

SYNTHETIC, STRUCTURAL, SPECTROSCOPIC AND CALCULATIONAL STUDIES OF A LITHIUM β -DIKETINIMATE COMPLEX

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Abstract—Reaction of malonaldehyde bis(phenylimine) monohydrochloride with two equivalents of *n*-BuLi in the presence of hexamethylphosphoric triamide (HMPA) yielded crystals of $[\text{PhN}(\text{CH})_2\text{NPhLi} \cdot \text{HMPA}]_2$. The two LiN_2C_3 metallacycles of the dimeric molecule are linked by two bridging oxygens from HMPA. No spectroscopic evidence for dissociative or other equilibria was obtained. The lithium projects above the mean plane of the metallacycles. MNDO calculations on model compounds reproduced bond lengths and angles well, except that all minima were planar, ascribing the envelope conformation to a packing effect. The molecule could best be described as a 1,5-diphenyl-1,5-diazapentadienyl lithium complex, the anion having contributions from diketinimate and two equivalent keteneimine-ene-amido resonance forms. In contrast, the protonated ligand exists in a localized keteneimine-ene-amine form only.

We have recently been engaged in study of early main-group metallation of multifunctional organic acids. These studies have concentrated on lithium, the smallest, most polarizing alkali metal, and its effect on the ligand in comparison to other metals or protons. Alteration of bond lengths within the anion,¹ or in some cases complete rearrangement² or decomposition of the covalent framework of the anion,³ has been observed in previous cases. This short paper focusses on the anion derived from tetrahydro-*N,N'*-diphenyl-1,3-propanediamine. This type of ligand, which may be described as a β -diketinimate by analogy with the widely studied β -diketonates, has in the past been studied using magnetic, UV-vis and NMR measurements of its transition metal complexes, especially those of nick-

el(II) and copper(II).⁴ Most of this work, on square planar/tetrahedral equilibria, predated the ready availability of X-ray diffraction information. However, there has been a recent reawakening of interest in the ligand type, its potential in providing stereochemical control being a stimulus to the synthetic chemist. Structure reports are nevertheless rare⁵ when compared with the β -diketonates. We report here the results of structural and NMR spectroscopic studies on a prototype early main-group metal β -diketinimate. This represents an extension of our earlier structural studies of lithium derivatives of potentially delocalized multidentate organic anions,¹⁻³ and also of our synthetic studies on the rational synthesis of mixed-anion complexes from hydrochlorides of protic bases.⁶ During the preparation of this manuscript the first structure determination of a lithium β -diketinimate was published.^{5d}

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EXPERIMENTAL

All manipulations were carried out under a protective argon blanket, either in a double-manifold argon/vacuum line or argon-filled recirculating glovebox. Solvents were purified using standard procedures. Malonaldehyde bis(phenylimine) monohydrochloride was used as-received. Hexamethylphosphoric triamide (HMPA) was dried over 13X molecular sieves.

CAUTION!: HMPA is a suspected carcinogen. Avoid skin contact and exposure to vapour.

