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Ab Initio Molecular Dynamics Investigation of Singlet $C_2H_2Li_2$: Determination of the Ground State Structure and Observation of LiH Intermediates

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Abstract: The structural, electronic, and dynamic properties of the organolithium compound $C_2H_2Li_2$ have been investigated via *ab initio* molecular dynamics simulations based on the Car−Parrinello method. Dynamical simulated annealing techniques applied to search for the low-energy configurations resulted in a structure that is not a dilithioethylene isomer as suggested by the stochiometric formula but an acetylenic derivative that can be visualized geometrically as a complex of lithioacetylene with lithium hydride $HC_2Li{\cdot}HLi$. However, the ground state electronic structure is more suggestive of an ionic complex $(H{-}C{=}C)^{-}{\cdot}(Li^{+}H^{-}Li^{+})$ in which the linear anion HCC^{-} binds to the two lithium cations in the triangular complex $Li^{+}H^{-}Li^{+}$. Several ethylene-like isomers were identified via high-temperature quenches, but these invariably turned out to lie at high energies (~>30 kcal/mol). Analysis of the high-temperature dynamics indicated that ethylene-like isomers are always unstable toward an intramolecular hydrogen migration mediated via a lithium hydride unit. The direct observation of these intramolecular rearrangement reactions revealed the role of the lithium atoms as hydrogen transfer reagents and confirmed the importance of lithium hydride as an intermediate species.

1. Introduction

Organolithium compounds have a widespread use in organic synthesis,[1,2] and a characterization of their structural and electronic properties is of fundamental interest for an understanding of their reactivity. Various mono− and polylithiated organic compounds can be readily prepared experimentally,[3,4] but apart from a few known crystal structures (e.g., $CH_{3.4}Li$[5a,b] and C_2H_5Li[5c]) and the structural determination of C_2H_2Li in an Ar matrix (IR[6] and ESR[7]), only the most general information concerning the structures of these species is available. The fact that organolithium compounds have a strong tendency to associate into oligomeric units[1] has prevented a detailed structural determination in many cases.

A characterization of the single molecule properties as the basis for an understanding of the more complex real systems thus mainly relies on theoretical investigations. Due to their unusual properties, such as their special ability of stabilizing unconventional forms of carbon (planar tetracoordinated carbon[8e] or perpendicular olefins[8b]), these molecules have fascinated theoreticians for more than two decades.[8]

A theoretical structural characterization and, in particular, the search for optimal geometries has turned out to be far from trivial. A large number of studies on different systems[8] have shown that organolithium compounds tend to adopt highly unorthodox structures that cannot easily be derived from the classical hydrocarbon analogues. Even for moderately complex isolated molecules in the gas phase, a comprehensive characterization of the potential energy surface (PES), e.g. the localization of the lowest-energy structure(s), is a time-consuming and demanding task.[9] The large number of geometrical possibilities as well as the occurrence of low-symmetry isomers and competing electronic states (see e.g. ref 8g) has so far precluded an extensive search for many systems.

Ab initio molecular dynamics (MD) simulations based on density functional theory[11] allow for an efficient minima search via simulated annealing techniques[25] and have proven to be a valuable tool in the investigation of disordered and amorphous

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Table 1. Comparison of Structural and Energetic Properties for Three Test Compounds[a]

	PP1-LDA	PP2-LDA	PP2-GC	NUMOL	G92-LDA	QCISD	CCSD/DZP	EXP
				C_2H_2				
d_{C-C}	1.211	1.203	1.204	1.201	1.212	1.211	1.221	1.203
d_{C-H}	1.082	1.078	1.067	1.074	1.078	1.069	1.072	1.061
				LiH				
r_e	1.524	1.643	1.651	1.603	1.640	1.653	1.621	1.595
D_e	65.9	58.8	61.6		57.5	44.1		56.0
				Li_2				
r_e	2.65	2.75	2.73	2.710	2.750	2.725	2.730	2.673
D_e	25.0	22.7	21.9		22.5	20.9		24.0

[a] PP1-LDA: LDA results with a norm-conserving pseudopotential and $E_{cut} = 35$ Ry. PP2-LDA: LDA results with an ultrasoft Vanderbilt pseudopotential and $E_{cut} = 25$ Ry. PP2-GC: gradient corrected (exchange only) results. NUMOL: all-electron LDA results (basis set free).[14] G92-LDA: all-electron LDA results (6-31G* basis set) (Gaussian92).[15] QCISD: quadratic configuration interaction including single and double excitations (6-31G* basis set).[15] CCSD/DZP: coupled-cluster method including single and double excitations with a double-ζ plus polarization[9] basis set. EXP: experimental values.[16] Dissociation energies D_e were calculated with the corresponding atomic energies obtained by correcting the LDA values in perturbation for spin polarization.[27] Bond distances are given in Å, energies in kcal/mol.

systems and clusters.[12] The possibility of a powerful optimization technique to determine energetically favorable configurations seems to be a natural tool for a study of molecular systems. The goal of our study is to probe the performance and possibilities of *ab initio* MD for an organometallic system. Furthermore, *ab initio* molecular dynamics simulations offer the additional possibility of investigating the dynamical properties of such aggregates, at finite temperature, and to also examine directly their chemical reactivity.

