Polymeric $[\text{N-Lithio-benzimidazole} \cdot \text{DMSO}]_x$
The Crystal Structure and ab initio Calculations

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Crystal Structure, Polymeric Organic Lithium Amide

That lithiated aromatic amines with more than one nitrogen atom can favor polymeric aggregates in the solid state is demonstrated by the single crystal X-ray diffraction structure of $[\text{N-lithio-benzimidazole} \cdot \text{DMSO}]_x$; $ab$ initio calculations on model compounds and simple electrostatic models indicate that the preference of the polymeric structure over dimeric alternatives is due to resonance stabilization and to Coulomb attraction between alternating benzimidazole anions and lithium cations.

Introduction

What is the effect of the second nitrogen atom on the nature of lithiated aromatic amines containing two ring N atoms? We have determined the X-ray crystal structure of N-lithio-benzimidazole. Simpler N-lithiated compounds — derived from amines, imines, heterocycles, etc. — exhibit a considerable variety of structures and degrees of aggregation in the solid state [1]. Dimers, exemplified by N-lithio-carbazole [2] and by N-lithio-indole [3], are quite common for heterocyclic lithium amides. Lithiated benzimidazole might behave similarly. Besides a dimeric structure like 1, planar (2) or pyramidal (3) monomers (which might be stabilized by additional ligands attached to lithium), and some aggregates based on these structures, were conceivable. Instead, we show in this paper that N-lithio-benzimidazole prefers an entirely different arrangement in the solid state: an infinite polymer with symmetrical aromatic units.

Abbreviations:
TMEDA = N,N,N',N'-Tetramethylethylenediamine; HMPA = Hexamethylphosphoric-triamide; ZPE = zero point energy.

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Results and Discussion

That 4 might be a polymer was indicated by its solubility properties. Like other N-lithiated aromatic amines with more than one nitrogen atom (e.g. benzotriazole), 4 is nearly insoluble in non-polar or weakly polar solvents (e.g. toluene, ether or THF). This behavior persists even when stoichiometric amounts of polar cosolvents are added,
e.g. TMEDA or HMPA, which have excellent ligating properties. Such lithio-amides are believed to be polymeric in the solid state [1c]. In order to investigate this hypothesis, we dissolved N-lithio-benzimidazole(THF)₂ (synthesized by adding n-BuLi to a solution of benzimidazole in THF) in warm DMSO. After cooling to room temperature, large prismatic, colorless crystals of N-lithio-benzimidazole(DMSO)₂ formed. X-ray analysis of these crystals reveals a polymeric structure (Fig. 1).

Each Li atom is bonded to only one N atom N(1) of a given benzimidazole anion but bonds also to an N atom (N 3) of a neighboring anion. In this way, infinite chains are formed. In addition, each lithium atom is coordinated to the oxygen centres of two DMSO molecules. Hence, approximately tetrahedral coordination results. To our knowledge, no X-ray structure of a DMSO-complexed lithiated organic compound has been reported before [4].

Important structural parameters are listed in Tables I, II and III. Problems with partial disorder are apparent: full-matrix least-squares refinement of the structure results in the final unweighted R value of 17.7; the \( R_w \) is 13.9 using non-Poisson weights (modified by the Dunitz-Seiler procedure [5] with a sharpening factor of 20). The atoms O2 and S2 are less intense than their counterparts in the alternate DMSO, but they are clearly evident from the electron density map. The composite isotropic temperature factors for O 2 (6.1), S2 (10.1), N 1 (2.9), N 3 (3.2), C2 (3.3), C6 (4.9) and O2 (4.3) are considerably larger than those for most of the other atoms in the structure. A difference map reveals two peaks of 2.5 and 1.3 electrons/Å\(^3\) near both S2 and O2; a third peak of 1.2 electrons/Å\(^3\) occurs 2.2 Å from S2. Also, two other peaks of 1.5 and 1.0 electrons/Å\(^3\) are located very near S1. No meaningful chemical relationship of these peaks to the remainder of the structure has been deduced. This unexplained disorder is certainly responsible for the poor \( R \) values. Nevertheless, the benzimidazole unit and the environs of the lithium atoms are well defined. These are the features in which we are interested.

