

A MNDO-STUDY OF SOLVENT FREE AND SOLVATED DIMERIC LITHIUM ION PAIRS OF ACETALDOXIME. MODELS FOR DIMERIC AGGREGATES OF LITHIATED OXIME ETHERS*

RAINER GLASER** and ANDREW STREITWIESER, Jr.

Department of Chemistry, University of California, Berkeley, California 94720 (U.S.A.)

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ABSTRACT

Cyclic and stack-type structures of solvent-free and solvated dimeric lithium ion pairs of isomeric carbanions of acetaldoxime were investigated as models for lithiated oxime ethers. The adequacy of MNDO is evaluated critically with reference to *ab initio* results. Severe overestimation of the pyramidalization at the carbanionic center and insufficient carbon lone-pair—lithium core repulsion are found to cause the following artifacts: excessive charge localization, the breakdown of the pseudo- π conjugation within the ligands, and orbital orientation towards the cation; standard MNDO calculations yield entirely unacceptable results. A simple method is proposed to counteract some of these deficiencies and results thus obtained are in significantly better agreement with *ab initio* data. Solvated cyclic (C_1 symmetric) dimers were found to be the most important aggregated species; they are preferred over *bis*-solvated monomeric ion pairs at the MNDO level. The magnitudes of the relative energies are such that a definitive conclusion regarding the predominance of monomeric or dimeric aggregates cannot be made. Mechanistic implications with regard to the experimentally observed *syn*-axial entry of electrophiles into configurationally fixed lithiated oxime ethers are discussed.

INTRODUCTION

The use of metalated enolate equivalents [1] has resolved many of the problems associated with classical carbonyl chemistry [2] and has opened a wide field of modern synthetic chemistry [3]. Many metalated N-derivatives of carbonyl compounds, $R_1R_2C=N-X$, such as imines [4], hydrazones [5, 6], oximes [7, 8] and oxime ethers [9, 10], have been used as enolate equivalents to achieve CC bond formation in the α position to a carbonyl group. One of the most important characteristics of these organometallic reagents is an extraordinary degree of regioselectivity in the formation of the metalated enolate equivalent. These reactions proceed in general with a remarkable preference for the formation of the *syn*-configured [11] intermediate. Furthermore, reaction of such intermediates with electrophiles often also proceeds stereoselectively [12]. Asymmetric inductions in the

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course of reactions of metalated enolates of N-derivatives of carbonyl compounds have been reported for cases with and without a chiral auxiliary. Quantitative *syn*-axial alkylation of several configurationally fixed lithiated dimethylhydrazones have been reported in a number of cases [4, 5]. Fraser and Dhawan [10] have found the exclusive *syn*-axial alkylation of configurationally rigid methyl oxime ethers and Lyle et al. [9] have found axial alkylation of oxime dianions of cyclic ketones.

We have performed ab initio calculations of various isomeric forms of isolated carbanions of oximes and their ion pairs with lithium and sodium [13, 14] in order to model metalated oxime ethers. In this ab initio work we considered monomeric ion pairs because most recent discussions have assigned a primary role to the monomeric metalated species. X-ray crystallographic data, however, show aggregation of such (solvated) ion pairs to be a common feature in the solid state; thus, such aggregation may also play an important role in solution [15–17]. Ab initio calculations of aggregated and solvated ion pairs of such oxime carbanions require considerable amounts of computer time and calculations of this size remain gigantic tasks even with the availability of super-computers. These calculations can, however, be done with the semi-empirical MNDO method quite readily and the results should provide a good starting point for tackling such systems at the ab initio level. Here we report results of a semi-empirical investigation of solvent-free and solvated dimeric aggregates of lithium ion pairs of acetaldoxime. The dimers investigated are isomerically pure with respect to the CN bond, i.e., only dimers formed by the combination of either two *syn*- or two *anti*-monomers were considered [18]. The structures of the dimeric aggregates are discussed with regard to their influence on the stereochemical course of the addition of electrophiles.

METHODOLOGICAL ASPECTS

The semi-empirical MNDO method [19] was used with the lithium parametrization of Thiel and Clark [20]. MNDO has been shown to reproduce ab initio and experimental structures quite well in many cases [21]. The lithium parametrization, however, is associated with some deficiencies. It is well known, for example, that LiC bonds are indicated to be too strong [22, 23]. The lithium parameters are clearly a compromise that is not completely satisfactory. Nevertheless, large lithium systems are so important that even a less-than-perfect computational performance is of significant use. For our present study it was clearly important to calibrate the method by comparison of MNDO results with our ab initio calculations [13, 14].

Figure 1 shows the structures of the monomeric and unsolvated lithium ion pairs of *syn*- and *anti*-acetaldoximes, 1a and 2a, as obtained from complete MNDO optimizations. The ab initio structures (3-21+G) of these compounds, 1c and 2c, are shown for comparison. Selected structural parameters are given in Table 1. Optimization of the *anti*-configured ion pair 2 by MNDO

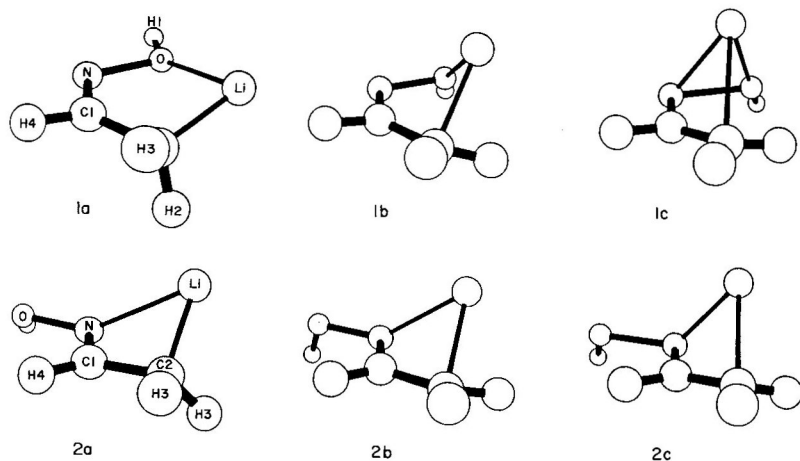


Fig. 1. The structures of the lithium ion pairs formed by the *syn*- and *anti*-carbanions of acetaldoxime, **1** and **2**, respectively. Structures were determined by complete (a) or partial (b) MNDO optimization (see text for details), and by (c) complete ab initio optimization (3-21+G).

and at the ab initio level indicates a η^3 coordination by lithium, but the MNDO optimization of the *syn*-isomer, **1a**, fails completely to reproduce the formal η^4 coordination. The structure **1a** is in fact very close to the ab initio transition-state structure for one of the possible racemization pathways of the chiral ion pair [24]. This unacceptable performance of the semi-empirical method is caused primarily by the severe pyramidalization of the carbanionic center that results in the breakdown of the pseudo- π -system of the anion and

TABLE 1

Selected structural parameters (in Å and degrees) for the lithium ion pairs formed by the *syn*- and the *anti*-acetaldoxime anions, **1** and **2**, as determined by complete MNDO (a), constrained MNDO (b) and ab initio (c) optimization

| Parameter | 1a | 1b | 1c | 2a | 2b | 2c |
|-----------|-------|-------|-------|-------|-------|-------|
| ON | 1.328 | 1.337 | 1.564 | 1.349 | 1.313 | 1.481 |
| NC | 1.320 | 1.364 | 1.378 | 1.338 | 1.389 | 1.349 |
| CC | 1.498 | 1.419 | 1.352 | 1.485 | 1.403 | 1.374 |
| ONC | 115.9 | 114.6 | 104.8 | 116.8 | 116.5 | 109.4 |
| NCC | 129.0 | 131.3 | 130.6 | 117.0 | 119.2 | 120.7 |
| LiO | 2.185 | 2.157 | 1.781 | 3.456 | 3.166 | 3.058 |
| LiN | 2.810 | 2.483 | 1.979 | 2.239 | 2.021 | 1.871 |
| LiC | 1.885 | 2.078 | 2.502 | 1.905 | 2.161 | 2.270 |
| LiCC | 100.1 | 79.5 | 63.6 | 85.9 | 74.4 | 69.2 |
| LiCCN | 14.9 | 47.5 | 41.9 | 32.0 | 38.3 | 37.0 |

artificial charge localization. Consequently, the MNDO calculations of **1** and **2** result in CC single bonds that are only slightly shorter than normal, and CN bond lengths that indicate CN double bonds. Moreover, pyramidalization at the carbanion carbon is accompanied by a rotation of the CH₂ group that results in orientation of the lone-pair orbital towards the lithium. In bonding situations containing several lone pairs, the direction of a single electron pair towards lithium along an internuclear axis is generally avoided whenever possible. Ab initio calculations of a variety of ion pairs provide strong evidence that lithium preferentially assumes positions in which at the same time maximal electrostatic attraction is assured and repulsion between lone-pair density and the lithium core electrons is avoided [25]. MNDO appears to embody only the first of these two factors and fails to account for the increased repulsion, introduced by the lithium core, associated with the placement of lithium directly at an oriented lone-pair.

Such artifacts are also observed in the determination of the structure of dimetalated oximes [26]. Similarly, McKee [23] found the global minimum of lithioacetaldehyde to have the lithium in close contact to carbon (C_s) and the correct global minimum was obtained only when the molecule was constrained to planarity. The underestimation of the carbon lone-pair–lithium core repulsion by MNDO may cause artifacts in other systems as well. For example, Lipkowitz and Burkett [27] studied the dimer of 7-norbornadienyllithium and found a global minimum in which the lithium atoms are located along the directional axes of the carbon lone-pairs. The structures suggested by Goldstein and Wenzel [28] appear, in fact, to be more reasonable as the lithium cations benefit from the electrostatic attraction to two carbon lone-pairs without suffering as much from lone-pair–lithium core repulsion. A comparable situation occurs from the dimer **10** (vide infra).

A great improvement in the agreement between the MNDO geometries and the ab initio structures is obtained when the following Kunstgriff [29] is applied. The ab initio calculations of the lithium ion pairs of acetaldoxime, **1c** and **2c**, show that the deprotonated carbon is only slightly pyramidalized. The relaxation pattern of the CCH₂ group upon ion-pair formation can be described to a good approximation as a small rotation of an essentially planar CCH₂ group around the CC axis. The direction of this rotation decreases the angle between the normal vector to the CCH₂ group and the C(H₂)–Li axis. We probed the potential of this idea by calculating the structures of **1** and **2** constraining the CCH₂ fragment to planarity. The results are shown in Fig. 1 as **1b** and **2b**, respectively. The position of the gegenion, characterized by the LiC bondlength, the LiCC angle and the LiCCN dihedral angle (see Table 1), is greatly improved. The delocalization of electron density within the pseudo- π system, not reflected in the completely optimized structures at all, manifests itself in significantly shortened CC bondlengths and increased CN bond distances. The LiC distances are increased by about 0.2 to 0.3 Å but still remain, especially in the *syn*-compound, too short, while the distances between the gegenion and the heteroatoms, although improved, remain

too long. As the interactions of lithium with nitrogen [30] and oxygen (vide infra), respectively, are satisfactory, the overestimated lithium—heteroatom distances are presumably caused by an additional limitation intrinsic to the MNDO method. Our ab initio calculations showed that the heteroatoms, and the nitrogen in particular, exhibit significant anionic character as a result of charge transfer within the carbanions [31]. As MNDO calculations are based on a minimal basis set and no augmentation by polarization functions is made, such charge transfer appears to be accounted for to an insufficient extent. Evidence for this statement stems also from the values of the ONC-angles. This angle is a sensitive parameter for the charge at nitrogen [14]. The MNDO derived values are all significantly larger than the angles obtained from ab initio calculations.

