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# α-Deprotonation of a β-shielded acrylamide creates a distorted lithium 1-aminoallen-1-olate

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ABSTRACT

The β-shielded acrylamide *N*,*N*-diisopropyl-α-(1,1,3,3-tetramethylindan-2-ylidene)acet-amide was prepared through ketone addition of an α-lithiated acetamide, followed by $H_2O$ elimination. Its α-deprotonation by *n*-butyllithium occurred readily in THF without any tendency towards addition reactions at C=O or C-β. The resultant single crystals of a dimeric lithio derivative had triple Li–O coordination and a weakly bonding, ion-pair type Li–C(α) relationship. In *tert*-butyl methyl ether as the solvent, up to seven pairs of diastereotopic nuclei (both $^{1}H$ and $^{13}C$) established a $C_S$-symmetric lithium 1-aminoallen-1-olate structure that is ascribed to either a thermal ground state or a very rapid (on the NMR time scales) oscillation between two chiral ground states that may resemble the solid-state structure.



## 1. Introduction

The rapidly interconverting alkenyllithium ground states **1** and **1'** (Scheme 1) contain the following atoms which are constitutionally pairwise equivalent yet magnetically (chemical-shift-) different ("diastereotopic") since they reside in spatially different (cis or trans) environments: C-1/-3, 1-/3-$CH_3$, C-7a/-3a, C-4/-7, and C-5/-6. The cis/trans environmentswill be interchanged on formation of **1**′ from **1**, so that all cis atoms become trans, and vice versa. For α-aryl [1] or α-cyano [2] as the electron-withdrawing groups ("EWG"), these "diastereotopomerizations" are so fast at about ambient temperatures that the separate resonance lines of (only) the diastereotopic nuclei become broadened up to signal "coalescence" at an averaged resonance position for each pair.

In search of a carboxyl derivative as an EWG that would tolerate a Li–C(α) bond as depicted for **1** (or **1**′), we chose carboxamide groups as the α-substituents. Such β-shielded acrylamide derivatives (**2**) were anticipated to be protected against interfering polymerization and Michael addition reactions at C-2, so that long-term NMR measurements might be used to establish the ground state structure in solutions: The envisioned alkenyllithium **2** would have a Li–C(α) bond and show separate signals for the above-mentioned diastereotopic pairs (cis and trans); with a suitable choice of the substituents $R^1$ and $R^2$, this arrangement would fit to a plane of symmetry ($C_S$) that coincides with the indane molecular plane and the amide group with its next neighbor atoms. The alternative allene-type isomer **3** would carry a Li–O bond and a close-to-linearly hybridized C-α center with the consequence of magnetically equivalent ("enantiotopic") indane sites and equal chemical NMR shifts of the two members in each of these pairs. Maximum symmetry would be achieved for **3** with a $C_S$ plane that is perpendicular to the indane ring plane and contains again the amide group and its next neighbor atoms. This work was designed to differentiate between **2** and **3**.

## 2. Results and discussion

The α-lithiated acetamides **4a**–**c** (Scheme 2) were added to 1,1,3,3-tetramethylindan-2-one [3] (**5**) and formed the β-hydroxycarboxamides **6a**–**c**, respectively. For the subsequent dehydration reaction to give **7a**–**c** without interference by the imminent [4] methyl migration, $SOCl_2$ was added to ice-cold solutions of **6a**–**c** and pyridine in dry $CCl_4$. More than one equivalent of $SOCl_2$ had to be added to **6b** and **6c** whose OC–NH functions can consume $SOCl_2$ with formation of imidchlorides (Cl–C=N) which, however, could quickly hydrolize to the desired amides **7b** and **7c** on workup with acid, as ascertained for **7c**.

In memory of Professor Heinrich Nöth.

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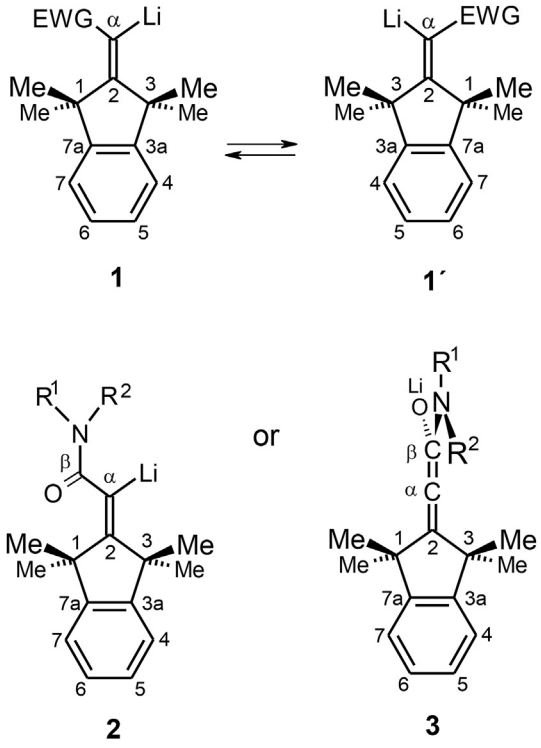
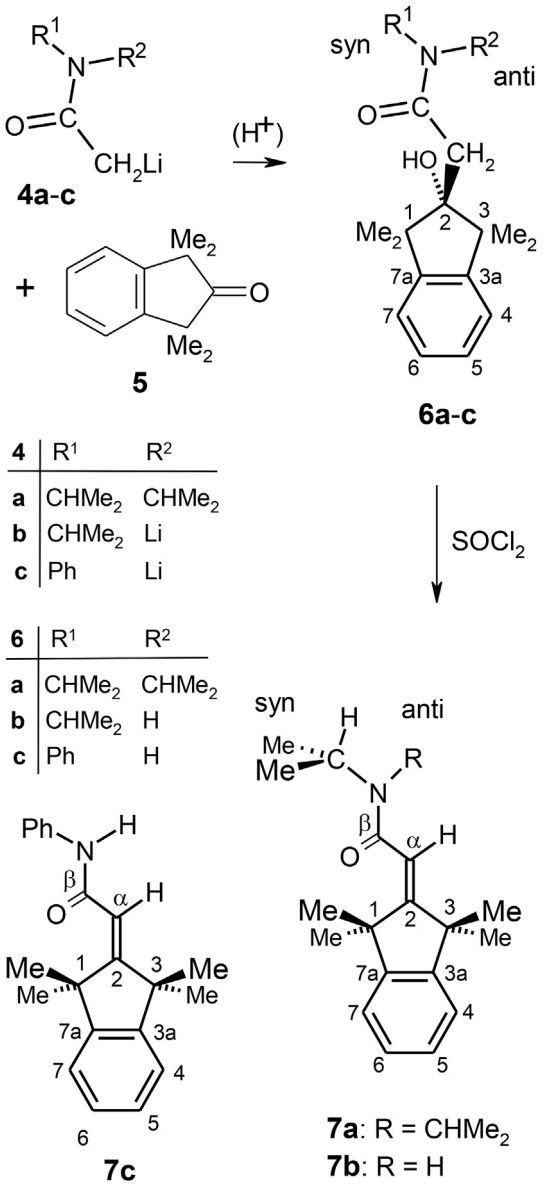



