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Crystal and Molecular Structure of a THF-solvated Lithium Amide Enolate Dimer

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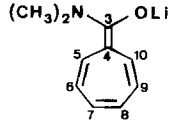
The structure of a crystalline complex with the composition [lithium 8-(dimethylamino)-8-heptafulvenolate]$_2 \cdot (THF)_4$ has been determined by *X*-ray analysis at $-115\,^{\circ}C$ ($R = 0.048$). The lithium atoms form a four-membered ring with the two oxygen atoms of the enolates and are solvated by two THF oxygens each. The π-system and the dimethylamino group are not involved in complexing the metal. The geometry of and the bonding in the nearly planar heptafulvene moiety of the enolate are discussed.

Kristall- und Molekülstruktur eines mit THF solvatisierten dimeren Lithiumenolats eines Carbonsäureamids

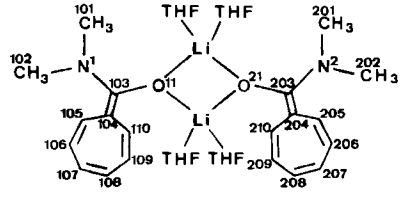
Die Struktur eines kristallinen Komplexes der Zusammensetzung [Lithium-8-(dimethylamino)-8-heptafulvenolat]$_2 \cdot (THF)_4$ wurde durch Röntgen-Strukturanalyse bei $-115\,^{\circ}C$ mit einem *R*-Wert von 0.048 bestimmt. Die Lithium-Atome bilden mit den beiden Enolat-Sauerstoffen einen Vierring und tragen als weitere Liganden je zwei THF-Sauerstoffe. Weder das π-System noch die Dimethylamino-Gruppe sind an der Komplexierung beteiligt. Die Geometrie und die Bindung im fast planaren Heptafulven-Teil des Enolates werden diskutiert.

In view of the importance of lithium enolates in modern synthetic organic chemistry, two years ago we started a project for determining the structure of some representative reagents of this type by *X*-ray crystal structure analysis. We found two tetrameric ketone enolates[3,4] as well as dimeric and tetrameric aggregates of ester enolates[5]. So far, no structure of a lithium enolate of a *N,N*-dialkylcarboxamide has been elucidated. An interesting example of this class of compounds is lithium 8-(dimethylamino)-8-heptafulvenolate (**1**) which is at the same time an amide enolate and a heptafulvene with inverse polarization[6,7].



1

(simplified numbering of the atoms of the enolate molecule used in the discussion)



(numbering of the atoms of the enolate molecules in the dimer as chosen in the *X*-ray structure determination)

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For the *X*-ray structure analysis, the enolate **1** was generated from *N,N*-dimethyl-1,3,5-cycloheptatriene-7-carboxamide (IUPAC name) with lithium diisopropylamide (LDA) and recrystallized from tetrahydrofuran (THF)/hexane. Both the solution and the crystals of **1** are deep violet[8-10]. Although "potentially antiaromatic", **1** is remarkably stable even at room temperature[11]. From the ^1H and ^{13}C NMR spectra of **1** there is evidence for an oxygen-bound lithium atom, as concluded from the facile rotation around the C(3) – N bond, and from a high barrier to rotation around the exocyclic C(3) – C(4) bond: there are signals due to anisochronous pairs of ring carbons in the ^{13}C spectrum, and there is only one signal from the methyl groups on nitrogen[7]. The same conclusion was drawn by *Woodbury* and *Rathke* from the NMR spectrum of the lithium enolate of *N,N*-dimethyl acetamide[12].

It was of interest to find out whether **1** is aggregated in the solid state as are other lithium enolates[2-5], whether the lone pair on nitrogen takes part in conjugation and/or in lithium complexation, and to what extent the ring geometry is determined by antiaromaticity.

A. Results

The lithium enolate **1** crystallized with two equivalents of tetrahydrofuran (THF) solvent. The crystal structure contains dimeric aggregates with approximate C_2-symmetry[13], see Figures 1 and 2. The enolate oxygen atoms and the lithium atoms form a nearly planar central four-membered ring. The heptafulvene rings in each dimer take a *cis*-position on the Li_2O_2 ring. Every lithium atom is coordinated by two THF molecules, thus achieving a tetrahedral environment of oxygen atoms. Neither the nitrogen atoms nor the π-systems are involved in Li-coordination.

