ELSEVIER

www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 584 (1999) 27–32

Journal of Organometallic Chemistry

An ab initio study on dilithiosulfoximines

Jürgen F.K. Müller [a,*], Rohit Batra [b,1]

[a] *Institute of Inorganic Chemistry, University of Basel, Spitalstrasse 51, CH-4056 Basel, Switzerland*
[b] *Institute of Organic Chemistry, University of Basel, St. Johanns-Ring 16, CH-4056 Basel, Switzerland*

Received 3 December 1998; received in revised form 12 January 1999

Abstract

The gas-phase structures of the dilithiosalts of (*N*-methyl)dimethylsulfoximine **1** were calculated by ab initio methods employing different levels of theory (HF, MP2, B3LYP and CBS). Three low-energy structures were found, with the 1,3-dilithiosulfoximine **2**, a metalla spiro structure, as the most stable isomer. The second minimum **3** contains a α,α dilithio motif forming two four-membered rings with the heteroatoms on sulfur, whereas isomer **4** shows one lithium coordinating to the two anionic carbon atoms and the other to the two heteroatoms bound to the sulfur. The values of the relative energies of the compounds **3** and **4** are 1–5 kcal mol^{-1} higher in energy than that of **2** and fairly close to one another depending on the applied level of theory. A comparison between DFT and CBS-Q calculations is made and reveals no significant discrepancies in the structures. The monolithium and lithium-free dianions **2a**,**b**$^{-}$–**4a**,**b**$^{-}$, **2**$^{2-}$–**4**$^{2-}$ and their complexation energies to the lithium cations were also calculated. NBO analyses were carried out to reveal donor–acceptor interactions in these dilithio salts. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Ab initio calculations; Dianions; Gas phase structures; Lithium; Sulfoximines

1. Introduction

The formation of more than one stereocentre in a single reaction step is one of the most challenging tasks in asymmetric synthesis. Several strategies have been developed and successfully applied to a variety of chemical reactions in which the creation of new stereogenic centres was achieved with (sub)stoichiometric or catalytic amounts of a chiral auxiliary [1]. Although chiral organolithium compounds are very useful reagents for stereoselective C–C bond formations [2] the extension to polylithiated chiral systems is restricted to a few examples and these have scarcely been applied in asymmetric synthesis [3]. In principle, such reagents may be employed for the multiplication of their chiral information in their reaction with prochiral (bis)electrophiles. Little is known about the existence, structure and chemical behaviour of chiral heteroatom stabilised dilithiocarbanions in which both lithiums are attached to the same carbon atom. In contrast, achiral polylithiocarbanions have already been the target of theoretical [4], structural [5] and experimental [6] investigations and heteroatom-stabilised dilithio compounds have been used for a wide range of synthetic applications [7]. For example, α,α-dilithiosulfones have already been used as reagents for the single-step formation of multiple C–C bonds. Performing such reactions in a stereoselective manner represents a challenge in organic synthesis, which was recently achieved by the use of the chiral aza analogues of the sulfones, the sulfoximines [8]. Our previous work on chiral sulfur-stabilised monolithiosulfoximines [9] prompted us to initially investigate the structures of the related dilithiated intermediates by ab initio methods (Scheme 1).

Ab initio calculations have been able to determine with considerable success the gas-phase structures of achiral and chiral oxygen- [10], nitrogen- [11], phosphorus- [12] and sulfur-stabilised (mono)lithiocarbanions [13]. It is our objective to extend these studies to chiral dilithiosulfoximines and to elucidate the possible structures and stabilities of these dilithio intermediates by classical ab initio methods and density functional the-

---

* Corresponding author. Tel.: +41-61-2671026; fax: +41-61-2671018.

E-mail address: muellerju@ubaclu.unibas.ch (J.F.K. Müller)

[1] Also corresponding author. Tel.: +41-61-2671157; fax: +41-61-2671105; e-mail: batra@ubaclu.unibas.ch

PII: S0022-328X(99)00081-9

ory (B3LYP), keeping in mind that such intermediates already serve as useful reagents for asymmetric transformations [8,14]. Natural bond orbital (NBO) analyses [15] were performed in order to investigate donor–acceptor interactions in such dilithio salts.

