with 5 N NaOH, and extracted with diethyl ether (3  $\times$  40 mL). Removal of the solvent from the dried ( $\text{MgSO}_4$ ) extract afforded a viscous oil, flash chromatography (eluant,  $\text{Et}_2\text{O}$ ) of which gave a white solid (0.6 g, 17%), mp 70–71 °C:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.12 (s, 6 H), 1.21 (t,  $J = 7.3$  Hz, 3 H), 2.41 (q,  $J = 7.3$  Hz, 2 H), 3.58 (s, 3 H), 6.70 (d,  $J = 8.2$  Hz, 1 H), 6.76

(s, 1 H), 7.38 (d,  $J = 8.4$  Hz, 1 H). Anal. Calcd for  $\text{C}_{13}\text{H}_{17}\text{NO}$ : C, 76.81; H, 8.43; N, 6.89. Found: C, 76.28; H, 8.32; N, 6.71.

**X-ray Structure Determination of Lithium 2,3,3-Trimethylindolenide Etherate.** The salt crystallized in the monoclinic space group  $P2_1/c$ . The unit cell parameters were determined to be  $a = 8.639$  (2) Å,  $b = 8.359$  (3) Å,  $c = 20.364$  (7) Å, and  $\beta = 96.60$  (3)° by least-squares fitting to the positions of 25 independent reflections in the range  $24^\circ \leq 2\theta \leq 26^\circ$ . This unit cell contained four asymmetric units of molecular formula  $\text{C}_{13}\text{H}_{22}\text{ONLi}$  in a volume of  $1460.87$  (1.0) Å<sup>3</sup>, which produces a calculated density of  $1.08$  g/cm<sup>3</sup>. A total of 2246 reflections were recorded in the range  $3.5^\circ \leq 2\theta \leq 45^\circ$  with a Nicolet R3m/E crystallographic system by the Wyckoff scan routine and graphite-monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71069$  Å) under a stream of dry nitrogen cooled to  $\approx -100$  °C. A total of 1551 unique reflections were observed with the criterion  $F_o \geq 3.0\sigma(F_o)$ . After Lorentz and polarization corrections, the structure was solved by the SHELXTL 5.1 programs. All non-hydrogen atoms were refined anisotropically. The approximate location of all hydrogen atoms was determined by Fourier difference syntheses. In the final stages of refinement the hydrogen atoms were placed in calculated positions and allowed to ride with the atom to which they are attached. The final agreement factors are  $R = 0.069$  and  $R_w = 0.075$  for 163 independent parameters where  $R = [\sum(w\Delta^2)/\sum(wF_o^2)]^{1/2}$ ,  $\Delta = |F_o - F_c|$ , and the weighting scheme is  $w = 1/[\sigma^2(F_o) + 0.0002F_o^2]$ .

**Sample Preparation.** The apparatus and procedures have been previously described in detail.<sup>11</sup> In general, the salts were recrystallized from diethyl ether, although the presence of the parent indolenines did not affect the  $^{13}\text{C}$  chemical shifts.

**Vapor Pressure Barometry.** The apparatus and procedure have been previously described.<sup>11</sup> The sample was recrystallized from diethyl ether.

**NMR Spectroscopy.** High-field spectra were obtained with a Bruker WH360 spectrometer, and the  $^{15}\text{N}$  spectrum was obtained with a JEOL PS-100-FT spectrometer.  $^{13}\text{C}$  chemical shifts are reported in ppm relative to internal  $\text{C}_6\text{D}_{12}$  (26.40) or THF (26.50), and  $^{15}\text{N}$  chemical shifts are referenced to external  $^{15}\text{N}$ methylamine 52.80 ppm).  $^{13}\text{C}$  spectra were assigned with the aid of semiselective  $^1\text{H}$  decoupling experiments. The temperatures in the  $\delta_{\text{C}(5)}$  vs  $T$  studies were calibrated against standard methanol and ethylene glycol samples; other temperatures are uncalibrated but are known to be accurate to  $\pm 2$  °C. The method of measurement of  $^{13}\text{C}$  and  $^7\text{Li}$  spin-lattice relaxation times used for the determination of  $^7\text{Li}$  quadrupole splitting constants has been previously described.<sup>20</sup>