To date only a few attempts have been made to investigate molecular or organometallic compounds with the Car–Parrinello method. We have performed *ab initio* molecular dynamics simulations for the organolithium compound $C_2H_2Li_2$ as a test case study to probe the capabilities of the method for systems of chemical interest.

Anticipating our results, we find that *ab initio* molecular dynamics is indeed a very powerful tool for the characterization of such systems. We did not attempt to perform an exhaustive search of the potential energy surface but mainly focused on a determination of the energetically most favorable structure(s) and likely thermally relevant isomers. Two relatively short molecular dynamics runs at high temperature (which took each ~50 h of CPU on a modern workstation) led to the identification of a number of isomeric structures and some of the corresponding transition states. They also revealed the role of the lithium atoms as intramolecular hydrogen transfer reagents. Subsequent cooling resulted in both cases in the same unexpected lowest-energy structure. In spite of what one could have guessed from the stochiometric formula, the ground state geometry has an acetylenic character and can be visualized as $C_2H^-(Li^+)_2H^-$ with the charges arranged in a quadrupole-like arrangement. Several ethylene-like isomers were also identified via quenches from high-temperature configurations. All of these, however, are energetically much less favorable than the lowest-energy structure.

2. Details of the Computational Scheme

The Car–Parrinello method for *ab initio* molecular dynamics simulations is well described in a number of publications.[11,12] In the following, we only give the relevant computational details for this particular case.

The electronic structure is described in the framework of density functional[26] and pseudopotential theory.[19,22] Calculations were performed using the local-density approximation (LDA) with the exchange-correlation functional described by the Perdew–Zunger parametrization[17] of the Ceperley–Alder[18] results for the homogeneous electron gas. The effects of generalized gradient corrections (GC) on the exchange functional[13] were examined as well.

In this approach, the valence orbitals are expanded in a basis of plane waves using a periodic face-centered cubic supercell of edge $a = 30$ au. The effect of the ionic cores is described via nonlocal *ab initio* pseudopotentials. We have tested different types of pseudopotentials, separable[19] norm-conserving (NC)[20] and also the supersoft Vanderbilt (VB)[21] type. Standard NC pseudopotentials from the literature have been used (Li,[22] C,[23] and H[24]) with an energy cutoff E_{cut} of the one-electron wave functions of 35 Ry. Angular-momentum-dependent terms up to $l_{max} = 1$ were included in the cases of lithium and carbon. Possible p-nonlocality effects were checked in the case of the lithium dimer and found to be negligible. Supersoft LDA and gradient-corrected LDA pseudopotentials have been constructed with cutoff radii r_c of 1.8, 1.25, and 0.8 for Li, C, and H, respectively. An energy cutoff of 25 Ry was used in this case.

The main motivation of our work was to probe the performance and capabilities of *ab initio* MD in the case of a particular organometallic system. We have therefore restricted our study to an investigation of the singlet potential energy surface of $C_2H_2Li_2$ even though triplet states are known to compete for the ground state in many organolithium compounds.[8b]

Examples of the performance of our computational scheme are given in Table 1 for acetylene, lithium hydride, and the lithium dimer. Results

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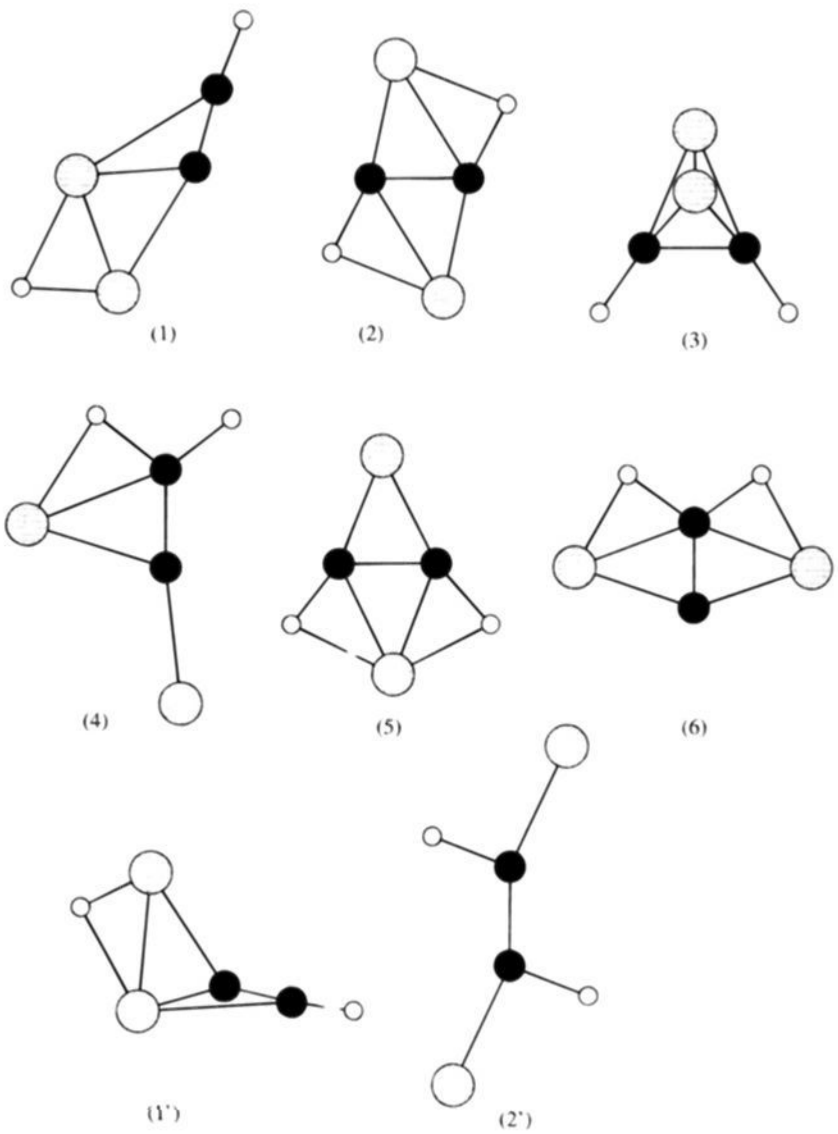

