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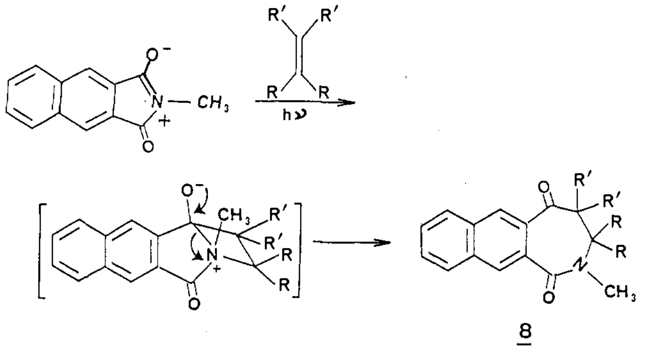

Figure 7. Reaction scheme of the photochemical addition of olefins to *N*-methyl-2,3-naphthalimide (**2**) leading to diazepinediones **8**.

from an excited imidol structure in which the C=N double bond has been created by double hydrogen transfer between two molecules.[25,39]

The creation of a double bond between the nitrogen atom and the carbonyl group of *N*-methyl-2,3-naphthalimide (**2**), which presents a rather long excited singlet lifetime (ca. 8 ns), would explain its $2\pi + 2\pi$ cycloaddition to an olefin[11] leading to the naphthazepinedione molecules **8** (Figure 7). Such an intermediate has also been proposed in the case of *N*-methylphthalimide[14,15] and of *N*-methyl-1,2-naphthalimide;[40] it is closely related to the product resulting from the photoaddition of olefins to ethoxyisoindolone where the four-membered ring intermediate could be isolated.[41]

In summary, both the short-wavelength and the long-wavelength emitting states of **3** are found to originate from, but are not, the Franck–Condon state. They decay with lifetimes differing from each other by about 2 orders of magnitude. In both the Franck–Condon state and the short-wavelength emitting state, the phenyl substituent is in a plane orthogonal to the naphthalimide moiety, while in the long-wavelength emitting state the two planes are coplanar.

Registry No. 1, 6247-15-0; **2**, 42896-23-1; **3**, 21815-18-9; **4**, 137769-13-2; 2,3-naphthalenedicarboxylic acid, 2169-87-1; 2,5-di-*tert*-butylaniline, 21860-03-7.

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Existence of Carbanion Triplet Structures As Evidenced by NMR Spectroscopy and MNDO/AM1 Calculations

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Abstract: Dilithium 2,2′-biindenide and 1,2′-biindenide have been taken as model systems to study the existence of carbanion triplet structures. Induced ^{13}C NMR chemical shifts by changing ether solvent indicated a polarization of charge toward the bridging positions as the cation solvation decreases. Moreover, in the unsymmetrical biindenide, a restricted rotation around the bridging bond could be manifested, governed by a negative entropy term. MNDO/AM1 calculations, where solvation and C–Li interactions were accounted for, supported a carbanion triplet arrangement where the rotational barrier decreased by increased cation solvation.

Introduction

The nature of the carbanion–alkali metal interaction is an important aspect of carbanion chemistry.[2] A variety of spectroscopic and theoretical approaches have been utilized to increase the understanding of this area of organometallic chemistry, where the role of covalency vs ionic interactions and also the presence of aggregation effects have been the greatest challenges. In the case of salts involving delocalized dicarbanions, an ion triplet arrangement has been proposed.[3] This proposal was based on the application of Coulomb's law, where the alkali ions were treated as point charges. The model was used to explain the unexpectedly small difference between the first and second acidity constants in a number of hydrocarbons, especially 2,2′-biindene and 9,9′-bifluorene where $\Delta pK_a < 1$. The ion triplet structure of dilithium 9,9′-bifluorenide has been confirmed in the solid state by X-ray crystallography.[4] This simple model, and extensions of it,[5] has further been used to account for the crystal structure of other dicarbanions. Of course, crystal packing or Madelung forces may be a complicating factor in the solid "lattices", but it is unclear to what extent such forces will favor or disfavor triplet structures in a given complex.

Some semiempirical MNDO calculations have also been performed in order to investigate the structures of dilithium dicarbanions.[5,6] In one MNDO study,[6d] the ion triplet structure was

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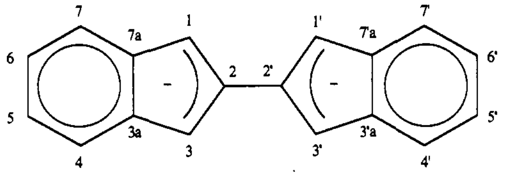
Table I. ^{13}C Chemical Shifts (δ) of 2,2′-Biindenide in Various Solvents and in the Solid State

	solvent				
position	THF/ DMEU	THF	2-MeTHF	solid	$\Delta\delta^a$
1,3,1′,3′	91.9	89.2	89.0	89.4	2.9
4,7,4′,7′	116.5	118.7	119.3	119.6; 121.7	−2.8
5,6,5′,6′	109.5	114.1	115.3	114.9; 115.8	−5.8
3a,7a,3′a,7′a	132.6	130.9	129.8	128.6	2.8
2,2′	137.7	132.5	131.6	131.8	6.1

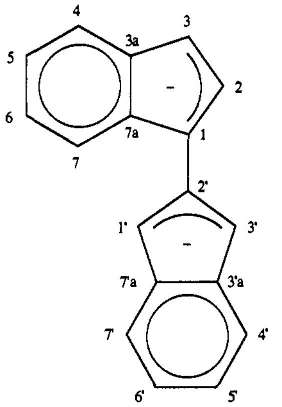
^{a} Difference in chemical shifts in THF/DMEU and 2-MeTHF.

found to be the global minimum if the cations were treated as "sparkles" or point charges. When lithium parameterization was used and a partly covalent contribution was introduced, a nonsymmetric structure was the most stable species, corresponding to the one found in crystals.