**Methylation of Lithium 2-Methyleneindolenides.** The following is a general procedure using methyl chloride:

A 50-mL round-bottom flask fitted with a sealed side arm was attached to a vacuum line and evacuated. After the flask was back-filled with dry  $\text{N}_2$ , the side arm was opened and a solution of 2,3,3-trimethylindolenine (0.318 g, 2 mmol) in dry diethyl ether (10 mL) was added through the side arm, which was then resealed. The solution was degassed by three freeze-pump-thaw cycles and cooled to 0 °C. The flask was back-filled with  $\text{N}_2$ , the side arm was opened, and after the addition of a solution (1.32 mL, 1.55 M) of butyllithium in hexane to the flask, the side arm was resealed. The solution was stirred at 0 °C for 3 h and the ether removed by pumping. Dry ( $\text{CaH}_2$ ), degassed THF (8 mL) was transferred to the flask, which was then back-filled with  $\text{N}_2$ . The side arm was reopened and fitted with a serum cap through which a fine-glass inlet tube was passed to the bottom of the flask. Methyl chloride was bubbled through the solution for 1 h after which the reaction mixture was quenched with water (5 mL). The aqueous mixture was extracted with ether (30 mL), the ethereal solution was dried ( $\text{MgSO}_4$ ), and the ether was removed by evaporation. The resulting oil was analyzed for starting material, and *C*- and *N*-methylated derivatives, by integration of the proton signals of 2-methyl ( $\delta$  2.18), aliphatic methylene ( $\delta$  2.46), and *N*-methyl ( $\delta$  2.97) protons, respectively.

### Results and Discussion

**X-ray Crystallographic Structure of Lithium 2,3,3-Trimethylindolenide.** The crystallographic asymmetric unit of this compound consists of one lithiated imine solvated by one diethyl ether with a molecular formula of  $\text{C}_{11}\text{H}_{12}\text{NLi}\cdot\text{C}_4\text{H}_{10}\text{O}$ . Short intermolecular contacts between the N and the Li with symmetrically equivalent atoms generated by inversion through a center of symmetry indicate the existence of a dimeric complex. A stereoplot of this dimer is given in Figure 1.

The core of the dimer is an approximately square-planar Li–N–Li–N four-membered ring. Each nitrogen atom exhibits distorted tetrahedral geometry and is approximately equidistant ( $\approx 2.0$  Å) from two lithium atoms. Selected internuclear distances and angles are given in Table I. One noteworthy aspect of the structure depicted in Figure 1 is the relatively short interatomic

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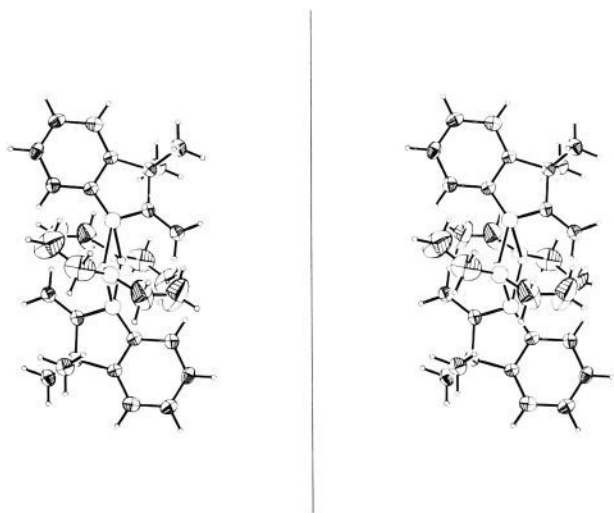


Figure 1. ORTEP stereodrawing of dimeric lithium 2,3,3-trimethylindolenide etherate.

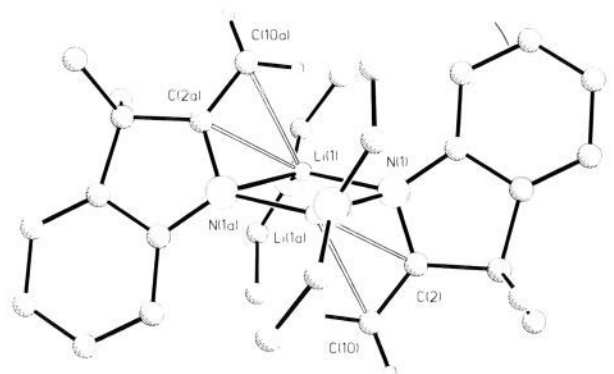


Figure 2. Molecular structure of dimeric lithium 2,3,3-trimethylindolenide, 4.

distance between the olefinic carbons and the lithium atoms. This is illustrated in fuller detail in Figure 2.

Significant differences exist among the structures of **2** and **3** and that of **4**, depicted in Figure 2, although all can be regarded as derivatives of the 1-phenyl-1-azaallyl anion. In the salt **3**, each lithium is tricoordinate with a trigonal-planar arrangement of ligands. The aromatic ring and the azaallyl anion are markedly noncoplanar with a dihedral angle of  $\sim 40^\circ$ , but there is no evidence of significant  $\pi$ -allyl or  $\pi$ -aryl bonding to lithium. In **2**, trigonal nitrogen and azaallyl systems are almost orthogonal. There is evidence of a significant  $\pi$ -aryl interaction in that the lithiums are no longer trigonal planar, being some 0.4 Å out of the planes of their  $\pi$ -ligands, and the aromatic ring assumes the position of a fourth ligand with Li-C(ipso) and one of the Li-C(ortho) distances of 2.44 and 2.66 Å, respectively. Finally, in the case of the indolenide **4**, the five-membered ring ensures coplanarity of the aromatic ring and the azaallyl anion. In this structure, the lithiums are again displaced by about 0.5 Å from the plane of the  $\pi$ -ligands, but it is now the carbon-carbon double bond of the azaallyl system that assumes the role of  $\pi$ -ligand with Li(1)-C(2a) and Li(1)-C(10a) distances of 2.37 and 2.51 Å, respectively.