Figure 1. Selected isomers of $C_2H_2Li_2$ (hydrogen, white circle; carbon, black circles; lithium, grey circles).

of all-electron LDA,[14,15] quadratic configuration interaction calculations with single and double substitutions (QCISD),[15] coupled-cluster calculations including single and double excitations (CCSD),[9] and the experimental values have also been given as references.

To demonstrate the quality of the pseudopotential approach, the results obtained with the two different pseudopotentials (PP1, NC; PP2, VB) can be compared to those of the all-electron LDA[14] and the CCSD of ref.[9]

In the case of acetylene, the structural quantities obtained with the two pseudopotentials are very similar and in close agreement with both the results of all-electron LDA or QCISD calculations and the experimental values. The effects of gradient corrections are minor and mainly correct for the slight overestimation of the length of the C−H bond within the LDA.

Larger variations exist in the case of lithium. PP1 underestimates the lithium−lithium as well as lithium−hydrogen bonds by ~4−5% compared to the all-electron LDA results. Therefore, the close agreement with the experimental values must be considered accidental. PP2 generates bond distances and dissociation energies in close agreement with the all-electron values. In comparison with experiment, bond distances are reproduced with a typical accuracy of ~1−2% and dissociation energies within a few kilocalories/mole (5−10%), i.e. with comparable or even better accuracy than the QCISD values[15] with a 6−31G* basis set. For these two test compounds, the inclusion of gradient correction does not seem to lead to a systematic improvement. The differences between the LDA and GC results are however too small (i.e., much smaller than the variation due to the use of different pseudopotentials) for a discussion of general trends of LDA versus gradient-corrected models.

We have used the slightly more economic pseudopotential PP1 for the molecular dynamics runs and relaxed the resulting structures with PP2 (LDA and GC). The effect of the finite box length was tested with respect to the relative energy difference of two isomers. Increasing the cell size to a = 35 au changed the relative energy difference by less than 0.1 kcal/mol, i.e. a value that is beyond the numerical accuracy of our scheme. PP1 was used with an energy cutoff of 35 Ry, which does not generate completely converged results, but an increase of E_{cut} to 45 Ry changed the structural quantities by less than 0.01 Å and the relative energy difference between the two isomers by less than 0.5 kcal/mol.

Molecular Dynamics and Simulated Annealing Runs. We have performed two independent simulated annealing optimizations initiated from two different starting configurations (structures **3** and **4** shown in Figure 1). All the atomic masses were set to an equal value of m = 7 amu. The pseudodynamics generated in this way allowed for an efficient exploration of the PES at finite temperature. A fictitious mass of the electronic degrees of freedom of μ = 500 au was used. Standard constant energy molecular dynamics simulations[11,12] were performed, and the equations of motion were integrated with a Verlet algorithm and a time step of 5 au (~0.1 fs). The heating cycles were initiated by choosing the atomic momenta from a Maxwell−Boltzmann distribution corresponding to an average temperature of 100 K. Subsequently, the system was heated (under temperature control via rescaling of atomic velocities) to an average temperature in the range of T = 1000−2000 K. After an initial equilibration of ~0.5 ps, we followed the evolution of the system during ~1−2 ps at high temperature. Subsequently, the system was cooled down via a rescaling of the atomic velocities with a factor of 0.9998 per time step. After a cooling run of ~1.5 ps, an examination of the root mean square displacements and the atomic trajectories showed that at $T \simeq$ 300 K the system was trapped in one energy minimum.