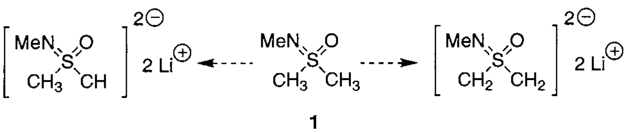
2. Computational methods

The ab initio calculations presented were performed with the Gaussian94 program suite [16]. All geometries were optimised at the Hartree–Fock (HF) level of theory with the basis sets 3-21G* and 6-31 + G** [17]. In order to assess the effect of electron correlation MP2(full)/6-31 + G** single-point calculations were calculated on the HF/6-31 + G** structures [18]. In addition, the structures of the dilithio compounds **2**–**4** were further optimised with the methods B3LYP/6-31 + G** and MP2(full)/6-31 + G**. The relative energies of the latter geometries were also computed with CBS-Q [19]. The natural bond orbital (NBO) method implemented in Gaussian94 was employed to analyse the HF/6-31 + G** wavefunctions. Hyperconjugative effects were evaluated based on the second order perturbation theory.

3. Results and discussion

3.1. Structures of dilithiosulfoximines

The model system (*N*-methyl)dimethylsulfoximine **1** was chosen for our computational investigations. Dilithiation afforded three different local energy minima (Figs. 1–3). The isomer **2** is lowest in energy and exhibits a dilithiospirostructure containing two Li–N–S–C and Li–O–S–C chelates with two different Cα atoms. A small change in both S–Cα bond lengths is observed compared with the protonated parent **1** (1.77 Å in **1** vs. 1.73 and 1.75 Å in **2**). The Li–C distances are 2.09 Å in either case. The lone pairs at the anionic C atoms point away from one other in the direction of each lithium atom, thus minimising the repulsion caused by the two negative charges. Structure **3** represents a local minimum which is only 2.7 kcal mol^{-1} higher in energy. It is characterised by a α,α-dilithiosulfoximine arrangement in which both lithiums are attached to the same Cα atom. In addition, each lithium is coordinated to one of the two heteroatoms of the sulfonimidoyl moiety, thereby forming (Li–N–S–C) and (Li–O–S–C) four-membered ring chelates, respectively. The S–Cα bond is significantly shortened after dimetallation from 1.77 to 1.66 Å. The lithium atom coordinating to the sulfoximine oxygen yields the longer Li–C bond with 2.11 Å. In contrast, in the *N*-chelate the Li–C bond is markedly shorter (2.04 Å). Both planes which are defined by the two four-membered ring chelates form the butterfly type structure depicted in Fig. 2. The lithium atoms are in a diastereotopic environment, which may be interesting for synthetic purposes [2,8]. The local minimum structure **4** lies 0.3 kcal mol^{-1} higher in energy than **3**. Remarkably, in **4** one lithium is exclusively coordinated to the heteroatoms of the sulfoximine group whereas



Scheme 1.

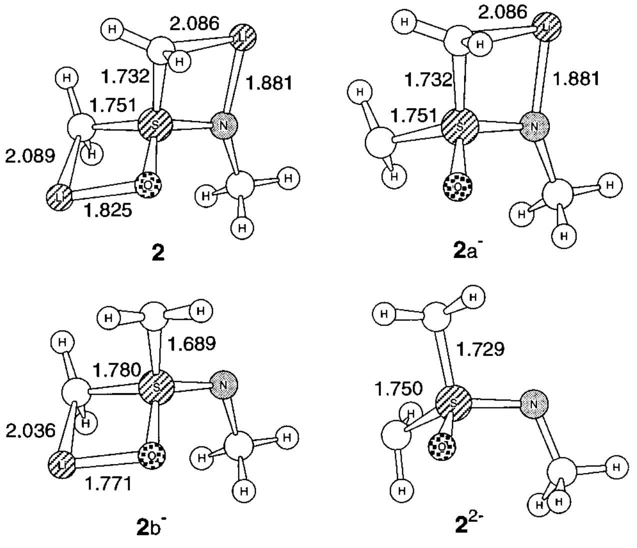


Fig. 1. α,α′-Dilithiosulfoximine **2** and the derived monolithioanions **2a,b**$^-$ with the lithium-free dianion $\mathbf{2}^{2-}$; bond distances in Å.

