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A DFT Study of Acetylenic Alkali Metal Thiolates

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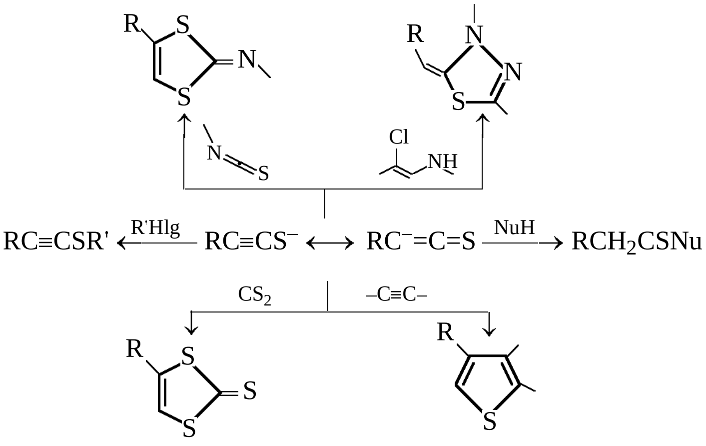
Abstract—Quantum-chemical calculations by the density functional theory (DFT) method showed that of acetylenic thiolates and their structural analogs, thioketene or thiirene anions, acetylenic thiolates and thioketene anions are only stable, and the negative charge in them is mostly localized on the sulfur atom.

Unstable acetylenic thiolates derived from alkali metal sulfides serve as reagents widely used in organic synthesis (for example, for preparing acetylenic sulfides, in cyclization reactions, or as synthetic equivalents of highly reactive thioketenes [1–9]).

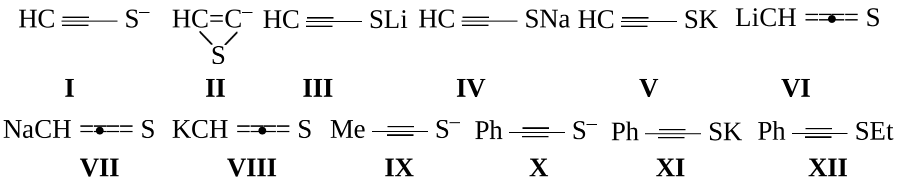


R, R' = Alk, Ar, Ac.

Reactivity and chemoselectivity in reactions of acetylenic thiolates depend on the nature of the solvent and metal [1, 3, 4, 8]. Thus, the direction of 1,3-anionic cycloaddition of acetylenic thiolates to esters of acetylenecarboxylic acids is primarily solvent-controlled [1]. In aprotic low-polarity solvents, such as benzene and THF, potassium 2-phenylethynethiolate reacts with acetylenecarboxylates to form thiophene derivatives. The reaction in more polar solvents, weak proton donors with pK_a ~20–25 (acetone, acetonitirle), results in nucleophilic addition of the thiolate by the triple bond, while in still more polar solvents with pK_a < 18 (water, alcohol), the starting acetylenuc thiolate undergoes «dimerization» to form 2-benzylidene-4-phenyl-2*H*-1,3-dithiol. The direction of reaction of acetylenic thiolates with isothiocyanates is much dependent on the nature of the cation: Lithium 2-arylethynethiolates are the only whose reaction with aryl isothiocyanates involve cycloaddition, whereas with potassium salt, the major reaction direction is “dimerization” of the starting acetylenic thiolate [1]. These data allowed us to suggest that the reaction direction and the reactivity of acetylenic thiolates depend on the state of the thiolates in the reaction medium, namely, ionicity of the sulfur–metal bond. Therefore, the structure of acetylenic tholates is interesting to study theoretically.