The diversity of structure noted above appears to have its origin in a subtle interplay of steric and electronic effects. Simple electrostatic considerations predict that dimers of the  $\text{Li}_2\text{A}_2\text{S}_2$  type will have a planar arrangement of the lithium and their ligand atoms. This arrangement is found in  $[\text{Li}\{\text{N}(\text{SiMe}_3)_2\}(\text{OEt}_2)]_2$ ,<sup>32</sup>  $[\text{Li}\{\text{N}(\text{CH}_2\text{Ph})_2\}(\text{OEt}_2)]_2$ ,<sup>33</sup>  $[\text{Li}(2,4,6\text{-tri-}t\text{-butylanilide})$

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Table I. Bond Lengths and Bond Angles in the Dimer of Lithium 2,3,3-Trimethylindolenide Etherate, 4

Bond Lengths, Å			
Li-N	2.004 (6)	Li-O	1.944 (6)
Li-Na	2.090 (6)	N-C(2)	1.393 (4)
N-C(9)	1.401 (4)	N-Lia	2.090 (6)
C(2)-C(3)	1.528 (4)	C(2)-C(10)	1.342 (5)
C(3)-C(4)	1.515 (5)	C(3)-C(11)	1.526 (4)
C(3)-C(12)	1.538 (5)	C(4)-C(5)	1.364 (4)
C(4)-C(9)	1.398 (4)	C(5)-C(6)	1.404 (5)
C(6)-C(7)	1.376 (5)	C(7)-C(8)	1.376 (5)
C(8)-C(9)	1.399 (5)	O-C(14)	1.437 (5)
O-C(15)	1.405 (5)	C(13)-C(14)	1.459 (8)
C(15)-C(16)	1.376 (8)		
Bond Angles, deg			
N-Li-O	126.8 (3)	N-Li-Na	101.5 (3)
O-Li-Na	125.0 (3)	Li-N-C(2)	121.0 (3)
Li-N-C(9)	128.4 (3)	C(2)-N-C(9)	106.3 (2)
Li-N-Lia	78.5 (3)	C(2)-N-Lia	83.4 (2)
C(9)-N-Lia	129.5 (3)	N-C(2)-C(3)	111.7 (3)
N-C(2)-C(10)	124.1 (3)	C(3)-C(2)-C(10)	124.1 (3)
C(2)-C(3)-C(4)	100.8 (2)	C(2)-C(3)-C(11)	111.8 (3)
C(4)-C(3)-C(11)	112.9 (2)	C(2)-C(3)-C(12)	111.0 (2)
C(4)-C(3)-C(12)	110.7 (3)	C(11)-C(3)-C(12)	109.4 (3)
C(3)-C(4)-C(5)	130.9 (3)	C(3)-C(4)-C(9)	107.7 (3)
C(5)-C(4)-C(9)	121.4 (3)	C(4)-C(5)-C(6)	119.3 (3)
C(5)-C(6)-C(7)	119.4 (3)	C(6)-C(7)-C(8)	121.7 (3)
C(7)-C(8)-C(9)	119.1 (3)	N-C(9)-C(4)	113.3 (3)
N-C(9)-C(8)	127.7 (3)	C(4)-C(9)-C(8)	119.0 (3)
Li-O-C(14)	122.7 (3)	Li-O-C(15)	126.5 (4)
C(14)-O-C(15)	109.7 (4)	O-C(14)-C(13)	109.9 (4)
O-C(15)-C(16)	114.6 (5)		

(OEt)<sub>2</sub>],<sup>34</sup> and disolvates of 4-substituted lithium 2,6-di-*tert*-butylphenolates.<sup>35</sup> This is also the structure adopted by **3**. The original conclusion of Streitwieser<sup>36</sup> that organolithium compounds involve essentially ionic Li-C bonds is well supported by recent ab initio calculations by Schleyer and his collaborators<sup>37</sup> and can obviously be extrapolated to lithium bonds to more electronegative atoms such as nitrogen.<sup>38</sup> It is, therefore, reasonable to discuss the structures **2-4** in terms of the  $\pi$ -electron distribution in the parent anions. Thus, the indolenide **4**, in which the planar azaallyl ion allows maximum delocalization, is most likely to involve a  $\pi$ -allyl interaction provided that, as appears to be the case, it is not accompanied by destabilizing nonbonded interactions. In **3**, both the aryl and cyclohexenyl rings are twisted out of the plane of the formally trigonal nitrogen atom, and no evidence of  $\pi$ -interactions is found. Finally, the presence of the *tert*-butyl group in **2** forces orthogonality between the trigonal nitrogen and the plane of the carbon-carbon double bond of the azaallyl ion, which evidently precludes a  $\pi$ -allyl interaction. On the other hand, the phenyl ring is now approximately coplanar with the trigonal nitrogen, can delocalize the  $\pi$ -charge, and is well positioned for a  $\pi$ -aryl interaction with one of the lithium atoms.