**Scheme 1.** Thermal interconversion of the non-linear ground states **1** and **1′** is known [1] to be accelerated by stronger electron-withdrawing groups (EWG); but will a non-linear (**2**) or a linearly hybridized (**3**) ground state be formed with a carboxamide as the EWG?.

The NMR observations at room temperature (rt) indicated a $C_S$-symmetric structure of the β-shielded *N*,*N*-diisopropyl acrylamide **7a**: The eight methyl substituents were grouped in four pairs of symmetry-equivalent ("enantiotopic") methyls, and all other atoms appeared to stay in the $C_S$ plane that coincides with the indane molecular plane. Conformations with deviations from this plane by, for example, rotation about the C(α)–C(β) single bond would result in up to eight (instead of only four) methyl resonances (both $^{1}H$ and $^{13}C$), as was observed for the later described carboxylic acid **11**. Actually, **7a** in $CH_2Cl_2$ solution displayed almost equal $^{1}H$ and $^{13}C$ spectra at rt and at −89 °C, which confirmed that we saw always the same (perhaps time-averaged?) $C_S$-symmeric species. Two-dimensional NOESY cross-peaks revealed that α-H was spatially close to the methyl protons of the R = $CHMe_2$ substituent that has an anti relationship with the O=C double bond; this isopropyl anti substituent was shown to carry the magnetically less shielded ("downfield") NC*H* and the more shielded ("upfield") C*Me*$_2$ protons. Thus, these indicators of close proximity supported a preferentially coplanar arrangement of the amide moiety and the indane rings of **7a**. Additionally, the NOESY correlation spectra exhibited also other cross-peaks that indicated an interconversion of the anti and syn isopropyl environments as caused by a slow (on the NMR time scale) rotation about the N–C(β) single bond at rt. If so, this intra-amide rotation would perturb the time-averaged $C_S$ symmetry of the ground state of **7a** only transiently.

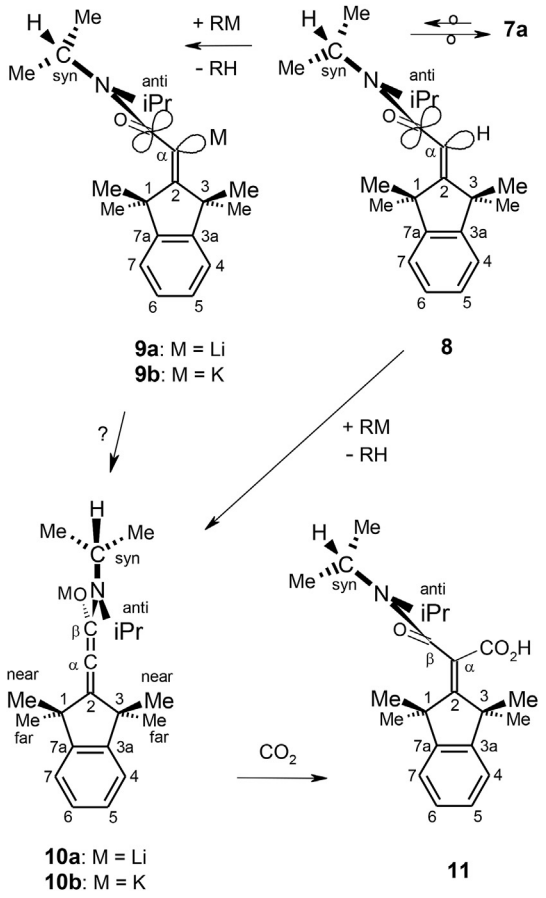
The α-deprotonation reaction of **7a** with [$^{6}$Li]*n*-butyllithium (n$Bu^{6}Li$) occurred rapidly and cleanly in the solvent tetrahydrofuran (THF). As a pleasing surprise, the lithiated product crystallized very soon and could be recrystallized in this THF solution at 40 °C for a subsequent purification through repeated washings with cyclopentane. The purified crystals were more soluble in *tert*-butyl methyl ether (tBuOMe), in which solvent the NMR spectra disclosed




**Scheme 2.** Preparation of the β-hydroxycarboxamides **6a**–**c** and β-shielded acrylamides **7a**–**c**.

that the crystals contained one equivalent of THF per carbanion unit. Down to −89 °C, most of the $^{1}H$ and $^{13}C$ NMR chemical shifts [5] $\delta$ were practically independent of the temperature (Tables S1–S4), which indicated that we observed always the same lithiated species. Spin-spin coupling [1,6] of the $^{6}Li$ isotope with any $^{13}C$ nucleus, as expected for C-α of **9a** in Scheme 3, could not be detected under these conditions, which suggested that there were no long-lived Li–C contacts. We emphasize that the established C(α)-angular topologies of the source **7a** and its derivative **11** (obtained through trapping by $CO_2$) do not provide topological evidence for **9a** or against the linear mode. **10a**. Therefore, more detailed analyses were necessary to attempt a differentiation of the alternative structural possibilities **9a** and **10a**.