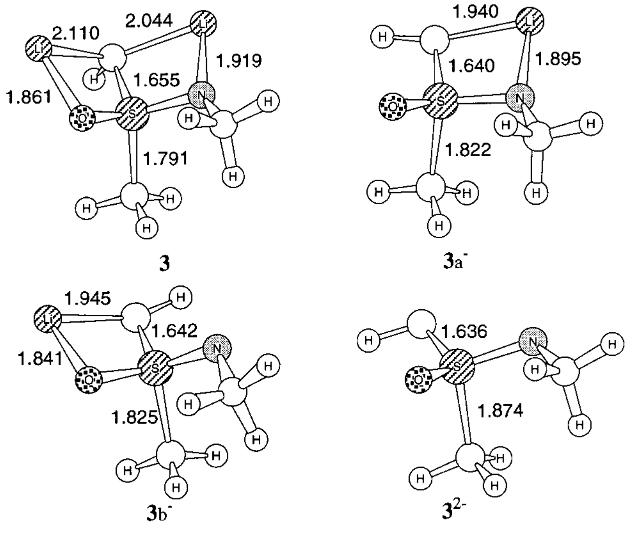


Fig. 2. α,α-Dilithiosulfoximine **3** and the derived monolithioanions **3a,b**$^-$ with the lithium-free dianion $\mathbf{3}^{2-}$; bond distances in Å.

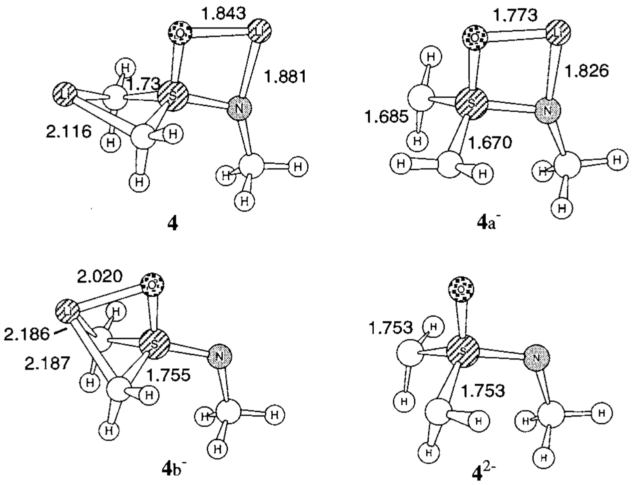


Fig. 3. α,α′-Dilithiosulfoximine **4** and the derived monolithioanions **4a,b**$^-$ with the lithium-free dianion **4**$^{2-}$; bond distances in Å.

the other shows a symmetrical bridging to the Cα atoms. The twofold carbon coordination of the lithium is unusual, because all other chelation modes of the lithium atoms correspond to structural motifs which have already been calculated for monolithiosulfoximines [9,20]. The Li–C distances are elongated to 2.23 Å in comparison to the structures **2** (2.09 Å) and **3** (2.04 and 2.11 Å). A common feature of all three isomers **2**–**4** is the strong pyramidalisation of the anionic carbon atoms described by their improper dihedral angles in Tables 1–4.

A comparison of these major structural minima with the results of MP2(full)/6-31 + G** calculations yielded only marginal changes in their geometries and energies. Greater accuracy in the determination of the relative energies may be achieved by applying CBS-Q [19]. These results show a reverse order in the relative stabilities: **4** becomes slightly energetically favoured over **3**, but the difference in their energies remains small (Table 5). The same observation is made for B3LYP/6-31 + G**, where **3** is about 2.1 kcal mol^{-1} higher in energy than **4**. In conclusion, all applied methods show compound **2** as the global minimum. The isomers **3** and **4** are in general 1–5 kcal mol^{-1} higher in energy and fairly close to one another, so that the order of these stabilities becomes exchangeable.

Relatively small structural changes have been noted for the dilithio salts going from HF/6-31 + G** to B3LYP/6-31 + G** and MP2(full)/6-31 + G**. This demonstrates that geometries derived from DFT are in good agreement with the results obtained from Hartree–Fock calculations. The use of smaller basis sets (6-31 + G** to 3-21G*) leads to an overestimation of the Li–O and S–C interaction [21] and is reflected in a strong contraction of the Li$_2$–O bond (2.001 Å) in **4** and a decrease of the S–C bond distances of the anionic carbons in **2**–**4**.

Table 1
Selected bond length (Å) and angles (°) of **1** [a]

S–O	1.453	O–S–N	121.82
S–N	1.517	C–S–C	103.34
S–C1	1.791	C–N–S	119.30
S–C2	1.769		

[a] The geometries were determined with HF/6-31+G**.