The interaction between a lithium cation and oxygen, important for the intramolecular chelation in the *syn* isomers as well as for the proper reproduction of solvation, is well accounted for by MNDO. The heats of hydration of the aquo complexes [32] $\text{Li}^+ \cdot n\text{OH}_2$ were found to be 31.3 (C_{2v} , $n = 1$), 59.8 (D_{2d} , $n = 2$) and 82.7 kcal mol⁻¹ (D_{3h} , $n = 3$), respectively, in excellent agreement with the experimental values obtained by high pressure mass spectroscopy [33]. The calculated equilibrium distances between lithium and the oxygen atom(s) are 2.05 Å, 2.06 Å and 2.10 Å, respectively; they are only slightly longer than high quality ab initio results [34].

Water molecules were used to model solvation. Only for the monomeric systems were the monohydrates, 3 (*syn*) and 4 (*anti*), and the dimethyl ether [35] solvated systems, 5 (*syn*) and 6 (*anti*), considered. Lithium is coordinated in a trigonal planar fashion in all of these cases. MNDO optimization does not give reasonable structures for the monosolvated ion-pairs; they can only be obtained when the geometry constraint proposed above is applied [36]. Major structural parameters for the monosolvated systems are summarized in Tables 2 (3 and 4) and 3 (5 and 6), respectively, and the hydrated species are shown in Fig. 2. Comparison of the data provided in Tables 2 and 3 shows that the structures of the ion-pairs are essentially invariant to the choice of either water or dimethyl ether as the solvent molecule. Solvation of the aggregates was therefore studied using water as the model for solvating molecules. This model should be a valid approximation to real solvation so long as the coordination of a solvent molecule is not affected by steric demands.

The errors associated with the heats of formation of the ion-pairs are large, because no compounds with NO bonds were used during the parametrization [17] and, more importantly, as a result of the deficiencies of the lithium parametrization. For example, the heats of formation [37] of 1b and 2b are -8.1 and -12.7 kcal mol⁻¹, respectively, and indicate the *anti*-isomer to be preferred by 4.6 kcal mol⁻¹. However, ab initio calculations [13] gave a *syn*-preference energy of 3.2 kcal mol⁻¹ at the 6-31+G*/3-21+G level. Similarly, the heats of formation of the monosolvated systems 3b–6b all indicate the *anti*-isomer to be more stable by about 4–4.5 kcal mol⁻¹,

TABLE 2

Selected structural parameters (in Å and degrees) for the monohydrates of the ion-pairs formed by lithium and the *syn*- or *anti*-carbanion of acetaldoxime, **3** and **4**, as determined by complete (a) and constrained (b) MNDO optimization

| Parameter | 3a | 3b | 4a | 4b |
|-----------|-------|-------|-------|-------|
| ON | 1.327 | 1.334 | 1.315 | 1.314 |
| NC | 1.322 | 1.369 | 1.344 | 1.389 |
| CC | 1.488 | 1.413 | 1.471 | 1.402 |
| ONC | 115.7 | 114.8 | 116.4 | 116.3 |
| NCC | 129.2 | 131.4 | 117.8 | 119.5 |
| LiO(sol) | 2.113 | 2.098 | 2.105 | 2.097 |
| LiO(H) | 2.222 | 2.196 | 3.452 | 3.187 |
| LiN | 2.826 | 2.475 | 2.262 | 2.054 |
| LiC | 1.914 | 2.120 | 1.941 | 2.183 |
| LiCC | 99.5 | 78.0 | 84.1 | 74.3 |
| LiCCN | 21.9 | 49.7 | 37.7 | 40.0 |

TABLE 3

Selected structural parameters (in Å and degrees) for the monoetherates of the ion-pairs formed by lithium and the *syn*- and *anti*-carbanions of acetaldoxime, **5** and **6**, as determined by complete (a) and constrained (b) MNDO optimization

| Parameter | 5a | 5b | 6a | 6b |
|-----------|-------|-------|-------|-------|
| ON | 1.327 | 1.334 | 1.316 | 1.314 |
| NC | 1.324 | 1.370 | 1.343 | 1.389 |
| CC | 1.486 | 1.421 | 1.471 | 1.401 |
| ONC | 115.5 | 114.9 | 116.3 | 116.2 |
| NCC | 129.1 | 131.2 | 117.8 | 119.5 |
| LiO(sol) | 2.132 | 2.108 | 2.116 | 2.107 |
| LiO(H) | 2.234 | 2.205 | 3.466 | 3.190 |
| LiN | 2.830 | 2.471 | 2.276 | 2.058 |
| LiC | 1.918 | 2.128 | 1.943 | 2.186 |
| LiCC | 99.3 | 77.7 | 84.4 | 74.3 |
| LiCCN | 24.1 | 50.2 | 38.1 | 40.2 |

whereas preliminary *ab initio* calculations of the systems **3** and **4** indicate that the *syn*-preference of the lithium ion pairs is preserved when one molecule of water is included in the calculation. The hydration enthalpies of 18.3 kcal mol⁻¹ of **3b** and **4b** appear to be reasonable [34]. A comparison of the relative stabilities of the various dimeric aggregates may lead to erroneous conclusions, but conclusions as to the importance of solvation may still be valid. The latter should be particularly true in cases where the structure of the unsolvated aggregate is essentially retained upon solvation.

In summary, the unacceptable discrepancies between the completely optimized MNDO and the *ab initio* structures are attributed to the overestimation of the pyramidalization at the carbanionic center introduced by the lithium

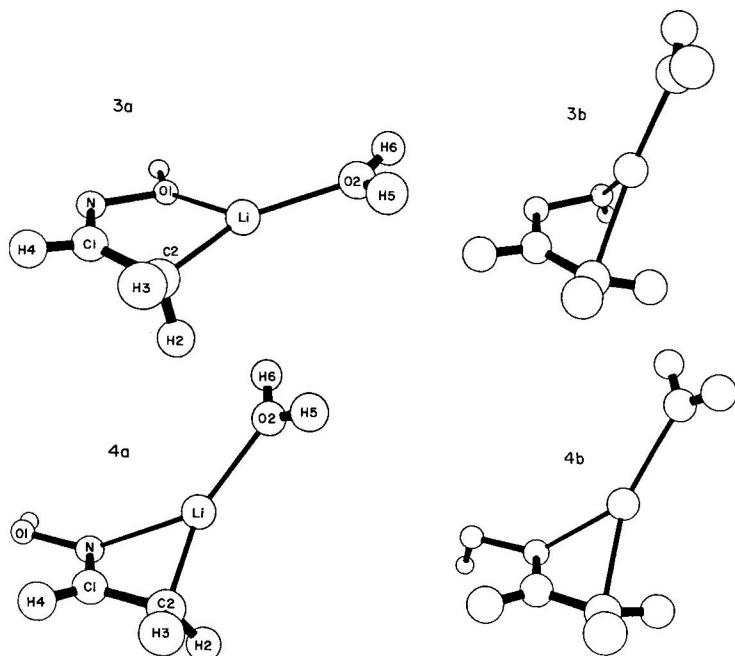


Fig. 2. The structures of the lithium ion-pairs formed by the *syn*- and *anti*-carbanions of acetaldoxime, 3 and 4, with inclusion of one water molecule as a model solvent. Structures were determined by complete (a) or partial (b) MNDO optimization.

parametrization and its consequences, and to the intrinsic limitation of the method to account adequately for strong internal charge transfer. The proposed Kunstgriff results in structures that are in better agreement with *ab initio* calculations. Solvation energies are reproduced quite well. Heats of formation of the ion-pairs, however, are associated with large errors and relative energies have to be interpreted with all necessary care dictated by the above discussion.

DIMERIC LITHIUM ION-PAIRS OF ACETALDOXIME

The structures of five solvent-free dimeric aggregates of the lithium ion-pairs of acetaldoxime, 7–11, and two solvated aggregates, 12 and 13, are presented. MNDO optimizations were performed without any constraints (method A) and under the constraint of keeping the CCH₂ fragment planar (method B). Structures obtained by method A (B) are shown on the right (left) side in the Figures. Major structural parameters of the ligands are summarized in Table 4. Important interatomic distances involving lithium are given in the Figures. A complete set of all the structures considered is given in the Appendix (Supplemental Material). The heats of formation are given in Table 5 and dimerization energies, solvation energies and relative stabilities are summarized in Table 6.

TABLE 4

Selected structural parameters (in Å and degrees) of the ligands in the dimeric aggregates

| Molecule | ON | NC | CC | ONC | NCC |
|-------------|-------|-------|-------|-------|-------|
| 7a | 1.328 | 1.357 | 1.426 | 119.3 | 132.3 |
| 7b | 1.327 | 1.375 | 1.399 | 118.9 | 132.1 |
| 8a, lig. I | 1.324 | 1.327 | 1.479 | 114.3 | 130.4 |
| 8a, lig. II | 1.327 | 1.431 | 1.506 | 114.7 | 128.3 |
| 8b, lig. I | 1.333 | 1.368 | 1.409 | 114.6 | 131.6 |
| 8b, lig. II | 1.330 | 1.338 | 1.476 | 115.2 | 130.5 |
| 9a, lig. I | 1.327 | 1.332 | 1.472 | 115.6 | 129.6 |
| 9a, lig. II | 1.329 | 1.337 | 1.473 | 115.6 | 128.1 |
| 9b, lig. I | 1.336 | 1.364 | 1.413 | 114.5 | 131.5 |
| 9b, lig. II | 1.335 | 1.389 | 1.410 | 115.4 | 130.5 |
| 10a | 1.312 | 1.330 | 1.512 | 116.8 | 119.3 |
| 10b | 1.318 | 1.368 | 1.420 | 115.4 | 121.0 |
| 11a | 1.329 | 1.370 | 1.418 | 117.1 | 121.6 |
| 11b | 1.328 | 1.381 | 1.398 | 116.2 | 122.4 |
| 12a | 1.326 | 1.355 | 1.422 | 119.4 | 132.7 |
| 12b | 1.324 | 1.37? | 1.397 | 118.2 | 131.8 |
| 13a | 1.314 | 1.332 | 1.496 | 116.2 | 120.3 |
| 13b | 1.321 | 1.367 | 1.414 | 114.9 | 121.4 |

TABLE 5

Heats of formation (in kcal mol⁻¹) of lithium ion-pair salts of acetaldoxime as determined by complete (a) and constrained (b) MNDO optimization

| Molecule ^{a,b} and point group | Heat of formation | |
|---|-------------------|--------|
| | a | b |
| 1 <i>syn</i> -X ⁻ Li ⁺ C ₁ | -21.1 | -8.1 |
| 2 <i>anti</i> -X ⁻ Li ⁺ C ₁ | -19.5 | -12.7 |
| 3 <i>syn</i> -X ⁻ Li ⁺ ·H ₂ O C ₁ | -98.2 | -87.3 |
| 4 <i>anti</i> -X ⁻ Li ⁺ ·H ₂ O C ₁ | -97.3 | -91.9 |
| 5 <i>syn</i> -X ⁻ Li ⁺ ·Me ₂ O C ₁ | -85.5 | -74.9 |
| 6 <i>anti</i> -X ⁻ Li ⁺ ·Me ₂ O C ₁ | -84.8 | -79.5 |
| 7 (<i>syn</i> -X ⁻ Li ⁺) ₂ C _i | -70.5 | -60.8 |
| 8 C ₁ | -57.8 | -46.6 |
| 9 C ₁ | -52.8 | -25.6 |
| 10 (<i>anti</i> -X ⁻ Li ⁺) ₂ C _i | -99.0 | -66.0 |
| 11 C _i | -68.6 | -61.4 |
| 12 (<i>syn</i> -X ⁻ Li ⁺) ₂ ·2H ₂ O C _i | -215.3 | -207.5 |
| 13 (<i>anti</i> -X ⁻ Li ⁺) ₂ ·2H ₂ O C _i | -237.1 | -213.0 |
| 14 <i>syn</i> -X ⁻ Li ⁺ ·2H ₂ O C ₁ | — | -159.4 |
| 15 <i>anti</i> -X ⁻ Li ⁺ ·2H ₂ O C ₁ | — | -164.3 |

^aHONCHCH₂ = X⁻. ^bH₂O in C_{2v}; O(CH₃)₂ was kept rigid in its C_{2v} structure.