3. Results and Discussion

Structure and Energetics. Both independent simulated annealing runs led to the same lowest-energy structure **1** (Figure 1). Eight systematic quenches of high-temperature configurations (via steepest descent (SD) minimizations) followed by subsequent relaxation (with combinations of low-temperature MD runs and SD) resulted in the local minima, depicted as structures **4**, **5**, and **6**. In addition, we have also relaxed structure **3**.[28] For comparative purposes, the stability of the conventional 1,2-dilithioethylene structure that can be derived from a substitution of the corresponding hydrocarbon was also exam-

Table 2. Structural and Energetic Properties of Different Isomeric Structures of $C_2H_2Li_2$ Shown in Figure 1[a]

structure	ΔE	d_{C-C}	d_{C-H}	d_{C-Li}	d_{Li-H}	d_{Li-Li}
1	0 (0)	1.242 (1.239)	1.078 (1.090)	2.14 (2.03) 2.24 (2.10)	1.81 (1.78) 1.83 (1.79)	2.505 (2.44)
2	35.2 (19.0)	1.377 (1.364)	1.138 (1.144)	1.97 (1.87) 2.37 (2.18)	2.08 (1.89)	
3	35.7 (19.5)	1.386 (1.373)	1.122 (1.128)	2.11 (2.00)		2.78 (2.60)
4	39.8 (25.1)	1.348 (1.331)	1.115 (1.120) 1.153 (1.193)	1.94 (1.70) 2.27 (2.02)	2.00 (1.75)	
5	42.7 (24.2)	1.367 (1.356)	1.170 (1.166)	2.04 (1.93) 2.19 (2.03)	1.83 (1.75)	
6	(29.9)	(1.339)	(1.182)	(1.92) (2.04)	(1.86)	

[a] Values are given for the gradient-corrected case (PP2-GC of Table 1); values in parentheses give the corresponding LDA results (PP2-LDA of Table 1). Isomer **6** is not a minimum for the GC model but transforms spontaneously into structure **4**. Bond distances are in Å, energies are given in kcal/mol relative to the lowest-energy structure **1**.

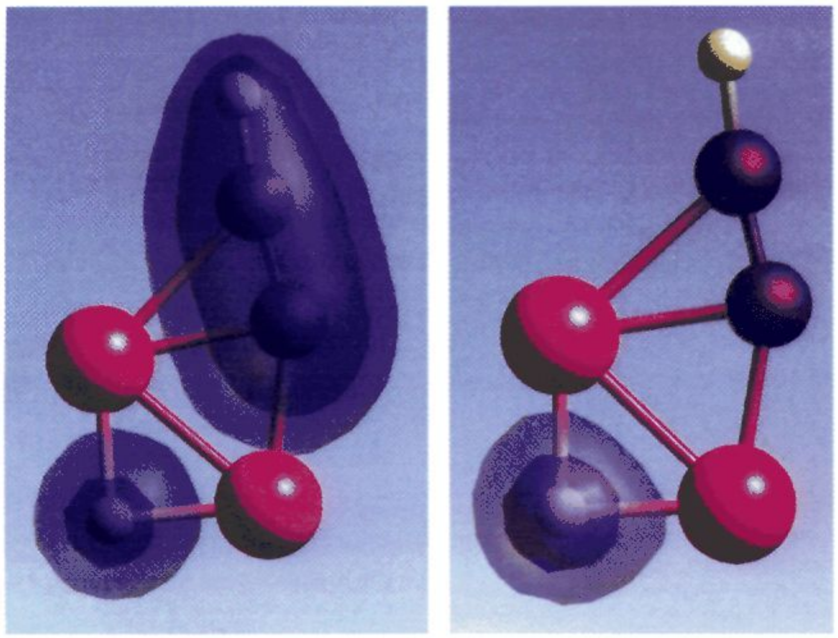

Figure 2. Electron density distribution of the lowest-energy structure (**1**): (left) total electron density (contours at 0.03 and 0.08 e/au^3) and (right) electron density distribution of the HOMO (contours at 0.025 and 0.06 e/au^3). The color coding of the atoms is white for hydrogen atoms, violet for carbon atoms, and magenta for lithium atoms.

ined. A steepest descent optimization results in geometry **2′** (Figure 1), which does not correspond to a minimum of the PES: an *ab initio* MD run starting from **2′** with initial zero momenta relaxed immediately to the local minimum structure **2**. We therefore suggest structure **2′** as a likely, energetically highly unfavorable transition state (>50 kcal/mol) (we did however not attempt to diagonalize the Hessian to further confirm the nature of **2′**). Characteristic structural and energetic properties of the equilibrium structures are summarized in Table 2. The lowest-energy structure **1** exhibits unique properties both with respect to energetics and in terms of chemical bonding. We did not perform an exhaustive search of the PES, and the isomers given in Figure 1 and Table 2 merely represent examples of typical minima encountered during the high-temperature dynamics rather than a comprehensive set of stationary points on the singlet potential energy surface. Nevertheless, we believe that the fact that all the local isomers found via quenching from high temperature are clearly much higher in energy (>30 kcal/mol) indicates strongly that the system $C_2H_2Li_2$ is dominated by the lowest-energy minimum **1** and that no other isomers seem to be relevant at moderate temperatures. All the minimum energy structures that resulted from the finite-temperature dynamics are planar. We found, however, that the ground state structure **1** can easily adopt a folded configuration **1′** (Figure 1), where the "linear" C−C−H unit is almost perpendicular to the plane of the triangular Li_2H. This strong deviation from planarity hardly costs the system any energy. Configuration **1′** is practically degenerate (~1 kcal/mol) with **1**, and within the limited numerical accuracy of our calculations, we could not decide if it corresponds to an additional minimum of the PES or merely to a "soft-mode" deformation of **1**. A further related configuration of **1** that could be observed in the high-temperature dynamics was its mirror equivalent (i.e., looking at the plane of structure **1** from above or below). An isomerization between these two completely equivalent configurations takes place via an in-plane swinging of the rigid triangular Li_2H unit with the neighboring carbon atom of the acetylene as a fixed point.