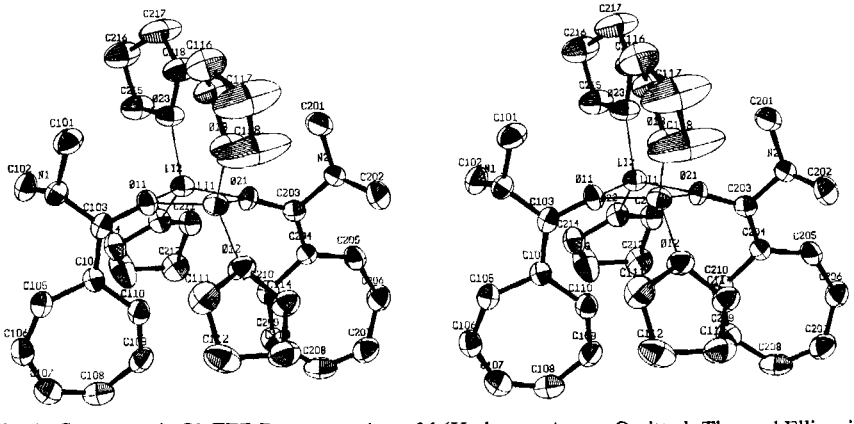
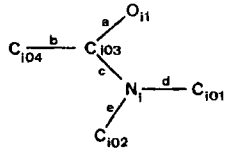


Fig. 1. Stereoscopic ORTEP Representation of **1** (Hydrogen Atoms Omitted, Thermal Ellipsoids are Drawn on the 50% Propability Level)

Like the ketone enolates, the amide enolate has a short olefinic double bond [C(3) – C(4)] and a long C – O single bond [C(3) – OLi] compared to the non-lithiated precursor. The C – N bond [C(3) – N] in the enolate moiety of **1** is significantly longer than the corresponding bond of carboxamides.

Table 1. Geometrical Data[a] of the Enolate Fragments in **1** and of Comparable Fragments in Topologically Similar Molecules. (The Letters on the Bonds Refer to the Corresponding Bonds in Molecules with Comparable Fragments. The Numbers at the Atoms Refer to **1**)



	1 (i = 1)	**1** (i = 2)	Pinacolone Li-Enolate	Enamines[b]	Carbox-amides	**8**
a	1.301 (5)	1.303 (6)	1.347 (3)	–	1.228 (9)	1.378
b	1.385 (7)[c]	1.381 (7)[c]	1.338 (4)	1.334 – 1.366	1.533 (14)	1.332
c	1.435 (7)	1.427 (5)	–	1.380 – 1.426	1.346 (10)	1.409
ab	125.0 (5)	125.1 (4)	122.3 (2)	–	119.2 (12)	118.9
bc	117.8 (4)	118.1 (4)	–	121.6 – 124.8	118.7 (12)	127.2
ac	117.3 (4)	116.9 (4)	–	–	122.0 (6)	113.8
cd	114.0 (4)	116.1 (4)	–	113 – 126.0	117.7 (14)	112.4
ce	113.6 (4)	116.4 (4)	–	115.7 – 122.1	124.4 (15)	115.1
de	111.0 (4)	111.6 (4)	–	108 – 111.9	117.5 (13)	112.0
bcd	+159.5 (5)	+164.1 (5)	–	119 – 180	–	126
bce	−72.0 (6)	−61.5 (6)	–	−8 – +11	–	−3
Δ	0.393	0.338	–	0.013 – 0.402	–	0.386
ref.	this work	this work	3)	14)	15)	22)

[a] Bond lengths and Δ in Å, angles and torsion angles in degrees. – [b] Ranges. – [c] Bond b interacts with the heptafulvene ring.

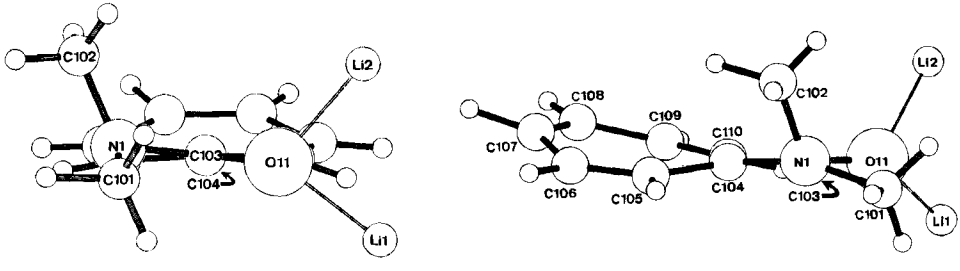
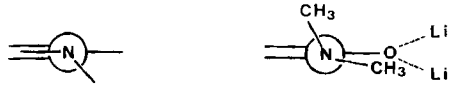


Fig. 2. Newman Projections Along the C(103) – C(104) Bond (Left Side) and Along the N(1) – C(103) Bond (Right Side) (The Corresponding Newman Projections of the Second Enolate Molecule are Similar)

The nitrogen atom of the dimethylamino group in **1** is pyramidal. The distance Δ[14] of the nitrogen above the plane formed by its bonding partners has an average value of 0.365 Å. This value is within the range of pyramidalities Δ found in enamines[14] in