A hexane solution of *n*-BuLi (10.2 cm³ of a 1.6 M solution) was added to a chilled suspension of malonaldehyde bis(phenylimine) monohydrochloride (2.11 g, 8.15 mmol) in toluene (10 cm³) and HMPA (1.42 cm³, 8.15 mmol). An exothermic reaction ensued, causing a clearing of the suspension and a darkening of colour. A fine precipitate of LiCl appeared towards the end of the *n*-BuLi addition. The mixture was heated to boiling and the LiCl was removed by filtration through a No. 4 glass frit. The solution was allowed to cool overnight, after which a crop of rod-like crystals had grown. The sample was maintained at -15°C for 24 h, then filtered under argon and washed with two 4-cm³ aliquots of hexane to yield 1.18 g (36%) of [PhN(CH)₃NPhLi·HMPA]₂ (**1**), m.p. = 87.0–87.5°C. ¹H NMR (300.1 MHz, toluene-*d*₈): δ 2.08 (d, ³J_{H-³¹P} = 9.5 Hz, 18H, MeN), 4.98 (t, ²J_{H-¹H} = 6.4 Hz, 1H, CHCHCH), 6.98–7.22 (m, 10H, NPh), 7.90 (d, ²J_{H-¹H} = 6.4 Hz, 2H, CHCHCH). ³¹P{¹H} NMR (121.5 MHz, toluene-*d*₈, referenced to 85% H₃PO₄): δ 36.52 (s, broadened in ¹H-coupled spectrum). ⁷Li NMR (116.6 MHz, toluene-*d*₈, referenced to 0.1 M Li₂SO₄ in D₂O): δ 0.15 (s). ¹³C NMR (75.5 MHz, benzene-*d*₆): δ 36.20 (d, ²J_{13C-³¹P} = 0.06 Hz, MeN), 94.08 (s, CHCHCH), 121.28, 121.40, 129.01, 156.15 (s, Ph), 156.42 (s, CHCHCH). All spectra were found to be essentially invariant to changes in concentration (over a 100-fold range) and temperature (over the range 207–293 K). IR (Nujol mull, NaCl plates): 1571 cm⁻¹, C=N str. Shifted to 1644 cm⁻¹ upon air exposure. Found: C, 62.0; H, 7.0; N, 17.0. Calc. for C₂₁H₃₁LiN₅OP: C, 61.9; H, 7.7; N, 17.2%.

A prism was selected direct from the liquor of a freshly grown crop of crystals and mounted on a Stoe-Siemens diffractometer in perfluoroether oil for low-temperature X-ray diffraction data collection. A summary of crystal data is presented in Table 1. The structure was solved by direct methods.⁷ All non-hydrogen atoms were refined anisotropically with hydrogens in calculated positions using full-matrix least squares refinement.⁸

MNDO calculations were performed using

Table 1. Crystallographic data and data collection parameters for [PhN(CH)₃NPhLi·HMPA]₂

Formula	C ₂₁ H ₃₁ LiN ₅ OP
Formula weight	407.42
Space group	monoclinic, <i>P</i> 2 ₁ / <i>c</i> (No. 14)
<i>a</i> (Å)	10.470(2)
<i>b</i> (Å)	18.836(4)
<i>c</i> (Å)	11.710(2)
β (°)	103.33(3)
<i>V</i> (Å ³)	2247.1(7)
<i>Z</i>	4
<i>D</i> _{calc} (g cm ⁻³)	1.204
Abs. coeff. (mm ⁻¹)	0.143
λ (Å)	0.71073
<i>T</i> (K)	153(2)
<i>R</i> ₁ ^a (%)	4.27
<i>R</i> _{w2} ^a (%)	12.03

^aRefinement based on *F*².

MOPAC version 6 via software programs from BIOSYM Technologies, San Diego run on a Silicon Graphics IP6 workstation. A planar starting geometry for 1-dehydro-1-lithia-2,6-diaza-benzene was generated from benzene using the Builder routine within INSIGHT II. This was energy optimized using the Keyword string GEO-OK PRECISE BONDS PI without constraint. The resultant planar optimized geometry is presented in Fig. 2. Distortion of this geometry into envelope conformations and re-optimization located the same minimum. Minima were re-calculated with addition of two water molecules coordinated to lithium.

RESULTS AND DISCUSSION

The parent “β-diimines” are most stable where aromatic substituents are present at nitrogen. Indeed, one such compound was commercially available as a hydrochloride salt. Since we have recently studied the metallation of hydrochlorides as a rational synthesis of mixed anion species,⁶ no attempt was made to obtain the free base. The product was simply dimetallated with two equivalents of butyl lithium in toluene solution in the presence of one equivalent of HMPA. In this case a mixed-anion complex was not isolated. However, a precipitate of LiCl appeared only in the last stages of reaction. Some metastable mixed aggregate species may therefore have been present in toluene solution. The lithium chloride produced was easily removed by filtration to yield a crop of the dimeric product **1**.