The $C_S$-symmetric (achiral) ground state of the precursor **7a** (Scheme 2) is stereoelectronically unfavorable for α-deprotonation. However, a ca. 90° rotation about the C(α)–C(β) bond would generate the NMR-invisible equilibrium component **8** whose H–C(α) bond orbital can overlap with the empty C=O π* orbital;




**Scheme 3.** Preparation, possible structures, and derivatization of the metalated amides (**9a**,**b** or **10a**,**b**?) in solution; "iPr" = $HCMe_2$, "RM" = either nBuLi or $PhCH_2K$.

this energetically stabilising orbital interaction would facilitate an α-deprotonation of **8** and would also stabilize the lithiated product if in a chiral conformation like **9a**. On the other hand, **10a** would provide an even better condition for the lateral overlap between the parallel $p_x$ orbitals at C-α and C-β and might be formed either from **9a** or directly from **8**.

Actually, the two isopropyl groups of lithiated **7a** had four equal NMR resonances at rt, namely, one 12-proton doublet, one 2-proton septet, and two $^{13}C$ signals, the latter with an intensity ratio of 4:2. At −64 °C, however, each of these two $^{13}C$ signals became extremely broad and changed into a pair (1:1) of signals on further cooling. Therefore, syn/anti converting rotation about the N–C(β) single bond was fast on the NMR time scale already at a much lower temperature than observed above for the slow carboxamide rotation at rt in **7a**. Such an accelerated rotation excluded the presence of a usual (almost undisturbed) carboxamide group as in **9a**; yet it was compatible with the N–C(β) single bond as formulated in the allenolate **10a** in accord with the proposal [7] that $Li^+$ favors a 1-methoxyallenolate strucuture whereas $Cu^+$ prefers the non-linear topology. Importantly, there was no further diastereotopic signal splitting down to −89 °C: The chemical shifts remained equal for the two members of each pair of constitutionally equivalent (and now enantiotopic) nuclei in the indane part, namely, C-1/-3, 1-$CH_3$/3-$CH_3$, C-7a/-3a, C-4/-7, and C-5/-6. In contrast with **7a**, this pointed to the presence of a (different) symmetry plane that cuts the tetramethylindane scaffold perpendicularly into two equivalent halves and lets the isochronous 1-/3-$CH_3$ groups above the molecular indane plane remain magnetically different from the other two 1-/3-methyls below that plane, as shown for **10a**. Of course, all singular (non-paired) atoms, such as C-2 and especially the O–C–N triad, should then reside within that perpendicular $C_S$ plane since otherwise the $C_S$ symmetry would be lost and the pairs of enantiotopic indane nulei would become diastereotopic (as they were in **7a** and would be in **9a**). In particular, the two different N–CH groups must also reside within the $C_S$ plane, whereas the two methyls of each isopropyl group will be equivalent by $C_S$ symmetry as depicted in **10a**. As a confirmatory NOESY interaction, the NCH protons generated a cross-peak with only those 1-/3-$CH_3$ protons which were on the same side ("near" to NCH) of the indane molecular plane, but not with the more distant 1-/3-$CH_3$ protons ("far" from NCH) on the other side. Selective proton decoupling of the two NC*H* groups narrowed (removed $^3J$ splitting from) the $^{13}C$ signal of C-β at $\delta = 171.9$ ppm. Similarly, selective decoupling of all twelve 1-/3-$CH_3$ protons identified (narrowed) C-2 at $\delta = 145$ ppm; therefore, $\delta = 180.1$ ppm remained for the allene-type C-α nucleus [8] in that spectral region. This defined a spectral distance of $\Delta\delta$(α,t-BuOMe) = 61.6 ppm from $\delta = 118.5$ ppm for the corresponding position (C-α) in **7a**. It left the oxygen atom as a reasonable place for Li within the symmetry plane of the allenolate model **10a**. These observations provided no evidence for a monomeric or aggregated nature of the ground state in tBuOMe solution.

The inferior solubility of **10a** in THF made NMR measurements less profitable; but the resultant chemical shifts (Tables S2 and S4) [5] were almost equal to those in tBuOMe (Tables S1 and S3) and again practically independent of the temperature. Diastereotopic splitting of the isopropyl resonances started with line broadening on cooling to −60 °C at which temperature **10a** began to precipitate and to disappear from the spectrum. The always separate and sharp NMR signals of the "near" and "far" (or "above" and "below" the indane plane) 1-/3-$CH_3$ groups revealed that rotation about the C(α) = C(β) double bond (which would be basically a single bond C(α)–C(β) in model **9a**) was still slow on heating to +55 °C. Perhaps except for a differing solvation pattern, **10a** was obviously the same species in THF as in tBuOMe.

The above observations of magnetically equivalent indane nuclei at low temperatures excluded the non-linear, chiral model **9a** from being a long-lived (static) ground state that should have displayed up to eight different $CH_3$ signals (both $^1H$ and $^{13}C$). They excluded also a very rapid (on the NMR time scales) equilibration of **9a** with its "optical antipode" *ent*-**9a** (not shown here): Such a highly mobile equilibrium should not display the above-mentioned allene-type resonance of $\delta_C = 180$ ppm that characterizes **10a**. However, these data did not exclude other chiral, equilibrating ground states with a C(α) = C(β) double bond as presented in the sequel.