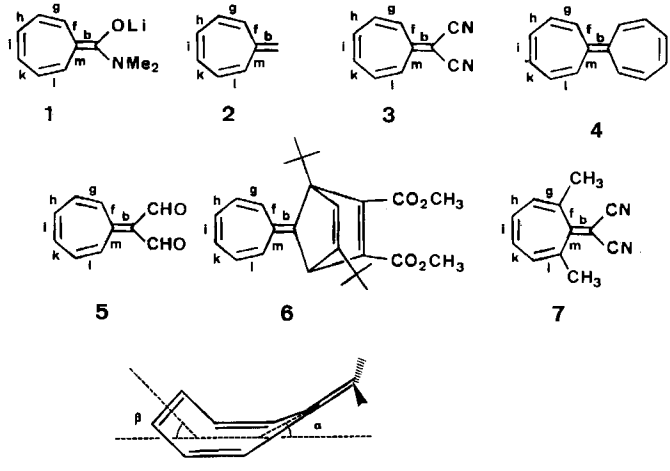


2a **2b**

which the structure **2a** is favoured. A Newman projection along the N – C(3) bond of **1** reveals, however, that one of the methyl groups is fully eclipsed with the C – O bond, see **2b**, rather than with the C = C bond, see **2a**, Figure 2, and Table 1.

As in other complexes of lithium with ethers[15] the O_{THF} – Li bond in **1** coincides with the bisector of the C – O – C angle of the THF molecules.

Table 2. Bond Lengths and Folding Angles of Heptafulvenes[d]



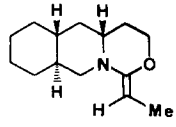
	b[a]	f	g	h	i	k	l	m	α[b]	β	ref.
1 (i=1)	1.385	1.461	1.340	1.456	1.331	1.460	1.338	1.451	14.8	12.6	this
1 (i=2)	1.381	1.458	1.342	1.463	1.331	1.447	1.336	1.461	20.8	17.9	work
2	1.350	1.450	1.365	1.470	1.334	1.470	1.365	1.450	0	0	16)
3	1.422	1.425	1.353	1.448	1.311	1.448	1.353	1.425	2.6	1.8	17)
4	1.373	1.454	1.341	1.430	1.332	1.427	1.343	1.459	24.7	15.7	18)
5	1.426	1.427	1.362	1.409	1.349	1.403	1.366	1.425	–[c]	---	19)
6	1.329	1.472	1.336	1.434	1.337	1.441	1.332	1.473	41.4	23.6	20)
7	1.361	1.465	1.339	1.415	1.338	1.415	1.339	1.465	45.3	20.1	21)

[a] Bond lengths in Å. – [b] Folding angles in °. – [c] Not stated and not calculable due to missing atom coordinates in ref.[19]. – [d] Data from *X*-ray structure (**1**, **3** – **7**) or microwave spectral analysis (**2**).

The heptafulvene unit in **1** has a shallow boat conformation. At the same time a clear-cut single bond/double bond alternation is present. The values of the bond lengths and the folding angles α,β are shown in Table 2 together with those of the other heptafulvenes. The seven-membered ring in **1** is surprisingly flat when compared to the other structures. The bond length alternation in **1** is more pronounced than in the dicyanoheptafulvene **3** but still lies within the range found in the other heptafulvenes. Of the double bonds in **1**, C(7) – C(8) (= bond i) is the shortest one as is the rule for most compounds shown in Table 2.

B. Discussion

Considering the bond lengths, the enolate unit in **1** can be classified as an amino substituted lithium enolate. This classification also holds if **1** is compared with enamines[14], and even better with the ketene *N,O*-acetal **8**[22]: the nitrogen is pyramidalized (sp^3-hybridized). This effect indicates[22,23] a low degree of p,π-overlap between the lone-pair on nitrogen and the double bond.



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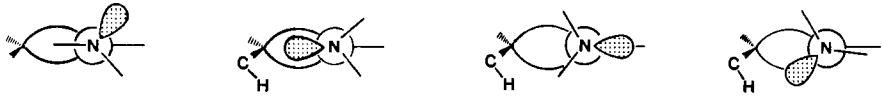
If the two-ring model description of double bonds is used[14,24], enamines can in principle occur in two staggered and two eclipsed conformations **9a, b** and **10a, b**, respectively. For simple enamines which have an H atom in the *cis*-position with respect to the dialkylamino group, the conformation **9a** has been found by *X*-ray crystal structure analysis[14,22,23].

In molecules with a potential leaving group such as Cl on the carbon bearing the nitrogen atom, conformation **9b** is favoured by an anomeric effect[25]: the lone pair on nitrogen is antiperiplanar to the geminal electronegative substituent.



9a **9b** **10a** **10b**

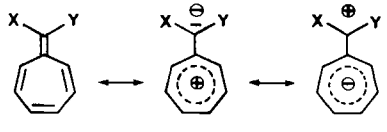
Enamines with the eclipsed conformation **10a** have not yet been observed. For conformation **10b** the amide enolate **1** is the first example.