In order to investigate the structures of such dicarbanion salts in solution, we undertook a NMR spectroscopic study of dilithium 2,2′-biindenide (**1**) and 1,2′-biindenide (**2**). This study is expected to give more direct structural evidence for a triplet arrangement than the more indirect proof given by the pK_a measurements. In an attempt to restrict certain dynamic processes, we also undertook a NMR study in the solid state using the CP/MAS technique. Moreover, semiempirical MNDO/AM1 calculations were carried out on both systems, where the counterion as well as solvation interactions were taken into account.



(**1**)



(**2**)

The choice of the 2,2′-biindenide system stems from the fact that this compound is one of the suggested systems where the proposed ion triplet structure is the most favored one, according to the small difference between the first and second acidity constant.[3] The less symmetric **2** was included to provide additional information since the charge pattern as reflected in the induced carbon shifts will be different for the two indenide subunits.

Table II. ^{13}C and ^{1}H Chemical Shifts (δ) of 1,2′-Biindenide in Various Solvents and ^{13}C Chemical Shifts (δ) in the Solid State

	solvent					
position	THF/ DMPU	THF	2-MeTHF	DEE^a	solid	$\Delta\delta^b$
1′,3′	88.0 (6.1)	87.3 (6.3)	87.3 (6.3)	87.2	88.0	0.8
4′,7′	116.3 (6.9)	117.6 (7.2)	118.1 (7.2)	119.1		−2.8
5′,6′	111.2 (6.1)	113.6 (6.4)	114.4 (6.4)	117.0		−5.8
3a′,7a′	131.1	131.0	129.7	129.1	128.9	2.0
2′	137.8	134.8	132.7	131.5	134.2	6.3
3	93.9 (5.8)	93.0 (5.9)	92.5 (6.0)	93.8	92.9	0.1
2	118.7 (6.8)	115.6 (6.9)	114.4 (6.9)	114.4		4.3
1	109.1	107.5	106.8	105.0	107.1	4.1
7	119.2 (7.8)	120.0 (8.0)	120.4 (8.1)	120.8		−1.6
6	111.3 (6.3)	114.3 (6.5)	115.6 (6.6)	116.3		−5.0
5	110.6 (6.2)	113.6 (6.4)	114.9 (6.5)	116.1		−5.5
4	118.4 (7.1)	120.0 (7.3)	120.5 (7.4)	121.4		−3.1
3a	133.1	131.8	129.8	130.0	128.9	3.1
7a	128.2	126.8	124.3	124.5	122.3	3.7

^{a} ^{1}H chemical shifts not reported due to broadened signals. ^{b} Differences in ^{13}C chemical shifts between THF/DMPU and DEE.

Results and Discussion

NMR Spectroscopy. ^{13}C NMR chemical shifts of **1** and **2** in different solvents and in the solid state are reported in Tables I and II, respectively. The shift changes observed in different solvents are interpreted as a result of a change in external solvation and/or a change in the relative amounts of contact ion pairs (cip) and solvent-separated ion pairs (ssip).[7] These induced shift changes are due to cation-induced polarization of the charge in the indenyl units under various ion pair conditions and could be compared to those shift changes previously observed in the 1- and 2-methyl-substituted indenide systems.[8]

In order to assess the ion-pair equilibrium, a variable-temperature ^{7}Li NMR study of **1** was performed in three solvent systems.[2b] A leveling effect at 253 K and higher temperatures could be noticed in 2-methyltetrahydrofuran (2-MeTHF) at $\delta = -6.0$ ppm, representing a cip. At low temperatures, a similar leveling was observed for the tetrahydrofuran/1,3-dimethylethyleneurea (THF/DMEU) system, indicating a ssip with a ^{7}Li shift of −0.8 ppm. In THF, no such leveling was observed within the studied temperature interval (213–293 K). The shift range in this inverval varied linearly between −5.4 and −4.0 ppm. Thus, the shift data in THF support a gradual change in the equilibrium between cip and ssip.

A comparison of the 2,2′-biindenide and the 2-methylindenide systems shows that the gross patterns of the shift changes are the same in both systems. Charge is polarized toward the five-membered rings when the equilibrium favors cip.[7,8] However, polarization of the biindenide system is greater with a more pronounced increase of the charge on the carbons joining the two subunits. This charge distribution, with a large increase of the electron density on two bridging carbons in the cip, is exactly opposite to the expected charge trend if only electrostatic repulsion within the dianion structure were operative. However, it is in good agreement with the charge pattern expected from a cip triplet structure (see below).

More conclusive support for an ion triplet structure comes from a study of the unsymmetrical **2**. The pattern of charge distribution in the 2′-substituted unit is approximately the same as observed in **1**. When the 1-substituted unit is compared to the analogously substituted 1-methylindenide, it is quite obvious that the charge is polarized toward the bridging position. The comparison between the 3- and 1-positions in the biindenide with the corresponding positions in the 1-methylindenide is especially revealing. The charge is polarized away from the methyl-substituted position in

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Table III. Line Broadening of ^{1}H Resonance 1′,3′ in 1,2′-Diindenide in Different Solvents, as a Function of the Temperature

solvent	temp (K)	$W^* - W_0$ (Hz)[a]	k (s^{-1})	ΔG^* (kcal mol^{-1})	ΔH^* (kcal mol^{-1})	ΔS^* (cal(mol·T)[a])
2-MeTHF	298	4	10000	12	2.0 ± 0.5	−31 ± 2
2-MeTHF	252	15	2700	11		
2-MeTHF	210	90	450	10		
DEE/THF	293	43	945	13	3.3 ± 0.9	−33 ± 5
DEE/THF	253	31	97	12		
DEE/THF	218	5	16	11		
DEE/THF	193	1.5	5	10		
THF[b]	293	0.4	100000	11		

[a] ($W^* - W_0$) is the difference in linewidths at half-height between the exchanging signals and a reference signal (H6). The ($W^* - W_0$) term refers to slow exchange in DEE/2-MeTHF solutions at 353 K and below, while fast-exchange conditions prevail at the other experimental conditions. [b] The energy barrier was estimated at room temperature based on the difference in T_1 and T_2, assuming that the reduction of T_2 is due to the exchange.

the latter system whereas in the biindenide system the charge is strongly polarized toward the bridging position. Again, these shift data correlate nicely with an ion triplet structure where the cations are located close to the junction of the two subunits.