TABLE 6

Relative stabilities, dimerization energies and solvation energies of monomeric and dimeric lithium ion-pairs of the isomeric carbanions of acetaldoxime as determined by MNDO (values in kcal mol⁻¹)

| Molecule | Dimerization ^a energy | | Solvation ^b energy | | Relative ^c stability | |
|----------|-------------------------------------|-------|----------------------------------|-------|------------------------------------|-------|
| | a | b | a | b | a | b |
| 1 | — | — | — | — | -21.1 | -8.1 |
| 2 | — | — | — | — | -19.5 | -12.7 |
| 3 | — | — | -16.2 | -18.3 | -37.3 | -26.4 |
| 4 | — | — | -16.9 | -18.3 | -36.4 | -31.0 |
| 5 | — | — | -13.2 | -15.5 | -34.2 | -23.6 |
| 6 | — | — | -14.1 | -15.5 | -33.6 | -28.3 |
| 7 | -14.2 | -22.3 | — | — | -35.3 | -30.4 |
| 8 | -7.9 | -15.2 | — | — | -28.9 | -23.3 |
| 9 | -5.3 | -9.6 | — | — | -26.4 | -17.8 |
| 10 | -30.0 | -20.3 | — | — | -49.5 | -33.0 |
| 11 | -14.8 | -18.0 | — | — | -34.3 | -30.7 |
| 12 | -9.5 | -16.4 | -11.5 | -12.4 | -46.7 | -42.8 |
| 13 | -21.2 | -14.6 | -8.1 | -12.6 | -57.6 | -45.6 |
| 14 | — | — | — | -29.3 | — | -37.5 |
| 15 | — | — | — | -29.7 | — | -42.4 |

^aDimerization energy: = $0.5 \cdot [H^0(\text{LiX} \cdot n \text{H}_2\text{O})_2 - 2 \cdot H^0(\text{LiX} \cdot n \text{H}_2\text{O})]$; $n = 0, 1$. ^bSolvation energy: = $m^{-1} \cdot [H^0(\text{LiX} \cdot n \text{E})_m - H^0(\text{LiX})_m - n \cdot m \cdot H^0(\text{E})]$; $n = 0, 1, 2$; $m = 1, 2$; $E = \text{H}_2\text{O}, \text{Me}_2\text{O}$. ^cRelative stability: = $m^{-1} \cdot [H^0(\text{LiX} \cdot n \text{E})_m - n \cdot m \cdot H^0(\text{E})]$; $n = 0, 1$; $m = 1, 2$; $E = \text{H}_2\text{O}, \text{Me}_2\text{O}$. ^dThe heat of formation of H_2O is -60.9 kcal mol⁻¹. ^eThe heat of formation of Me_2O is -51.2 kcal mol⁻¹.

Solvent-free dimeric aggregates

The most stable dimer formed by the *syn*-configured ion-pair, 1, was found to be the inversion symmetric structure 7 shown in Fig. 3. Li1 is trigonally coordinated by the carbanionic center of ligand I and the heteroatoms O2 and N2 of the second ligand. Repulsion between the lithium atoms (Li—Li in 7a, 3.93 Å; in 7b, 3.84 Å) causes the coordination around lithium to be non-planar. In contrast to the structures of the monomeric system, 7 exhibits significantly shorter LiN distances and increased LiO distances independent of the optimization procedure. In 7b the Li1—N2 distance is 2.10 Å and shorter than the shortest LiC contact of 2.11 Å, while the Li1—O2 distance is comparatively long at 2.44 Å. This finding is in good agreement with the electrostatic properties of the oxime carbanion [13]. The possibility for each lithium cation to coordinate strongly with one nitrogen atom and a carbanionic center of the other ligand, the centers of highest charge accumulation, reduces the importance of chelation by oxygen.

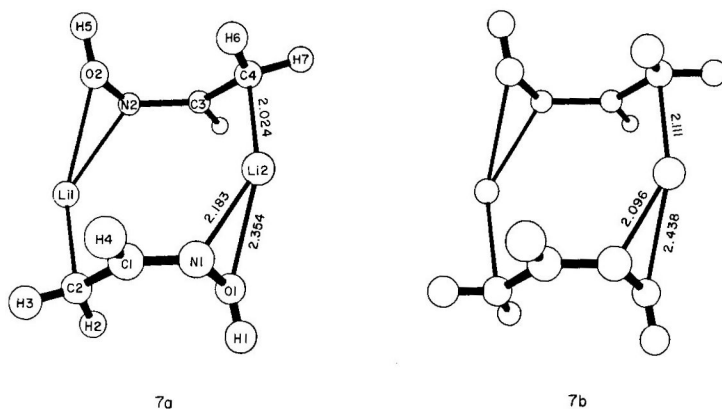


Fig. 3. The structure of the most stable dimeric aggregate of the *syn*-configured lithium ion-pair of the carbanion of acetaldoxime, **7**. Structures were determined by complete (a) or partial (b) MNDO optimization.

Two stack structures of **1** (Figs. 4 and 5) were found to be local minima. While the structures obtained for the methods A and B for the dimer **7** are not too different (the tendency for pyramidalization at the deprotonated carbon is reduced compared to the monomeric system), molecules **8a** and **9a** suffer severely from the discussed deficiencies and therefore only the structures obtained by method B are discussed. In **8b** the lithium of ion-pair I is additionally coordinated by the carbanionic center of the second ion-pair and a distorted tetrahedral coordination about lithium results. All the distances involving Li1 and atoms of ligand I are slightly increased as compared to the monomeric ion-pair. Additional coordination of Li1 by the nitrogen lone-pair of N2 characterizes the stack structure **9**. Such an arrangement was found by X-ray crystallography for a related lithium dimethylhydrazone [6]. The coordination of Li1 is surprisingly far from a tetrahedral arrangement. Attempts to find a local minimum with a more tetrahedral coordination were unsuccessful.

Both methods employed resulted in the same ordering of the relative stabilities (see Table 6) of these *syn*-dimers: **7** > **8** > **9**. The dimerization energy of **8** is undoubtedly overestimated, because an additional LiC contact is formed during aggregation. The relative ordering of the stack structures may therefore be inverted. Furthermore, the gap of 7.1 kcal mol⁻¹ in the relative energies of the cyclic dimer **7** and the stack structure **8** presumably represents only a lower limit. The possibility for **8** and **9** to form chiral helical polymers or, for **9** to form cyclic polymers, would increase the relative stabilities of the stack structures. However, the magnitude of the dimerization energies of **8** and **9** as compared to **7**, and the entropy factor in favor of the formation of small aggregates, suggest that higher aggregates of the stack-types are unlikely. Solvation is expected to reduce the probability for stack-type aggregates further. Stack polymers, whether cyclic or acyclic, always

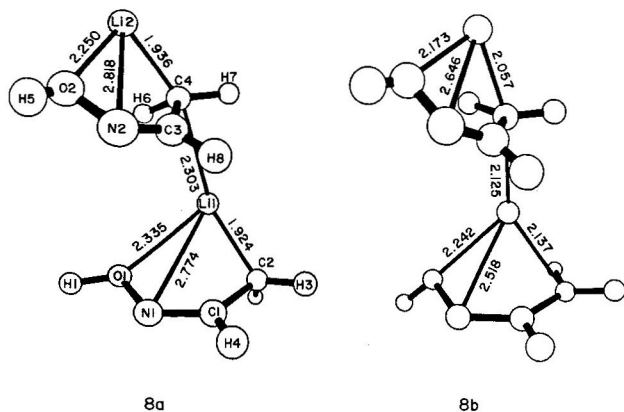


Fig. 4. The structure of the stack-type dimeric aggregate of the *syn*-configured lithium ion-pair of the carbanion of acetaldoxime that is characterized by an additional LiC contact, **8**. Structures were determined by complete (a) or partial (b) MNDO optimization.

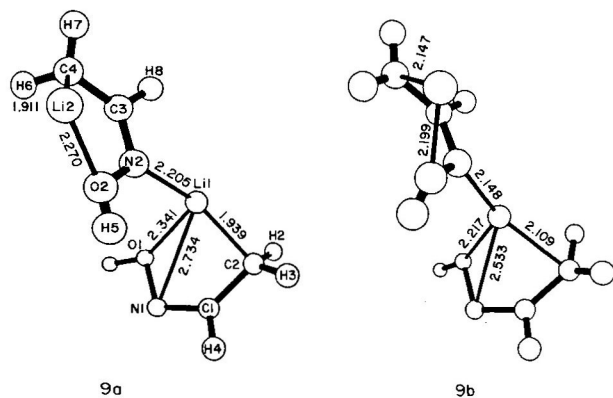


Fig. 5. The structure of the stack-type dimeric aggregate of the *syn*-configured lithium ion-pair of the carbanion of acetaldoxime that is characterized by an additional LiN contact, **9**. Structures were determined by complete (a) or partial (b) MNDO optimization.

contain tetra-coordinated lithium cations (except for the gegenion in the terminal monomeric unit of a non-cyclic polymer). Coordination of solvent molecules to these cations would be less effective as compared to a tris-coordinated lithium cation (as in **7**) and, most likely, would lead to fragmentation into smaller units. Stack-type aggregates of the *anti*-monomer **2** are unlikely for similar reasons and were not considered.

Two minima were found for aggregates composed of the *anti*-configured ion-pairs, **2**, and their structures, **10** and **11**, are shown in Figs. 6 and 7, respectively. Dimer **10** provides an extreme example of how misleading the results of an MNDO calculation can become when applied mechanically.

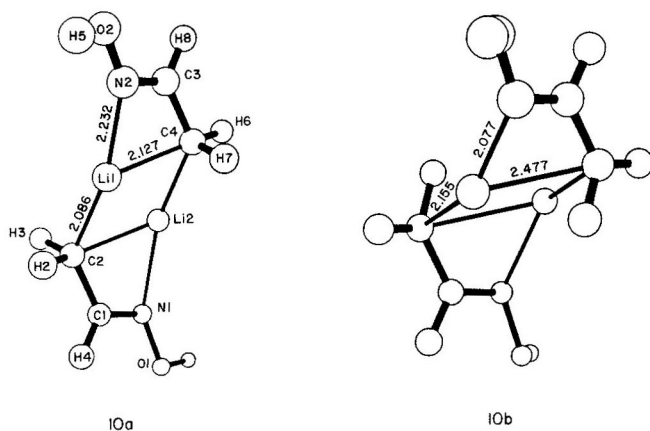


Fig. 6. The structure of the C_1 symmetric dimer of the lithium ion-pair of the *anti*-configured carbanion of acetaldoxime that is characterized by the four-membered ring formed by the lithiums and the carbanionic centers, **10**. Structures were determined by complete (a) or partial (b) MNDO optimization.