We assume that the eclipsed conformation of the C(3) – N bond in our structure is a compromise between two factors:

a) Minimun van der Waals interaction of the *N*-methyl [C(2)] and the neighboring methine groups [C(5)] (the shortest $H_{C(2)}$-$H_{C(5)}$ distance is 2.27(6) Å), i.e., steric repulsion disfavors conformation **9a** and **10a**.

b) Maximum deviation from a conformation with antiperiplanar arrangement of the virtual N-lone pair and the C(3) – O bond, i.e., conformation **9b** should be disfavored by two opposing anomeric effects.

The ring geometry in heptafulvenes is governed by steric and electronic factors[26].



11a **11b** **11c**

Heptafulvenes **11** with normal polarization (X,Y = acceptors) tend to be flat due to the contribution of resonance structure **11b** (cf. **3** in Table 2). Due to the canonical form **11c** heptafulvenes with inverse polarization (X,Y = donors) might be expected to adopt a boat shape to avoid "antiaromaticity" in the cycloheptatrienyl anion moiety. MNDO/3 calculations, however, predict energy minima for *planar* structures of the unsubstituted cycloheptatrienyl anion with charge and electron distributions as indicated in the formulae **12** and **13**[27].

12 **13** **14**

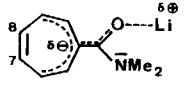
For the anion of methyl 1,3,5-cycloheptatriene-7-carboxylate (IUPAC name) such a calculation[28] produced an energy minimum with a planar seven-membered ring, alternating bond lengths, the ester group twisted around 60° with respect to the ring plane, and a charge and electron distribution as indicated by the formula **14**.

We believe that the experimentally found flat boat conformation of the seven-membered ring in **1** is controlled by two effects:

a) Inverse polarization in **1** favors reduced π-orbital overlap in the ring which is achieved by deviation of the folding angles α,β from zero.

b) Folding causes reduction of the C(5) – C(4) – C(10) angle in heptafulvenes **11**. Since the corresponding angle in **1** already has the ideal sp^2 value of 120°, increasing α would produce strain.

Because of the tight bond of lithium to oxygen and due to the high C(7) – C(8) double bond character[29] we prefer the description of **1** as a "cross conjugated lithium enolate" with an electron distribution as indicated in formula **15**.



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Experimental Part

Preparation of **1**: To a solution of 0.35 ml (2.50 mmol) of diisopropylamine in 2 ml of THF was added at 0°C 1.46 ml (2.45 mmol) of 1.68 M *n*-butyllithium in hexane. After stirring at room temperature for 10 min and subsequently cooling to – 50°C, a solution of 400 mg (2.45 mmol) of *N,N*-dimethyl-1,3,5-cycloheptatriene-7-carboxamide[30] in 2 ml of THF was added dropwise. The deep violet solution was stirred for 1 h and warmed to room temperature. After addition of 8 ml of hexane the solution was rapidly cooled to – 78°C, warmed again to 0°C and slowly cooled to

– 27 °C (24 h). Crystals of appropriate size grew under these conditions, were separated from the mother liquor, washed with small portions of hexane and dried in vacuo.

Table 3. Atomic Coordinates and Thermal Parameters of **1** (2 **1** · 4 C_4H_8O)

THE TEMPERATURE FACTOR HAS THE FORM OF EXP(-T) WHERE
T = 8*(PI**2)*U*(SIN(THETA)/LAMBDA)**2 FOR ISOTROPIC ATOMS
T = 2*(PI**2)*SUM(I,(H(I)*H(J)*U(I,J)*ASTAR(I)*ASTAR(J)), FOR
ANISOTROPIC ATOMS, ASTAR(I) ARE RECIPROCAL AXIAL LENGTHS AND
H(I) ARE MILLER INDICES.
THE E.S.D. OF THE LAST SIGNIFICANT DIGIT IS GIVEN IN PARENTHESES.