The Li–N distances, 2.06(2) and 2.07(2) Å, are equal within experimental error. These values lie

![Fig. 1. Infinite Li-benzimidazole chain of 4 in the solid state.](image)

| Table I. Positional parameters and their estimated standard deviations. |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| Atom   | \( x \)         | \( y \)         | \( z \)         | \( B(A^2) \)   |
| S1     | 0.6708(4)       | 0.2449(4)       | 0.9545(2)       | 4.94(8)       |
| S2     | 0.9946(5)       | 0.4823(6)       | 0.7626(4)       | 10.1(1)       |
| O1     | 0.7679(9)       | 0.290(1)        | 0.8951(5)       | 4.1(2)        |
| O2     | 0.873(1)        | 0.379(1)        | 0.7351(7)       | 6.1(2)        |
| N1     | 0.623(1)        | 0.5626(9)       | 0.7987(6)       | 2.9(2)        |
| N3     | 0.535(1)        | 0.243(1)        | 0.7152(6)       | 3.2(2)        |
| C2     | 0.502(1)        | 0.124(1)        | 0.7436(8)       | 3.3(2)        |
| C3A    | 0.422(1)        | 0.262(1)        | 0.6476(7)       | 2.8(2)        |
| C4     | 0.389(2)        | 0.368(1)        | 0.5899(8)       | 4.2(3)        |
| C5     | 0.264(2)        | 0.360(2)        | 0.5253(9)       | 4.9(3)        |
| C6     | 0.168(1)        | 0.252(2)        | 0.5176(9)       | 4.6(3)        |
| C7     | 0.325(1)        | 0.151(1)        | 0.6369(7)       | 2.5(2)        |
| C7A    | 0.192(1)        | 0.144(1)        | 0.5711(8)       | 3.8(3)        |
| C10    | 0.504(1)        | 0.348(2)        | 0.9310(9)       | 5.4(3)        |
| C11    | 0.753(2)        | 0.320(2)        | 1.0493(9)       | 7.0(5)        |
| C20    | 1.171(2)        | 0.414(4)        | 0.768(2)        | 14(1)         |
| Li     | 0.695(2)        | 0.374(2)        | 0.780(1)        | 2.7(4)        |

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: \( 4/3 \times (a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab\cos\gamma B(1,2) + ac\cos\beta B(1,3) + bc\cos\alpha B(2,3)) \).

| Table II. Bond distances [Å]. |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| Atom 1          | Atom 2 Distance | Atom 1          | Atom 2 Distance |
| O1               | 1.53(1)          | N3              | C3A             | 1.35(1)          |
| C10              | 1.80(1)          | N3              | Li              | 2.07(2)          |
| C11              | 1.75(2)          | C3A             | C4              | 1.42(2)          |
| C2               | 1.72(2)          | C4              | C5              | 1.37(2)          |
| C3A              | 1.72(2)          | C4              | C5              | 1.37(2)          |
| O2               | 2.04(2)          | C5              | C6              | 1.38(2)          |
| C3A              | 1.92(2)          | C6              | C7              | 1.38(2)          |
| N1               | 2.06(2)          | C7A             | C7              | 1.43(1)          |
| N3               | 1.340(8)         | N1              | C2              | 1.349(7)         |
| C2               | 1.340(8)         | N1              | C7A             | 1.373(7)         |

Numbers in parentheses are estimated standard deviations in the last significant digits.
within the normal range of 1.90–2.10 Å, found for Li–N distances in other lithium amides [1]. Notably, they are in good agreement with the Li–N distances (2.063(5) and 2.086(6) Å) in the only other known polymeric aromatic lithium amide structure, [2-lithio(2-mercaptopyrimidine)HMPA]₆ [6].

![Structure 5]

In the structure of 4, the metal atoms bend out of the benzimidazole plane by ca. 6° for the Li–N1 bond and 11° for the Li–N3 bond. Hence, the nitrogen atoms can be regarded as roughly sp²-hybridized and as forming a σ-bond to the lithium atoms, in contrast to the lithio-carbazole(THF)₂ dimer in which both σ- and π-bonding contributions occur [2]. The quite similar Li–N and N1–C2 and N3–C2 distances (1.349(7) and 1.340(8) Å) in 4 show that the structure is not that of a lithium amide, loosely complexed with an amine. (Note for comparison: the quite different N1–C2 and N3–C2 distances of 1.315(8) and 1.361(7) Å, respectively, of neutral benzimidazole [7]). For monomeric lithium amides complexed with an amine (e.g. TMEDA), one would expect Li–N(amide) distances of about 1.90–2.00 Å and Li–N(amine) distances of about 2.14–2.24 Å [8].