The structure of acetylenic thiolates has scarcely been studied, unlike the situation with their analogs, alkali metal enolates and enethiolates [10–12]. In the present work we report the results of a theoretical study of three groups of acetylenic thiolates. The first group includes ethynethiolate (**I**) and its structural analog, thiirene anion (**II**); the second group includes lithium, sodium, and potassium ethynethiolates (**III**–**V**, respectively) and their thioketene analogs **VI**–**VIII**; and the third group includes 1-propynethiolate (**IX**), phenylethyenethiolate (**X**), potassium phenylethynethiolate (**XI**) and, for comparison, (ethylsulfanyl)phenylethyne (**XII**) (for preliminary results of our quantum-chemical study of acetylenic thiolates, see [13]).

The aim of the present work was comparative analysis of the geometric and electronic structures of the above structures, obtained by DFT quantum-chemical calculations [14].



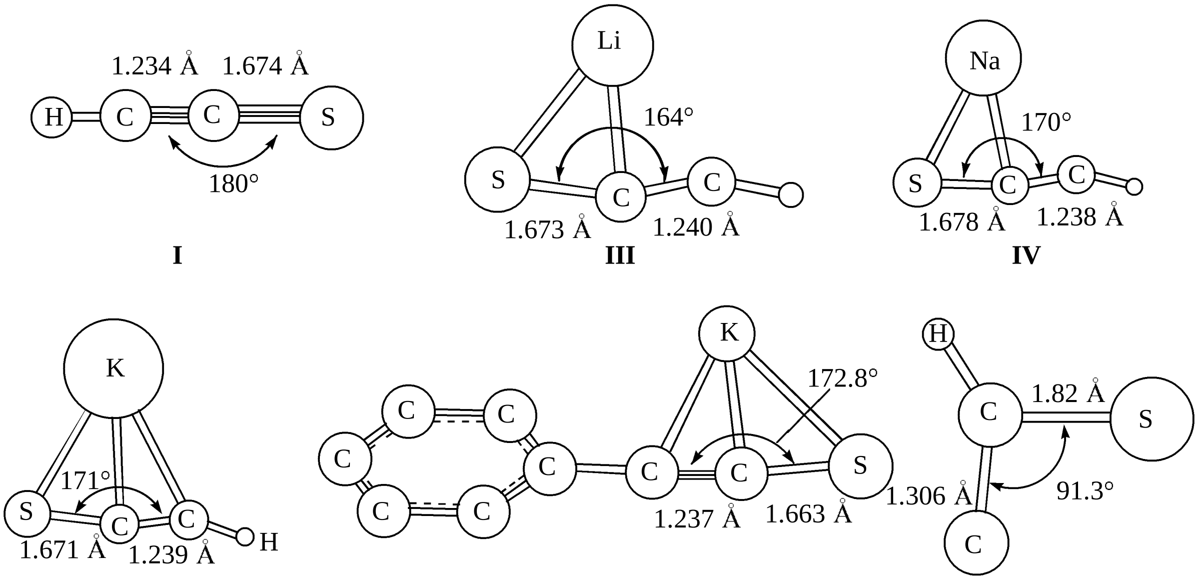
Search for and identification of stationary points were performed using B3LYP/6-31+G(d) calculations [15–17] with full geometry optimization under the assumption of C_1 symmetry and subsequent calculation of force fields. All stationary points on the potential energy surface correspond to minima (NIMAG = 0). The calculations were performed using the GAUSSIAN-98W program package [18]. Analysis of the populations obtained at the B3LYP/6-31+G(d) level was performed by the method of natural bond orbitals (NBO, Version 3.1, link 607, GAUSSIAN-98W) [19], which allowed us to go around drawbacks of the Mulliken analysis. The population analysis involved construction of a set of natural bond orbitals, natural populations that are always positive, and their sum is equal to the number of electrons in the molecule. Accordingly, charges obtained on the basis of natural populations (natural charges) provide a more accurate description of the electron density distribution than Mulliken's total atomic charges [20].

As seen from Table 1, there are two stable structures for ethynethiolate (**I**) and its structural isomer, thiirene anion (**II**): ethynethiolate (**I**) with the CCS bond angle of 180° (thioketene anion) and structure **XIII** with a strongly distorted CCS bond angle of 91.3° and unusually long $C^2{\equiv}C^1$, C–S, and $H–C^2$ bonds (1.306, 1.820, and 1.086 Å, respectively; see figure and Table 1). The optimized $H–C^2$ bond length in ethynethiolate (**I**) and its alkali metal salts **III**–**V** is 1.067±2 Å (standard value 1.06 Å) [21].