ATOM	X	Y	Z	U11(OR U)	U22	U33	U12	U13	U23
O11	0.7010(1)	-0.0018(3)	0.3504(2)	0.034(2)	0.031(2)	0.045(2)	0.006(2)	-0.009(2)	0.002(2)
N1	0.5965(2)	0.0737(4)	0.3439(2)	0.038(2)	0.038(3)	0.033(2)	-0.001(2)	-0.014(2)	0.006(2)
C101	0.6194(3)	0.0334(6)	0.2698(3)	0.056(3)	0.069(4)	0.038(3)	-0.005(3)	-0.019(3)	0.001(3)
C102	0.5384(2)	-0.0105(6)	0.3805(3)	0.035(3)	0.048(4)	0.061(4)	-0.005(3)	-0.018(3)	0.004(3)
C103	0.6479(2)	0.0740(5)	0.3790(2)	0.033(3)	0.027(3)	0.042(3)	-0.004(2)	-0.015(2)	0.012(3)
C104	0.6370(2)	0.1539(5)	0.4407(2)	0.034(3)	0.030(3)	0.032(3)	0.001(2)	-0.008(2)	0.006(2)
C105	0.5804(2)	0.2512(5)	0.4634(2)	0.029(3)	0.034(3)	0.039(3)	-0.005(3)	-0.008(2)	0.009(3)
C106	0.5545(2)	0.3186(5)	0.5250(3)	0.035(3)	0.032(3)	0.055(3)	0.000(3)	-0.009(3)	0.003(3)
C107	0.5730(3)	0.3058(6)	0.5907(3)	0.052(3)	0.038(3)	0.047(3)	-0.004(3)	-0.008(3)	0.002(3)
C108	0.6292(3)	0.2502(6)	0.5980(3)	0.070(4)	0.042(3)	0.042(3)	-0.008(3)	-0.023(3)	0.000(3)
C109	0.6852(2)	0.1892(6)	0.5443(3)	0.046(3)	0.042(3)	0.052(3)	-0.002(3)	-0.027(3)	0.003(3)
C110	0.6875(2)	0.1482(5)	0.4786(3)	0.037(3)	0.030(3)	0.048(3)	0.001(2)	-0.014(2)	0.003(3)
LI1	0.7939(4)	0.0180(9)	0.3159(4)	0.042(5)	0.037(5)	0.028(4)	-0.001(4)	-0.008(4)	0.002(4)
O12	0.8385(2)	0.1893(4)	0.3402(2)	0.032(2)	0.030(2)	0.053(2)	0.000(2)	-0.024(2)	-0.005(2)
C111	0.8077(3)	0.3317(7)	0.3441(4)	0.068(4)	0.037(4)	0.078(5)	0.003(3)	-0.036(4)	0.007(4)
C112	0.8294(3)	0.4126(6)	0.3996(3)	0.080(5)	0.038(4)	0.068(4)	-0.004(3)	-0.011(3)	-0.012(3)
C113	0.8965(3)	0.3495(7)	0.3966(3)	0.060(4)	0.053(4)	0.055(4)	-0.013(3)	-0.019(3)	-0.009(3)
C114	0.8870(2)	0.1916(6)	0.3791(3)	0.052(3)	0.036(3)	0.059(3)	-0.003(3)	-0.025(3)	0.001(3)
O13	0.8241(2)	0.0361(4)	0.2116(2)	0.066(2)	0.061(3)	0.032(2)	-0.031(2)	-0.011(2)	0.007(2)
C115	0.8009(3)	-0.0491(8)	0.1627(3)	0.061(4)	0.061(5)	0.041(3)	-0.020(4)	-0.018(3)	0.000(3)
C116	0.8145(3)	0.0359(7)	0.0963(3)	0.094(5)	0.061(4)	0.057(4)	-0.014(4)	-0.029(4)	0.014(3)
C117	0.8699(5)	0.132(1)	0.1005(4)	0.21(1)	0.148(8)	0.059(5)	-0.130(8)	-0.040(6)	0.037(5)
C118	0.8695(5)	0.137(1)	0.1721(4)	0.24(1)	0.182(9)	0.052(5)	-0.181(9)	-0.022(6)	0.021(6)
O21	0.8122(1)	-0.1571(3)	0.3601(2)	0.029(2)	0.035(2)	0.039(2)	0.003(2)	-0.015(1)	0.004(2)
N2	0.9194(2)	-0.2499(4)	0.3196(2)	0.037(2)	0.044(3)	0.036(2)	0.007(2)	-0.011(2)	-0.009(2)
C201	0.9027(3)	-0.2917(6)	0.2558(3)	0.060(4)	0.065(4)	0.046(3)	0.021(3)	-0.021(3)	-0.017(3)
C202	0.9809(2)	-0.1680(7)	0.3038(3)	0.037(3)	0.084(5)	0.047(3)	0.004(3)	-0.001(3)	-0.010(3)
C203	0.8660(2)	-0.1957(5)	0.3759(2)	0.036(3)	0.018(3)	0.039(3)	-0.003(2)	-0.010(2)	0.000(2)
C204	0.8749(2)	-0.1890(5)	0.4425(2)	0.030(3)	0.024(3)	0.032(3)	-0.004(2)	-0.007(2)	0.003(2)
C205	0.9303(2)	-0.2659(5)	0.4576(2)	0.039(3)	0.037(3)	0.045(3)	0.010(3)	-0.013(2)	-0.003(3)
C206	0.9579(2)	-0.2467(6)	0.5102(3)	0.045(3)	0.064(4)	0.046(3)	0.010(3)	-0.021(3)	0.001(3)
C207	0.9438(3)	-0.1342(7)	0.5637(3)	0.054(4)	0.076(5)	0.044(3)	-0.001(4)	-0.023(3)	-0.004(3)
C208	0.8877(3)	-0.0585(6)	0.5659(3)	0.081(4)	0.052(4)	0.033(3)	-0.003(4)	-0.022(3)	-0.006(3)
C209	0.8283(2)	-0.0677(6)	0.5612(3)	0.049(3)	0.044(3)	0.038(3)	0.005(3)	-0.009(3)	0.003(3)
C210	0.8240(2)	-0.1200(5)	0.4992(2)	0.037(3)	0.037(3)	0.037(3)	-0.001(2)	-0.011(2)	0.007(3)
LI2	0.7205(4)	-0.1924(8)	0.3810(4)	0.039(4)	0.030(5)	0.033(4)	-0.006(4)	-0.009(4)	0.002(4)
O22	0.6696(1)	-0.2536(4)	0.4767(2)	0.041(2)	0.039(2)	0.033(2)	0.001(2)	-0.009(2)	0.008(2)
C211	0.6935(3)	-0.3688(6)	0.5127(3)	0.047(4)	0.035(4)	0.048(4)	0.004(3)	-0.015(3)	0.007(3)
C212	0.6643(3)	-0.3372(8)	0.5903(3)	0.067(4)	0.057(4)	0.039(3)	0.004(4)	-0.017(3)	0.017(3)
C213	0.5975(3)	-0.2713(8)	0.5917(3)	0.080(4)	0.123(6)	0.041(3)	0.050(5)	0.003(3)	0.021(4)
C214	0.6078(2)	-0.1986(6)	0.5228(3)	0.036(3)	0.052(4)	0.046(3)	0.003(3)	-0.004(2)	0.007(3)
O23	0.6940(2)	-0.3586(4)	0.3268(2)	0.054(2)	0.042(2)	0.036(2)	-0.020(2)	-0.006(2)	-0.002(2)
C215	0.6355(3)	-0.4452(9)	0.3570(3)	0.063(4)	0.070(5)	0.049(4)	-0.040(4)	-0.004(3)	-0.002(4)
C216	0.6166(3)	-0.5135(8)	0.2956(3)	0.078(5)	0.096(5)	0.053(4)	-0.045(4)	-0.011(4)	-0.001(4)
C217	0.6782(4)	-0.5103(9)	0.2365(3)	0.108(6)	0.128(7)	0.049(4)	-0.058(5)	-0.016(4)	-0.016(4)
C218	0.7163(4)	-0.3827(8)	0.2526(3)	0.070(5)	0.071(5)	0.039(3)	-0.030(4)	-0.010(3)	0.000(3)
H101	0.659(3)	0.089(6)	0.245(3)	0.08(2)					
H102	0.624(2)	-0.073(6)	0.260(3)	0.07(2)					
H103	0.577(2)	0.052(6)	0.248(2)	0.07(2)					