Additional information regarding the 1,2′-system can be obtained from the ^{1}H NMR data. All proton signals in the 2′-substituted indenide unit exposed temperature- and solvent-dependent line shape changes. For the H1′ and H3′ resonances, the region of slow exchange was reached at cip conditions at low temperatures; see Table III. The shift difference between these exchanging resonances was found to be 160 Hz at a ^{1}H resonance frequency of 500 MHz. The shift differences for the other protons are smaller, since they were still in the fast-exchange region at the lowest temperatures investigated. The observed dynamic process is obviously caused by the rotation around the 1,2′-bond.

The energy barrier for this rotation was estimated by studying the exchange rate as a function of temperature in 2-MeTHF and diethyl ether (DEE)/2-MeTHF (100:3; see the Experimental Section). The exchange rate in 2-MeTHF was not affected by the concentration in a range between 0.1 and 0.01 M. The lack of concentration dependence implies that the restricted rotation is probably not associated with a change in aggregation state, i.e., the formation of dimers, trimers, or higher aggregates. There were no significant changes in line broadening in THF solution in the measured temperature interval. The NMR results and the calculated activation parameters are reported in Table III. From this table, it is evident that the exchange rate is slower in less cation solvating media.

It was also found that addition of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) to a 2-MeTHF solution reduced the exchange rate. It is known that addition of TMEDA inhibits the interaction between THF and the cation, thereby favoring the cip situation.[9] It has also been observed that the exchange between free and complexed TMEDA can be slow on the NMR time scale.[10]

Hence, we propose that the rotation preferably takes place in a more solvated state. Further support for this view comes from the activation parameters (Table III). It can be noted that the major contribution to the free energy of activation is found in the relatively large and negative entropy term. This indicates that the transition state has a more ordered structure, i.e., "freezing" of solvent molecules, which is expected when the solvation is increased (compare cip ⇄ ssip).[7,8] In this context, it must be borne in mind that the exchange rate between cip and ssip is fast on the proton NMR time scale and will not influence the observed rotational process. The proposed model also rationalizes the lack of temperature dependence on the exchange rate in THF. A temperature decrease will stabilize the transition state (TS) for the rotational process and thereby compensate for the reduced thermal energy available.

A partial double-bond character of the bridging bond would also reduce the rotational rate about this bond. However, the semiempirical calculations discussed below for this system suggest that the bond order for the bridging bond is close to unity.

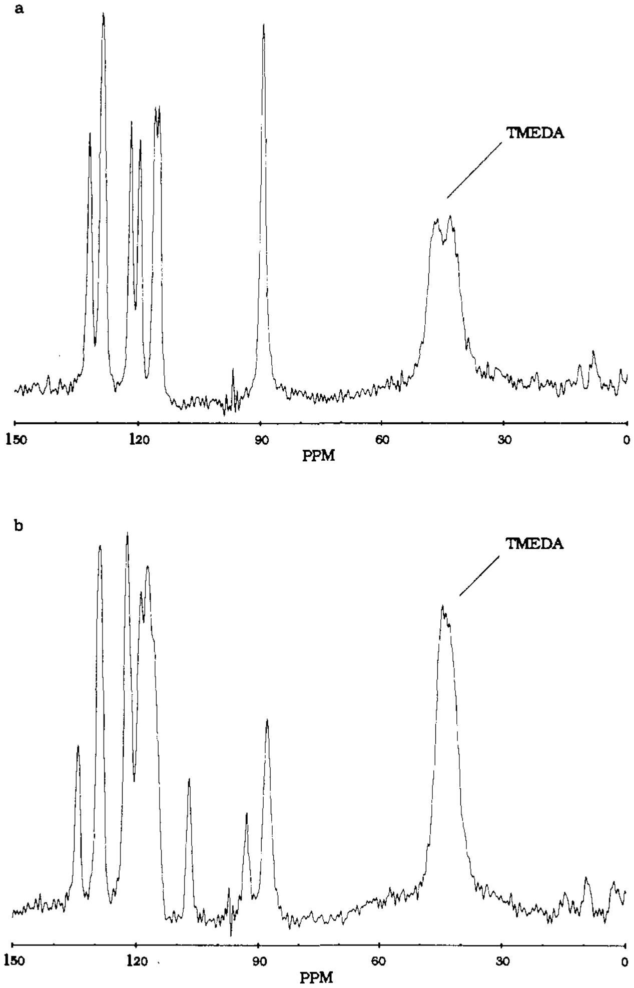

Figure 1. ^{13}C CP/MAS NMR spectra of the ^{7}Li isotopomers of (a) 2,2′-biindenide and (b) 1,2′-biindenide.

At this point, it is illuminating to compare our findings to the (phenylallyl)lithium system,[11] where restricted rotation has been attributed to a change in double-bond character as the ion pair situation varies. In that case, an increased rotational rate was observed when the relative cip concentration increased. Moreover, the activation parameters for that system were dominated by the activation enthalpy, and the activation entropy was positive. Both of these findings are opposite to the situation in the present case.