Table 2
Selected bond lengths (Å) and angles (°) of **2**

	HF/6-31+G**	B3LYP/6-31+G**	CBS-Q	HF/3-21G*
Li$_1$–N	1.881	1.869	1.904	1.854
Li$_2$–O	1.825	1.826	1.861	1.797
Li$_1$–C	2.086	2.063	2.089	2.115
Li$_2$–C	2.089	2.061	2.088	2.123
S–C$_1$	1.732	1.746	1.726	1.703
S–C$_2$	1.751	1.770	1.754	1.729
S–N	1.589	1.626	1.611	1.581
S–O	1.515	1.562	1.551	1.524
O–S–N	111.43	110.47	110.43	110.51
S–C–Li$_1$	82.77	82.81	83.33	81.82
S–C–Li$_2$	79.93	79.92	80.67	79.60
S–C–Li$_1$–H$_1$	109.72	108.74	109.54	112.91
S–C–Li$_1$–H$_2$	105.19	105.04	104.81	108.49
S–C–Li$_2$–H$_1$	107.36	106.24	107.48	109.97
S–C–Li$_2$–H$_2$	105.40	104.75	104.63	108.32

3.2. *Structures of the monolithio anions and lithium-free dianions*

The successive removal of a lithium cation in **2** resulted in two different monolithiated anions **2a**$^-$ and

Table 3
Selected bond lengths (Å) and angles (°) of **3**

	HF/6-31+G**	B3LYP/6-31+G**	CBS-Q	HF/3-21G*
Li$_1$–N	1.919	1.902	1.932	1.893
Li$_2$–O	1.861	1.858	1.894	1.845
Li$_1$–C	2.044	2.034	2.059	2.090
Li$_2$–C	2.110	2.099	2.123	2.117
S–C$_1$	1.655	1.664	1.651	1.640
S–C$_2$	1.791	1.836	1.815	1.780
S–N	1.583	1.619	1.607	1.575
S–O	1.517	1.567	1.558	1.522
O–S–N	111.15	110.84	110.62	110.79
S–C–Li$_1$	82.55	82.02	82.33	81.10
S–C–Li$_2$	77.24	76.73	77.42	78.33
Li–C–Li	118.10	118.29	117.91	115.08
S–C–Li$_1$–H	111.78	110.85	111.01	115.75
S–C–Li$_2$–H	108.24	107.68	107.82	113.95
S–C–Li–Li	74.23	73.21	71.35	74.27

Table 4
Selected bond lengths (Å) and angles (°) of **4**

	HF/6-31+G**	B3LYP/6-31+G**	CBS-Q	HF/3-21G*
Li_1–N	1.881	1.866	1.899	1.867
Li_1–O	1.843	1.843	1.866	1.821
Li_2–O	2.940	2.743	2.200	2.001
Li_2–C	2.116	2.103	2.216	2.289
S–C_1	1.730	1.746	1.715	1.681
S–C_2	1.730	1.746	1.715	1.681
S–N	1.604	1.648	1.630	1.600
S–O	1.507	1.553	1.567	1.553
O–S–N	99.67	98.54	98.65	97.57
O–Li_1–N	79.36	81.70	80.21	79.99
S–C–Li_2	80.96	77.97	70.94	67.89
C–Li_2–C	78.36	79.36	73.91	70.51
S–C–Li_2–H_1	108.00	104.40	99.03	103.83
S–C–Li_2–H_2	106.67	106.03	103.51	108.07

2b$^-$, in which the Li–N–S–C chelate **2a**$^-$ is energetically favoured over the Li–O–S–C complexation in **2b**$^-$ by ca. 7 kcal mol^{-1} (Table 6 and Fig. 1). The analogous procedure was also performed with the dilithiosalt **3**. After removal of one lithium the Li–N–S–C complexation is energetically favoured over the Li–O–S–C coordination. The resulting monolithio intermediates **3a**$^-$ and **3b**$^-$ differ distinctly from the structures derived from **2** although the complexation energies are similar (Table 6). The unusual coordination mode of the lithium cations in **4** (Fig. 3) leads after decomplexation of one lithium either to an exclusively heteroatom-*N*,*O*-coordinated monolithioanion **4a**$^-$ or to a threefold lithium coordinated monolithioanion **4b**$^-$. The removal of the second lithium produces a naked 1,3-dianionic species **2**$^{2-}$, which delithiation requires 437 kcal mol^{-1} when starting from the dilithiosulfoximine **2**. The energy required for the second delithiation amounts to 266 kcal mol^{-1} from **2a**$^-$ and 259 kcal mol^{-1} from **2b**$^-$. Removal of the second lithium cation affords the α,α-dianion **3**$^{2-}$. The energy required for the twofold delithiation of **3** amounts to 451 kcal mol^{-1} (Fig. 2). After removal of the second lithium ion, the 1,3-dianion **4**$^{2-}$ is generated (439 kcal mol^{-1}), which is closely related to the dianionic species **2**$^{2-}$ with only a small difference in their conformations and energies ($\Delta E = 2.3$ kcal mol^{-1}).