To our knowledge, this is only the second dimeric *s*-block metal complex to be structurally

Table 2. Selected bond lengths (Å) and bond angles (°) for $[\text{PhN}(\text{CH}_3)_3\text{NPhLi} \cdot \text{HMPA}]_2$ (1); methyl and phenyl hydrogens are omitted for clarity

O(1)—Li(1)	1.970(4)	O(1)—Li(1')	2.060(4)
Li(1)—N(2)	2.038(4)	Li(1)—N(1)	2.052(5)
N(1)—C(1)	1.326(3)	N(2)—C(3)	1.322(3)
C(1)—C(2)	1.394(4)	C(2)—C(3)	1.387(4)
Li(1)—O(1)—Li(1')	85.9(2)	O(1)—Li(1)—N(2)	114.6(2)
O(1)—Li(1)—N(1)	122.4(2)	N(2)—Li(1)—N(1)	93.7(2)
O(1)—Li(1)—O(1')	94.1(2)	N(2)—Li(1)—O(1')	115.4(2)
N(1)—Li(1)—O(1')	118.4(2)	C(1)—N(1)—C(11)	117.3(2)
C(1)—N(1)—Li(1)	116.8(2)	C(11)—N(1)—Li(1)	124.8(2)
C(3)—N(2)—C(21)	118.3(2)	C(3)—N(2)—Li(1)	118.0(2)
C(21)—N(2)—Li(1)	123.7(2)	N(1)—C(1)—C(2)	127.1(2)
C(3)—C(2)—C(1)	126.7(2)	N(2)—C(3)—C(2)	127.1(2)

characterized.^{5d} Relevant bond lengths and angles are presented in Table 2. The asymmetric unit consists of one bidentate chelating diketiminato bonded through N(1) and N(2) to Li(1), which is further coordinated to O(1) of the neutral HMPA ligand. The dimeric molecule (Fig. 1) is generated by inversion of the asymmetric unit through a centre such that O(1) and Li(1) form two corners of a central four-membered ring. This four-membered ring is joined via corner-sharing lithiums to the two orthogonal six-membered LiC_3N_2 rings of the metallacycles. The bridging mode for HMPA, once thought unusual,⁹ is becoming a characteristic motif among lithium complexes of multidentate anions.³ The bulky dimethylamino groups of the HMPA, and phenyl groups of the diimides, effectively shield the lithium cations such that further intermolecular catenation is prohibited.

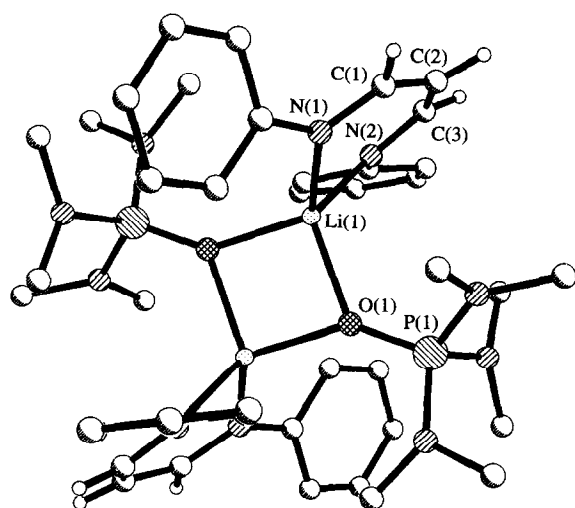


Fig. 1. Molecular structure of $[\text{PhN}(\text{CH}_3)_3\text{NPhLi} \cdot \text{HMPA}]_2$.