The clear difference between the properties of the ground state structure with respect to all the other isomers also manifests itself in the type of chemical bonding it exhibits. From an inspection of the carbon−carbon distance in Table 2, it is evident that in contradiction to what one could expect from the stochiometric formula the lowest-energy structure is *not ethylene-like* but *acetylene-like*, with a C−C bond of 1.23 Å only slightly larger than a normal C−C triple bond of ~1.20 Å (or a C−C bond in the carbanion C_2^{2-}). In contrast, all the other

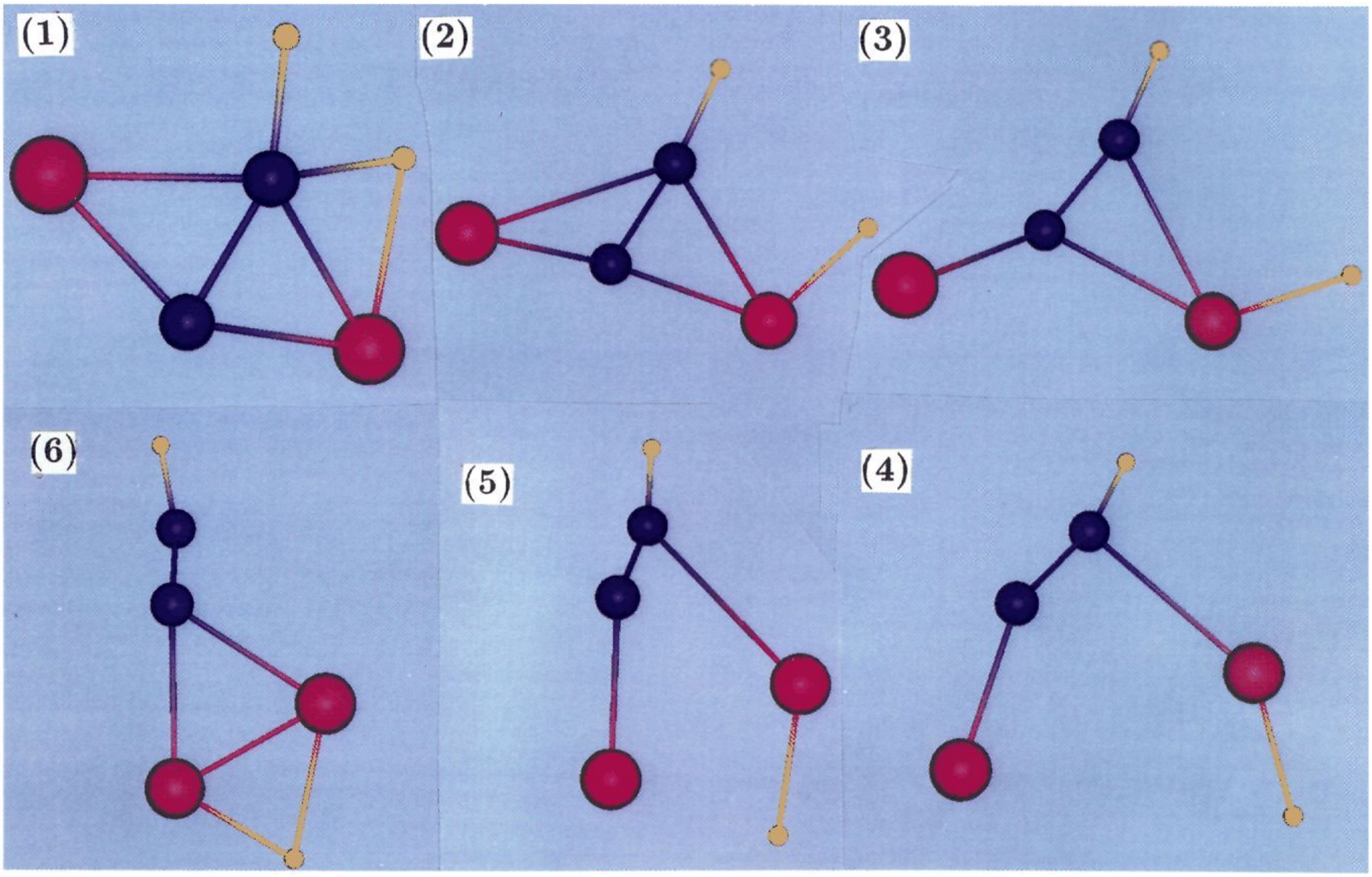

Figure 3. Snapshots **1**−**6** of high-temperature configurations during an intramolecular hydrogen transfer reaction. Color coding of the atoms corresponds to yellow (hydrogen), violet (carbon), and red (lithium).