More insight into the electronic structure of the title compound is provided by ab initio calculations on several monomeric, dimeric, and polymeric structures of lithio-imidazole as models. We find two minima for monomeric lithio-imidazole: one with the lithium σ-bound to a nitrogen atom (8) and another with the lithium π-bound over the five membered ring (9). The latter is favoured in energy by 10.9 kcal mol⁻¹ (6-31G*/6-31G*) (see Table IV and Fig. 2). This agrees with ab initio
Fig. 2. Some monomeric, dimeric, and polymeric structures of lithiated imidazoles optimized at the 6–31G* level (distances in Å).
Table IV. Absolute (− a.u.) and relative (kcal mol\(^{-1}\)) energies of monomeric, dimeric, and polymeric lithiated imidazoles per mole monomer unit.

<table>
<thead>
<tr>
<th>Basis set</th>
<th>6 (\text{C}_2\text{H}_3\text{N}_2^\cdot )</th>
<th>7 (\text{C}_2\text{H}_3\text{N}_2\text{Li}^+ )</th>
<th>8 (\text{C}_2\text{H}_3\text{N}_2\text{Li}-\sigma )</th>
<th>9 (\text{C}_2\text{H}_3\text{N}_2\text{Li}-\pi )</th>
<th>10 ([\text{C}_2\text{H}_3\text{N}_2\text{Li}]_2 )</th>
<th>11 ([\text{C}_2\text{H}_3\text{N}<em>2\text{Li}]</em>\infty )</th>
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<tbody>
<tr>
<td>3−21 G//</td>
<td>222.94348(^a)</td>
<td>237.71801</td>
<td>230.39226</td>
<td>230.40120</td>
<td>230.44381</td>
<td>230.48608</td>
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<tr>
<td>3−21 G</td>
<td>224.22470</td>
<td>239.05705</td>
<td>231.70066</td>
<td>231.71810</td>
<td>231.74536</td>
<td>231.78118</td>
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<tr>
<td>6−31 G*</td>
<td>36.26</td>
<td>36.62</td>
<td>37.06</td>
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<td>12.6</td>
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\(^a\) Absolute electronic energy in − a.u.; \(^b\) relative energy in kcal mol\(^{-1}\); \(^c\) zero point energy in kcal mol\(^{-1}\) (scaled by 0.89) on the 3−21 G geometry.

calculations on lithio-pyrrole and reflects the better coordination of the lithium cation [2, 9]. Aggregation of two lithio-imidazole units leads to a dimer (Fig. 2, 10) with \(C_{2v}\) symmetry. Such dimeric aggregates with a central \(\text{Li}_2\text{N}_2\) ring are quite common [1] (notably in the crystal structure of N-lithio-indole [3], which is the isoelectronic counterpart of N-lithio-benzimidazole). Originally, we expected this feature to be exhibited by N-lithio-benzimidazole as well. Dimer 10 is 17.1 kcal mol\(^{-1}\) (per monomeric unit) more stable than the \(\pi\)-bound monomer 9. The dimer 10 shows almost the same geometry of the ring as the \(\sigma\)-bonded monomeric system (8). In both species, the \(N_1-C_2\) and \(N_3-C_2\) distances are quite different, and similar to those in neutral benzimidazole (see above). In contrast, the imidazole anion (6) displays \(C_{2v}\) symmetry with equal \(C_2-N\) separations. Adding a second lithium cation within a \(C_2\) symmetry constraint to 8 leads to a structure 7 with \(C_{2v}\) symmetry and equidistant Li−N and C−N separations. The high natural charges on lithium (+0.973) and on nitrogen (−0.851) indicate almost fully ionic Li−N bonding. Thus, we reasoned that the symmetrical imidazole geometry afforded by two lithium cations with equidistant Li−N bonds would be preferred due to better resonance delocalization in the anion moiety. The 3−21 G optimized geometry of such a species was used for \textit{ab initio} calculations on polymeric lithio-imidazole 11 (see Table V). While keeping the ring geometry fixed only the Li−N distance was optimized by calculating several single points with slightly different Li−N separations at the 3−21 G level with \(2_1\)-screw axis symmetry restriction (fourth neighbors approximation proved to be sufficient for energy comparison). This shows that a geometry with a Li−N distance of 1.847 Å is the most stable one (GEO1). Several cases with unsymmetrical bridging of the imidazole units by lithium cations were also examined. In all cases, the energy was calculated to be higher than that of the symmetrically bridged form (11). In addition, a second 3−21 G calculation was performed on a polymer derived from the 6−31 G* geometry of 7 with a Li−N separation of 1.890 Å (GEO2). This revealed that the total energy is only slightly dependent on the geometry. The highest level of theory calculations on lithio-pyrrole and reflects the better coordination of the lithium cation [2, 9]. Aggregation of two lithio-imidazole units leads to a dimer (Fig. 2, 10) with \(C_{2v}\) symmetry. Such dimeric aggregates with a central \(\text{Li}_2\text{N}_2\) ring are quite common [1] (notably in the crystal structure of N-lithio-indole [3], which is the isoelectronic counterpart of N-lithio-benzimidazole). 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employed in the polymer calculation was a HF/6-31G*/GEO2 single point. MP2 calculations on the monomeric and dimeric species show that the electron correlation corrections to the relative energies are negligible. Hence, MP2 computations were not performed on the polymers.