The X-ray diffraction analysis of lithiated **7a** disclosed a chiral dimer (Fig. 1) with one THF ligand per anion unit. In terms of the crystallographic numbering of one of the two symmetry-equivalent monomer units of the solid dimer, one can see a substantially distorted allene system whose backbone C15–C14–C2 is almost coplanar with the indane molecular plane [5]. As appropriate for allene substituents, the indane plane is almost perpendicular (95°) to the terminal triad O1–C15–N1 (which is almost coplanar with the C16–N1–C19 triad of the $NiPr_2$ part). The distortion culminates in the bond angle C15–C14–C2 = 142° instead of ca. 180° as expected for a "perfect" allene. As a possible reason for that, the oxygen-connected atom Li1 deviates from both the O1–C15–N1 and the indane planes: With Li1–O1–C15 = 94° and the dihedral angle Li1–O1–C15–C14 = 60°, Li1 is close to C14 (= C-α), but the distance of Li1–C14 = 2.36 Å is somewhar too long for a true Li–C bond. Nevertheless, the close approach of Li1 appears to draw negative electric charge from the enolate moiety (O1–C15–C14)

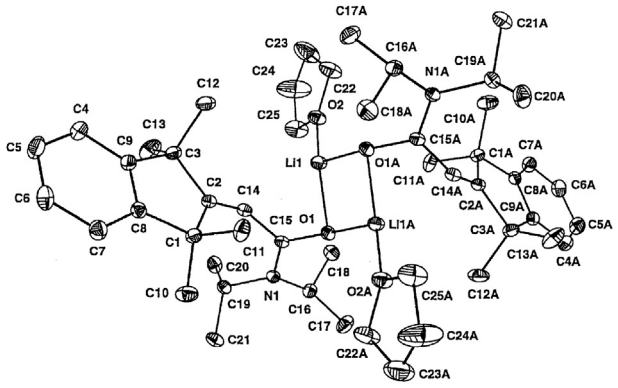



**Fig. 1.** X-ray diffraction analysis of the dimer of lithiated **7a** with one equivalent of THF per anion unit at −90 °C, showing the crystallographic numbering (hydrogens omitted); the allene-type part is C2=C14 = C15.

toward C14 with the consequence of a reduced (albeit not eliminated) double-bond character of C(α) = C(β) = C14 = C15 = 1.39 Å, whereas the semicyclic double bond C(2) = C(α) retained C2=C14 = 1.32 Å. In fact, the dihedral angle [5] of Li1–C14–C2–C1 = 76° (rather than ca. 180°) points to some directional indifference as appropriate for an ion-pair relationship of Li1 and C14. Since this chiral structure depends on Li bonding, it can be expected to be configurationally labile and to enantiomerize very rapidly unless fixed within a crystal. Thus, structures like that in Fig. 1 may be the actual ground states also in solution and may enantiomerize rapidly across a low energy barrier that might resemble the model **10a**. The short yet labile distance of a cation to the C2=C14 [or C(2) = C(α)] double bond may perhaps explain why the $^{13}$C NMR chemical shifts of C2 and C14 (= C-α) change remarkably on the following replacement of $Li^+$ in **10a** by $K^+$ in **10b**.

Deprotonation of **7a** by benzylpotassium ($PhCH_2K$) in THF produced **10b** that was more soluble than lithiated **7a** and hence unsuitable to be purified through crystallization from THF. The $^{13}$C NMR data resembled those of lithiated **7a** in THF, except for the allene-type nuclei of **10b** whose δ values were lower by 5 ppm for C-2 yet higher by 5 ppm for C-β and by ca. 10 ppm for C-α so that Δδ(α,THF) = 190.0–118.5 = 71.5 ppm. The perpendicular symmetry plane as for model **10a** applied also to **10b** down to at least −87 °C: As the only diastereotopic splittings, the members of the isopropyl NCH and $HCMe_2$ pairs became magnetically nonequivalent at ca. −75(7) °C in accord with formula **10b** (to be compared with −64 °C for **10a**). This potassium allenolate **10b** was less basic than $iPr_2NK$ but more basic than $(Me_3Si)_2NK$ in THF. Derivatization of **10b** with solid $CO_2$ occurred at the allene-typ C-α position to afford the thermally stable carboxylic acid **11** that did not yet undergo decarboxylation even at 203 °C due to its unsuitable topology.

## 3. Conclusion

(i) Dimeric lithiated **7a** crystallized from a THF solution suggesting that $Li^+$ favored coordination to additional THF ligands less than to a negatively charged oxygen atom. The ion-pair relationship of Li and C-α (Fig. 2) appeared to create a certain carbanionic character of C-α in competition with a counteracting allene-type rehybridization of C-α whose $^{13}$C NMR resonance absorption at $\delta_C$ = 180 ppm (in tBuOMe solution) or at 182 ppm (in THF) was established through selective {$^1$H} NMR decoupling. Judging from the solid-state angle of C(β)–C(α)–C(2) = 142° as compared with the angles of ca. 120° expected for model **9** and up to 180° for model **10**, lithiated **7a** may be called a lithium 1-aminoallen-1-olate (according to $^{13}$C-α) with some traits of an α-lithiated acrylamide derivative (Li–C ion pair relationship).

## 4. Experimental

### 4.1. General remarks

All organometallics were handled, as described previously [6], under inert-gas cover with a stream of dry argon gas. $^1$H and $^{13}$C NMR shifts δ were referenced against internal $Me_4Si$. NMR abbreviations were as follows: d = doublet, m = multiplet, q = quartet, quat = quaternary, sept = septet, t = triplet.