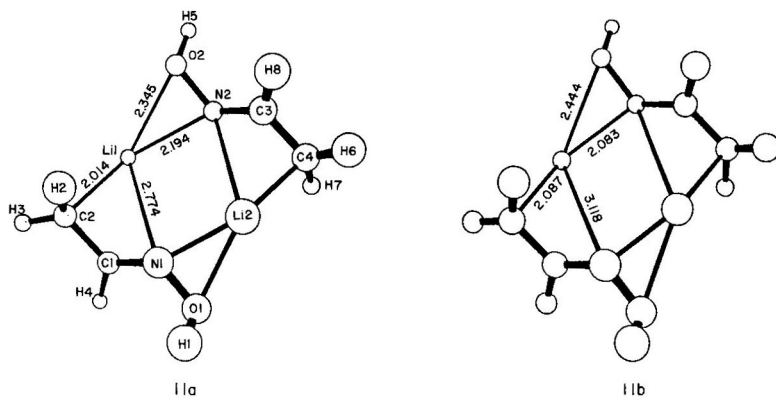


Fig. 7. The structure of the second C_1 symmetric dimer of the lithium ion-pair of the *anti*-configured carbanion of acetaldoxime, **11**. Structures were determined by complete (a) or partial (b) MNDO optimization.

This dimer, formed by the combination of two monomeric units with opposite chirality, contains a characteristic four-membered ring formed by the two lithium cations and the carbon atoms at the carbanionic centers. In **10a** each lithium is coordinated by the carbanionic carbon and the nitrogen atom of the same ligand and, in addition, by the CH_2 carbon of the other ligand; a trigonal and almost planar coordination around lithium results. The proximity of two lithium cations to the carbanionic centers, C2 and C4, causes

complete charge localization on the carbons. The CC bonds (1.51 Å) are the longest and the CN bonds (1.33 Å) are the shortest for all the molecules studied. The LiC distances are of comparable magnitude, 2.09 Å (Li1—C2) and 2.13 Å (Li2—C2), and the stabilization resulting from the four LiC contacts is apparently so strong as to outweigh the repulsion between the cations, which are only 2.16 Å apart. We regard this structure as a complete artifact of the MNDO lithium parametrization. A more reasonable structure, 10b, is obtained under the constraint of method B. The characteristic four-membered ring is preserved but the LiC bondlengths are increased to values of 2.16 Å (Li1—C2) and 2.48 Å (Li1—C4). As a consequence of these increased LiC distances and the non-planar coordination of lithium, the distance between the cations is increased to 2.72 Å.

The structure of the second dimer composed of monomer 2, 11, is comparatively less affected by the methods used. The shortest distances involving the Li1 atom are (in 11a) the Li1—C2 distance (2.01 Å), the Li1—N2 distance (2.19 Å) and the Li1—O2 distance (2.35 Å). The distance between the Li1 atom and N1 is 2.77 Å and suggests that this nitrogen might be engaged in coordination to both of the lithium cations. However, in 11b the Li1—N1 distance is increased to a value of 3.12 Å. The structure is probably best described as the *anti*-version of dimer 7; i.e., the lithium cations are trigonally coordinated by the carbanionic center of one of the ligands and by the heteroatoms of the other ligand. The Li—Li distance in 11b is 3.37 Å, essentially identical with the values of 3.38 Å in 11a. Dimer 11 is ranked as less stable than 10. However, this ranking is far from being established and, in fact, the opposite may be true. According to the heats of formation resulting from normal MNDO calculations, 10 is 15.2 kcal mol⁻¹ (per ion-pair) more stable than 11. If method B is used to correct, to a first approximation, for the inadequate description of the LiC contact, then 10 still remains favored, but only by 2.3 kcal mol⁻¹. Moreover, the fact that 10 contains twice the number of LiC contacts as compared to 11 suggests that 11 > 10 could be the correct ordering.

Solvated dimeric aggregates

The most stable solvated aggregate composed of two monomers of the *syn*-configured monomeric units, 7, was also considered with the inclusion of two water molecules, 12. Inversion symmetry, established for 7, was assumed for 12 and its structure is shown in Fig. 8. The structural parameters of the ligands are essentially unaffected by the presence of the water molecules (see Table 4) and the dimeric unit 7 remains virtually unchanged. The LiC and LiN distances are slightly increased (by 0.04 Å or less). Only the third coordination of lithium, the chelation by the oxime oxygen, becomes significantly less important. The water molecules cause an enhancement of the movement of the lithium atoms out of the plane defined by the heteroatoms of one ligand and the carbanionic center of the other ligand.

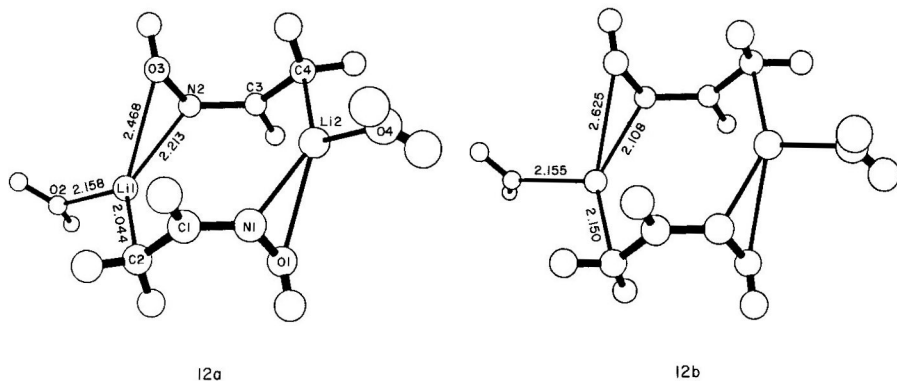


Fig. 8. Structure of the bis-solvated derivative of 7, **12**. Structures were determined by complete (a) or partial (b) MNDO optimization.

The solvent-free dimers **10** and **11** merge to one and the same solvated dimer **13** (Fig. 9). As above, inversion symmetry was assumed for the solvated *anti*-dimer **13**. The relation between **13** and **10** is obvious and similar methodological limitations apply. Only the structures derived with method B will therefore be considered. The characteristics of dimer **10** are retained in **13**. The water molecules cause the LiN and the Li2—C4 distances to be increased by 0.06 Å or less. Only the Li2—C2 and the Li1—C4 distances are increased by more than 0.1 Å. The increase of these bond lengths cause the skeleton of **13**, i.e., the eight-membered ring formed by the ligands and the cations, to be flattened out. As for **12**, the resulting coordination of lithium is close to tetrahedral geometry with one elongated and three short contacts. Our finding that the structures **10** and **11** merge into the same solvated structure can be rationalized quite readily. The comparison between **7** and **13** has shown that chelation of lithium by the hydroxy oxygen becomes less important in the presence of solvent molecules. As this chelation becomes less important one can easily envision that the ligand II of **11** (top in Fig. 7) would undergo a translation, approximately along the C3—N2 axis, to yield **10** or **13**, respectively. Chelation by the oxime oxygen is replaced by the newly formed coordination to a carbanionic center (Li2—C2 and Li1—C4, respectively).

The dimers **10**, **11** and **13** give rise to an interesting speculation. We have stated above that the MNDO ordering of the relative stabilities of the *anti*-dimers, $10 > 11$, may be erroneous. If indeed the ordering is $11 > 10$, then different structures of *anti*-dimers could exist depending on the reaction conditions. Under conditions that disfavor solvation (e.g., sterically demanding solvent or solvent with low nucleophilicity), a loose solvation would presumably result in formation of **11**-type aggregates, whereas a strongly coordinating solvent would favor the formation of aggregates of the type **13**.

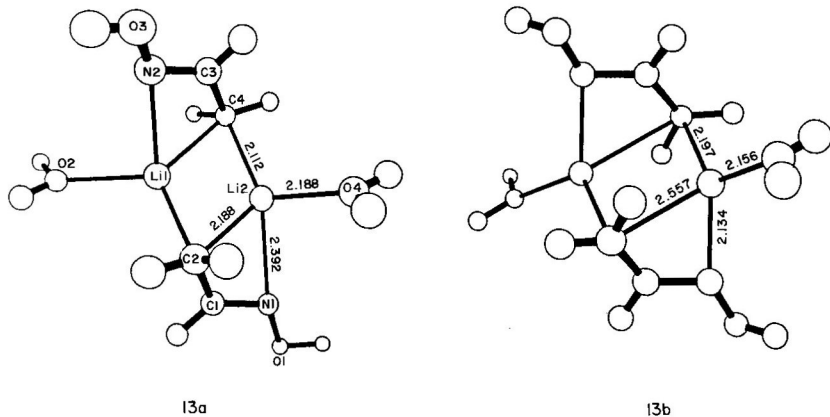


Fig. 9. Structure of the bis-solvated dimeric aggregate resulting from 10 and 11 upon inclusion of model solvent molecules into the calculation, 13. Structures were determined by complete (a) or partial (b) MNDO optimization.

The relative stability of solvated dimers vs. desolvated monomers

The values in Table 6 indicate that aggregation leads to large increases in the stabilities relative to the corresponding monomers or unsolvated species (Table 5). In order to assess the possibility that the solvated dimers 12 and 13 may play a role in solution, their relative stabilities can be compared to the relative stabilities of the corresponding bis-solvated monomers [38], 14 (*syn*) and 15 (*anti*), shown in Fig. 10. As dimerization of the bis-solvated monomers leads to dimers associated with four solvent molecules, the comparison of 14 (15) to 12 (13) neglects a small portion of the stabilization energy of the dimers and gives a lower limit for the preference, if any, of the aggregated species. Such a comparison needs to be done among energy values derived with method B (*vide supra*).

The relative stabilities of the bis-solvated monomers are $-37.5 \text{ kcal mol}^{-1}$ (14) and $-42.4 \text{ kcal mol}^{-1}$ (15), respectively, and the relative stabilities are $-42.8 \text{ kcal mol}^{-1}$ and $-45.6 \text{ kcal mol}^{-1}$ for the solvated aggregates 12 and 13, respectively. These values indicate the solvated dimers 12 and 13 to be favored over the bis-solvated monomers by $5.3 \text{ kcal mol}^{-1}$ and $3.2 \text{ kcal mol}^{-1}$, respectively. Although the number of short LiC contacts is preserved during aggregation and a cancellation of errors is possible, these numbers are certainly not large enough to allow a reliable conclusion as to the predominant species to be made, but they should rather be taken as an indication that aggregation may play a role. Clearly, *ab initio* calculations are needed to obtain quantitative data that will allow for such conclusions. These calculations are now being pursued.

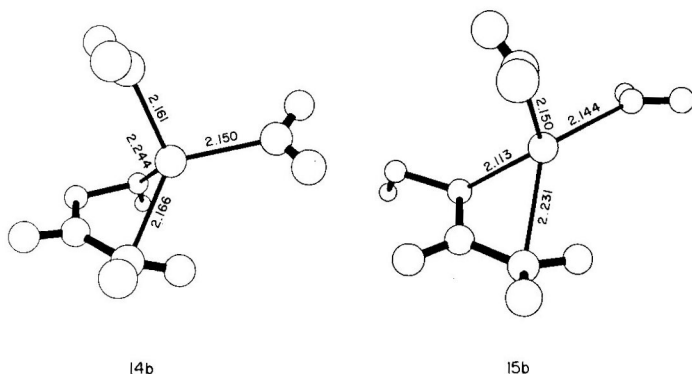


Fig. 10. The structures of the bis-solvated lithium ion-pairs of the *syn*- and *anti*-configured carbanions of acetaldoxime, 14 and 15. The structures were determined by MNDO optimization under the constraint of the CCH₂ fragments to planarity (method B, see text for details).