The bond lengths within the diketiminato anions indicate complete delocalization of charge throughout the NCCCN ligand core, although there is no structural evidence for participation of the phenyl groups. In this feature it is closely similar to the related lithium diazaallyl complex, which we published recently.¹ It differs in one regard. In the aforementioned complex, the LiNCN four-membered ring was planar. However, the planarity in the LiNCCCN rings of **1** is very approximate. While the organic portion of the ring is near planar (r.m.s. deviation: 0.03 Å), consistent with an all- sp^2 hybridization scheme, the lithium lies 0.69 Å above this plane, giving the six-membered ring an envelope conformation. The sum of bond angles around N(1) and N(2) (356.6 and 360.0°, respectively) confirms the sp^2 hybridization at nitrogen, with one sp^2 hybridized lone pair from each nitrogen coordinating to lithium. This being the case, the envelope conformation dictates that both phenyl groups of each anionic ligand lie to one side of the ring, with lithium lying to the other. This leaves one side less crowded and able to accommodate two dimethylamino groups of the HMPA ligands, while the other single dimethylamino group fits between the two phenyls of the opposite diiminate. The alternative conformation, where lithium lies co-planar with the delocalized NCCCN core and one phenyl group lies on either side, would seem less favourable since the dimethylamino groups of the HMPA would be less comfortably accommodated. The two monomers are bound by the HMPA ligands in a near-symmetric fashion, so as to suggest that the molecule is a true dimer rather than monomers associated in the solid state.¹⁰ In support of this interpretation, an extensive study of proton, carbon, phosphorus and lithium NMR spectra at variable concentration and temperature failed to reveal any evidence of dissociative equilibria.

The structure contrasts with the recently published $\{\text{Li}[\text{N}(\text{Me}_3\text{Si})\text{C}(\text{Ph})\text{C}(\text{H})\text{C}(\text{Ph})\text{N}(\text{SiMe}_3)]\}_2$.^{5d} While also a dimer, this molecule has no ancillary donor molecules, relying on the bulk of its substituents to prevent the polymerization that occurs when $\text{PhN}(\text{CH}_3)_3\text{NPhLi}$ is prepared in the absence of donor solvents. The absence of ancillary donors in the previously published compound forces one nitrogen of each ligand into a bridging position, which in turn reduces symmetry such that the delocalization of the ligand core is not so complete [$\text{Me}_3\text{SiN}-\text{C}$: 1.337(6), 1.299(6) Å;^{5d} *cf.* $\text{PhN}-\text{C}$: 1.326(3), 1.322(3) Å]. A further effect of HMPA solvation is to increase lithium–nitrogen bond lengths [$\text{Li}-\text{N}$ 1.965(9), 1.952(10) Å;^{5d} *cf.* $\text{Li}(1)-\text{N}(2)$ 2.038(4), $\text{Li}(1)-\text{N}(1)$ 2.052(5) Å].

Structures are available for Ni^{II} ,^{5a} Gd^{III} and Sm^{III} ^{5b} complexes of [N,N' -(1,3-dimethylpropane-diylidene)-diaminato-] anion, the 2,4-dimethyl equivalent of the ligand in $[\text{PhN}(\text{CH}_3)_3\text{NPhLi} \cdot \text{HMPA}]_2$. $\text{M}-\text{N}$ distances range from 1.95^{5a} to 2.48 Å,^{5b} but the metallaheterocyclic chelate rings are never far from planarity. Aside from packing forces, there is an alternative explanation of ring puckering in **1**. The system might profitably be considered as the lithium salt of a 1,5-diazapentadienide anion. The puckering might then be seen as an attempt by the lithium to gain some overlap with the π -system of the delocalized anion. There is a further possibility of participation of lithium p -orbitals in the delocalization, the system then being viewed as a diaza-lithiabenzene. To probe these possibilities, a semi-empirical molecular orbital calculational study was undertaken on a model lithium diketeniminate monomer, firstly with no solvation and secondly with solvation by two water molecules, in order to model the tetrahedral geometry provided by the HMPA ligands. Figure 2 shows bond angles and

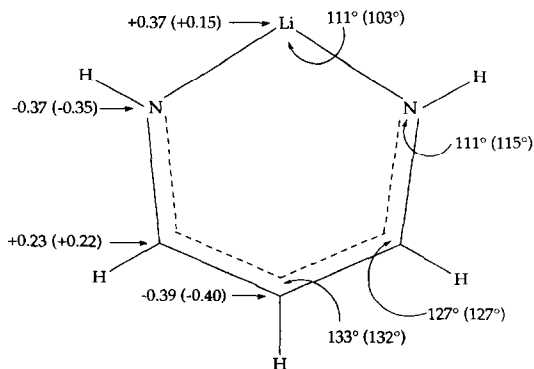


Fig. 2. MNDO-optimized bond angles and atomic charges for $\text{HN}(\text{CH}_3)_3\text{NHLi}$ and $\text{HN}(\text{CH}_3)_3\text{NHLi}(\text{H}_2\text{O})_2$.