### 4.2. *N,N-Diisopropyl-α-(2-hydroxy-1,1,3,3-tetramethylindan-2-yl) acetamide (**6a**)*

A solution of $iPr_2NLi$ (LDA), prepared from $iPr_2NH$ (9.70 mL, 69 mmol) in anhydrous THF (25 mL) and nBuLi (76 mmol) in hexane (34.5 mL), was added dropwise under argon gas cover to a stirred solution of *N,N*-diisopropylacetamide (9.13 g, 63.7 mmol) in dry THF (25 mL) at ca. 0 °C to give **4a**. The yellow solution was stirred at rt for 30 mim and then treated at 0 °C with a solution of 1,1,3,3-tetramethylindan-2-one (**5**, 10.0 g, 53.1 mmol) in dry THF (25 mL). After another 60 min at rt, the mixture was diluted with water (300 mL), treated with aqueous HCl (2 M) until all precipitates were dissolved, and extracted with $Et_2O$ (3 × 100 mL). The combined $Et_2O$ extracts were washed with distilled water until neutral, dried over $Na_2SO_4$, filtered, and concentrated. The resultant oil was distilled at 155–165 °C (bath temp.)/0.03 mbar to give a glassy, colorless resin (12.3 g, 70%) that began to crystallize slowly after 10 days at rt. The analytically pure crystals **6a** had mp

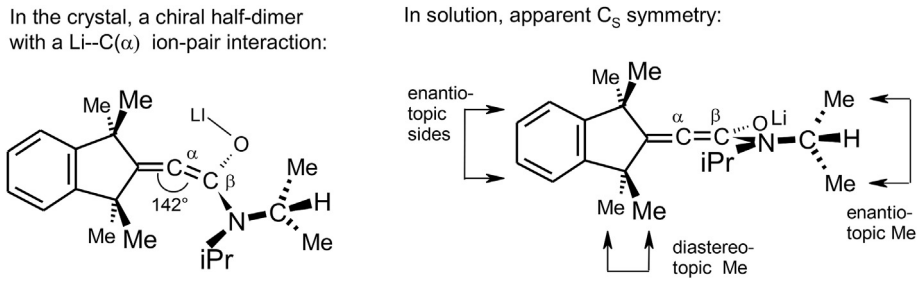



**Fig. 2.** Lithiated **7a** is "frozen" in chiral conformations in the crystal but liberated in solution to be (apparently) $C_S$ symmetric per evidence from stereotopic $^{13}$C reporter nuclei.

(ii) If the chiral solid-state structure (Figs. 1 and 2) resembles a chiral ground state (but not **9a**) in solution, it has to enantiomerize in a double-well potential so rapidly that its NMR spectra display an apparent (because averaged) $C_S$ symmetry as suggested by model **10a**. In a single-well potential, on other hand, **10a** (and also **10b**) would be the $C_S$ symmetric ground state.

89–91 °C (from propan-2-ol).

IR (KBr) $\nu$ 3287 (sharp O–H), 2970, 1606 (s), 1439, 1380, 1340, 1043, 763 $cm^{-1}$.

$^1H$ NMR ($CDCl_3$, 400 MHz) $\delta$ 1.23 and 1.410 (2 s, 2 × 6H, 2 × 1-/3-$CH_3$), 1.25 (sharp d, $^3J = 6.8$ Hz, 6H, 2 × isopropyl-$CH_3$ syn to C=O), 1.445 (sharp d, $^3J = 6.9$ Hz, 6H, 2 × isopropyl-$CH_3$ anti), 2.56 (s, 2H, $CH_2$), 3.55 (unresolved, 1H, NC*H* anti), 4.12 (sept, $^3J = 6.8$ Hz, 1H, NC*H* syn), 6.62 (s, 1H, OH), 7.14 (m, 2H, 4-/7-H), 7.19 (m, 2H, 5-/6-H) ppm, assigned through comparison with **6b**;

$^{13}C$ NMR ($CDCl_3$, 100.6 MHz) $\delta$ 20.6 (q, 2 × isopropyl-$CH_3$ syn), 21.0 (broadened q, 2 × isopropyl-$CH_3$ anti), 24.2 and 29.4 (2 q, 2 × 1-/3-$CH_3$), 33.2 (t, $CH_2$), 46.2 (d, NCH syn), 48.6 (broadened d, NCH anti), 50.7 (quat, C-1/-3), 86.0 (quat, C-2), 122.6 (d, C-4/-7), 127.0 (d, C-5/-6), 149.1 (quat, C-3a/-7a), 172.7 (quat, C=O) ppm, assigned as above.

Anal. calcd for $C_{21}H_{33}NO_2$ (331.5): C, 76.09; H, 10.03; N, 4.23. Found: C, 75.84; H, 10.04; N, 4.19.

### 4.3. *N*-Isopropyl-α-(2-hydroxy-1,1,3,3-tetramethylindan-2-yl) acetamide (**6b**)

The procedure described for **6a** was followed, using LDA (175 mmol) in THF (30 mL) for the deprotonation of *N*-isopropylacetamide (8.13 g, 80.0 mmol) in dry THF (30 mL) to give **4b**. The subsequent treatment with 1,1,3,3-tetramethylindan-2-one (**5**, 10.0 g, 53.1 mmol) in dry THF (30 mL) and final work-up afforded a brown solid that was recrystallized from toluene (30 mL) to give colorless needles (5.09 g, 33%) with mp 157–160 °C.

IR IR (KBr) $\nu$ 3600–2900 (broad O–H), 3294 (sharp N–H), 2961, 1631 (s, C=O), 1484, 751 $cm^{-1}$.