Mechanistic implications

The calculations presented indicate that aggregation of lithiated oxime ethers may be important at normal concentrations. Consequently, such species must be considered in discussions of reaction mechanism. For example, there is a minor dispute as to the facial preference of the entry of the electrophile in the presence of *syn*-axial alkylation [6, 8, 10]. Such discussions should also take into consideration monomeric ion-pairs and dimeric aggregates.

For the alkylation of a configurationally fixed oxime ether, e.g., 4-tert-butylcyclohexanoneoxime methyl ether, four possible pathways need a priori to be considered. Lithiation of the oxime ether results in two rapidly interconverting [14] enantiomeric ion-pairs; the gegenion can coordinate in either a *cisoid* (*c*) or a *transoid* (*t*) fashion with respect to the substituent in the 4 position. Each of these diastereomeric intermediates can be approached by the electrophile from either the coordinated (*syn*, *s*) side or the opposite (*anti*, *a*) side. Two of these pathways (*ta*, *cs*) result in equatorial alkylation and proceed through transition structures with boat-like conformations; they are therefore kinetically disfavored. Axial alkylation results either by entry of the electrophile on the coordination face of a *transoid* ion-pair (*ts* path) or by entry from the opposite side of the *cisoid* ion-pair (*ca* path). Both of these pathways involve conformationally favored chair-type transition states. Collum et al. [6] recently proposed a mechanism for the alkylation of closely related hydrazone derivatives; they argued that the presumed η^4 coordination would preclude entry of the electrophile from the coordinated face and, therefore, the observed *trans* stereochemistry with axial entry of the electrophile requires an attack opposite the side of metal coordination (the *ca* path). Our *ab initio* structures, however, show that the

reacting carbanion is only weakly coordinated to the cation with a rather long bondlength. Reaction from the *syn* side should not be seriously impeded. Indeed, such a reaction (the *ts* path) should be favored over the alternative *ca* pathway because precoordination can place the nucleofug of the electrophilic reagent close to the cation of the metalated intermediate and lower the energy of the reaction transition state.

This situation could change if the reacting species is a dimeric aggregate. In the dimers found in the present study the lithium is more fully coordinated and precoordination of the electrophile is perhaps less important. This factor, if of dominating importance, could lead to a preference for the *ca* pathway. On the other hand, the carbanion carbon is now more fully a part of the lithium coordination and may be less reactive. Furthermore, precoordination to a dimeric aggregate places the electrophile R^+ in a significantly worse position with respect to the carbanionic center than in the case of precoordination to a monomeric ion-pair. Such precoordination to the aggregate does not allow the electrophile to approach the carbanionic center. Structural reorganization is necessary in the dimer to lead to a better positioning of the electrophile and would involve at least partial fragmentation of the aggregate with concomitant energy increase. In contrast, in the monomeric ion-pair the cation is placed in a central position above the face of the ligand, thus allowing the electrophile to approach closely towards the reactive center of the ligand. Thus, there is no apparent advantage of the dimer over monomer in reaction of these metalated systems with an electrophile.

SUMMARY

Several structures of solvent-free and solvated dimeric aggregates of lithium ion-pair salts of isomeric acetaldoximes were presented as models for lithiated oxime ethers. Complete structural optimizations by MNDO revealed methodological deficiencies, which have been accounted for in part by constraining the CCH_2 fragments of the oxime anions to planarity. Comparison of *ab initio* data to MNDO results show this constraint to effectively reduce these deficiencies. The inversion-symmetric solvated dimers **12** and **13**, formed by the association of two enantiomeric units of **1** or **2**, respectively, were shown to be the most stable dimers. Larger aggregates, such as helical acyclic or cyclic polymers, are less likely. Comparison of the relative stabilities of **12** and **13** to the bis-solvated monomers **14** and **15**, respectively, indicates the dimeric aggregates to be preferred by 5.3 and 3.2 kcal mol⁻¹, respectively. A definitive conclusion as to the predominance of monomeric or dimeric ion-pairs cannot be made because of the methodological deficiencies of the MNDO method with lithium compounds. The results presented indicate that aggregation may occur and suggest that such aggregates be considered in mechanistic studies. Some stereochemical implications with regard to the addition of electrophiles to dimeric metalated oxime ethers of 4 substituted cyclohexanones have been discussed. Axial entry of the

electrophile, proceeding via a chair-type transition state and therefore preferred over the equatorial entry, can occur either on the coordinated face of the metalated intermediate (*ts* path) or from the opposite face (*ca* path). It is suggested that monomeric ion-pairs in general involve such *syn* reaction. This pathway could become less likely if dimeric aggregates are the reactive species but no advantage of such species is apparent in reaction with electrophiles.

ACKNOWLEDGEMENT

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APPENDIX

Optimized geometries (in Å and degrees) and heats of formation (in kcal mol⁻¹).

syn-HON=CH-CH₂ Li⁺, C₁, 1.

MNDO, 1a.

Heat of formation = -21.05 kcal mol⁻¹.

| Center | Bond length | with | Angle | with | Dihedral | with |
|--------|-------------|------|---------|------|----------|------|
| N | — | — | — | — | — | — |
| C1 | 1.320 | N | — | — | — | — |
| O | 1.328 | N | 115.892 | C1 | — | — |
| H1 | 0.954 | O | 108.053 | N | 175.629 | C1 |
| C2 | 1.498 | C1 | 129.037 | N | -2.516 | O |
| H2 | 1.119 | C2 | 109.700 | C1 | -95.493 | N |
| H3 | 1.109 | C2 | 110.195 | C1 | 146.537 | N |
| H4 | 1.104 | C1 | 112.830 | N | 177.002 | O |
| Li | 1.885 | C2 | 100.134 | C1 | 14.882 | N |

MNDO, CCH₂ group constrained to planarity, 1b.

Heat of formation = -8.14 kcal mol⁻¹.

| Center | Bond length | with | Angle | with | Dihedral | with |
|--------|-------------|------|---------|------|----------|------|
| N | — | — | — | — | — | — |
| C1 | 1.364 | N | — | — | — | — |
| O | 1.337 | N | 114.588 | C1 | — | — |
| H1 | 0.952 | O | 109.633 | N | 138.558 | C1 |
| C2 | 1.419 | N | 131.305 | N | -5.140 | O |
| H2 | 1.111 | C2 | 126.052 | C1 | -15.159 | N |
| H3 | 1.094 | C2 | 119.712 | C1 | 180.000 | H2 |
| H4 | 1.107 | C1 | 111.214 | N | 175.541 | O |
| Li | 2.078 | C2 | 79.509 | C1 | 47.502 | N |

MNDO/ab initio, 1c.

Heat of formation = 29.00 kcal mol⁻¹.

| Center | Bond length | with | Angle | with | Dihedral | with |
|--------|-------------|------|---------|------|----------|------|
| N | — | — | — | — | — | — |
| C1 | 1.378 | N | — | — | — | — |
| O | 1.564 | N | 104.816 | C1 | — | — |
| H1 | 0.962 | O | 106.504 | N | 135.066 | C1 |
| C2 | 1.352 | C1 | 130.591 | N | 5.237 | O |
| H2 | 1.072 | C2 | 121.883 | C1 | -16.766 | N |
| H3 | 1.073 | C2 | 119.430 | C1 | 175.085 | N |
| H4 | 1.077 | C1 | 109.031 | N | 177.800 | O |
| Li | 2.052 | C2 | 63.593 | C1 | 41.876 | N |

anti-HON=CH-CH₂⁻ Li⁺, C₁, 2.

MNDO, 2a.

Heat of formation = -19.48 kcal mol⁻¹.

| Center | Bond length | with | Angle | with | Dihedral | with |
|--------|-------------|------|---------|------|----------|------|
| N | — | — | — | — | — | — |
| C1 | 1.338 | N | — | — | — | — |
| O | 1.313 | N | 116.751 | C1 | — | — |
| H1 | 0.958 | O | 107.984 | N | 194.348 | C1 |
| C2 | 1.485 | C1 | 116.984 | N | 178.308 | O |
| H2 | 1.115 | C2 | 113.542 | C1 | -68.994 | N |
| H3 | 1.103 | C2 | 112.546 | C1 | 116.653 | N |
| H4 | 1.103 | C1 | 123.182 | N | -2.758 | O |
| Li | 1.905 | C2 | 85.858 | C1 | 32.022 | N |

MNDO, CCH₂ group constrained to planarity, 2b.Heat of formation = -12.71 kcal mol⁻¹.

| Center | Bond length | with | Angle | with | Dihedral | with |
|--------|-------------|------|---------|------|----------|------|
| N | — | — | — | — | — | — |
| C1 | 1.389 | N | — | — | — | — |
| O | 1.313 | N | 116.511 | C1 | — | — |
| H1 | 0.961 | O1 | 108.897 | N | 247.466 | C1 |
| C2 | 1.403 | C1 | 119.183 | N | 175.424 | O |
| H2 | 1.113 | C2 | 125.923 | C1 | -13.040 | N |
| H3 | 1.091 | C2 | 120.301 | C1 | 180.000 | H2 |
| H4 | 1.103 | C1 | 121.448 | N | -3.082 | O1 |
| Li | 2.161 | C2 | 74.367 | C1 | 38.274 | N |

MNDO/ab initio, **2c**.Heat of formation = 8.76 kcal mol⁻¹.

| Center | Bond length | with | Angle | with | Dihedral | with |
|--------|-------------|------|---------|------|----------|------|
| N | — | — | — | — | — | — |
| C1 | 1.349 | N | — | — | — | — |
| O | 1.481 | N | 109.440 | C1 | — | — |
| H1 | 0.967 | O | 105.224 | N | 233.050 | C1 |
| C2 | 1.374 | C1 | 120.660 | N | 184.574 | O |
| H2 | 1.081 | C2 | 120.370 | C1 | -27.069 | N |
| H3 | 1.071 | C2 | 120.094 | C1 | 173.648 | N |
| H4 | 1.077 | C1 | 117.779 | N | -3.568 | O |
| Li | 2.270 | C2 | 69.217 | C1 | 37.039 | N |

syn-HON=CH-CH₂ Li⁺·OH₂, C₁, H₂O in C_{2v}, **3**.MNDO, **3a**.Heat of formation = -98.20 kcal mol⁻¹.

| Center | Bond length | with | Angle | with | Dihedral | with |
|--------|-------------|------|---------|------|----------|------|
| N | — | — | — | — | — | — |
| C1 | 1.323 | N | — | — | — | — |
| O1 | 1.327 | N | 115.673 | C1 | — | — |
| H1 | 0.954 | O1 | 107.979 | N | 174.084 | C1 |
| C2 | 1.488 | C1 | 129.193 | N | -3.424 | O1 |
| H2 | 1.120 | C2 | 110.808 | C1 | -83.301 | N |
| H3 | 1.107 | C2 | 110.915 | C1 | 157.097 | N |
| H4 | 1.104 | C1 | 112.631 | N | 175.646 | O1 |
| Li | 1.914 | C2 | 99.455 | C1 | 21.863 | N |
| O2 | 2.113 | Li | 152.428 | N | 34.339 | O1 |
| H5 | 0.944 | O2 | 123.043 | Li | 161.415 | N |
| H6 | 0.944 | O2 | 108.089 | H5 | 178.777 | Li |