The  $\eta^3$ -azaallyl structure has been clearly documented by Colgan, Papasergio, Raston, and White<sup>39</sup> for  $\omega$ -lithio derivatives of  $\omega$ -(trimethylsilyl)- and  $\omega,\omega$ -bis(trimethylsilyl)-2-picoline **5** and **6** and in the case of the dimer **6** the lithium is rather symmetrically situated above the azaallyl system with N, C(1), and C(2) distances of 2.19, 2.34, and 2.35 Å, respectively. The interaction

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**Table II.**  $^{13}\text{C}$  Chemical Shifts (ppm) for Lithium 2,3,3-Trimethylindolenide in Various Solvents at 90 MHz

solvent	concn, M	T, °C	C(2)	C(4)	C(5)	C(6)	C(7)	C(1a)	C(3a)	=CH <sub>2</sub>
Et <sub>2</sub> O <sup>a</sup>	0.24	26	178.4	121.7	115.6	127.8	109.4	159.4	141.8	66.5
		-40	177.6	121.7	115.2	127.8	110.0	159.8	141.6	66.5
dioxolane <sup>a</sup>	0.50	26	177.5	121.7	114.0	127.7	109.5	161.1	142.3	66.4
		-100	176.6	122.2	113.9	128.1	110.0	161.4	142.2	66.7
THF <sup>b</sup>	0.27	80	178.3	121.0	112.6	127.3	108.5	161.9	142.3	c
		26	178.0	120.8	111.8	127.3	108.1	162.2	142.1	c
		-70	177.3	120.2	110.3	127.3	107.3	162.7	141.8	c
		-100	177.2	120.5	110.2	127.4	107.2	162.8	141.7	c
		80	178.2	121.7	113.3	127.4	108.9	161.5	142.3	67.0
pyridine <sup>a</sup>	0.62	26	178.7	121.3	111.6	128.0	108.6	163.2	143.2	68.7
		26	178.6	121.4	111.3	128.1	108.6	163.6	143.2	69.0
		-40	178.5	121.7	111.4	128.5	108.8	163.8	143.3	69.5
Et <sub>2</sub> O/HMPT <sup>a</sup> (4.1 equiv)	0.24	26	177.8	120.1	109.9	127.0	107.7	163.0	142.1	c
		-100	176.9	119.8	109.3	127.5	108.0	164.2	141.7	c
			176.5 <sup>d</sup>	119.6	108.3	127.0	e	163.7	141.5	c

<sup>a</sup>Referenced to internal C<sub>6</sub>D<sub>12</sub> (10%),  $\delta$  26.40. <sup>b</sup>Referenced to THF,  $\delta$  26.50. <sup>c</sup>Obscured by solvent. <sup>d</sup>Major species. <sup>e</sup>Overlapping with C(5) resonance.

**Table III.** Degree of Association (*n*) of Lithium 2,3,3-Trimethylindolenide in THF at 17 °C

concn, M	<i>n</i>	<i>K</i> <sub>eq</sub> , mol <sup>-1</sup>
0.076	1.04	
0.089	1.04	
0.105	1.08	
0.122	1.08	
0.153	1.14	
0.191	1.16	2.8
0.253	1.22	3.5
0.338	1.25	3.3
0.580	1.33	3.4

of lithium with a  $\pi$ -bond has also been postulated for the lithium enolate of acetaldehyde<sup>40</sup> and has been observed in the unsolvated lithium enolates of pinacolone<sup>41</sup> and in the lithium dienolate of 2,2,5,6,6-pentamethylhept-4-en-3-one.<sup>42</sup> These weak bonds must also be electrostatic, reflecting static and induced partial  $\pi$ -negative charges in the conjugated systems.

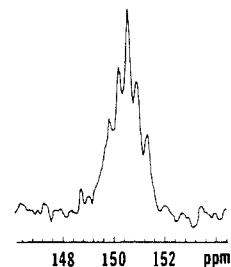
**<sup>13</sup>C Chemical Shifts.** The  $^{13}\text{C}$  chemical shifts for lithium 2,3,3-trimethylindolenide in several solvents are presented in Table II. The most significant changes are observed for C(5), which is "para" to the nitrogen atom. We have previously established that chemical shifts of the analogous carbon atom in simple arylamides reflect the degree of delocalization of the negative charge. In contrast, chemical shifts of positions "ortho" to the anionic center are also influenced by proximity effects associated with the lithium cations and their attached solvent and are, therefore, less easily interpreted.