The energy eigenvalues for the polymer 11 (6-31G*/GEO2) exhibit a band structure with quite narrow band widths. The gap \( (\pi-\pi^* \text{excitation}) \) between the valence and the conduction band is 10.277 eV. The rather narrow band widths indicate that the \( \pi \)-electrons are mainly delocalized on the five-membered rings; the lithium cations are not involved in this respect. Nevertheless, the N–Li distances were calculated to be equal. This is due to the optimal Coulomb attraction of imidazole anions and lithium cations. At the HF/6-31G* level, the polymer (11) is calculated to be 22.5 kcal mol\(^{-1}\) (per monomeric unit) lower in energy than the hypothetical dimer 10.

Simple electrostatic models provide insight: if a square planar dipolar arrangement of four alternating unit charges is taken as a model for the dimer, a Coulomb energy of \(-1.29/r \text{ a.u.} (r = +, - \text{distance}) [10, 11] \) results. For an infinite chain of alternating unit charges (a model for the polymer), the Coulomb energy is higher, \(-1.39/r \text{ a.u.} \). If a constant Li–N separation of 1.9 Å and full unit charges, Li\(^+\) and N\(^-\), are assumed, an energetic preference for the chain of 15.7 kcal mol\(^{-1}\) (per monomeric unit) results. Considering the crudeness of the approximation, this is in reasonable agreement with the \textit{ab initio} result.

We conclude that resonance stabilization in the five-membered rings of 4 is responsible for the essentially equidistant C2–N bonds. On the other hand, Coulomb attractions of alternating benzimidazole anions and lithium cations result in equidistant Li–N separations. These effects lead to the polymeric structure of the title compound. Hence, \textit{ab initio} calculations indicate that the preference for polymeric lithio-benzimidazole is an electronic effect, rather than being favored by crystal packing.

**Experimental**

Benzimidazole (1.18 g = 10 mmol) was dissolved in 10 ml THF. To this solution, 6.3 ml (10.1 mmol) of 1.6 M n-BuLi in hexane was added drop-wisely at -50 °C. Near the end of the addition a white precipitate formed. After stirring for about 2 h, the suspension was filtered and washed twice with 5 ml hexane. The composition of the white powder was determined to be lithio-benzimidazole(THF)\(_2\) by integration of a \(^1\)H NMR spectrum. This powder dissolved on warming in an appropriate amount of DMSO. After a few days, colorless crystals of N-Lithio-benzimidazole (DMSO), formed. Yield 1.74 g (62%).

\(^1\)H NMR (400 MHz, d\(_6\)-DMSO, RT, numbering according Formula 4) \( \delta = 7.83 \) (s, 1H, H2), 7.51 (m, 3.3 Hz, 2H, H4,7), 6.84 (m, 3.3 Hz, 2H, H5,6), 2.62 (s, 12H, DMSO); \(^13\)C NMR (100.6 MHz, d\(_6\)-DMSO, RT) \( \delta = 152.8 \) (C2), 146.2 (C3a, 7a), 116.1/116.4 (C5, C6), 40.4 (DMSO).

\( \text{C}_{11}\text{H}_{22}\text{N}_2\text{O}_2\text{S}_2\text{Li} \) (280.36)

Caled C 47.13 H 6.11 N 9.99.

Found C 47.21 H 6.35 N 10.05.

**Crystal data**

Monoclinic, \( P2_1/c \) (\# 14), \( a = 9.046(2), b = 10.074(3), c = 16.515(9) \text{ Å}, \beta = 102.90(3), V = 1467.1 \text{ Å}^3 \), \( \rho_{\text{calc}} = 1.328 \text{ g cm}^{-3}, Z = 4 \), absorption coefficient \( \mu = 31.9 \text{ cm}^{-1} \).