Table 5
Relative energies [a]

	2	3	4
MP2/6-31+G**//HF/6-31+G**	0.00	2.74	3.01
B3LYP/6-31+G**	0.00	4.87	2.79
CBS-Q (0K)	0.00	2.23	1.07
CBS-4 (0K)	0.00	0.72	2.23
MP2 (full)/6-31+G**	0.00	3.02	3.55

[a] Energies in kcal mol^{-1}.

Table 6
Relative energies of the resulting anions after removal of the lithium cations [a]

	Geometries		
	Optimised	Non-optimised	ΔE
2a$^-$	171.6	180.9	9.3
3a$^-$	172.0	181.4	9.4
4a$^-$	169.1	188.3	9.2
2b$^-$	178.4	187.0	8.6
3b$^-$	177.8	192.1	12.3
4b$^-$	170.2	177.1	6.9
2^{2-}	437.6	449.4	11.8
3^{2-}	451.7	465.8	14.1
4^{2-}	439.9	447.6	7.5

[a] Energies in kcal mol^{-1} based on MP2(full)/6-31+G**//HF/6-31+G** calculations.

3.3. NBO analyses

For the isomer **2**, the interaction of the carbon lone pair (n_C) of the Li–O–S–C chelate with the σ* orbital of the S–N bond and the hyperconjugation between the n_C of the Li–N–S–C chelate with the σ* orbital of the S–O bond provide important stabilisation of the negative charge (17.2 and 15.3 kcal mol^{-1}) [22]. Stabilisation along the lithium carbon and the lithium heteroatom bonds in **2** are also confirmed by the interaction of the LP* on lithium and the lone pairs of the anionic carbons (24.5 kcal mol^{-1} for each Li–C interaction) which surpass the donor contribution of the lone pairs of the two hetero atoms (8.1 kcal mol^{-1} for Li–O and 17.1 kcal mol^{-1} for Li–N). The predominant hyperconjugative contribution for the stabilisation of the dianionic carbon in **3** is the interaction between the α-C lone pairs and the antibonding σ* orbital of the S–O bond (35.8 kcal mol^{-1}), it is found to be more effective than the corresponding n_C–σ^*_{S-C} interaction (20.3 kcal mol^{-1}). The latter causes a significant shortening of the S–C(α) bond in **3** compared to **2** and **4**. However the σ^*_{S-C} hyperconjugation for such dilithio salts is obviously not as pronounced as for the corresponding monolithio compounds, where it is known to be the dominating mechanism [4,9,19,23]. Another type of negative hyperconjugation is observed in the 1,3-dianion **4**: in this case a strong interaction between the carbon lone pairs and the σ* orbital of the S–N bond (23.1 kcal mol^{-1} for each anionic C-atom) is responsible for the stabilisation of the anionic charge. The interactions of the LP* of the lithium atoms with the two n_Cs (20.7 kcal mol^{-1} per lithium) and the lone pairs of the heteroatoms (17.5 kcal mol^{-1} for Li–N and 7.5 kcal mol^{-1} for Li–O), respectively are less

Table 7
NBO atomic partial charges

	2	3	4
O	−1.20287	−1.21693	−1.19426
S	+2.09336	+2.08754	+2.10737
N	−1.23452	−1.24306	−1.25481
Li_1	+0.91948	+0.90977	+0.89544
Li_2	+0.90794	+0.90499	+0.94204
C_1	−1.30310	−1.71948	−1.28893
C_2	−1.28435	−0.88220	−1.28896
C_3	−0.42562	−0.42233	−0.42510

effective but still contribute distinctly to the distribution of the two anionic charges. The atomic partial charges (see Table 7) indicate a significant degree of negative charge located at the lithium bound carbon atoms in **2**–**4**, which explains especially the formation of that unusal intermediate **4**, where one lithium bridges two carbon atoms (−1.28893 vs. −1.28896) rather than hetero atoms.