ATOM	X	Y	Z	U11(OR U)	ATOM	X	Y	Z	U11(OR U)
H104	0.519(2)	0.027(4)	0.436(2)	0.04(1)	H206	0.982(3)	-0.083(6)	0.272(3)	0.09(2)
H105	0.504(2)	0.007(5)	0.355(2)	0.05(1)	H207	0.954(2)	-0.339(4)	0.422(2)	0.04(1)
H106	0.545(2)	-0.108(5)	0.377(2)	0.06(2)	H208	0.994(2)	-0.311(5)	0.513(2)	0.06(1)
H107	0.553(2)	0.267(4)	0.431(2)	0.03(1)	H209	0.983(2)	-0.117(4)	0.588(2)	0.04(1)
H108	0.516(2)	0.370(4)	0.531(2)	0.03(1)	H210	0.888(2)	0.009(5)	0.620(2)	0.06(1)
H109	0.534(2)	0.340(5)	0.639(2)	0.07(1)	H211	0.784(2)	-0.029(5)	0.591(2)	0.05(1)
H110	0.636(2)	0.251(5)	0.643(2)	0.05(1)	H212	0.779(2)	-0.115(4)	0.492(2)	0.03(1)
H111	0.726(2)	0.173(4)	0.560(2)	0.03(1)	H217	0.5810	-0.1951	0.6343	0.1243
H112	0.731(2)	0.109(4)	0.451(2)	0.02(1)	H218	0.5603	-0.3578	0.5978	0.1300
H115	0.7955	0.3923	0.4511	0.0970	H219	0.6107	-0.08218	0.5293	0.1341
H116	0.8324	0.5284	0.3894	0.1058	H220	0.5672	-0.2236	0.5011	0.09210
H119	0.8702	0.1294	0.4271	0.0951	H223	0.5788	-0.4475	0.2811	0.1000
H120	0.9334	0.1469	0.3470	0.06290	H224	0.5977	-0.6218	0.3078	0.1000
H123	0.7719	0.1010	0.09455	0.1000	H225	0.7067	-0.6113	0.2400	0.1500
H124	0.8282	-0.03448	0.05082	0.1000	H226	0.6692	-0.5035	0.1879	0.1102
H125	0.8629	0.2411	0.08509	0.1331	H213	0.747(2)	-0.367(5)	0.495(2)	0.04(1)
H126	0.9166	0.08942	0.06472	0.2200	H214	0.681(2)	-0.457(6)	0.498(2)	0.05(2)
H127	0.8648	0.2443	0.1936	0.1681	H215	0.695(3)	-0.260(6)	0.608(3)	0.08(2)
H128	0.9189	0.09338	0.1731	0.2500	H216	0.659(2)	-0.419(6)	0.618(3)	0.06(2)
H113	0.820(3)	0.376(6)	0.300(3)	0.06(2)	H221	0.589(4)	-0.375(8)	0.381(4)	0.14(3)
H114	0.756(3)	0.324(6)	0.350(3)	0.07(2)	H222	0.640(4)	-0.50(1)	0.392(4)	0.18(4)
H117	0.937(3)	0.392(7)	0.355(3)	0.11(2)	H227	0.705(3)	-0.288(8)	0.227(4)	0.13(3)
H118	0.913(2)	0.356(5)	0.443(3)	0.06(2)	H228	0.765(3)	-0.390(7)	0.235(3)	0.09(2)
H121	0.751(3)	-0.069(6)	0.187(3)	0.08(2)					
H122	0.621(4)	-0.141(8)	0.158(4)	0.12(3)					
H201	0.859(2)	-0.340(6)	0.268(2)	0.07(2)					
H202	0.896(2)	-0.204(5)	0.228(2)	0.07(2)					
H203	0.940(2)	-0.355(4)	0.227(2)	0.04(1)					
H204	0.994(2)	-0.149(5)	0.349(2)	0.07(2)					
H205	1.017(2)	-0.219(5)	0.276(2)	0.04(1)					