MNDO, CCH₂ group constrained to planarity, **3b**.Heat of formation = -87.35 kcal mol⁻¹.

| Center | Bond length | with | Angle | with | Dihedral | with |
|--------|-------------|------|---------|------|----------|------|
| N | — | — | — | — | — | — |
| C1 | 1.369 | N | — | — | — | — |
| O1 | 1.334 | N | 114.848 | C1 | — | — |
| H1 | 0.954 | O1 | 125.584 | N | 288.895 | C1 |
| C2 | 1.413 | C1 | 131.361 | N | -4.551 | O1 |
| H2 | 1.109 | C2 | 126.233 | C1 | -12.008 | N |
| H3 | 1.093 | C2 | 119.802 | C1 | 180.000 | N |
| H4 | 1.107 | C1 | 111.128 | N | 176.463 | O1 |
| Li | 2.120 | C2 | 78.009 | C1 | 49.655 | N |
| O2 | 2.098 | Li | 140.292 | N | 88.313 | O1 |
| H5 | 0.944 | O2 | 126.962 | Li | 142.025 | N |
| H6 | 0.944 | O2 | 108.170 | H5 | 175.760 | Li |

MNDO, HONCHCH₂Li in ab initio structure, 3c.Heat of formation = -48.60 kcal mol⁻¹.

| Center | Bond length | with | Angle | with | Dihedral | with |
|--------|-------------|------|---------|------|----------|------|
| N | — | — | — | — | — | — |
| C1 | 1.378 | N | — | — | — | — |
| O1 | 1.564 | N | 104.816 | C1 | — | — |
| H1 | 0.962 | O1 | 106.504 | N | -135.066 | C1 |
| C2 | 1.352 | C1 | 130.591 | N | -5.237 | O1 |
| H2 | 1.072 | C2 | 121.883 | C1 | 16.766 | N |
| H3 | 1.073 | C2 | 119.430 | C1 | -175.085 | N |
| H4 | 1.077 | C1 | 109.031 | N | -177.800 | O1 |
| Li | 2.502 | C2 | 63.593 | C1 | -41.876 | N |
| O2 | 2.114 | Li | 145.128 | N | -130.725 | O1 |
| H5 | 0.944 | O2 | 126.087 | Li | -88.840 | N |
| H6 | 0.944 | O2 | 107.885 | H5 | -168.629 | Li |

anti-HON=CH-CH₂ Li⁺·OH₂, C₁, H₂O in C_{2v}, 4.

MNDO, 4a.

Heat of formation = -97.34 kcal mol⁻¹.

| Center | Bond length | with | Angle | with | Dihedral | with |
|--------|-------------|------|---------|------|----------|------|
| N | — | — | — | — | — | — |
| C1 | 1.344 | N | — | — | — | — |
| O1 | 1.315 | N | 116.359 | C1 | — | — |
| H1 | 0.958 | O1 | 107.753 | N | -160.664 | C1 |
| C2 | 1.471 | C1 | 117.814 | N | 178.947 | O1 |
| H2 | 1.114 | C2 | 115.438 | C1 | -58.149 | N |
| H3 | 1.101 | C2 | 113.593 | C1 | 173.904 | N |
| H4 | 1.104 | C1 | 122.824 | N | -2.428 | O1 |
| Li | 1.941 | C2 | 84.143 | C1 | 37.651 | N |
| O2 | 2.105 | Li | 138.624 | N | -38.141 | O1 |
| H5 | 0.944 | O2 | 127.031 | Li | -4.688 | N |
| H6 | 0.944 | O2 | 108.146 | H5 | 179.601 | Li |

MNDO, CCH₂ group constrained to planarity, 4b.Heat of formation = -91.91 kcal mol⁻¹.

| Center | Bond length | with | Angle | with | Dihedral | with |
|--------|-------------|------|---------|------|----------|------|
| N | — | — | — | — | — | — |
| C1 | 1.389 | N | — | — | — | — |
| O1 | 1.314 | N | 116.293 | C1 | — | — |
| H1 | 0.961 | O1 | 117.479 | N | 82.230 | C1 |
| C2 | 1.402 | C1 | 119.516 | N | 175.720 | O1 |
| H2 | 1.111 | C2 | 125.896 | C1 | -11.331 | N |
| H3 | 1.091 | C2 | 120.291 | C1 | 180.000 | H2 |
| H4 | 1.104 | C1 | 121.363 | N | -2.370 | O1 |
| Li | 2.183 | C2 | 74.296 | C1 | 39.969 | N |
| O2 | 2.097 | Li | 141.822 | N | -32.319 | O1 |
| H5 | 0.944 | O2 | 123.061 | Li | -3.056 | N |
| H6 | 0.944 | O2 | 108.161 | H5 | 180.617 | Li |

MNDO, HONCHCH₂Li in ab initio structure, 4c.

Heat of formation = -69.82 kcal mol⁻¹.

| Center | Bond length | with | Angle | with | Dihedral | with |
|--------|-------------|------|---------|------|----------|------|
| N | — | — | — | — | — | — |
| C1 | 1.349 | N | — | — | — | — |
| O1 | 1.481 | N | 109.440 | C1 | — | — |
| H1 | 0.967 | O1 | 105.224 | N | 126.999 | C1 |
| C2 | 1.374 | C1 | 120.660 | N | 175.425 | O1 |
| H2 | 1.081 | C2 | 120.370 | C1 | 27.069 | N |
| H3 | 1.071 | C2 | 120.094 | C1 | -173.648 | N |
| H4 | 1.077 | C1 | 117.779 | N | -3.568 | O1 |
| Li | 2.270 | C2 | 69.217 | C1 | -37.039 | N |
| O2 | 2.110 | Li | 139.843 | N | 54.430 | O1 |
| H5 | 0.944 | O2 | 124.954 | Li | -42.349 | N |
| H6 | 0.944 | O2 | 108.113 | H5 | -169.663 | Li |

syn-HON=CH-CH₂ Li⁺·O(CH₃)₂, C₁, 5.

MNDO, CH₃OCH₃ in its optimized C_s structure, 5a.

Heat of formation = -85.47 kcal mol⁻¹.

| Center | Bond length | with | Angle | with | Dihedral | with |
|--------|-------------|------|---------|------|----------|------|
| N | — | — | — | — | — | — |
| C1 | 1.324 | N | — | — | — | — |
| O1 | 1.327 | N | 115.530 | C1 | — | — |
| H1 | 0.954 | O1 | 108.020 | N | 172.965 | C1 |
| C2 | 1.486 | C1 | 129.100 | N | -3.627 | O1 |
| H2 | 1.119 | C2 | 111.097 | C1 | -80.224 | N |
| H3 | 1.107 | C2 | 111.081 | C1 | 159.772 | N |
| H4 | 1.104 | C1 | 112.684 | N | 175.391 | O1 |
| Li | 1.918 | C2 | 99.267 | C1 | 24.130 | N |
| O2 | 2.132 | Li | 209.796 | N | -137.619 | O1 |
| C3 | 1.396 | O2 | 113.549 | Li | 167.964 | N |
| C4 | 1.396 | O2 | 119.868 | C3 | 176.080 | Li |
| H5 | 1.116 | C3 | 107.323 | O2 | 180.000 | C4 |
| H6 | 1.116 | C4 | 107.323 | O2 | 180.000 | C3 |
| H7 | 1.118 | C3 | 112.604 | O2 | 118.923 | H5 |
| H8 | 1.118 | C3 | 112.604 | O2 | -118.923 | H5 |
| H9 | 1.118 | C4 | 112.604 | O2 | 118.923 | H6 |
| H10 | 1.118 | C4 | 112.604 | O2 | -118.923 | H6 |

MNDO, CCH₂ group constrained to planarity, CH₃OCH₃ in its optimized C_s structure, 5b.

Heat of formation = -74.85 kcal mol⁻¹.

| Center | Bond length | with | Angle | with | Dihedral | with |
|--------|-------------|------|---------|------|----------|------|
| N | — | — | — | — | — | — |
| C1 | 1.370 | N | — | — | — | — |
| O1 | 1.334 | N | 114.860 | C1 | — | — |
| H1 | 0.954 | O1 | 110.203 | N | 122.929 | C1 |
| C2 | 1.412 | C1 | 131.233 | N | -4.344 | O1 |

| Center | Bond length | with | Angle | with | Dihedral | with |
|--------|-------------|------|---------|------|----------|------|
| H2 | 1.110 | C2 | 126.212 | C1 | -11.432 | N |
| H3 | 1.093 | C2 | 119.849 | C1 | 180.000 | H2 |
| H4 | 1.107 | C1 | 111.160 | N | 176.543 | O1 |
| Li | 2.128 | C2 | 77.664 | C1 | 50.240 | N |
| O2 | 2.108 | Li | 218.624 | N | -91.372 | O1 |
| C3 | 1.396 | O2 | 123.207 | Li | 182.543 | N |
| C4 | 1.396 | O2 | 119.868 | C3 | 179.584 | Li |
| H5 | 1.116 | C3 | 107.323 | O2 | 180.000 | C4 |
| H6 | 1.116 | C4 | 107.323 | O2 | 180.000 | C3 |
| H7 | 1.118 | C3 | 112.604 | O2 | 118.923 | H5 |
| H8 | 1.118 | C3 | 112.604 | O2 | -118.923 | H5 |
| H9 | 1.118 | C4 | 112.604 | O2 | 118.923 | H6 |
| H10 | 1.118 | C4 | 112.604 | O2 | -118.923 | H6 |

anti-HON=CH-CH₂ Li⁺·O(CH₃)₂, C₁, **6**.

MNDO, C₁, CH₃OCH₃ in its optimized C_s structure, **6a**.

Heat of formation = -84.79 kcal mol⁻¹.

| Center | Bond length | with | Angle | with | Dihedral | with |
|--------|-------------|------|---------|------|----------|------|
| N | — | — | — | — | — | — |
| C1 | 1.343 | N | — | — | — | — |
| O1 | 1.315 | N | 116.327 | C1 | — | — |
| H1 | 0.958 | O1 | 107.745 | N | 198.971 | C1 |
| C2 | 1.471 | C1 | 117.842 | N | 178.789 | O1 |
| H2 | 1.114 | C2 | 115.329 | C1 | -58.170 | N |
| H3 | 1.101 | C2 | 113.554 | C1 | 174.069 | N |
| H4 | 1.104 | C1 | 122.902 | N | -2.512 | O1 |
| Li | 1.943 | C2 | 84.436 | C1 | 38.076 | N |
| O2 | 2.116 | Li | 138.021 | N | -41.286 | O1 |
| C3 | 1.396 | O2 | 123.041 | Li | 0.653 | N |
| C4 | 1.396 | O2 | 119.868 | C3 | 178.708 | Li |
| H5 | 1.116 | C3 | 107.323 | O2 | 180.000 | C4 |
| H6 | 1.116 | C4 | 107.323 | O2 | 180.000 | C3 |
| H7 | 1.118 | C3 | 112.604 | O2 | 118.923 | H5 |
| H8 | 1.118 | C3 | 112.604 | O2 | -118.923 | H5 |
| H9 | 1.118 | C4 | 112.604 | O2 | 118.923 | H6 |
| H10 | 1.118 | C4 | 112.604 | O2 | -118.923 | H6 |

MNDO, CCH₂ group constrained to planarity, CH₃OCH₃ in its optimized C_s structure, **6b**.

