



DFT theoretical studies of alkali metal acetylenic thiolates

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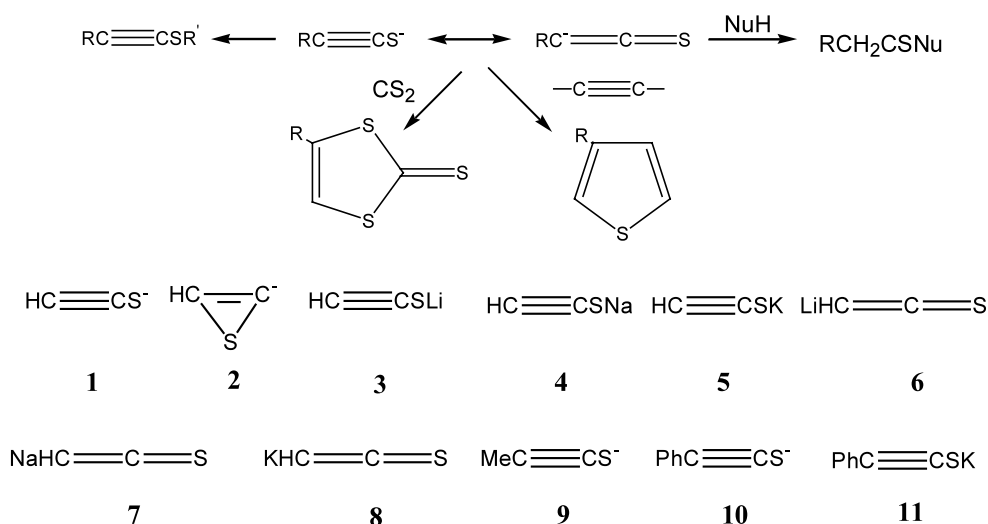
Received 5 June 2002; revised 31 October 2002; accepted 8 November 2002

Abstract—It follows from DFT calculations of acetylenic thiolates and their structural isomers—thioketenes and thiirenes that only the acetylenic type is stable. Most of the negative charge is concentrated on the sulfur atom. The influence of the cation (Li, Na, K) and the acetylenic substituent on the electronic structure and geometry of the thiolates is investigated. DFT calculations of IR and ^{13}C NMR spectra of phenylethynethiolate potassium are in agreement with experimental data. © 2002 Elsevier Science Ltd. All rights reserved.

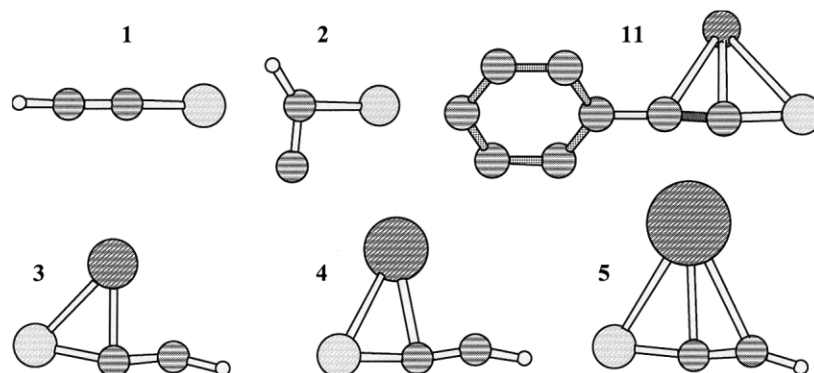
Unstable alkali metal acetylenic thiolates have been widely used in organic synthesis for the preparation of acetylenic sulfides, in cyclization reactions or as a source of reactive thioketenes.¹

Structures of acetylenic thiolates have not been studied in contrast to their analogous alkali metal enolates.² In this work we present the results of theoretical studies on ethynethiolate **1** and the isomeric anion of thiirene **2**; ethynethiolate lithium **3**, sodium **4** and potassium **5** and analogues of thioketene **6–8**; and also 1-propynethiolate **9**, phenylethynethiolate **10** and phenylethynethiolate potassium **11**.

DFT calculations were performed using the GAUSSIAN 98W program package. Geometries were optimized with C_1 -symmetry at the B3PW91/6-31+G* level of theory.³ The B3PW91 density function is a standard one from the Gaussian program and uses Becke's three parameter hybrid correction for exchange and that of Perdew's and Wang's for correlation. All structures were characterized as minima. It was shown that the two stable structures are ethynethiolate **1** with a bond angle of C–C–S 180° and the structural isomeric anion thiirene **2** with a strongly distorted bond angle C–C–S of 91.3° .



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However, the anion of ethynethiolate **1** is appreciably more stable than anion **2** (ΔE 43.7 kcal/mol). Therefore, the thiirenes or structures with a strongly distorted C–C–S bond angle were not considered. The calculations of the geometry of the alkali salts of ethynethiolates **3–5** and analogues of thioketenes **6–8** led to the same structures as structures of type **3–5**.