$^1H$ NMR ($CDCl_3$, 400 MHz) $\delta$ 1.21 (d, $^3J = 6.6$ Hz, 6H, 2 × isopropyl-$CH_3$ syn to C=O), 1.26 and 1.36 (2 s, 2 × 6H, 2 × 1-/3-$CH_3$), 2.47 (s, 2H, $CH_2$), 4.16 (pseudo-octet, 1H, $^3J$ = ca. 6 Hz, NC*H* syn), 4.96 (s, 1H, OH), 5.80 (broadened d, $^3J$ = ca. 6 Hz, 1H, NH), 7.14 (m, 2H, 4-/7-H), 7.20 (m, 2H, 5-/6-H) ppm, assigned through comparison with **6a** and **7b**;

$^{13}C$ NMR ($CDCl_3$, 100.6 MHz) $\delta$ 22.6 (q, 2 × isopropyl-$CH_3$ syn), 23.8 and 29.4 (2 q, 2 × 1-/3-$CH_3$), 37.0 (t, $CH_2$), 41.5 (d, NCH syn), 50.6 (quat, C-1/-3), 85.9 (quat, C-2), 122.7 (d, C-4/-7), 127.2 (d, C-5/-6), 148.7 (quat, C-3a/-7a), 172.1 (quat, C=O) ppm, assigned as above.

Anal. calcd for $C_{18}H_{27}NO_2$ (289.42): C, 74.70; H, 9.40; N, 4.84. Found: C, 74.51; H, 9.26; N, 4.88.

### 4.4. α-(2-Hydroxy-1,1,3,3-tetramethylindan-2-yl)acetanilide (**6c**) [5]

See the Supporting Information for the preparation and characterization of **6c**.

### 4.5. *N,N*-Diisopropyl-α-(1,1,3,3-tetramethylindan-2-ylidene) acetamide (**7a**)

A clear solution of the *N,N*-diisopropylacetamide **6a** (2.00 g, 6.03 mmol) and dry pyridine (0.52 mL, 6.40 mmol) in dry $CCl_4$ (5 mL) was cooled in an ice-bath and treated with thionyl chloride ($SOCl_2$, 0.93 mL, 12.8 mmol). The mixture deposited a yellow resin and was stirred at rt overnight, then poured into conc. HCl with added ice. The acidic aqueous layer was shaken at rt with $Et_2O$ (3 × 50 mL). These $Et_2O$ extracts were combined with the $CCl_4$ layer and washed with distilled water until neutral, dried over $Na_2SO_4$, filtered, and concentrated to give a viscous oil (almost pure **7a**, 1.01 g, 53%) that was distilled at 120–135 °C (bath temp.)/0.04 mbar, affording pure **7a** (627 mg, 33%) that crystallized very slowly with mp 51–54 °C.

IR (KBr) $\nu$ 2963, 2929, 2864, 1630 (C=O), 1435, 1369, 1339, 1305, 1215, 1155, 1134, 1047, 756 $cm^{-1}$.

$^1H$ NMR ($CDCl_3$, 400 MHz) $\delta$ 1.15 (d, $^3J = 6.7$ Hz, 6H, 2 × isopropyl-$CH_3$ anti to C=O), 1.41 (s, 6H, 2 × 3-$CH_3$), 1.48 (d, $^3J = 6.8$ Hz, 6H, 2 × isopropyl-$CH_3$ syn), 1.58 (s, 6H, 2 × 1-$CH_3$), 3.48 (broadened sept, $^3J = 6.8$ Hz, 1H, NC*H* syn), 4.10 (sept, $^3J = 6.7$ Hz, 1H, NC*H* anti), 5.97 (s, 1H, α-H), 7.16 (m, 2H, 4-/7-H), 7.23 (m, 2H, 5-/6-H) ppm, assigned through comparison with **7b**, selective decoupling at {$\delta_H = 1.15$ ppm} or at {$\delta_H = 1.48$ ppm} that simplified NC*H* to a singlet at $\delta_H = 4.10$ ppm or $\delta_H = 3.48$ ppm}, respectively, and the following NOESY cross-peaks: α-H ↔ isopropyl-$CH_3$ → doublet at $\delta_H = 1.15$ ppm is anti to C=O, 3-$CH_3$ ↔ α-H ↔ NC*H* → septet at $\delta_H = 4.10$ ppm is anti to C=O, isopropyl-$CH_3$ doublet at $\delta_H = 1.48$ ppm ↔ NC*H* → septet at $\delta_H = 3.48$ ppm are syn to C=O;

$^1H$ NMR ($CH_2Cl_2$, 400 MHz, 25 °C) $\delta$ 1.09, 1.38, 1.44, 1.54, 3.39, 4.06, 7.13, 7.18 ppm;

$^1H$ NMR ($CH_2Cl_2$, 400 MHz, −89 °C) $\delta$ 1.02, 1.38, 1.42, 1.52, 3.24, 4.00, 7.13, 7.20 ppm;

$^{13}C$ NMR ($CH_2Cl_2$, 100.6 MHz, 25 °C) $\delta$ 20.5 (qqi, $^1J = 126.2$ Hz, $J = 4.9$ Hz, 4 × isopropyl-$CH_3$), 30.1 (qq, $^1J = 126.4$ Hz, $^3J = 4.6$ Hz, 2 × 1-$CH_3$), 31.7 (qq, $^1J = 126.4$ Hz, $^3J = 4.6$ Hz, 2 × 3-$CH_3$), 45.5 (dm, $^1J = 132.4$ Hz, $^3J = 4.0$ Hz, NCH syn), 47.81 (broadened, C-3), 47.94 (broadened, C-1), 49.9 (broadened d, $^1J = 135$ Hz, NCH anti), 118.5 (sharp d, $^1J = 151.0$ Hz, C-α), 122.56 and 122.68 (2 dm, $^1J = 156$ Hz, C-4/-7), 127.29 and 127.60 (2 ddd, $^1J = 159$ Hz, $^3J = 7$ Hz, $^2J$ = ca. 1.2 Hz, C-5/-6), 148.2 (unresolved m, C-3a), 150.5 (unresolved m, C-7a), 166.2 (m, apparent $J = 3.6$ Hz, C-2), 167.85 (broadened td, apparent $^3J = 5.3$ Hz, $^2J = 1.6$ Hz, C=O) ppm;