An irregular fragment which measured approximately 250 x 300 x 450 microns was cut from a larger crystal. This sample was mounted inside a glass capillary and sealed under nitrogen. Data were collected on an Enraf-Nonius CAD-4 diffractometer equipped with a graphite monochromator at room temperature using CuK\(_\alpha\) and \( \omega-2\theta \) technique. Scan range = 0.6 + 0.14tan\( \theta \), 20 range = 0 to 150°. A total of 3405 diffraction maxima were measured over the \( h k l \) range \( h 0 \) to 11, \( k 0 \) to 12, \( l -20 \) to +20. Data analysis was performed using the suite of programs in the Enraf-Nonius structure determination package, MolEN [12]. After data reduction, averaging and rejection of systematic absences, a total of 1610 unique reflections above 3.0*\( \sigma_l \) were used in the analysis. The structure was solved using the direct methods program SIR88 [13]. Full matrix least-squares refinement of the 157 atomic position parameters and anisotropic temperature factors provided the present structural model. An extinction coefficient was refined to a final value of 1.25 · 10\(^{-5} \).*

* Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-W-7514 Eggenstein-Leopoldshafen 2 (FRG), on quoting the depository number CSD 55690, the names of the authors, and the journal citation.
**Computational methods**

The geometry of all monomeric and dimeric species were optimized in the symmetries indicated, using gradient optimization techniques at Hartree-Fock levels with the 3–21G [14] and the 6–31G* [15] split valence basis sets (the latter augmented by a set of polarization functions on all non-hydrogen atoms). The program packages Gaussian 90 [16] and Cadpac 4.1 [17] were employed. Electron correlation corrections were evaluated with second order Moller-Plesset perturbation theory using the frozen core approximation (MP2(FC)/6–31G*). All geometries were characterized to be minima on the hypersurface by diagonalization of the 3–21G force constant matrix. The zero point energies (ZPE) were also determined at 3–21G and scaled by an empirical factor of 0.89. Natural charges were calculated by using the natural population analysis (NPA) on the basis of natural atomic orbitals (NAO) [18] at 6–31G*.

The electronic and the energy band structures of the periodic polymers were calculated by the *ab initio* Hartree-Fock crystal orbital method [19, 20]. The details of the formalism have been discussed elsewhere [21, 22]. Therefore we restrict ourselves here to only those mathematical expressions which are needed for a better understanding.

In the case of a one-dimensional chain with translational or helical symmetry the wave vector \(k\) and the vector \(q\) denoting the cells become scalars and the Hartree-Fock equation, in matrix form, reduces to

\[
\mathbf{F}(k) \mathbf{c}_n(k) = \varepsilon_n(k) \mathbf{S} \mathbf{c}_n(k) \]

with

\[
\mathbf{F}(k) = \sum_{q=-N}^{N} \exp(ikqa) \mathbf{F}(q),
\]

\[
\mathbf{S}(k) = \sum_{q=-N}^{N} \exp(ikqa) \mathbf{S}(q)
\]

where \(a\) is the elementary translation and \(n\) is the band index.

\[
[S(q)]_{rs} = \langle \chi_r^q | \chi_s^q \rangle
\]

The elements of the matrices \(\mathbf{F}(q)\) are defined by

\[
[F(q)]_{rs} = \langle \chi_r^0 | -\frac{1}{2} \Delta - \sum_{q_1=-N}^{N} \sum_{\alpha=1}^{M} \frac{Z_\alpha}{r} | \chi_s^q \rangle + \sum_{q_1,q_2=-N}^{N} \sum_{u,v=1}^{m} \mathbf{P}(q_1-q_2)_{uv} \langle \chi_r^0 \chi_u^q | \chi_s^q \chi_v^q \rangle - \frac{1}{2} \langle \chi_r^0 \chi_u^q | \chi_s^q \chi_v^q \rangle
\]

with

\[
P(q_1-q_2)_{uv} = (a/2\pi) \int_{-\pi/a}^{\pi/a} \sum_{n=1}^{n^*} c(k)_u^* c(k)_v \exp(ika(q_1-q_2)) \, dk
\]

where \(\chi^q_u\) stands for an atomic basis function placed in cell \(q\). \(m\) is the number of basis functions and \(M\) is the number of atoms in one cell of the polymer. The number of filled bands is denoted by \(n^*\). The calculations have been performed in the fourth neighbors’ approximation. This means the electronic interactions were taken into account up to the fourth elementary cell to the left and to the right of the given cell.

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[4] proved by a search in the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1 EW, U. K.