Heat of formation = -79.48 kcal mol⁻¹.

| Center | Bond length | with | Angle | with | Dihedral | with |
|--------|-------------|------|---------|------|----------|------|
| N | — | — | — | — | — | — |
| C1 | 1.389 | N | — | — | — | — |
| O1 | 1.314 | N | 116.244 | C1 | — | — |
| H1 | 0.961 | O1 | 108.803 | N | 248.011 | C1 |
| C2 | 1.401 | C1 | 119.521 | N | 175.686 | O1 |
| H2 | 1.111 | C2 | 125.850 | C1 | -11.115 | N |
| H3 | 1.091 | C2 | 120.304 | C1 | 180.000 | H2 |

| Center | Bond length | with | Angle | with | Dihedral | with |
|--------|-------------|------|---------|------|----------|------|
| H4 | 1.104 | C1 | 121.332 | N | -2.380 | O1 |
| Li | 2.186 | C2 | 74.306 | C1 | 40.205 | N |
| O2 | 2.107 | Li | 143.336 | N | -33.586 | O1 |
| C3 | 1.396 | O2 | 114.856 | Li | -9.077 | N |
| C4 | 1.396 | O2 | 119.868 | C3 | 181.084 | Li |
| H5 | 1.116 | C3 | 107.323 | O2 | 180.000 | C4 |
| H6 | 1.116 | C4 | 107.323 | O2 | 180.000 | C3 |
| H7 | 1.118 | C3 | 112.604 | O2 | 118.923 | H5 |
| H8 | 1.118 | C3 | 112.604 | O2 | -118.923 | H5 |
| H9 | 1.118 | C4 | 112.604 | O2 | 118.923 | H6 |
| H10 | 1.118 | C4 | 112.604 | O2 | -118.923 | H6 |

Dimer of *syn*-HON=CH-CH₂; Li⁺, C₁, 7.

MNDO, 7a.

Heat of formation = -70.53 kcal mol⁻¹.

Inversion center: $x = 0.625$, $y = 0.355$, $z = 1.922$.

| Center | Bond length | with | Angle | with | Dihedral | with |
|--------|-------------|------|---------|------|----------|------|
| N | — | — | — | — | — | — |
| C1 | 1.357 | N | — | — | — | — |
| O | 1.328 | N | 119.306 | C1 | — | — |
| H1 | 0.958 | O | 111.228 | N | 91.106 | C1 |
| C2 | 1.426 | C1 | 132.343 | N | 2.512 | O |
| H2 | 1.105 | C2 | 120.512 | C1 | -14.991 | N |
| H3 | 1.105 | C2 | 116.500 | C1 | 204.367 | N |
| H4 | 1.111 | C1 | 110.569 | N | 183.439 | O |
| Li | 2.024 | C2 | 93.341 | C1 | 93.246 | N |

MNDO, CCH₂ group constrained to planarity, 7b.

Heat of formation = -60.78 kcal mol⁻¹.

Inversion center: $x = 0.740$, $y = 0.126$, $z = 1.896$.

| Center | Bond length | with | Angle | with | Dihedral | with |
|--------|-------------|------|---------|------|----------|------|
| N | — | — | — | — | — | — |
| C1 | 1.375 | N | — | — | — | — |
| O | 1.327 | N | 118.858 | C1 | — | — |
| H1 | 0.960 | O | 110.841 | N | 91.181 | C1 |
| C2 | 1.399 | C1 | 132.100 | N | -1.018 | O |
| H2 | 1.102 | C2 | 124.669 | C1 | 8.243 | N |
| H3 | 1.105 | C2 | 120.583 | C1 | 180.000 | H2 |
| H4 | 1.114 | C1 | 110.050 | N | 185.127 | O |
| Li | 2.111 | C2 | 87.755 | C1 | 100.689 | N |

Dimer of *syn*-HON=CH—CH₂ Li⁺, C₁, **8**.

MNDO, **8a**.

Heat of formation = -57.82 kcal mol⁻¹.

| Center | Bond length | with | Angle | with | Dihedral | with |
|--------|-------------|------|---------|------|----------|------|
| N1 | — | — | — | — | — | — |
| C1 | 1.328 | N1 | — | — | — | — |
| O1 | 1.324 | N1 | 114.281 | C1 | — | — |
| H1 | 0.955 | O1 | 107.906 | N1 | 170.740 | C1 |
| C2 | 1.479 | C1 | 130.352 | N1 | -1.225 | O1 |
| H2 | 1.115 | C2 | 112.486 | C1 | -65.742 | N1 |
| H3 | 1.105 | C2 | 111.454 | C1 | 171.378 | N1 |
| H4 | 1.106 | C1 | 111.847 | N1 | 176.898 | O1 |
| Li1 | 1.924 | C2 | 93.309 | C1 | 38.940 | N1 |
| N2 | 4.201 | N1 | 97.687 | C1 | 104.958 | H4 |
| C3 | 1.331 | N2 | 69.723 | N1 | 37.634 | C1 |
| O2 | 1.327 | N2 | 114.703 | C3 | -118.179 | N1 |
| H5 | 0.955 | O2 | 108.739 | N2 | 168.483 | C3 |
| C4 | 1.506 | C3 | 128.338 | N2 | -6.268 | O2 |
| H6 | 1.131 | C4 | 117.945 | C3 | -63.090 | N2 |
| H7 | 1.120 | C4 | 114.795 | C3 | 162.229 | N2 |
| H8 | 1.121 | C3 | 113.131 | N2 | 170.355 | O2 |
| Li2 | 1.936 | C4 | 96.321 | C3 | 33.742 | N2 |

MNDO, CCH₂ group constrained to planarity, **8b**.

Heat of formation = -46.64 kcal mol⁻¹.

| Center | Bond length | with | Angle | with | Dihedral | with |
|--------|-------------|------|---------|------|----------|------|
| N1 | — | — | — | — | — | — |
| C1 | 1.368 | N1 | — | — | — | — |
| O1 | 1.333 | N1 | 114.569 | C1 | — | — |
| H1 | 0.954 | O1 | 109.873 | N1 | 124.630 | C1 |
| C2 | 1.409 | C1 | 131.591 | N1 | -5.154 | O1 |
| H2 | 1.110 | C2 | 125.665 | C1 | -10.860 | N1 |
| H3 | 1.093 | C2 | 120.195 | C1 | 180.000 | H2 |
| H4 | 1.108 | C1 | 110.961 | N1 | 176.566 | O1 |
| Li1 | 2.137 | C2 | 78.607 | C1 | 51.155 | N1 |
| N2 | 4.733 | N1 | 93.586 | C1 | 96.265 | H4 |
| C3 | 1.338 | N2 | 57.586 | N1 | 31.060 | C1 |
| O2 | 1.330 | N2 | 115.197 | C3 | -110.827 | N1 |
| H5 | 0.953 | O2 | 108.951 | N2 | 156.566 | C3 |
| C4 | 1.476 | C3 | 130.472 | N2 | -6.563 | O2 |
| H6 | 1.126 | C4 | 123.650 | C3 | -31.824 | N2 |
| H7 | 1.114 | C4 | 119.840 | C3 | 180.000 | H6 |
| H8 | 1.116 | C3 | 111.303 | N2 | 171.056 | O2 |
| Li2 | 2.059 | C4 | 86.309 | C3 | 41.134 | N2 |

Dimer of *syn*-HON=CH-CH₂ Li⁺, C₁, **9**.

MNDO, **9a**.

Heat of formation = -52.78 kcal mol⁻¹.

| Center | Bond length | with | Angle | with | Dihedral | with |
|--------|-------------|------|---------|------|----------|------|
| N1 | — | — | — | — | — | — |
| C1 | 1.332 | N1 | — | — | — | — |
| O1 | 1.327 | N1 | 115.164 | C1 | — | — |
| H1 | 0.954 | O1 | 108.142 | N1 | 169.121 | C1 |
| C2 | 1.472 | C1 | 129.584 | N1 | -1.523 | O1 |
| H2 | 1.114 | C2 | 114.318 | C1 | -61.089 | N1 |
| H3 | 1.105 | C2 | 112.937 | C1 | 173.555 | N1 |
| H4 | 1.106 | C1 | 112.156 | N1 | 173.405 | O1 |
| Li1 | 1.939 | C2 | 91.676 | C1 | 41.792 | N1 |
| O2 | 4.562 | N1 | 82.056 | C1 | 100.184 | H4 |
| N2 | 1.329 | O2 | 62.955 | N1 | 81.260 | C1 |
| C3 | 1.337 | N2 | 115.580 | O2 | 144.527 | N1 |
| H5 | 0.957 | O2 | 109.032 | N2 | 169.801 | C3 |
| C4 | 1.473 | C3 | 128.135 | N2 | -3.046 | O2 |
| H6 | 1.120 | C4 | 113.134 | C3 | -71.405 | N2 |
| H7 | 1.105 | C4 | 112.316 | C3 | 165.158 | N2 |
| H8 | 1.111 | C3 | 113.027 | N2 | 173.807 | O2 |
| Li2 | 1.911 | C4 | 99.488 | C3 | 28.558 | N2 |

MNDO, CCH₂ group constrained to planarity, **9b**.

Heat of formation = -35.56 kcal mol⁻¹.

| Center | Bond length | with | Angle | with | Dihedral | with |
|--------|-------------|------|---------|------|----------|------|
| N1 | — | — | — | — | — | — |
| C1 | 1.364 | N1 | — | — | — | — |
| O1 | 1.336 | N1 | 114.471 | C1 | — | — |
| H1 | 0.951 | O1 | 108.394 | N1 | 151.382 | C1 |
| C2 | 1.413 | C1 | 131.457 | N1 | -7.137 | O1 |
| H2 | 1.114 | C2 | 125.463 | C1 | -12.926 | N1 |
| H3 | 1.093 | C2 | 120.858 | C1 | 180.000 | H2 |
| H4 | 1.107 | C1 | 111.050 | N1 | 173.828 | O1 |
| Li1 | 2.109 | C2 | 79.705 | C1 | 50.564 | N1 |
| O2 | 4.921 | N1 | 78.874 | C1 | 103.921 | H4 |
| N2 | 1.335 | O2 | 55.837 | N1 | 83.802 | C1 |
| C3 | 1.389 | N2 | 115.433 | O2 | 135.949 | N1 |
| H5 | 0.957 | O2 | 111.085 | N2 | 120.090 | C3 |
| C4 | 1.410 | C3 | 130.462 | N2 | -1.844 | O2 |
| H6 | 1.110 | C4 | 122.241 | C3 | -13.156 | N2 |
| H7 | 1.085 | C4 | 119.246 | C3 | 180.000 | H6 |
| H8 | 1.113 | C3 | 111.102 | N2 | 176.458 | O2 |
| Li2 | 2.147 | C4 | 78.231 | C3 | 47.978 | N2 |

Dimer of *anti*-HON=CH—CH₂ Li⁺, C_i, 10.

MNDO, 10a.

Heat of formation = -98.96 kcal mol⁻¹.

Inversion center: $x = 1.246$, $y = -2.539$, $z = 0.957$.

| Center | Bond length | with | Angle | with | Dihedral | with |
|--------|-------------|------|---------|------|----------|------|
| N | — | — | — | — | — | — |
| C1 | 1.330 | N | — | — | — | — |
| O | 1.312 | N | 116.825 | C1 | — | — |
| H1 | 0.960 | O | 108.144 | N | 173.346 | C1 |
| C2 | 1.512 | C1 | 119.310 | N | -176.131 | O |
| H2 | 1.127 | C2 | 108.245 | C1 | 74.787 | N |
| H3 | 1.127 | C2 | 107.404 | C1 | 188.599 | N |
| H4 | 1.105 | C1 | 122.758 | N | 2.549 | O |
| Li | 2.127 | C2 | 82.631 | C1 | -26.287 | N |

MNDO, CCH₂ group constrained to planarity, 10b.