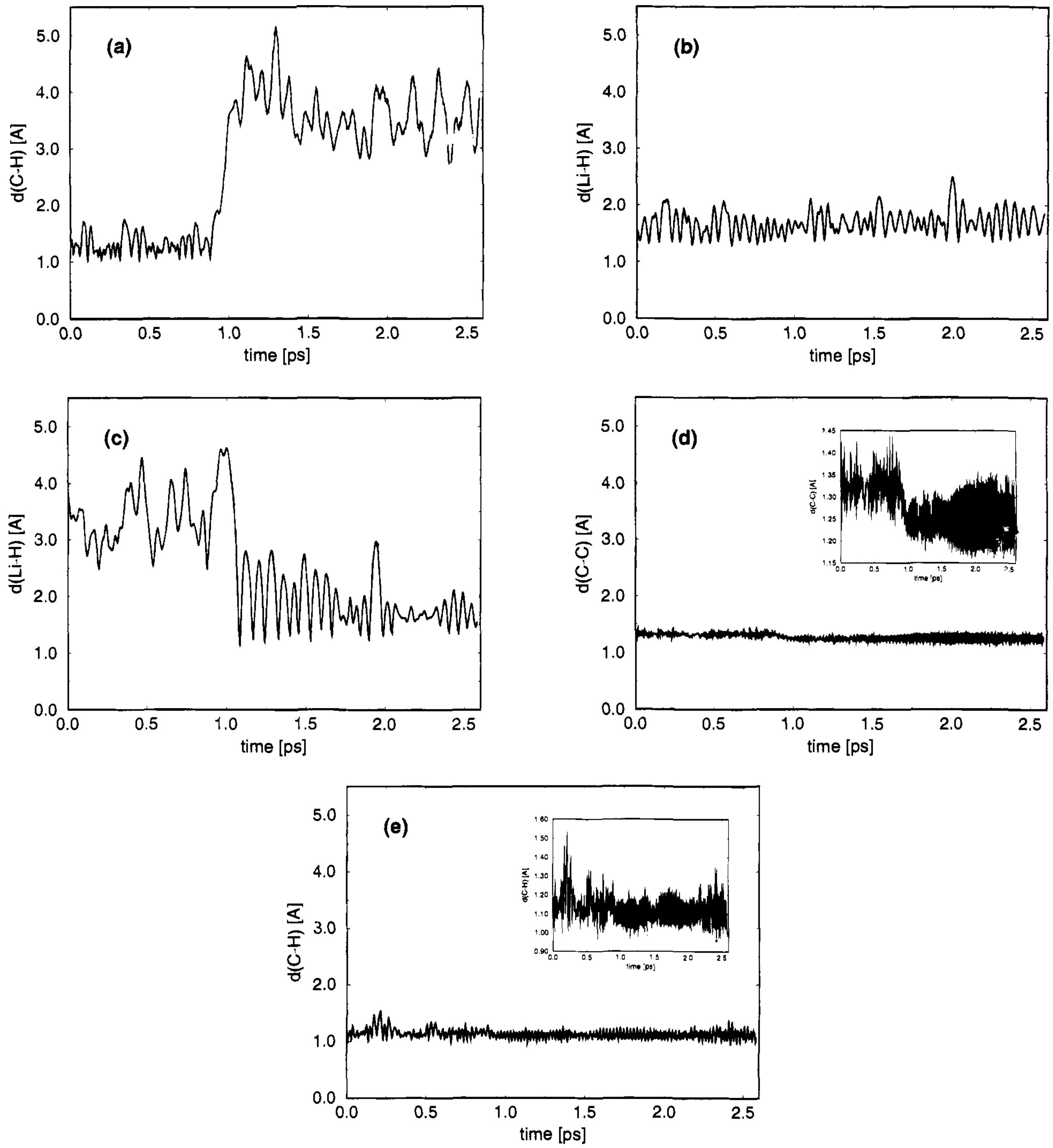

Figure 4. Temporal evolution of characteristic interatomic distances during the reaction in Figure 3: (a) C−H distance of the migrating hydrogen, (b) Li−H distance of the LiH transfer unit, (c) Li−H distance between the other lithium atom and the migrating hydrogen, (d) C−C bond distance (the inset has a magnification of scale), and (e) C−H bond distance of the nonmigrating hydrogen (the inset has a magnification of scale).