All experimental data, namely charge distribution in the cip, the dilution experiments, and the activation parameters, indicate that this system exists as ion triplet like structures in the cip and that this ion arrangement is causing the restricted rotation in **2**.

Solid-state ^{13}C CP/MAS NMR data of the TMEDA-complexed ^{7}Li systems **1** and **2** are presented in Figure 1, parts a and b, respectively. The chemical shifts are reported in Tables I and

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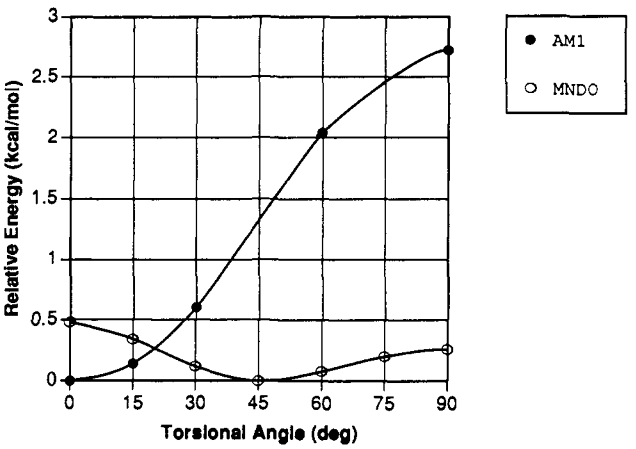

Figure 2. Comparison of MNDO and AM1 relative energies of the 2,2′-biindenide dianion as functions of twist angle.

II, respectively. As evident from Table I, the chemical shifts of the 2,2′ system in the solid state correspond most closely to a cip in 2-MeTHF, and we therefore propose the ion pair to be a contact ion pair triplet structure. From Figure 1a, it is evident that there is an asymmetry in the crystal structure, as the 4,7- and 5,6-positions are nonequivalent. However, the question as to whether the asymmetry is between or within the monomer units cannot be decided on NMR data only. A similar asymmetry has been reported previously for the TMEDA-complexed dilithium 9,9′-bifluorenide system determined by X-ray crystallography.[4]

The situation is different for the 1,2′-biindenide system. First, all resonances could not be unambiguously assigned due to the restricted resolution in the solid-state NMR spectrum (Figure 1b). However, the nonprotonated positions, together with some of the protonated positions, could be assigned (see Table II). It is clear that the differences between the solution- and solid-state data for this system are much larger than in the previous symmetric case. Moreover, the shift pattern in the solid does not correspond well to any ion pair situation observed in solution. Charge seems to be polarized away from the bridging position toward the non-proton-bearing benzene carbons. Hence, the observed differences between solution- and solid-state NMR data for **2** merely point toward a solid-state structure where the lithiums are shifted toward the five-membered rings. The conclusion is that the crystal structure does not correspond to the structure, or the time-averaged structure in solution. We have noticed in a previous study of lithium fluorenide that the preferred cation positions can be altered depending on the ligand used,[12] possibly due to crystal packing forces.

MNDO/AM1 Calculations. In an attempt to rationalize the interpretation of the NMR results, we carried out semiempirical MNDO[13] and AM1[14] calculations on the 2,2′- and 1,2′-biindenide systems. As a first approximation, we considered structures of the isolated dianions without any countercations. The dependencies of 2,2′- and 1,2′-biindenide dianion stabilities on the twist angle around the central C2–C2′ or C1–C2′ bonds, as calculated by both MNDO and AM1 methods, are shown in Figures 2 and 3, respectively. The striking feature of these calculated results is the substantial difference between the two methods. For the 2,2′-dianion, AM1 predicts the planar structure to be the global minimum and the 90° rotamer to be a TS for rotation with a barrier equal to 2.7 kcal/mol. In contrast, MNDO predicts a very shallow potential energy curve with a minimum around 45° and the planar rotamer (TS) 0.5 kcal/mol higher in energy. Similarly, 1,2′-biindene dianion is predicted by AM1 to be slightly nonplanar in its lowest energy conformation with a twist angle of 18.5°, whereas MNDO gives a shallow minimum around 65° with the 90° rotamer higher in energy by only 0.1 kcal/mol and the planar form (TS) less stable by 2.5 kcal/mol. The difference in results between the two methods may be explained as follows. The major factors contributing to the calculated structures for the biindene system are steric repulsions, which favor nonplanar rotamers, and conjugation, which favors planarity. It is well established that MNDO in its original formulation and parameterization seriously overestimates steric repulsions and underestimates conjugation in organic molecules: a defect which was reportedly overcome in the later released AM1 method.[14] Thus, we believe the AM1 results to be more reliable than MNDO and consequently favor the former calculations that predict the 2,2′-dianion to be planar and the 1,2′-isomer to be slightly twisted in their lowest energy conformations.

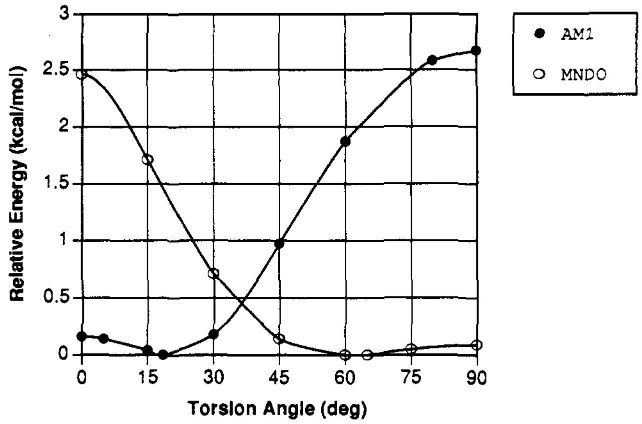

Figure 3. Comparison of MNDO and AM1 relative energies of the 1,2′-biindenide dianion as functions of twist angle.