$^{13}C$ NMR ($CH_2Cl_2$, 100.6 MHz, −89 °C) $\delta$ 19.9, 20.1, 29.8, 31.5, 45.2, 47.47, 47.67, 50.2, 118.4, 122.6, 122.8, 127.3, 127.6, 148.0, 149.9, 165.0, 167.7 ppm;

$^{13}C$ NMR ($CDCl_3$, 100.6 MHz) $\delta$ 20.38 (2 × isopropyl-$CH_3$ syn), 20.43 (2 × isopropyl-$CH_3$ anti), 30.0, 31.6, 45.3, 47.61, 47.70, 49.6, 117.9, 122.27, 122.37, 127.00, 127.33, 147.8, 150.0, 166.4, 168.0 ppm, assigned through HETCOR, the above NOESY correlations, comparison with **7b**, and the selective decoupling experiments {3-C*H*$_3$} → C-2 narrowed, C-3 as a dd with $^3J = 5.5$ Hz (cis) and 2.3 Hz, and C-3a as a quasi-t with apparent $J = 6$ Hz; {1-C*H*$_3$} → C-1 as a dd with $^3J = 8.5$ Hz (trans) and 2.3 Hz, and C-7a as a quasi-t with apparent $J = 6.2$ Hz; {NC*H* anti at $\delta_H = 4.10$ ppm} → C=O as a d with $^3J = 6.5$ Hz. These assignments were supported by the following COLOCS(6 Hz) cross-peaks: 3-C*H*$_3$ ↔ C-2 and C-3 and C-3a, 1-C*H*$_3$ ↔ C-1 and C-2 and C-7a, α-H ↔ C-2 and C=O, isopropyl-C*H*$_3$ anti ↔ NCH anti, isopropyl-C*H*$_3$ syn ↔ NCH syn.

Anal. calcd for $C_{21}H_{31}NO$ (313.5): C, 80.46; H, 9.97; N, 4.47. Found: C, 80.12; H, 9.71; N, 4.45.

### 4.6. *N*-Isopropyl-α-(1,1,3,3-tetramethylindan-2-ylidene)acetamide (**7b**)

A solution of the *N*-isopropylacetamide **6b** (2.00 g, 6.91 mmol) and dry pyridine (at least 1.60 mL, 20.5 mmol) in dry $CCl_4$ (10 mL) was stirred until **6b** was completely dissolved. The mixture was cooled in an ice-bath for the addition of thionyl chloride ($SOCl_2$, 0.61 mL, 8.34 mmol). The yellow-brown suspension was stirred at rt overnight. The resultant solid cake was dissolved in a mixture of ice (30 g) and conc. HCl (8 mL). The acidic aqueous layer was shaken at rt with $Et_2O$ (3 × 30 mL). These $Et_2O$ extracts were combined with the $CCl_4$ layer and washed with aqueous HCl (2 M, 15 mL) and then with distilled water until neutral, dried over $Na_2SO_4$, filtered, and concentrated to leave a crude material (1.76 g) that was recrystallized from ethanol (7 mL). The pure, faintly yellow crystals (880 mg, 47%) had mp 196–197 °C.

IR (KBr) $\nu$ 3253 (sharp N–H), 2962, 1654, 1622 (C=O), 1552, 1266, 757 $cm^{-1}$.

$^1H$ NMR ($CDCl_3$, 400 MHz) $\delta$ 1.21 (d, $^3J = 6.5$ Hz, 6H,

2 × isopropyl-$CH_3$ syn to C=O), 1.38 (s, 6H, 2 × 3-$CH_3$), 1.66 (s, 6H, 2 × 1-$CH_3$), 4.15 (octet, $^3J$ = 6.5 Hz, 1H, NC*H* syn), 5.39 (broadened d, $^3J$ = ca. 6.5 Hz, 1H, NH), 5.76 (s, 1H, α-H), 7.15 (m, 1H, 4-H), 7.19 (m, 1H, 7-H), 7.24 (m, 2H, 5-/6-H) ppm, assigned through comparison with **6b** and **7a**;

$^{13}$C NMR ($CDCl_3$, 100.6 MHz) δ 22.9 (q, 2 × isopropyl-$CH_3$ syn), 28.8 (q, 2 × 1-$CH_3$), 32.1 (q, 2 × 3-$CH_3$), 41.4 (d, NCH syn), 48.1 (quat, C-3), 48.6 (quat, C-1), 116.3 (d, C-α), 122.3 and 122.6 (2 d, C-4/-7), 127.0 and 127.5 (2 d, C-5/-6), 147.0 (quat, C-3a), 150.0 (quat, C-7a), 165.6 (quat, C-2), 174.7 (quat, C=O) ppm, assigned as above.

Anal. calcd for $C_{18}H_{25}NO$ (271.4): C, 79.66; H, 9.29; N, 5.16. Found: C, 79.50; H, 9.03; N, 5.21.

### 4.7. α-(1,1,3,3-Tetramethylindan-2-ylidene)acetanilide (**7c**) [5]

See the Supporting Information for the preparation and characterization of **7c**.

### 4.8. Lithium β-(N,N-diisopropylamino)-α-(1,1,3,3-tetramethylindan-2-ylidene)ethen-β-olate ($C_S$-symmetric model **10a**)

A dry NMR tube (5 mm) was charged with the *N*,*N*-diisopropylacrylamide **7a** (119 mg, 0.38 mmol) and anhydrous THF (0.60 mL) and cooled to −78 °C under argon cover gas for the addition of nBuLi (0.50 mmol) in hexane (0.29 mL). After 30 min at rt, the yellow solution began to precipitate a copious amount of the crystalline dimer. A majority of these crystrals could be dissolved at 40 °C in the tightly closed NMR tube and was then cooled slowly to rt for the precipitation of the purified crystals which were washed with dry cyclopentane under argon gas and then subjected either to X-ray diffraction or to NMR studies in fresh anhydrous solvents.