A d_s–p_c π-interaction for the stabilisation of all the dianions **2**–**4** is unlikely due to the low d character on sulfur in the σ bond orbitals (< 2%). The d orbitals of the sulfur therefore appear to play no role in the charge distribution.

4. Conclusions

Three equilibrium structures for the dilithiated *N*,*S*,*S*-trimethylsulfoximine system were found, with the dilithiospiro structure **2** representing the most stable isomer. Only ca. 1–5 kcal mol^{-1} higher in energy were the α,α dilithiosulfoximine **3** and the isomer **4** with heteroatom contacts to one lithium while the second lithium is associated with both anionic carbon atoms. All levels of theory revealed no significant discrepancies in the geometries of the isomers **2**–**4**. Important contributions for the dicarbanion stabilisation are due to hyperconjugative effects. The structures and relative energies of the derived monolithio dianions and lithium free dianions have been also computed. In conclusion, these results have some important implications for asymmetric synthesis: because reactions with achiral dilithio salts are already meaningful in synthetic sequences [7] one can imagine further synthetic approaches with chiral dilithio compounds derived from the discussed dilithiosulfoximine intermediates **2** or **3**. Multiple stereoselective C–C bond formations with prochiral biselectrophiles already have been applied in cyclisation reactions and have led to a new and powerful methodology for the synthesis of new carbo- and heterocyclices [8]. Further work in our group now concentrates on the exploration of the synthesis, reactivity and selectivity of such chiral dilithio compounds.

References

[1] Reviews: (a) J.D. Morrison, Asymmetric Synthesis, vol. 5, Academic Press, New York, 1985. (b) R. Noyori, Asymmetric Catalysis in Organic Synthesis, Wiley, New York, 1994. (c) G.R. Stephenson, Advanced Asymmetric Synthesis, Chapman and Hall, London, 1996.

[2] (a) W.C. Still, A. Mitra, J. Am. Chem. Soc. 100 (1978) 1927. (b) J.S. Sawyer, A. Kucerovy, T.L. Macdonald, G.J. MacGarvey, J. Am. Chem. Soc. 110 (1988) 842. (c) K. Rein, M. Goicoechea-Pappas, T.V. Anklekar, G.C. Hart, G.A. Smith, R.E. Gawley, J. Am. Chem. Soc. 111 (1989) 2211. (d) R.E. Gawley, G.C. Hart, C.J. Bartolotti, J. Org. Chem. 54 (1989) 175. (e) D. Hoppe, F. Hintze, P. Tebben, Angew. Chem. Int. Ed. Engl. 29 (1990) 1422. (f) S.T. Kerrick, P. Beak, J. Am. Chem. Soc. 113 (1991) 9708. (g) W.H. Pearson, A.C. Lindbeck, J. Am. Chem. Soc. 113 (1991) 8546.

[3] (a) T. Hayashi, A. Yamamoto, M. Hojo, Y. Ito, J. Chem. Soc. Chem. Commun. (1989) 495. (b) R.C. Petter, C.I. Milberg, Tetrahedron Lett. 30 (1989) 5085. (c) D. Seebach, H. Bossler, H. Gründler, S.-I. Shoda, Helv. Chim. Acta 74 (1991) 197. (d) D. Seebach, A.K. Beck, A. Studer, in: B. Ernst, C. Leumann, (Eds.), Modern Synthetic Methods, vol. 7, VCH, Weinheim, 1995, p. 1. (e) D. Seebach, O. Bezencon, B. Jaun, T. Pietzonka, J.L. Matthews, F.N.M. Kühnle, W.B. Schweizer, Helv. Chim. Acta 79 (1996) 588.

[4] D.A. Bors, A. Streitwieser Jr., J. Am. Chem. Soc. 108 (1986) 1397.

[5] (a) W. Hollstein, K. Harms, M. Marsch, G. Boche, Angew. Chem. Int. Ed. Engl. 26 (1987) 1287. (b) H.-J. Gais, J. Vollhardt, H. Günther, D. Moskau, H.J. Lindner, S. Braun, J. Am. Chem. Soc. 110 (1988) 978. (c) G. Boche, Angew. Chem. Int. Ed. Engl. 28 (1989) 277. (c) J.F.K. Müller, M. Neuburger, B. Spingler, Angew. Chem. Int. Ed. Engl. 111 (1999) 92.