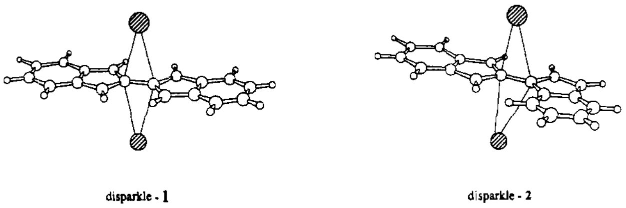
disparkle - 1
disparkle - 2

Figure 4. AM1 calculated structures of 2,2′- and 1,2′-biindenide disparkle ion triplets.

It is important to be aware of this deficiency in MNDO in handling the balance between repulsion and conjugation since we are forced to use MNDO when lithium is included as a counterion (see below); the lithium parameterization for AM1 is not yet available. The extent of this error may be estimated from Figures 2 and 3. It appears that MNDO underestimates the stability of the planar structure relative to the perpendicular one by at least 3 kcal/mol in the case of 2,2′-biindenide and approximately 5 kcal/mol for the 1,2′-biindenide dianion. Of course, for rotamers with twist angles lower than 90°, the error will be lower than these upper limits given for the extreme case.

The next step in the computational investigation was the inclusion of counterions. First we utilized "sparkles" available in the MOPAC[15] program package. Sparkles are unpolarizable +1 point charges located in a center of a sphere with an effective radius of 0.7 Å.[15] In previous theoretical studies of lithiated polyaromatic compounds, we showed the usefulness of such calculations in providing models for externally solvated species where alkali-metal ions interact with organic anions by Coulombic forces only.[6d,16] The optimal AM1 structures of the biindenide-disparkle ion triplets are given in Figure 4. Both disparkle 2,2′-biindenide and 1,2′-biindenide show planarity of the organic portion of the molecules in the minimum energy rotamers as calculated by AM1. Those structures reveal a typical ion triplet arrangement as proposed for such systems.[3] That is, the count-

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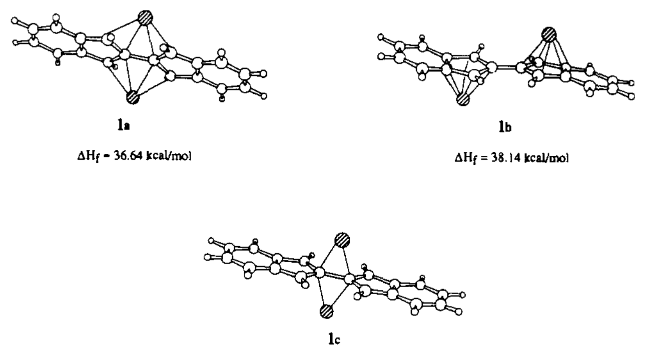
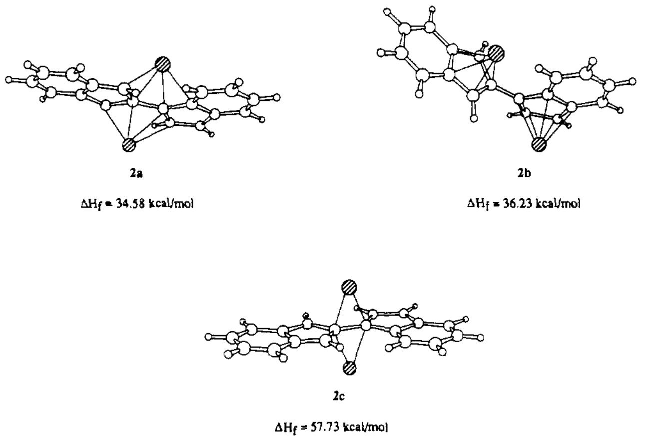


1a $\Delta H_f = 36.64$ kcal/mol

1b $\Delta H_f = 38.14$ kcal/mol

1c $\Delta H_f = 57.00$ kcal/mol

Figure 5. MNDO optimized structures of dilithium 2,2′-biindenide haptomers.



2a $\Delta H_f = 34.58$ kcal/mol

2b $\Delta H_f = 36.23$ kcal/mol

2c $\Delta H_f = 57.73$ kcal/mol

Figure 6. MNDO optimized structures of dilithium 1,2′-biindenide haptomers.

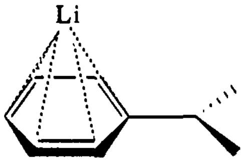
ercations are located over and under the central C1–C2′ and C2–C2′ bonds and the electron densities on those carbons are increased, due to polarization, as compared to the isolated dianions. This is in full agreement with the NMR results discussed earlier. MNDO, on the other hand, while also predicting a planar structure for disparkle 2,2′-biindenide, indicated a slightly twisted rotamer for the 1,2′-isomer disparkle compound (twist angle 22°). The planar form was calculated by MNDO to be 0.3 kcal/mol higher in energy in this latter case. Keeping in mind the comparison of the MNDO and AM1 results for the isolated dianions, we conclude that planar structures will be favored for the organic moieties in the ion triplets of both 1,2′- and 2,2′-biindenide systems if only Coulombic forces are operative.

Closer inspection of the AM1 and MNDO results for disparkle biindenides shows that the overestimation of the relative stabilities of the nonplanar vs the planar rotamers, although still present, is significantly lower than for the isolated anions. This is probably due to repulsions between the sparkles and the carbon framework present in the nonplanar rotamers. Since these repulsions are overestimated by MNDO, the overall error is expected to be partially canceled. We would also expect a similar reduction in the error for calculations performed with dilithio derivatives.