energetically less favorable structures **2**−**6** have C−C bond distances in the range of 1.32−1.38 Å close to a C−C double bond.[31] The acetylene unit in **1** is deprotonated, and the proton is bound to the two lithium atoms. The resulting configuration can be rationalized as a complex of lithium hydride with lithioacetylene $LiH{\cdot}LiC_2H$. A closer inspection of the interatomic distances shows that the two lithium−hydrogen bonds are practically equivalent. No clear distinction between the two lithium atoms could be found either in the analysis of the electron density or in the dynamic properties at finite temperature. Therefore, an even more appropriate way of describing **1** would probably be a formula like $HLi_2{\cdot}C_2H$. **1** has a remarkably short lithium−lithium distance of 2.505 Å (LDA result: 2.441 Å). This is shorter (recall Table 1) than the interatomic distance in the neutral dimer (experimental value of 2.673 Å[16]). Considering the fact that the Li−Li distance in the singly ionized molecule Li_2^+ is enlarged (3.12 Å),[29] this seems surprising at first sight. A short Li−Li distance can however be rationalized with the enhanced stabilization due to the quadrupole-like arrangement of the charges in structure **1**.[10]

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[31] We use the terms "ethylene-" or "acetylene-like", respectively, according to the length of the C−C bond.

The analysis of the electronic structure presents a similar picture. Figure 2 shows the distribution of (a) the total electron density and (b) the electron density distribution of the highest occupied state (HOMO). It is clearly evident from Figure 2a that both lithium atoms are essentially ionized with the valence electron density located on the acetylenic unit and the hydrogen atom of the lithium hydride part generating a distribution of charges of the form $Li^+H^-Li^+(C_2H)^-$. The enhanced stability of quadrupole-like ion multiplets has been observed in the case of carbanionic systems and is also well-known for ionic models of organolithium compounds.[10] In the HOMO (Figure 2b), the electron density is located around the hydrogen atom of the lithium hydride unit.

Dynamic Properties. High-Temperature Dynamics. The high-temperature dynamics of the two simulated annealing runs have been analyzed in some detail. Even though the use of unrealistic masses (all atomic masses set equal to $m = 7$ amu) generates a pseudodynamics, it serves as an efficient way to explore the PES. In both cases the system stayed in an ethylene-like state, similar to the starting geometries, for the first few hundred femtoseconds. After this time a spontaneous collapse of the ethylene-like configurations was observed. In both runs an intramolecular hydrogen transfer reaction occurred whereby one of the hydrogen atoms was eliminated from the carbon unit and transferred via a lithium hydride intermediate to the lithium atoms. This transformed the system from an ethylene-like to an acetylene-like configuration. Figure 3 illustrates one of these hydrogen transfer reactions by a sequence of snapshots of the system, and Figure 4 monitors the simultaneous temporal evolution of some characteristic interatomic distances. All distances in Figure 4 are given with the same scale for a better appreciation of the relative magnitude of the changes involved. The temporal evolution of the C−H distance of the migrating hydrogen (Figure 4a) shows clearly the breaking of the C−H bond. For the first 100 fs, the bond distance is, on average, around a value of ~1.2 Å with rapid oscillations as can be expected for the stretching motion of a strong intramolecular bond. Then, a sudden change occurs to an average value of 3.5 Å with much lower frequency oscillations. Simultaneously, the C−C bond distance changes from a value close to that of a C−C double bond $\langle d_{CC}\rangle$, ~ 1.32, to a value of ~1.25 Å close to that of a triple bond, as can be seen in the magnified view of the inset of Figure 4d. The transfer of the hydrogen is mediated via a lithium hydride intermediate as is shown in Figure 3 and confirmed in Figure 4b by the preservation of the corresponding Li−H distance throughout the reaction. Figure 4c shows the distance of the other lithium atom to the migrating hydrogen, indicating the formation of an additional Li−H bond. Beside the LiH species, the acetylenic unit C_2H is another structural unit that is conserved during the whole dynamics as can be seen from Figure 4d,e showing the rapid intramolecular bond vibrations of the C−C bond and the C−H bond distance to the nonmigrating hydrogen.

The direct observation of this hydrogen elimination reaction reveals the importance of lithium as a hydrogen transfer reagent and confirms the occurrence of a LiH as an intermediate species. Our findings seem to be in close agreement with the experimental observation that 1,3-dilithiopropane eliminates easily LiH[4a] and the suggested mechanism of intermolecular rearrangement to thermodynamically more favorable LiH complexes. The same argument has been invoked to explain the fact that it was so far impossible to prepare 1,2-dilithioethane. Calculations confirmed the experimental findings that both systems are unstable toward conversion to LiH complexes.[8i] Recent attempts to synthesize *cis*- and *trans*-1,2-dilithioethylene showed a rapid decomposition with a splitting off of lithium hydride and possible further metalation to dilithioacetylene.[4b] On the other hand, neither the elimination of Li_2 nor that of H_2 could be observed experimentally. The authors of ref 4b suggest therefore that lithioacetylene can form a relatively stable complex with lithium hydride. According to our calculations of the isolated molecule in the gas phase, the decompositions to $Li_2 + C_2H_2$, $LiH + LiC_2H$, and $H_2 + C_2Li_2$ are all endothermic (by at least 30 kcal/mol).[30]