Heat of formation = -66.04 kcal mol⁻¹.

Inversion center: $x = 1.348$, $y = -1.819$, $z = 1.499$.

| Center | Bond length | with | Angle | with | Dihedral | with |
|--------|-------------|------|---------|------|----------|------|
| N | — | — | — | — | — | — |
| C1 | 1.368 | N | — | — | — | — |
| O | 1.318 | N | 115.435 | C1 | — | — |
| H1 | 0.959 | O | 107.858 | N | 142.535 | C1 |
| C2 | 1.420 | C1 | 121.004 | N | -174.218 | O |
| H2 | 1.120 | C2 | 125.409 | C1 | 0.857 | N |
| H3 | 1.113 | C2 | 119.091 | C1 | 180.000 | H2 |
| H4 | 1.106 | C1 | 120.988 | N | -0.265 | O |
| Li | 2.479 | C2 | 72.836 | C1 | -33.898 | N |

Dimer of *anti*-HON=CH—CH₂ Li⁺, C_i, 11.

MNDO, 11a.

Heat of formation = -68.59 kcal mol⁻¹.

Inversion center: $x = -0.225$, $y = -1.048$, $z = -1.504$.

| Center | Bond length | with | Angle | with | Dihedral | with |
|--------|-------------|------|---------|------|----------|------|
| N | — | — | — | — | — | — |
| C1 | 1.370 | N | — | — | — | — |
| O | 1.329 | N | 117.138 | C1 | — | — |
| H1 | 0.961 | O | 111.510 | N | 83.330 | C1 |
| C2 | 1.418 | C1 | 121.610 | N | 179.879 | O |
| H2 | 1.111 | C2 | 121.524 | C1 | 25.221 | N |
| H3 | 1.100 | C2 | 117.006 | C1 | 170.335 | N |
| H4 | 1.108 | C1 | 120.454 | N | -3.002 | O |
| Li | 2.014 | C2 | 88.871 | C1 | 63.467 | N |

MNDO, CCH₂ group constrained to planarity, **11b**.

Heat of formation = -61.44 kcal mol⁻¹.

Inversion center: $x = 0.262$, $y = -1.078$, $z = 1.719$.

| Center | Bond length | with | Angle | with | Dihedral | with |
|--------|-------------|------|---------|------|----------|------|
| N | — | — | — | — | — | — |
| C1 | 1.381 | N | — | — | — | — |
| O | 1.328 | N | 116.199 | C1 | — | — |
| H1 | 0.961 | O | 110.657 | N | 92.080 | C1 |
| C2 | 1.398 | C1 | 122.431 | N | 183.647 | O |
| H2 | 1.110 | C2 | 124.345 | C1 | -0.199 | N |
| H3 | 1.102 | C2 | 120.336 | C1 | 180.000 | H2 |
| H4 | 1.108 | C1 | 119.619 | N | -3.598 | O |
| Li | 3.118 | N | 53.320 | C1 | 55.285 | C2 |

Dimer of *syn*-HON=CH-CH₂; Li⁺ with 2 H₂O, C₁, H₂O in C_{2v}, **12**.

MNDO, **12a**.

Heat of formation = -215.32 kcal mol⁻¹.

Inversion center: $x = 0.605$, $y = 0.357$, $z = 1.890$.

| Center | Bond length | with | Angle | with | Dihedral | with |
|--------|-------------|------|---------|------|----------|------|
| N | — | — | — | — | — | — |
| C1 | 1.355 | N | — | — | — | — |
| O1 | 1.326 | N | 119.358 | C1 | — | — |
| H1 | 0.960 | O1 | 110.938 | N | 88.597 | C1 |
| C2 | 1.422 | C1 | 132.750 | N | 1.990 | O1 |
| H2 | 1.106 | C2 | 120.302 | C1 | -19.377 | N |
| H3 | 1.106 | C2 | 116.403 | C1 | 201.195 | N |
| H4 | 1.111 | C1 | 110.549 | N | 182.180 | O1 |
| Li | 2.044 | C2 | 99.162 | C1 | 89.835 | N |
| O2 | 2.158 | Li | 119.872 | C2 | 179.819 | C1 |
| H5 | 0.943 | O2 | 122.069 | Li | 91.823 | C2 |
| H6 | 0.943 | O2 | 125.768 | H5 | -113.054 | C2 |

MNDO, CCH₂ group constrained to planarity, **12b**.

Heat of formation = -207.53 kcal mol⁻¹.

Inversion center: $x = 0.793$, $y = -0.033$, $z = 1.828$.

| Center | Bond length | with | Angle | with | Dihedral | with |
|--------|-------------|------|---------|------|----------|------|
| N | — | — | — | — | — | — |
| C1 | 1.373 | N | — | — | — | — |
| O1 | 1.324 | N | 118.226 | C1 | — | — |
| H1 | 0.961 | O1 | 110.639 | N | 87.011 | C1 |
| C2 | 1.397 | C1 | 131.828 | N | -1.669 | O1 |
| H2 | 1.100 | C2 | 124.748 | C1 | 9.659 | N |
| H3 | 1.105 | C2 | 120.149 | C1 | 180.000 | H2 |
| H4 | 1.113 | C1 | 110.683 | N | 184.619 | O1 |
| Li | 2.150 | C2 | 90.777 | C1 | 102.458 | N |
| O2 | 2.155 | Li | 117.637 | C2 | 161.465 | C1 |
| H5 | 0.944 | O2 | 123.702 | Li | 94.108 | C2 |
| H6 | 0.944 | O2 | 122.899 | H5 | -114.359 | C2 |

Dimer of *anti*-HON=CH—CH₂ Li⁺ with 2 H₂O, C_i, H₂O in C_{2v}, **13**.

MNDO, **13a**.

Heat of formation = -237.12 kcal mol⁻¹.

Inversion center: $x = 1.515, y = -2.063, z = 1.450$.

| Center | Bond length | with | Angle | with | Dihedral | with |
|--------|-------------|------|---------|------|----------|------|
| N | — | — | — | — | — | — |
| C1 | 1.332 | N | — | — | — | — |
| O1 | 1.314 | N | 116.162 | C1 | — | — |
| H1 | 0.958 | O1 | 107.766 | N | 176.673 | C1 |
| C2 | 1.496 | C1 | 120.255 | N | -177.265 | O1 |
| H2 | 1.126 | C2 | 112.267 | C1 | 50.270 | N |
| H3 | 1.122 | C2 | 109.132 | C1 | 166.919 | N |
| H4 | 1.105 | C1 | 122.270 | N | 1.236 | O1 |
| Li | 2.188 | C2 | 84.932 | C1 | -32.028 | N |
| O2 | 2.188 | Li | 95.995 | N | 218.395 | C1 |
| H5 | 0.943 | O2 | 125.766 | Li | 71.422 | N |
| H6 | 0.943 | O2 | 125.990 | Li | -100.759 | N |

MNDO, CCH₂ group constrained to planarity, **13b**.

Heat of formation = -213.01 kcal mol⁻¹.

Inversion center: $x = 1.331, y = -1.546, z = 1.627$.

| Center | Bond length | with | Angle | with | Dihedral | with |
|--------|-------------|------|---------|------|----------|------|
| N | — | — | — | — | — | — |
| C1 | 1.367 | N | — | — | — | — |
| O1 | 1.321 | N | 114.858 | C1 | — | — |
| H1 | 0.958 | O1 | 107.621 | N | 149.430 | C1 |
| C2 | 1.414 | C1 | 121.395 | N | -177.928 | O1 |
| H2 | 1.117 | C2 | 125.967 | C1 | -5.100 | N |
| H3 | 1.109 | C2 | 120.029 | C1 | 180.000 | H2 |
| H4 | 1.108 | C1 | 120.469 | N | -4.965 | O1 |
| Li | 2.557 | C2 | 74.397 | C1 | -30.675 | N |
| O2 | 2.156 | Li | 110.028 | N | 224.397 | C1 |
| H5 | 0.944 | O2 | 121.670 | Li | 42.507 | N |
| H6 | 0.944 | O2 | 126.887 | Li | -113.886 | N |

syn-HON=CH—CH₂ Li⁺·2 H₂O, C₁, H₂O in C_{2v}, **14**.

MNDO, CCH₂ group constrained to planarity.

Heat of formation = 159.35 kcal mol⁻¹.

| Center | Bond length | with | Angle | with | Dihedral | with |
|--------|-------------|------|---------|------|----------|------|
| N | — | — | — | — | — | — |
| C1 | 1.367 | N | — | — | — | — |
| O1 | 1.331 | N | 114.843 | C1 | — | — |
| H1 | 0.955 | O1 | 123.598 | C1 | 285.281 | C1 |
| C2 | 1.409 | C1 | 131.812 | N | -7.029 | O1 |
| H2 | 1.106 | C2 | 126.148 | C1 | -11.927 | N |
| H3 | 1.094 | C2 | 119.852 | C1 | 180.000 | H2 |
| H4 | 1.094 | C1 | 110.983 | N | 174.418 | O1 |

| Center | Bond length | with | Angle | with | Dihedral | with |
|--------|-------------|------|---------|------|----------|------|
| Li | 2.166 | C2 | 79.822 | C1 | 50.610 | N |
| O2 | 2.161 | Li | 124.004 | C2 | 62.520 | C1 |
| H5 | 0.944 | O2 | 125.734 | Li | 47.644 | C2 |
| H6 | 0.944 | O2 | 118.898 | Li | 261.910 | C2 |
| O3 | 2.161 | Li | 102.400 | O2 | 213.621 | C2 |
| H7 | 0.944 | O3 | 125.402 | Li | -65.633 | O2 |
| H8 | 0.944 | O3 | 125.140 | Li | 130.216 | O2 |

anti-HON=CH-CH₂; Li⁺·2 H₂O, C₁, H₂O in C_{2v}, 15.

MNDO, CCH₂ group constrained to planarity.

Heat of formation = -164.25 kcal mol⁻¹.

| Center | Bond length | with | Angle | with | Dihedral | with |
|--------|-------------|------|---------|------|----------|------|
| N | — | — | — | — | — | — |
| C1 | 1.387 | N | — | — | — | — |
| O1 | 1.316 | N | 115.804 | C1 | — | — |
| H1 | 0.961 | O1 | 117.002 | C1 | 83.103 | C1 |
| C2 | 1.398 | C1 | 120.333 | N | 177.462 | O1 |
| H2 | 1.108 | C2 | 126.192 | C1 | -9.620 | N |
| H3 | 1.092 | C2 | 120.110 | C1 | 180.000 | H2 |
| H4 | 1.105 | C1 | 121.143 | N | -0.560 | O1 |
| Li | 2.231 | C2 | 74.344 | C1 | 42.020 | N |
| O2 | 2.150 | Li | 119.241 | C2 | 88.668 | C1 |
| H5 | 0.944 | O2 | 125.189 | Li | 23.611 | C2 |
| H6 | 0.944 | O2 | 121.241 | Li | 233.414 | C2 |
| O3 | 2.144 | Li | 106.098 | O2 | 210.441 | C2 |
| H7 | 0.944 | O3 | 130.781 | Li | 80.615 | O2 |
| H8 | 0.944 | O3 | 118.176 | Li | -121.951 | O2 |

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