The results of MNDO calculations where two lithium cations are included as counterions are shown in Figures 5 and 6. Included are the global minima, **1a** and **2a**, local minima where the cations are associated with the five-membered rings (**1b** and **2b**), and structures analogous to those obtained by sparkle AM1 calculations as well as by predictions based on triplet structures (**1c** and **2c**).[3] All the above structures exhibit antifacial selectivity with the lithium cations located on the opposite faces of the organic dianion. This is in accord with the results of similar calculations published earlier,[6b,d,e] as well as with the available X-ray crystal structure determination results.[17] This preference is at least partially due to favorable interactions of lithium-based dipoles in such orientations. Moreover, synfacial orientation may further be destabilized in real systems by steric crowding of the cation solvation molecules.

The most stable haptomers of both dilithium **1** and **2** complexes are similar to the ion triplet arrangements represented by the disparkle structure. The only significant difference between those arrangements is that in the dilithio derivatives, **1a** and **2a**, the lithium cations are shifted toward C1 and C3, respectively, each being within bonding distance of four carbon atoms. The organic dianions in both **1a** and **2a** are essentially planar, with small distortions from planarity most likely resulting from interactions with the lithium cations.

The second most stable haptomers of dilithium **1** and **2** complexes are **1b** and **2b** where the lithiums are located over and under the five-membered rings. The calculated heats of formation of these haptomers are higher in energy than **1a** and **2a** by 1.5 and 1.6 kcal/mol, respectively. Given the small energy differences, it could be argued that **1b** and **2b** should also be considered as candidates for the optimum structure of these dilithio derivatives. However, MNDO overestimates the degree of covalency of the carbon–lithium bond, as well as its energy,[18] and as a consequence, the relative stabilities of structures with more formal C–Li bonds are overestimated relative to those with fewer C–Li bonds. For example, MNDO predicts the η^6-haptomer of benzyllithium (**3**) to be more stable than **4** by 3.3 kcal/mol[17] even though **4** is the preferred arrangement in the crystal (as a triethylenediamine complex).[19] The calculated result is no doubt influenced by the fact that there are six formal C–Li bonds in **3** whereas there are only three such bonds in **4**. Hence, in the case of the dilithium diindenides, the relative stabilities of **1b** and **2b** (with 10 formal C–Li bonds) are probably overestimated as compared to the cases **1a** and **2a** (with 8 such bonds). This suggests that the real differences in energy are actually greater than the calculated ones in favor of **1a** and **2a**. Therefore, we exclude **1b** and **2b** as possible minimum energy haptomers for monomeric, unsolvated dilithium **1** and **2** complexes.



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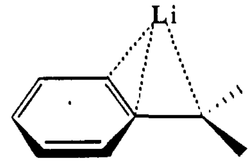

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Structures **1c** and **2c** were calculated by forcing the dianions to be planar with the lithiums located over and under the central C2–C2′ or C1–C2′ bond in a plane perpendicular to the dianion. Partial optimization ended with heats of formation higher in energy by 20.4 kcal/mol for **1c** and 23.2 kcal/mol for **2c**, as compared to **1a** and **2a**, respectively. The differences are probably overestimated since only four C–Li bonds are present in c-type haptomers, whereas there are eight in **1a** and **2a**. It should be stressed that those structures are neither local minima nor transition states on the MNDO potential energy surface; force constant calculations exhibit more than one imaginary frequency for both **1c** and **2c**.

We also calculated the structures of dilithio-**1** and dilithio-**2** with six water molecules mimicking the ethereal solvent molecules. The minimum energy conformations are similar to those given in Figures 5 and 6. The general trend is that solvation of the cations significantly reduces the energy differences between the haptomers in question. This is in accord with the previously reported results of MNDO calculations for the dilithio biphenylene system.[6e] In both 2,2′- and 1,2′-biindenide, the haptomers with lithiums located over and under the five-membered rings become the preferred arrangements when water molecules are included (**1b**·6H_2O, $\Delta H_f = -389.38$ kcal/mol; **2b**·6H_2O, $\Delta H_f = -387.65$

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kcal/mol). However, the small differences in energy, when compared to the cases of **1a**·6H_2O and **2a**·6H_2O (1.8 and 2.9 kcal/mol, respectively), together with the previously discussed deficiencies of the MNDO method lead us to believe that the predicted preference of the η^5-haptomers over the a-type arrangements in the solvated systems is due to the overestimation of C–Li interaction by the MNDO method. However, the comparison between solution- and solid-state NMR data of **2** indicates that the energies of **2a** and **2b** are comparable, since **2a** seems to be the valid structure in solution but a **2b** type in the solid. More interestingly, the difference in energies between the a-type haptomers and the c-type haptomers decreases from over 20 kcal/mol in unsolvated systems to 7.5 and 7.7 kcal/mol for **1c**·6H_2O and **2c**·6H_2O, respectively. Moreover, overestimation of the C–Li bond energy artificially stabilizes a-type haptomers vs c-type haptomers. At this point, it is not possible to judge the magnitude of the overestimation or whether or not the calculated differences are sufficiently small so as to be significantly affected but such a correction. This question must await additional information such as X-ray structure determination of dilithium biindenides or high-level ab initio calculation results for model systems.