The shifts for C(5) for enamide salt in diethyl ether and pyridine are both concentration and temperature independent over the ranges examined. They, therefore, appear to correspond to limiting degrees of aggregation, which, by analogy with lithium arylamides, are most likely 2 (dimer) and 1 (monomer), respectively. The temperature-independent value of  $\delta_{\text{C}(5)}$  for the salt in dioxolane is at a slightly higher field from that of the species in diethyl ether and clearly corresponds to dimer but one which is more highly solvated. This conclusion is confirmed by an argument based on quadrupole splitting constants (see below). In THF, however,  $\delta_{\text{C}(5)}$  exhibits both concentration and temperature dependences with values at higher concentrations and temperatures intermediate between those for the species in pyridine and diethyl ether. Under these conditions, the salt appears to exist as monomer-dimer mixtures.

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**Figure 3.**  $^{15}\text{N}$  resonance of [ $^6\text{Li}$ ]lithium [ $^{15}\text{N}$ ]-2,3,3-trimethylindolenide in diethyl ether at  $-80^\circ\text{C}$  and 10.13 MHz.

**Degree of Association.** Vapor pressure barometry has been used to determine the degree of association of the indolenide salt in THF, and the results are given in Table III. The values obtained confirm that the salt is indeed an equilibrium mixture of monomer and dimer and, in the range of total concentration for which the relative concentrations of the two species are not too different, a reasonably good equilibrium constant is obtained.

**$^6\text{Li}$ ,  $^{15}\text{N}$  Spin-Spin Coupling.**  $^{15}\text{N}$ -Labeled (33%) 2,3,3-trimethylindolenine was synthesized from [ $^{15}\text{N}$ ]aniline by literature methods and its  $^6\text{Li}$  salt prepared. The  $^{15}\text{N}$  resonance of this salt is diethyl ether at  $-80^\circ\text{C}$  is observed at  $\delta$  150.2 as a fairly well-resolved 1:2:3:2:1 pentet (Figure 3) with  $J_{^6\text{Li}-^{15}\text{N}} = 3.5$  Hz. This multiplicity established that each nitrogen atom is associated with two lithium cations, which, considered with the results discussed above, unambiguously establishes the bridged dimeric structure of the salt in diethyl ether. The magnitude of the coupling constant is the same as observed for similar structures in the lithium arylamide series.

We attempted to obtain similar data for the monomer in pyridine, but, unfortunately, exchange is too fast on the NMR time scale at the freezing point ( $-38^\circ\text{C}$ ) of the solvent to allow resolution of the fine structure. Line broadening of the  $^{15}\text{N}$  resonance for both the  $^6\text{Li}$  and  $^7\text{Li}$  isotopomers was, however, observed. The line widths are roughly proportional to the ratio of the magnetogyric ratios of the two lithium isotopes, indicating that they are controlled by spin-spin coupling. The  $^{15}\text{N}$  chemical shift for the salt in pyridine is 171.0 ppm, and the difference between this value and that for the dimer in diethyl ether is similar in magnitude and direction to that (ca. 25 ppm) for monomers and dimers in lithium *N*-alkylanilides.

**$^7\text{Li}$  Quadrupole Splitting Constants.** The quadrupole splitting constant (QSC), defined as  $(1 + \eta^2/3)^{1/2}(e^2Qq_{zz}/h)$  where the asymmetry parameter  $\eta = (q_{xx} - q_{yy})/q_{zz}$ , has been shown to be characteristic of the degree of aggregation and, particularly, of the formal coordination of the lithium cation.<sup>20</sup> The dependence on the latter can provide evidence for the degree of solvation of the aggregate. Determination of QSC for lithium salts in solution requires measurements of spin-lattice relaxation times for  $^{13}\text{C}$

**Table IV.**  $^{13}\text{C}$  and  $^7\text{Li}$  Spin-Lattice Relaxation Times and  $^7\text{Li}$  QSC's for Lithium 2,3,3-Trimethylindolenide in Various Solvents

solvent	concn, M	$T$ , °C	$T_1$ , s				$^7\text{Li}$	QSC, kHz
			C(4)	C(5)	C(6)	C(7)		
$\text{Et}_2\text{O}$	0.24	26	2.44	2.05	2.48	2.55	0.225	228
	0.50	26	2.39	1.92	2.35	2.37	0.204	233
		10	1.84	1.55	1.87	1.83	0.160	233
dioxolane	0.50	26	0.62	0.70	0.69	0.77	0.141	156
pyridine	0.50	26	0.60	0.66	0.71	0.61	0.068	216
		10	0.45	0.49	0.46	0.42	0.047	218
THF	0.27	26	1.38	1.14	1.43	1.17	0.193	180
	0.75	26	1.04	0.94	1.05	0.96	0.136	190

nuclei having attached protons and for  $^7\text{Li}$ . The appropriate data are presented in Table IV. The values of QSC have been calculated with the average of the relaxation times for the four unsubstituted carbon atoms of the aromatic ring.