[6] (a) J. Vollhardt, H.-J. Gais, L. Lukas, Angew. Chem. Int. Ed. Engl. 24 (1985) 608. (b) J. Vollhardt, H.-J. Gais, L. Lukas, Angew. Chem. Int. Ed. Engl. 24 (1985) 696. (c) H.-J. Gais, J. Vollhardt, Tetrahedron Lett. 29 (1988) 1529.

[7] (a) S. Brenner, M. Bovete, Tetrahedron 31 (1975) 153. (b) E.M. Kaiser, J.D. Petty, P.L.A. Knutson Synthesis (1977) 509. (c) C.J. Kowalsky, M.L. O'Dowd, M.C. Burke, K.W. Fields, J. Am. Chem. Soc. 102 (1980) 5411. (d) H.-H. Vogt, R. Gompper, Chem. Ber. 114 (1981) 2884. (e) D. Seebach, M. Pohmakotr, Tetrahedron 37 (1981) 4047. (f) A. Maerker, M. Theis, Top. Curr. Chem. 138 (1987) 1. (g) C.M. Thomson, Dianion Chemistry in Organic Synthesis, CRC Press, Boca Raton, FL, 1994, p. 1. (h) F. Caturia, C. Nájera, Tetrahedron Lett. 37 (1996) 2833. (i) P. Bonete, C. Nájera, Tetrahedron 52 (1996) 4111. (j) I. Marek, J.-F. Normant, Chem. Rev. 96 (1996) 3241.

[8] J.F.K. Müller, M. Neuburger, M. Zehnder, Helv. Chim. Acta 80 (1997) 2182.

[9] (a) J.F.K. Müller, R. Batra, B. Spingler, M. Zehnder, Helv. Chim. Acta 79 (1996) 820. (b) J.F.K. Müller, M. Neuburger, M. Zehnder, Acta Crystallogr. Sect. C53 (1997) 419.

[10] (a) G.W. Spitznagel, T. Clark, J. Chandrasekhar, P. v. R. Schleyer, J. Comput. Chem. 3 (1982) 363. (b) F. Bernardi, A. Bottoni, A. Venturini, A. Mangini, J. Am. Chem. Soc. 108 (1986) 8171.

[11] (a) T. Clark, P. v. R. Schleyer, K.N. Houk, N.G. Rondan, J. Chem. Soc. Chem. Commun. (1981) 579. (b) P. v. R. Schleyer, T. Clark, A.J. Kos, G.W. Spitznagel, G. Rohde, D. Arad, K.N. Houk, N.G. Rondan, J. Am. Chem. Soc. 106 (1984) 6467. (c) G. Boche, J.C.W. Lohrenz, A. Opel, in: A.-M. Sapse, P. v. R. Schleyer (Eds.), Lithium Chemistry, Wiley, New York, 1995, pp. 195–226. (d) A.M. El-Nahas, P. v. R. Schleyer, J. Comput. Chem. 15 (1994) 596.

[12] (a) A. Streitwieser Jr., A. Rajca, R.S. McDowell, R. Glaser, J. Am. Chem. Soc. 109 (1987) 4184. (b) S.E. Denmark, C.J. Cramer, J. Org. Chem. 55 (1990) 1806. (c) W. Zarges, M. Marsch, K. Harms, F. Haller, G. Frenking, G. Boche, Chem. Ber. 124 (1991) 861. (d) C.J. Cramer, S.E. Denmark, P.C. Miller, R.L. Dorow, K.A. Swiss, S.R. Wilson, J. Am. Chem. Soc. 116 (1994) 2437. (e) R. Koch, E. Anders, J. Org. Chem. 60 (1995) 5861. (f) M. Kranz, S.E. Denmark, J. Org. Chem. 60 (1995) 5867. (g) M. Kranz, S.E. Denmark, K.A. Swiss, S.R. Wilson, J. Org. Chem. 61 (1996) 8551.