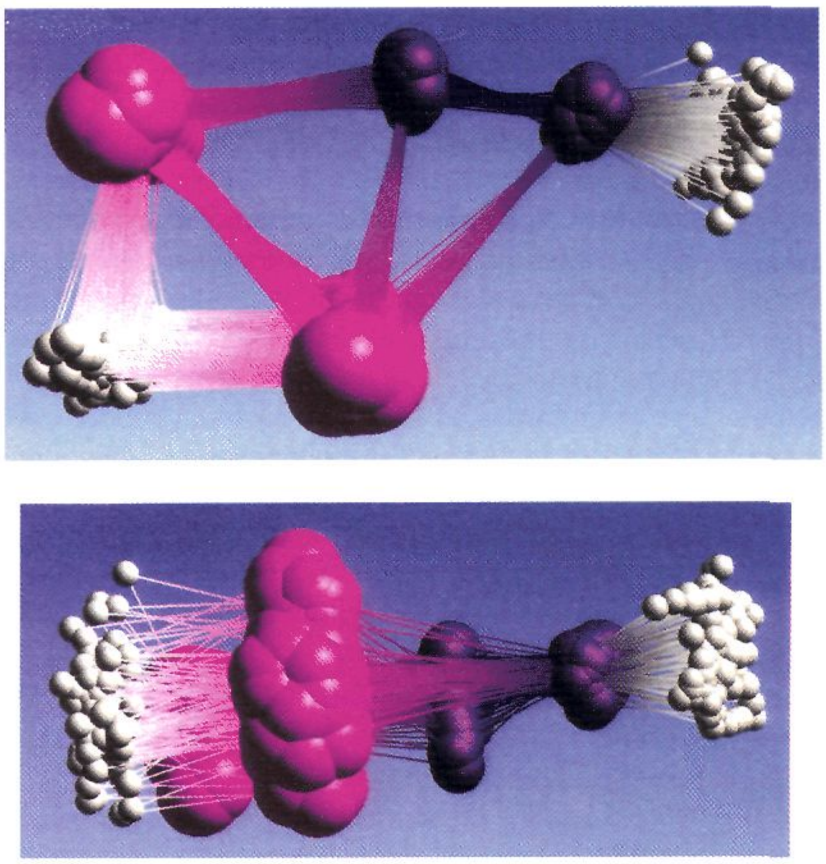

Figure 5. Superposition of instantaneous configurations at room temperature: (a) on-plane view and (b) out-of-plane view of the atomic trajectories spanning 10 ps. Color coding of the atoms is the same as in Figure 2.

Room-Temperature Dynamics. We have also followed the room-temperature dynamics of the molecule using realistic atomic masses. Figure 5a,b shows a superposition of instantaneous configurations generated in this fashion to give an impression of the magnitude of the atomic movements. As is indicated by the on-plane view of Figure 5a, the system is essentially oscillating around the equilibrium structure **1**. Even though the out-of-plane movement (illustrated in Figure 5b) is considerable, the root mean square displacements of the lithium, carbon, and hydrogen atoms do not exceed maximal values of 0.9, 0.4, and 1.4 Å, respectively. Thus, the structure is not fluxional on the time scale of our observation (10 ps). However, recall our earlier discussion of the isomerization of structure **1**.

4. Summary and Conclusions

Many organolithium compounds are known to adopt highly unconventional structures, and traditional chemical experience from analogous hydrocarbon molecules seems to be no guide for structural predictions. The search for the optimum structures of organolithium compounds is therefore a challenging task that has motivated many studies over the last two decades. We have chosen the organolithium compound $C_2H_2Li_2$ as a test case to study the capabilities of *ab initio* molecular dynamics methods in the characterization of these systems. The search for the most favorable equilibrium structure was conducted by applying a simulated annealing optimization technique.[25] Two independent optimizations lead to the same ground state structure that can be visualized as an ionic acetylide lithium hydride complex. A limited further exploration of the (singlet) potential energy surface showed that the finite-temperature properties of the system are very likely dominated by this minimum configuration only. An examination of the dynamic properties of the system further confirmed the importance of LiH as a key structural unit and intermediate species. Ethylene-like isomers were observed to be unstable toward a spontaneous intramolecular hydrogen transfer reaction mediated via a LiH species. Our findings seem to be in very good agreement both with the experimental suggestion that related compounds such as 1,3-dilithiopropane and dilithioethylene can easily undergo a LiH elimination reaction and with theoretical predictions for similar organolithium compounds such as 1,2-dilithioethane.

Being one of the first applications of the Car–Parrinello scheme to organometallic compounds, this study shows that the method is a very valuable and efficient tool even for the characterization of the properties of the isolated species in the gas phase. The application of the same technique to other organometallic systems or to more realistic, i.e. associated organolithium, compounds in the condensed phase is feasible and seems to be extremely promising.

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Supplementary Material Available: Table of the total energies of the $C_2H_2Li_2$ isomers and of the molecules H_2, LiH, Li_2, C_2H_2, C_2HLi, and C_2Li_2 (1 page). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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