It has been shown that lithium indolide **7** in diethyl ether exists as the dimeric species  $\text{Li}_2\text{A}_2\text{S}_2$ , which is characterized by a QSC of 317 kHz. The  $^{13}\text{C}$  relaxation times of the unsubstituted carbon atoms have relative magnitudes similar to those observed for the indolenide salt in the same solvent. In the case of the former system, it has been argued that the use of the average  $T_1$  is a valid approximation, and, similarly, no serious error should be introduced into the calculation of QSC for the present system. The value (233 kHz) for the indolenide salt in diethyl ether is approximately midway between the values for the  $\text{Li}_2\text{A}_2\text{S}_2$  (317 kHz) and  $\text{Li}_2\text{A}_2\text{S}_4$  (~150 kHz) species. QSC and the  $^{13}\text{C}$  chemical shifts for this system are independent of both concentration and temperature. It is therefore unlikely that we are dealing either with a mixture of the two species or with the trisolvate,  $\text{Li}_2\text{A}_2\text{S}_3$ , since diethyl ether shows no tendency to disolvate the individual lithium cations in the dimers of the relatively less hindered indolide or *N*-methylanilide salts. An alternative explanation is that the  $\pi$ -bonding, noted above to be present in the crystal structure of lithium indolenide etherate, is preserved in solution and is responsible for the low value of QSC for this particular  $\text{Li}_2\text{A}_2\text{S}_2$  salt. In the absence of the  $\pi$ -interaction, the three ligands (N, N, and O) would be coplanar with the lithium atom and would give rise to a large field gradient,  $q_{zz}$ , at the lithium in a direction perpendicular to the plane of the four atoms. In terms of a point charge model,<sup>20</sup>  $q_{zz} = -\sum c_i/r_i^3$  where  $c_i$  is the effective charge of the ligand atoms and  $r_i$  its distance from lithium. Very approximately,  $c_i$  and  $r_i$  are the same for the three ligands so that  $q_{zz} = -3p$  ( $p = c_N/r_N^3$ ). The  $\pi$ -interaction changes the field gradient in two ways. First, it introduces a ligand, which lies above the plane of the  $\sigma$ -ligands, the contribution of which is  $+2p'$ . Because of the delocalized nature of the  $\pi$ -charge and because it is further away (2.5 vs 2 Å),  $p' < p$ , but its contribution will be significant. Second, the  $\pi$ -interaction lifts the lithium out of the plane of the  $\sigma$ -ligands, thus reducing their contribution to  $q_{zz}$ . This second effect is quite small (~6%) since the angles that the  $\sigma$ -ligand bonds subtend with are only changed from 90° to 98°.

The  $^{13}\text{C}$  chemical shift data for the salt in dioxolane show it to be dimer in the temperature range -100 to +26 °C, and the observed value of 156 kHz for QSC is in excellent agreement with those found for the tetrasolvated dimers ( $\text{Li}_2\text{A}_2\text{S}_4$ ) of the lithium *N*-alkylanilides<sup>20</sup> in THF. Dioxolane is a poorer Lewis base than diethyl ether,<sup>20</sup> but it is less sterically demanding and is evidently able to disolvate each lithium.

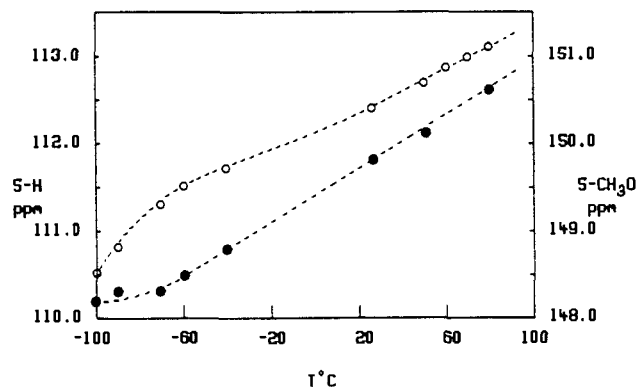
The QSC values for the salt in pyridine and THF are in the range appropriate for the  $\text{LiAS}_3$ . We have pointed out,<sup>20</sup> however, that the QSC's for such species are rather sensitive to the A-Li-S bond angles and differences of perhaps 40 kHz could well arise in this way. For this reason, no conclusion regarding  $\pi$ -bonding in the  $\text{LiAS}_n$  species can be reached from a consideration of QSC's.