[13] (a) S. Wolfe, A. Rauk, I.G. Csizmadia, J. Am. Chem. Soc. 91 (1969) 1567. (b) S. Wolfe, A. Rauk, L.M. Tel, I.G. Csizmadia, J. Chem. Soc. Chem. Commun. (1970) 96. (c) A. Streitwieser Jr., J.E. Williams Jr., J. Am. Chem. Soc. 97 (1975) 191. (d) S. Wolfe, A. Stolow, L.A. La John, Tetrahedron Lett. 24 (1983) 4071. (e) S. Wolfe, L.A. La John, D.F. Weaver, Tetrahedron Lett. 25 (1984) 2863. (f) T. Clark, in: C. Chatgiliaoglu, K.-D. Asmus (Eds.), Sulfur Centered Reactive Intermediates In Chemistry and Biology, NATO ASI Series A, Life Sciences, vol. 197, Plenum Press, New York, 1990, p. 13. (g) R. Koch, E. Anders, J. Org. Chem. 59 (1994) 4529.

[14] (a) P. Hohenberg, W. Kohn, Phys. Rev. 136 (1964) B 864. (b) W. Kohn, L. Sham, J. Phys. Rev. 140 (1965) A1133. (c) J.C. Slater, Quantum Theory of Molecular and Solids, vol. 4: The Self-Consistent Field of Molecular and Solids, McGraw-Hill, New York, 1974. (d) A.D. Becke, Phys. Rev. A 38 (1988) 3098. (e) A.D. Becke, J. Chem. Phys. 98 (1993) 1372. (f) J.P. Perdew, Y. Wang, Phys. Rev. B 45 (1992) 13244. (g) R.G. Parr, Y. Wang, Density-Functional Theory of Atoms and Molecules, Oxford University Press, Oxford, 1989.

[15] (a) A.E. Reed, F. Weinhold, J. Chem. Phys. 78 (1983) 4066. (b) A.E. Reed, F. Weinhold, R.B. Weinstock, J. Chem. Phys. 83 (1985) 735. (c) A.E. Reed, F. Weinhold, J. Chem. Phys. (1985) 83, 1736. (d) A.E. Reed, P. v. R. Schleyer, J. Am. Chem. Soc. 109 (1987) 7362. (e) A.E. Reed, L.A. Curtiss, F. Weinhold, Chem. Rev. 88 (1988) 899.

[16] M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.A. Robb, J.R. Cheeseman, T. Keith, G.A. Petersson, J.A. Montgomery, K. Raghavachari, M.A. Al-Laham, V.G. Zakrzewski, J.V. Ortiz, J.B. Foresman, J. Cioslowski, B.B. Stefanov, A. Nanayakkara, M. Challacombe, C.Y. Peng, P.Y. Ayala, W. Chen, M.W. Wong, J.L. Andres, E.S. Replogle, R. Gomperts, R.L. Martin, D.J. Fox, J.S. Binkley, D.J. Defrees, J. Baker, J.P. Stewart, M. Head-Gordon, C. Gonzalez, J.A. Pople, Gaussian 94, Revision B.2, Gaussian, Inc., Pittsburgh, PA, 1995.

[17] W.J. Hehre, L. Radom, P. v. R. Schleyer, J.A. Pople, Ab Initio Molecular Orbital Theory, Wiley Intersience, New York, 1986.

[18] (a) C. Møller, M.S. Plesset, Phys. Rev. 46 (1934) 618. (b) J.S. Binkley, J.A. Pople, Int. J. Quant. Chem. 9 (1975) 229.

[19] (a) J.W. Ochterski, G.A. Petersson, K.B. Wiberg, J. Am. Chem. Soc. 117 (1995) 11299. (b) J.W. Ochterski, G.A. Petersson, J. Montgomery Jr., J. Chem. Phys. 104 (1996) 2598.

[20] H.-J. Gais, D. Lenz, G. Raabe, Tetrahedron Lett. 36 (1995) 7437.

[21] (a) J.B. Collins, P. v. R. Schleyer, J.S. Binkley, J.A. Pople, J. Chem. Phys. 64 (1976) 5142. (b) J. Chandrasekhar, J. Andrade, P. v. R. Schleyer, J. Am. Chem. Soc. 103 (1981) 5609. (c) M.M. Francl, W.J. Pietro, W.J. Hehre, J.S. Binkley, M.S. Gordon, D.J. DeFrees, J.A. Pople, J. Chem. Phys. 77 (1982) 3654.

[22] U. Salzner, P. v. R. Schleyer, J. Am. Chem. Soc. 115 (1993) 10231.

[23] G. Raabe, H.-J. Gais, J. Fleischhauer, J. Am. Chem. Soc. 118 (1996) 4622.