In conclusion, critical evaluation of the MNDO-calculated results allows us to propose both a- and c-type haptomers as possible candidates for monomeric, solvated dilithium **1** and **2** complexes. Actually, both a and c reveal the features of the ion triplet arrangement expected for such systems. The c-type structures are "pure" ion triplets governed by Coulombic interactions of the organic dianion with the countercations as demonstrated by sparkle calculations, and the a-type haptomers are ion triplet structures modified by some carbon–lithium bond covalency. Although it has been generally accepted that the carbon–lithium bond is mostly ionic,[20] the fact that partial covalency of the bond may influence the lowest energy structures of certain organolithiums cannot be excluded. For example, we showed that pure Coulombic interactions of the lithium cations with polyaromatic dianions in dilithium naphtalenide and dilithium anthracenide lead to ion triplet structures as the global minima.[6d] On the other hand, MNDO calculations performed with lithium parameterization gave distinctly different global minima for those compounds, in full agreement with X-ray data. Consequently, turning back to the biindenide systems, we expect that, in the systems with solvation of the countercations (i.e., with longer C–Li distances and a higher degree of ionic character), the preferred structures will be like those presented in Figures 5 and 6, or similar to **1** and **2**. On the other hand, in systems with poor solvation of the cations (i.e., shorter C–Li distances), structures similar to **1a** or **2a** are expected to represent minimum energy arrangements for dilithium 2,2′- and dilithium 1,2′-biindenide, respectively.

Strong support for a triplet arrangement, similar to the **a**,**c** structures discussed above, is provided by a ^{6}Li,^{1}H two-dimensional heteronuclear Overhauser effect experiment (HOESY).[21] In such an experiment, the cross-peak intensity will reflect the proximity of lithium and hydrogen nuclei. As seen in Figure 7a, the proton intensities of lithium indenide nicely correlate to the expected distances if the lithium ion is almost centrally located above the five-membered ring. This observation is in nice agreement with earlier HOESY observations in THF of lithium fluorenide.[21c] Only the distant H5,6 proton signal is absent in that system under cip conditions. The proton slice of dilithium **2** complex (Figure 7b) reveals quite a different pattern under the same cip conditions (2-MeTHF). The H2 and H1′,3′ signals are clearly seen at a 1:2 intensity ratio, while the more remote H3 peak is of much lower intensity. Hence, a situation where the two lithium ions are close to the bridging bond seems to be prevalent.

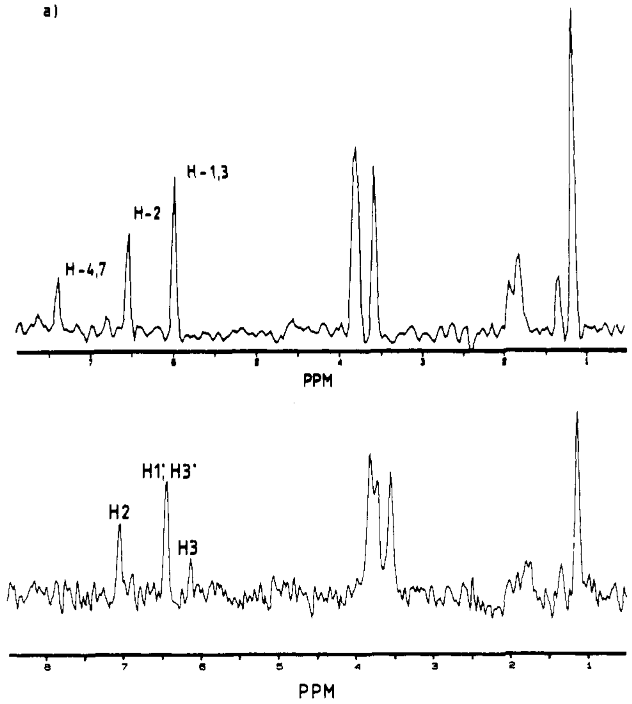

Figure 7. Proton slice (f_1 trace of ^{6}Li signal) from a ^{6}Li,^{1}H HOESY experiment of (a) lithium indenide and (b) dilithium **2** complex dissolved in 2-MeTHF.

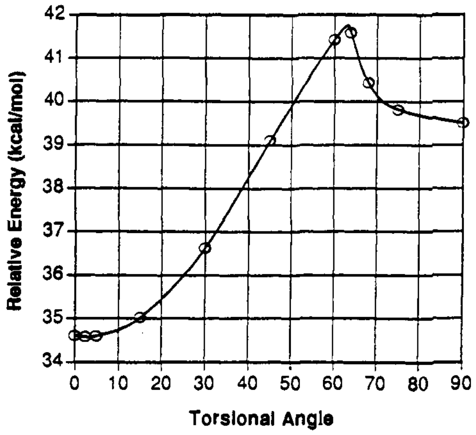

Figure 8. MNDO heat of formation of dilithium 1,2′-biindenide as a function of rotation around the C1–C2′ bond.

Barrier for Rotation in 1,2′-Biindenide. Additional calculations were performed on **2** in an attempt to rationalize the interpretation of the NMR results concerning internal rotation around the C1–C2′ bond. Figure 3 shows the calculated barrier for rotation of the isolated dianion (2.7 kcal/mol by AM1) with the minimum energy structure having the torsional angle C7a–C1–C2′–C1′ = 18.5° and the transition state for the rotation with ϕ = 90°. Hence, loss of conjugation appears to be responsible for the barrier. However, conjugation is not very important in this system as manifested by the low energy barrier to rotation and as supported by the small changes in calculated bond lengths and bond orders between the perpendicular and nearly planar rotamers (1.443 Å and 0.995 for 90°; 1.433 Å and 1.047 for 18.5°).

The addition of two lithium cations to the dianionic system significantly increases the calculated barrier for rotation. In this case, the transition state for rotation is a rotamer with a twist angle of ca. 64° (Figure 8) that is 7.1 kcal/mol higher in energy than the optimal structure **2a**. Moreover, in view of the previously discussed overestimation of nonplanar rotamer stabilities by MNDO, this calculated barrier may be underestimated by roughly 2–3 kcal/mol (cf. Figure 3 and the disparkle calculation results). Hence, the calculated barrier for rotation in monomeric, unsolvated dilithium 1,2′-biindenide is significantly higher than the experimental values of 2.9 kcal/mol in 2-MeTHF and 3.6 kcal/mol in

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DEE/2-MeTHF.