**Effect of Hexamethylphosphoric Triamide.** We have shown<sup>43</sup> that the addition of HMPT to a diethyl ether solution of lithium

**Table V.**  $^{13}\text{C}$  Chemical Shifts (ppm) for Lithium 5-Methoxy-2,3,3-trimethylindolenide in Various Solvents at 26 °C and 90 MHz

carbon	dioxolane <sup>a</sup>	THF <sup>b</sup>	pyridine <sup>c</sup>
1a	155.2	156.6	158.1
2	178.7	178.5	179.0
2a	67.5	<i>d</i>	67.1
3	47.7	47.2	47.5
3a	143.5	143.2	144.1
4	110.3	109.8	110.6
5	151.6	150.4	149.6
6	112.6	112.3	113.3
7	108.5	107.1	107.1
3-Me	31.1	31.2	31.7
O-Me	56.5	56.5	57.2

<sup>a</sup>0.5 M. <sup>b</sup>0.27 M. <sup>c</sup>0.50 M. <sup>d</sup>Obscured by solvent.

**Figure 4.** Temperature dependencies of  $\delta_{\text{C}(5)}$  for 0.27 M solutions of lithium 2,3,3-trimethylindolenide (●) and its 5-methoxy derivative (○) in tetrahydrofuran.

*N*-isopropylanilide converts the species  $\text{Li}_2\text{A}_2\text{S}_2$  first to  $\text{LiAS}_3$  and then to the triple ion  $[\text{LiA}_2\text{S}_n]^-[\text{Li}(\text{HMPT})_4]^+$ , approximately 90% of the latter being formed on the addition of 4 equiv/Li of HMPT. Lithium 2,2,3-trimethylindolenide in diethyl ether behaves similarly. Thus, the addition of 4 equiv of HMPT gives a solution that at -60 °C exhibits  $^7\text{Li}$  resonances at  $\delta$  2.3, 3.4, and 5.1, those at  $\delta$  2.3 and 5.1 being equal to each other and much more intense than that at 3.4. The analogous values for lithium *N*-isopropylanilide are  $\delta$  2.3, 3.7, and 4.6. In addition, the line widths of the three bands are similar for the two systems, with that at  $\delta$  2.3, assigned to  $\text{Li}(\text{HMPT})_4^+$ , being very sharp (lwhh 7 Hz). We conclude that the lithium indolenide is also converted to the triple-ion species by HMPT.

**Lithium 5-Methoxy-2,3,3-trimethylindolenide.** In a study of substituted lithium phenolates, it was found that electron-donating substituents tended to increase the degree of aggregation.<sup>44</sup> Since we anticipate the usefulness, in a mechanistic investigation of C- vs N-alkylation, of being able to change the degree of aggregation by varying a remote substituent, we have included in the present study a brief survey of lithium 5-methoxy-2,3,3-trimethylindolenide.

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**Table VI.** Products of the Reactions of Lithium 2,3,3-Trimethylindolenide and Its 5-Methoxy Derivative with Methyl Chloride at 19 °C

5-substituent	solvent	concn, M	C/N	% reactn <sup>a</sup>
H	THF	0.27	4.9	46
			5.2	80
CH <sub>3</sub> O	THF	0.25	13	50
			11	69
			8.3	72
H	dioxolane	0.50	9.3	58
			9.9	62
CH <sub>3</sub> O	dioxolane	0.50	9.6	67
			12	77

<sup>a</sup>The reactions were terminated at these values, which therefore do not reflect absolute yields.

The <sup>13</sup>C chemical shift data for the 5-methoxy derivative are given in Table V. Because of the presence of the methoxy substituent, a direct comparison of the absolute chemical shifts of C(5) with those for the unsubstituted indolenide cannot be made. The changes in  $\delta_{C(5)}$  from one solvent to another, however, are rather similar to those for the unsubstituted salt. The main difference is found in the temperature dependences (Figure 4) for the THF solutions. The changes in  $\delta_{C(5)}$  in the lower end of the temperature range are a result of the conversion of monomer to dimer with increasing temperature, and this process begins at a much lower temperature in the case of the 5-methoxy derivative. This result is consistent with our findings in the lithium phenolate series in which conversion of dimers to tetramers occurs as the basicity of the phenolate ion is increased by appropriate para substitution. At the higher end of the temperature range, desolvation of the dimers is presumably also occurring, as has been observed for lithium *N*-isopropylanilide in THF.<sup>11</sup>

**Methylation of Lithium Indolenides.** The C- and N-methylation products of both indolenides have characteristic <sup>1</sup>H NMR spectra, which readily permit the total analysis of mixtures of starting material and products. Both gave essentially complete C-methylation when reacted with methyl iodide in either THF or dioxolane. In contrast, dimethyl sulfate yielded only the N-methylated products. Methyl chloride, however, gave mixtures of both C- and N-methylated derivatives and was selected for this preliminary study. Pyridine is too readily alkylated itself to be

used as a solvent, and the 5-methoxyindolenide was too insoluble in diethyl ether for this solvent to be used. Accordingly, only reactions in THF and dioxolane were screened. The results are presented in Table VI. Although they are of a preliminary nature, they appear to indicate that aggregation does play a role in controlling the regiochemistry in the alkylation of lithium enamides, with C-methylation being favored by increased association.