The acetylenic bond length 1.237 ± 3 Å and the C–S distance 1.674 ± 4 Å are almost unchanged with addition of an alkali metal (Li, Na, K). The acetylenic substituent has a more serious influence on these distances. The bond angle C–C–S changes depending on the presence and type of the alkali metal (Li, Na, K). It is equal at 180° for ethynethiolate **1**, 1-propynethiolate **9** and phenylethynethiolate **10**; lithium ethynethiolate **3** 163.9° ; sodium ethynethiolate **4** 169.6° ; potassium ethynethiolate **5** 170.5° and potassium phenylethynethiolate **11** 172.8° .

The calculation of the electronic structures of these acetylenic thiolates **1–11** revealed that Mulliken atomic charges are dependent on the presence and type of alkali metal (Li, Na, K) and on the acetylenic substituent (H, Me, Ph) (Table 1). The negative charges of acetylenic thiolates **1**, **9**, **10** are on the atoms of the C–S bond. At the same time, the contribution of the resonance structure of $R-C^+=C^--S^-$ grows from ethynethiolate **1** to phenylethynethiolate **10**. The negative charges of the alkali metal acetylenic thiolates **3–5** are on all the atoms of the C–C–S fragment. For given structures the contributions of the other resonance structure $H-C^-=C^+-S^-M^+$ are important. This contribution increases from lithium ethynethiolate **3** to potas-

sium ethynethiolate **5**. Thus the ionic degree of the M^+S^- bond increases.

For comparison, the geometry of potassium phenylethynethiolate **11** was optimized assuming C_1 -symmetry at the HF/6-31+G* level of theory. The calculated results of both HF and DFT methods are in agreement.

Though acetylenic thiolates are unstable we were earlier able to isolate an individual compound potassium phenylethynethiolate **11**.⁴ The structure of thiolate **11** was characterized by IR and ^{13}C NMR spectra and the spectra compared with calculated DFT counterparts. DFT calculations of IR spectra of the potassium phenylethynethiolate **11** were performed at the B3LYP/6-31G** level of theory. This method was found to give the best agreement with reference values from higher levels of theory.⁵ A strong $C\equiv C$ absorption band was observed at 2200 cm^{-1} , in agreement with the DFT calculated counterpart of 2174 cm^{-1} for this thiolate **11**.

DFT/IGLO calculations of ^{13}C NMR spectra were performed for phenylethynethiolate **10** and these calculations were compared with the experimental ^{13}C NMR (DMSO) spectra of potassium phenylethynethiolate **11**. We previously showed that potassium phenylethynethiolate **11** is dissociated in this solvent.⁶ The calculated signals of C_1-S are at 128.8 ppm, and C_2-C-S at 60.4 ppm, while the experimental signals are 110 and 69.1 ppm, respectively. The comparison of these values with the signals of the carbon atoms in the ^{13}C NMR spectra of 2-phenyl-1-ethylthioethyne **13** (the uncharged neutral

Table 1. Geometries (d Å, \angle °) and Mulliken atomic charges (q) of acetylenic thiolates $R-C\equiv C_1-SM$ ($M=Li, Na, K$)

Molecule	dC_1-C_2	dC_1-S	$dS-M$	$\angle C_2C_1S$	$\angle MSC_1$	qC_2	qC_1	qS	qM
1	1.234	1.674		180		−0.194	−0.204	−0.602	
3	1.240	1.673	2.341	163.9	57.6	−0.015	−0.040	−0.191	0.240
4	1.238	1.678	2.653	169.6	62.1	−0.252	−0.096	−0.205	0.553
5	1.239	1.671	3.032	170.5	64.9	−0.392	−0.103	−0.340	0.835
9	1.232	1.682		180		2.725	−2.753	−0.649	
10	1.240	1.656		180		3.452	−7.415	−0.526	
11 ^a	1.237 (1.207)	1.663 (1.693)	3.032 (3.031)	172.8 (174.2)	64.39 (67.8)	2.235 (1.03)	−5.150 (−2.695)	−0.513 (−0.597)	0.838 (0.863)

^a HF values are given for comparison in parentheses.

molecule), C_1-S (79.9 ppm) and C_2-C-S (93.7 ppm), showed that the charge leads to the downfield shift of the C_1-S signal (31.1 ppm) and highfield shift of the C_2-C-S signal (24.6 ppm). It is known that the shift of signals of C atoms in ^{13}C NMR spectra is correlated with the electronic density of these C atoms⁷ and that these data confirm the calculated electronic structure of the ion **11** $Ph-C^+=C^--S^-$.

Thus the calculated data for acetylenic thiolates are in agreement with the direction of alkylation, acylation and 1,3-anionic cycloaddition reactions of these thiolates.¹

Acknowledgements

This work was supported by the Russian Foundation for Basic Research (Grant no. 00-03-32740).

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