These calculations provide us with two boundary models: (1) isolated dianions wherein the countercations are removed by solvation to the extent that the dianion does not "see" them at all (barrier 2.7 kcal/mol) and (2) an unsolvated, contact ion pair (barrier ca. 9–10 kcal/mol). We would expect the real solvated system to be somewhere in between those extremes. Thus, increasing solvation of the cations should result in a decrease of the barrier in accord with the experimental results (see above). To provide additional support to this conclusion, we have recalculated the transition-state structure for rotation of dilithium **2** complex, while fixing the torsional angle at 64° and adding six molecules of water. The final energy of that system, serving as an approximate model for the solvated transition state, was only 3.6 kcal/mol higher in energy than **2a**$\cdot$6H_2O. Even though the "corrected" value will be higher, it is still acceptably close to the experimental values. More importantly, these calculations demonstrate that the transition state for rotation in 1,2′-biindenide is more strongly stabilized by solvation than the minimum energy structure, providing a rationale for the NMR results indicating that increased cation solvation lowers the barrier for rotation in that system.

Experimental Section

1,2′-Biindene was synthesized from commercially available 1-indanone according to standard procedures.[22]

2,2′-Biindene was synthesized according to an earlier published procedure.[23]

The biindenide salts were prepared by addition of *n*-butyllithium (1.0 M in hexane) to the corresponding biindene in ethereal solution at −78 °C. The solid material was prepared in hexane solution with 1 equiv of TMEDA added. The crystals were filtered under an argon atmosphere and dried in vacuum.

The solvents used in order of decreasing solvation ability were: THF/*N*,*N*,*N*′,*N*′-tetramethylpyrimidinone (DMPU) or THF/DMEU; THF; 2-MeTHF; and DEE. In some cases, a mixture of ethers was used to increase the solubility of the salt. The solid materials were isolated as TMEDA complexes.

Solution NMR spectra were obtained on Bruker ACP 250 and AM 500 spectrometers, using cyclohexane as internal reference and converted to the δ scale using the ^{13}C NMR chemical shift of cyclohexane, 27.7 ppm.

The assignment of the ^1H NMR resonances of the dilithium 1,2′-biindenide was done by double-quantum filtered COSY in combination with NOE difference experiments. The ^{13}C resonances were assigned by C,H-correlated methods. The nonprotonated carbons were assigned by the COLOC pulse sequence optimized for a coupling constant of 18 Hz.

The phase-sensitive HOESY experiments[21b] were performed at room temperature using a mixing time of 2 s.

Solid-state CP/MAS NMR spectra were obtained using a Bruker MSL 100 NMR spectrometer. The samples were rotated at 3 kHz, the repetition time was 2.5 s, and the contact time was 1 ms. The methylene carbon of adamantane was used as external reference at 38.3 ppm relative to TMS.

The ^{13}C CP/MAS spectra were assigned based on similarities to the shifts obtained in solution. Protonated and nonprotonated carbons were distinguished based on the differences in cross-polarization rates.[24]

The activation parameters were derived from the NMR data according to earlier described procedures.[25] In the fast-exchange region the exchange rate was calculated according to $k = \pi\delta\nu^2/(2(W^* - W_0))$; in the slow-exchange region the exchange was calculated according to $k = \pi(W^* - W_a)$.

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Kinetics of Alkylhalocarbene Rearrangements: Modulation by Fluorine Substituents

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Abstract: Rate constants were measured by laser flash photolytic methods for hydrogen and carbon 1,2-migrations in four different alkylchlorocarbenes and in the analogous alkylfluorocarbenes. The carbenes, products, and rate constants (s^{-1}) were as follows: phenoxymethylchlorocarbene to (*Z*)- and (*E*)-1-chloro-2-phenoxyethene ($Z/E \sim 4/1$), $k = 3.6 \times 10^7$; phenoxymethylfluorocarbene to (*Z*)-1-fluoro-2-phenoxyethene ($Z/E > 10/1$), $k = 1.3 \times 10^7$; neopentylchlorocarbene to (*Z*)- and (*E*)-1-*tert*-butyl-2-chloroethene ($Z/E = 1/12$), $k = 1.4 \times 10^7$; neopentylfluorocarbene to (*Z*)- and (*E*)-1-*tert*-butyl-2-fluoroethene ($Z/E = 1/2.5$), $k = 2.6 \times 10^6$; cyclobutylchlorocarbene to 1-chlorocyclopentene (C migration) and chloromethylenecyclobutane (H migration), $k_c = 4.6 \times 10^7$, $k_H = 2.1 \times 10^7$; cyclobutylfluorocarbene to 1-fluorocyclopentene (C migration) and fluoromethylenecyclobutane (H migration), $k_c = 1.8 \times 10^6$, $k_H = 5.3 \times 10^5$; cyclopropylchlorocarbene to 1-chlorocyclobutene, $k = 9 \times 10^5$; cyclopropylfluorocarbene to 1-fluorocyclobutene, $k = 1.4 \times 10^5$. Activation energies for several of these processes were in the range of 2–4 kcal/mol, with $A \sim 10^8$–10^9 s^{-1}.

Hydride and carbon 1,2-shifts are fundamental intramolecular carbene reactions.[1] The simultaneous availability of nanosecond laser flash photolytic (LFP) equipment, appropriate (diazirine) precursors,[2] and Platz's ylide kinetic methodology[3] permits us to determine kinetic parameters for these processes. Although alkyl and dialkylcarbenes often rearrange too quickly for nanosecond

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