$^1$H NMR (tBuOMe, 400 MHz, 25 °C) δ 1.18 (d, $^3J$ = 6.8 Hz, 12H, 4 × isopropyl-$CH_3$), 1.33 (s, 6H, 1-/3-$CH_3$ "near" to NCH), 1.38 (s, 6H, 1-/3-$CH_3$ "far" from NCH), 3.59 (sept, $^3J$ = 6.8 Hz, 2H, 2 × NCH), 7.08 (m, 4H, 4-/5-/6-/7-H) ppm, assigned through the NOESY cross-peaks isopropyl-C*H*$_3$ ↔ NC*H* ↔ 1-/3-C*H*$_3$ "near" ↔ 4-/7-H, but 1-/3-$CH_3$ "far" ↔ 4-/7-H only (see Table S1 for the temperature dependence);

$^{13}$C NMR (tBuOMe, 100.6 MHz, −14 °C) δ 21.7 (qm, $^1J$ = 124.5 Hz, 4 × isopropyl-$CH_3$), 30.8 (qq, $^1J$ = 125.5 Hz, 1-/3-$CH_3$ "far"), 33.9 (qq, $^1J$ = 125.5 Hz, 1-/3-$CH_3$ "near"), 46.7 (dm, $^1J$ = 133 Hz, 2 × NCH), 47.9 (unresolved, C-1/-3), 123.0 (dd, $^1J$ = 155 Hz, C-4/-7), 126.5 (dd, $^1J$ = 157.5 Hz, C-5/-6), 143.4 (unresolved, C-2), 151.4 (unresolved, C-3a/-7a), 170.9 (unresolved, C-β), 180.6 (unresolved, C-α) ppm, assigned through the selective decoupling experiments {all 1-/3-C*H*$_3$} → C-1/-3 sharp and C-2 narrowed, and {NC*H*} → C-β narrowed and isopropyl-$CH_3$ as clean qq (see Table S3 for the temperature dependence); NMR spectra in THF: See Table S4.

### 4.9. Potassium β-(N,N-diisopropylamino)-α-(1,1,3,3-tetramethylindan-2-ylidene)ethen-β-olate (**10b**) [5]

The NMR spectra of **10b** did not change on introduction of $iPr_2NH$ (0.018 mL, 0.13 mmol), whereas the addition of $(Me_3Si)_2NH$ (0.030 mL, 0.14 mmol) led to the appearance of the $^1$H and $^{13}$C NMR resonances of **7a** as formed from **10b**.

### 4.10. N,N-Diisopropyl-α-(1,1,3,3-tetramethylindan-2-ylidene) malonamide (**11**)

A THF solution of **10a** (0.38 mmol) as obtained above was poured onto solid $CO_2$ and worked up with $Et_2O$ and aqueous NaOH (2 M). Acidification of the NaOH layer afforded the carboxylic acid **11** (70 mg) that was recrystallized from toluene (4 mL). The analytically pure, colorless needles (53 mg, 39%) had mp 203–205 °C. This unusual high thermal stability against decarboxylation is due to the mechanistically unfavorable fixation of the keto group in the chiral conformation.

IR (KBr) ν 3600–2500 (O–H), 2968, 2931, 1732 (C=O), 1586 (s), 1454, 1440, 1337, 1205, 753 cm$^{-1}$.

$^1$H NMR ($CDCl_3$, 400 MHz) δ 1.12 and 1.19 (2 d, $^3J$ = 6.6 Hz, 2 × 3H, 2 × isopropyl-$CH_3$ anti to C=O), 1.42 and 1.52 (2 d, $^3J$ = 6.7 Hz, 2 × 3H, 2 × isopropyl-$CH_3$ syn), 1.51 and 1.53 (2 s, 2 × 3H, 2 × 3-$CH_3$), 1.57 and 1.64 (2 s, 2 × 3H, 2 × 1-$CH_3$), 3.45 (sept, $^3J$ = 6.7 Hz, 1H, NC*H* syn), 4.35 (sept, $^3J$ = 6.6 Hz, 1H, NC*H* anti), 7.11 and 7.12 (2 m, 2H, 4-/7-H), 7.23 (m, 2H, 5-/6-H) ppm, assigned through comparison with **7a**;

$^{13}$C NMR ($CDCl_3$, 100.6 MHz) δ 19.5, 19.7, 20.0, and 20.5 (4 q, 4 × isopropyl-$CH_3$), 27.9 and 29.1 (2 q, 2 × 1-$CH_3$), 31.8 and 32.7 (2 q, 2 × 3-$CH_3$), 46.5 (d, NCH syn), 48.9 (quat, C-3), 49.4 (quat, C-1), 51.0 (d, NCH anti), 121.8 (d, C-4), 122.1 (d, C-7), 127.31 (d, C-5), 127.44 (d, C-6), 127.6 (quat, C-α),147.9 (quat, C-3a), 148.9 (quat, C-7a), 165.4 (quat, $CO_2H$), 166.0 (quat, C-2), 167.9 (quat, amide C=O) ppm, assigned as above.

Anal. calcd for $C_{22}H_{31}NO_3$ (357.5): C, 73.92; H, 8.74; N, 3.92. Found: C, 73.60; H, 8.96; N, 3.82.

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## Appendix A. Supplementary data

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[8] In agreement with δ = 185.1 ppm as reported for $tBu_2C{=}C{=}C(OLi){-}OCH_3$ (compound 12b in Table 2 of Ref [7]).