Table 3. MNDO-optimized bond properties for $\text{HN}(\text{CH}_3)_3\text{NHLi}$ and $\text{HN}(\text{CH}_3)_3\text{NHLi}(\text{H}_2\text{O})_2$

Bond	Length (Å)	($p-p$) π overlap	Bond indices
C—N	1.33 (1.33)	0.58 (0.61)	1.54 (1.58)
C—C	1.42 (1.41)	0.35 (0.33)	1.27 (1.26)
N—Li	1.95 (2.03)	0.09 (0.05)	0.50 (0.44)

charges, while Table 3 lists lengths, ($p-p$) π overlap and total bond indices¹¹ of selected bonds. In both cases, values for the bis-water complex are given in parentheses. MNDO bond lengths and, in most cases, angles are in excellent agreement with the solid-state data. The one angle which deviates significantly (the C—C—C angle is 5° larger in the calculated data) does so as a direct result of the “gas-phase” planarity. Deliberate distortion from the planar minima, followed by re-optimization, caused structures to relax to planar minima in both the solvated and unsolvated cases. The lithium, even when merely two-coordinate, appears to prefer to maximize direct σ overlap with the nitrogens than to engage in pentadienyl-type π -bonding. In this it mimics its diaza-allyl analogue.¹ The main effect of solvation is to lengthen the N—Li bonds, consistent both qualitatively and quantitatively with experiment. The quality of agreement lends weight to the conclusion that the solid-state envelope conformation is a simple packing effect. However, the computed atomic charges betray the tendency of MNDO to overestimate covalency in lithium bonding. Nevertheless, the significant negative charge on the central carbon is noteworthy. If the deprotonated anion had simply been derived from a “resonance hybrid” of the two keteneimine-ene-amido anions, the bond indices within the anion core should all approximate to 1.5. Contributions from a β -diketenimine form would increase C—N and decrease C—C bond indices, as well as confer negative charge on the carbon, all of which are seen in the calculations. The results suggest that approximately equal contributions from the three canonical forms of the anion describe the system accurately. The term “diazapentadienyl lithium” thus seems reasonable. While there is evidence for a quasi-aromatic planar 6 π -electron anion, the lithium neither coordinates to nor contributes significantly to [as judged by ($p-p$) π overlap] this π -system.

The IR spectrum showed a C—N stretch at 1571 cm^{-1} , shifted 73 cm^{-1} to higher frequency upon exposure of the plates to atmospheric moisture. IR data reported for the lanthanide complexes^{5b} would

seem to be contaminated with hydrolysis products showing vibrations consistent with a localized form of ligand (1633, 1615 cm^{-1}),^{5b} which became apparent only upon air exposure of **1**. This reconfirms experimentally the fundamental difference between the proton and the lithium nucleus in how they bind to potentially conjugated systems. The protonated ligand adopts a localized keteneimino-ene-amine form, as judged from solid-state IR data. In solution, a rapid tautomerism exists between the two equivalent forms, but with no detectable contribution from a β -diketiminato form.⁴ The lithiated congener prefers a delocalized, pseudo-aromatic six-membered six- π -electron ring, a "resonance hybrid" of approximately equal contributions from β -diketiminato and two equivalent keteneimino-ene-amido resonance forms. In older literature, a non-classical delocalized form has even been suggested for the protonated 2-benzylamino-4-benzylimino-2-pentene, on the basis of NMR and UV spectral measurements.¹² Even at 300 MHz the room-temperature NMR is inconsistent with a static, localized form,¹³ but IR data settle the question. It seems that in moving from proton to lithium "cations" the appropriate description of bonding changes from keteneimino-ene-amine to lithium diazapentadienyl, from a rapidly tautomerizing double-minimum situation to a delocalized single-minimum one. Further studies of the coordination chemistry and spectroscopy of main-group complexes of this ligand class will be directed towards making use of the close steric control offered by the ligands, and towards tuning the contributions of the different canonical forms by varying the metal.

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