**Conclusions.** The combination of observations of <sup>13</sup>C chemical shifts and <sup>6</sup>Li-<sup>15</sup>N coupling constants, together with colligative measurements, used to study lithium arylamides also provides evidence for the solution structures of lithium enamides, which also appear to exist as either monomeric or dimeric ion pairs in weakly polar solvents.

A consideration of <sup>7</sup>Li quadrupole splitting constants leads to the conclusion that the lithium indolenide has the same  $\pi$ -bonded structure in solution in diethyl ether as found in the crystalline diethyl ether solvate. In the less sterically demanding solvent, dioxolane, the tetrasolvated dimer is formed.

A total of 4 equiv of HMPT appears to induce the same conversion to a triple-ion salt, [LiA<sub>2</sub>S<sub>n</sub>]<sup>-</sup>[Li(HMPT)<sub>4</sub>]<sup>+</sup>, as found for lithium *N*-isopropylanilide.

Lithium 5-methoxy-2,3,3-trimethylindolenide also forms monomeric and dimeric ion pairs but with a greater propensity for the latter than the unsubstituted indolenide.

Methylation by methyl chloride gives both C- and N-methyl derivatives, the former being favored by the dimeric salts. These preliminary studies do not preclude the complex interplay of salt effects found in analogous reactions of lithium enolates.<sup>12b</sup>

The 2,3,3-trimethylindolenide system, with its fixed stereochemistry and variable regiochemistry, appears to be eminently suitable for a detailed mechanistic study of its alkylation.

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**Registry No.** HMPT, 680-31-9; Li(HMPT)<sub>4</sub><sup>+</sup>, 56929-83-0; <sup>15</sup>N, 14390-96-6; <sup>6</sup>Li, 14258-72-1; Li<sup>+</sup>, 17341-24-1; C<sub>11</sub>H<sub>12</sub>NLi·C<sub>4</sub>H<sub>10</sub>O, 115560-36-6; 2,3,3-trimethylindolenine, 1640-39-7; 3,3-dimethyl-2-ethylindolenine, 18781-53-8; (4-methoxyphenyl)hydrazine, 3471-32-7; 2-methyl-3-pentanone, 565-69-5; 3,3-dimethyl-2-ethyl-5-methoxyindolenine, 115560-34-4; 1-methyl-2-methylene-2,3-dihydro-1*H*-indole, 115560-35-5; lithium 2,3,3-trimethylindolenide, 115590-27-7; lithium 5-methoxy-2,3,3-trimethylindolenide, 115603-36-6.

## Thermodynamic Studies of Competitive Adduct Formation: Single- and Double-Insertion Reactions of Carbon Monoxide with Rhodium Octaethylporphyrin Dimer

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**Abstract:** Reactions of carbon monoxide with (octaethylporphyrin)rhodium dimer, [(OEP)Rh]<sub>2</sub>, in toluene produce an equilibrium system involving four species: [(OEP)Rh]<sub>2</sub> (1), [(OEP)Rh]<sub>2</sub>(CO) (2), (OEP)RhC(O)Rh(OEP) (3), and (OEP)RhC(O)C(O)Rh(OEP) (4). No evidence is found for the formation of a dicarbonyl adduct of 1, which is accounted for on the basis of required structural features of metal-metal-bonded porphyrin dimers. <sup>1</sup>H and <sup>13</sup>C NMR evidence is presented for double insertion of CO into the Rh-Rh bond. NMR methods are used to determine enthalpy and entropy changes for the reaction of 1 with CO to form the following: 2,  $\Delta H_2^\circ = -10 \pm 1$  kcal/mol ( $-41 \pm 4$  kJ/mol),  $\Delta S_2^\circ = -26 \pm 4$  cal/K·mol ( $-109 \pm 17$  J/K·mol); 3,  $\Delta H_3^\circ = -12 \pm 2$  kcal/mol ( $-50 \pm 8$  kJ/mol),  $\Delta S_3^\circ = -31 \pm 5$  cal/K·mol ( $-130 \pm 21$  J/K·mol); 4,  $\Delta H_4^\circ = -21 \pm 2$  kcal/mol ( $-88 \pm 8$  kJ/mol),  $\Delta S_4^\circ = -62 \pm 5$  cal/K·mol ( $-259 \pm 30$  J/K·mol). Thermodynamic criteria for the double insertion of CO into metal-metal bonds are presented and applied to the (OEP)Rh system.

Binding and activation of CO by transition-metal complexes has occupied a focal point in organometallic catalysis research.

Reactions of coordinated CO with nucleophiles and CO insertions into M-R (R = alkyl, aryl) bonds are ubiquitous organometallic