Table 4. Bond Lengths (Å) and Angles (Degrees) in **1** ($2\,\mathbf{1}\cdot 4\,C_4H_8O$) with Standard Deviations in Parentheses

C101	-N1	1.455(6)	C102	-N1	1.453(6)	C103	-C104	1.385(7)	C103	-N1	1.435(7)
C103	-O11	1.301(5)	C104	-C105	1.451(6)	C104	-C110	1.461(8)	C105	-C106	1.338(7)
C106	-C107	1.460(8)	C107	-C108	1.331(8)	C108	-C109	1.496(7)	C109	-C110	1.340(7)
C111	-C112	1.50(1)	C111	-O12	1.449(7)	C112	-C113	1.500(9)	C113	-C114	1.504(8)
C114	-O12	1.439(7)	C115	-C116	1.484(9)	C115	-O13	1.430(8)	C116	-C117	1.48(1)
C117	-C118	1.41(1)	C118	-O13	1.40(1)	C201	-N2	1.452(7)	C202	-N2	1.449(7)
C203	-C204	1.381(7)	C203	-N2	1.427(5)	C203	-O21	1.303(6)	C204	-C205	1.461(7)
C204	-C210	1.458(6)	C205	-C206	1.336(8)	C206	-C207	1.447(8)	C207	-C208	1.331(8)
C208	-C209	1.463(9)	C209	-C210	1.342(7)	C211	-C212	1.511(8)	C211	-O22	1.440(7)
C212	-C213	1.52(1)	C213	-C214	1.475(8)	C214	-O22	1.449(5)	C215	-C216	1.51(1)
C215	-O23	1.444(8)	C216	-C217	1.459(8)	C217	-C218	1.49(1)	C218	-O23	1.427(7)
LI1	-LI2	2.58(1)	LI1	-O11	1.884(8)	LI1	-O12	1.956(9)	LI1	-O13	1.987(8)
LI1	-O21	1.917(9)	LI2	-O11	1.931(9)	LI2	-O21	1.878(8)	LI2	-O22	1.973(7)
LI2	-O23	2.028(9)									

C104	-C103	-N1	117.8(4)	C104	-C103	-O11	125.0(5)	N1	-C103	-O11	117.2(4)
C103	-C104	-C105	121.0(5)	C103	-C104	-C110	117.9(4)	C105	-C104	-C110	120.9(4)
C104	-C105	-C106	130.8(5)	C105	-C106	-C107	129.1(5)	C106	-C107	-C108	126.4(4)
C107	-C108	-C109	128.9(5)	C108	-C109	-C110	128.1(5)	C104	-C110	-C109	130.7(4)
C112	-C111	-O12	105.2(6)	C111	-C112	-C113	103.6(5)	C112	-C113	-C114	102.1(5)
C113	-C114	-O12	106.1(5)	C116	-C115	-O13	107.0(5)	C115	-C116	-C117	102.9(6)
C116	-C117	-C118	107.0(7)	C117	-C118	-O13	110.3(8)	C204	-C203	-N2	118.1(4)
C204	-C203	-O21	125.1(4)	N2	-C203	-O21	116.9(4)	C203	-C204	-C205	120.1(4)
C203	-C204	-C210	119.1(4)	C205	-C204	-C210	120.3(4)	C204	-C205	-C206	129.8(5)
C205	-C206	-C207	128.2(5)	C206	-C207	-C208	126.3(6)	C207	-C208	-C209	128.2(5)
C208	-C209	-C210	127.4(4)	C204	-C210	-C209	129.4(5)	C212	-C211	-O22	105.2(4)
C211	-C212	-C213	101.7(5)	C212	-C213	-C214	105.5(4)	C213	-C214	-O22	107.2(4)
C216	-C215	-O23	106.3(5)	C215	-C216	-C217	103.7(6)	C216	-C217	-C218	106.1(6)
C217	-C218	-O23	106.1(5)	LI2	-LI1	-O11	48.3(3)	LI2	-LI1	-O12	137.7(4)
LI2	-LI1	-O13	123.5(4)	LI2	-LI1	-O21	46.6(3)	O11	-LI1	-O12	120.5(4)
O11	-LI1	-O13	112.2(5)	O11	-LI1	-O21	94.2(3)	O12	-LI1	-O13	98.8(4)
O12	-LI1	-O21	113.0(5)	O13	-LI1	-O21	119.8(4)	LI1	-LI2	-O11	46.8(3)
LI1	-LI2	-O21	47.9(3)	LI1	-LI2	-O22	141.1(4)	LI1	-LI2	-O23	120.9(4)
O11	-LI2	-O21	94.0(4)	O11	-LI2	-O22	116.9(4)	O11	-LI2	-O23	113.6(4)
O21	-LI2	-O22	120.3(5)	O21	-LI2	-O23	115.4(4)	O22	-LI2	-O23	97.9(3)
C101	-N1	-C102	111.0(4)	C101	-N1	-C103	114.0(4)	C102	-N1	-C103	113.6(4)
C201	-N2	-C202	111.6(4)	C201	-N2	-C203	116.1(4)	C202	-N2	-C203	116.4(4)
C103	-O11	-LI1	141.2(4)	C103	-O11	-LI2	125.4(3)	LI1	-O11	-LI2	84.9(4)
C111	-O12	-C114	109.3(4)	C111	-O12	-LI1	120.0(4)	C114	-O12	-LI1	127.0(4)
C115	-O13	-C118	107.1(5)	C115	-O13	-LI1	125.9(4)	C118	-O13	-LI1	127.0(5)
C203	-O21	-LI1	129.4(4)	C203	-O21	-LI2	143.5(4)	LI1	-O21	-LI2	95.5(4)
C211	-O22	-C214	108.6(3)	C211	-O22	-LI2	120.8(3)	C214	-O22	-LI2	130.6(4)
C215	-O23	-C218	109.5(5)	C215	-O23	-LI2	121.5(4)	C218	-O23	-LI2	126.9(4)

Crystal Structure Analysis[31]: $2\,C_{10}H_{12}LiNO\cdot 4\,C_4H_8O$, M = 626.74. A single crystal (approximated size 0.3 mm × 0.3 mm × 0.6 mm) was mounted in a Lindeman glass tube under Ar with hexadecane as adhesive. The unit cell has been determined after a search run with 15 reflections. Monoclinic, space group $P2_1/c$, a = 20.987 (17), b = 9.170 (3), c = 19.761 (9) Å, β = 73.65 (5)°, V = 3649.2 Å^3, at −115 °C, Z = 4, d_x = 1.14 g · cm^{-3}. Intensity measurements were carried out at −115 °C with an Enraf Nonius CAD 4 diffractometer, equipped with graphite

monochromator and cooling device (Mo-K_α radiation, λ = 0.7107 Å, 4468 independent reflexions with $\Theta \leqslant 22°$, 2574 with $I > 3\sigma(I)$). The structure was solved by MULTAN 80[32] and refined by bloc full-matrix analysis using SHELX[33]. All hydrogen positions have been found, but those at C(112), C(114), C(116), C(117), C(118), C(213), C(214), C(216), C(217) were substituted by calculated positions. After anisotropic refinement of the non-hydrogen atoms, isotropic refinement of H atoms (with ride-mode for the calculated H atoms) in the SHELX system and anisotropic refinement of the non-hydrogen atoms and isotropic refinement of the experimentally found H atoms in the *X*-ray[34] system, the final *R* value was 0.048 (R_w = 0.050). Some large vibrational parameters in the THF molecules point to a certain amount of orientational disorder in the crystal structure. Atomic coordinates and thermal parameters are listed in Table 3, bond lengths and angles in Table 4.

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