However, anion **XIII** is much less stable than ethynethiolate (**I**) ($\Delta E = E_p^{\mathbf{I}} - E_p^{\mathbf{XIII}} = 182.8$ kJ mol^{-1}) (Table 1). Therefore, we omitted thiirene structures and structures with a strongly distorted CCS bond angle from further calculations. With lithium, sodium, and potassium ethynethiolates (**III**–**V**), the calculations resulted in ethynethiolate structures **III**–**V** exclusively (see figure).

The lengths of the C≡C (1.239±1 Å) and C–S bonds (1.674±3 Å) scarcely vary, irrespective of whether the metal is present or absent and what is its nature (Li, Na, K). The nature of the substituent at the triple bond stronger affects these bond lengths. At the same time, the presence or absence of the alkaline metal (Li, Na, K) and its nature much affect the value of the CCS bond angle. Thus, the CCS bond angle in ethynethiolate (**I**), 1-propynethiolate (**IX**), and phenylethynethiolate (**X**) is 180°, and in lithium, sodium, potassium ethynethiolates (**III**–**V**) and potassium phenylethynethiolate (**XI**), 163.9, 169.6, 170.5, and 172.8°, respectively (see figure and Table 1). Thus, in going from potassium to lithium, the CCS bond angle stronger and stronger departs from the normal value.

As seen from the calculated normal charges in thiolates **I**–**XI** (Table 2), they depend on the presence and type of the alkaline metal (Li, Na, K) and on the nature of the substituent at the triple bond (H, Me, Ph). The negative charge in thiolates **I**–**XI** is distributed over all atoms of the C≡CS fragment, the $R–C^-{=}C^+–S^-M^+$ resonance structure contributing significanly. In going from salts **III**–**V** to thei anions **I** and **IX**, the negative charge on the sulfur atom increases, which is consistent with the reported reactivity order of the acetylenic thiolates. Acetylenic metal thiolates react as nucleophiles in strongly solvating solvents and are prone to 1,3-anionic cycloaddition in aprotic or weakly solvating solvents [1]. At the same time, the substituents at the triple bond in compounds **X** and **IX** decrease the contribution of the resonance structure



I **III** **IV** **V** **XI** **XIII**

Calculated structures of acetylenic thiolates **I, III–V, XI**, and **XIII**

$R–C^-{=}C^+–S^-$. On the other hand, the contribution of the alternative resonance structure $R–C^+{=}C^-–S^-$ increases in going from ethynethiolate (**I**) to phenylethynethiolate (**X**). With thiolates **III**–**V**, the contribution of the resonance structure $R–C^-{=}C^+–S^-$ increases from lithium ethynethiolate (**III**) to potassium ethynethiolate (**V**), with increasing ionicity of the $M^+–S^-$ bond. Comparison of the electronic structure of (ethylsulfanyl)phenylethyne (**XII**) with those of potassium phenylethynethiolate (**XI**) and ion **X** provide evidence showing that the resonance structure $R–C^-{=}C^+–S^-$ contributes much into the charge distribution.

For the sake of comparison, we calculated the geometric and electronic structures of phenylethynethiolate (**X**), potassium phenylethynethiolate (**XI**), and

Table 1. Total energies (E_{tot}) and optimized bond lengths (*d*) and bond angles in acetylenic thiolates $RC^2{\equiv}C^1SM$ (M = Li, Na, K) and $PhC^2{\equiv}C^1SEt$

Comp. no.	$-E_{tot}$, au	$d(H–C^2)$, $d(C–C^2)$, Å	$d(C^1–C^2)$, Å	$d(C^1–S)$, Å	$d(S–M)$, Å	$\angle C^2C^1S$, deg	$\angle MSC^1$, deg
I	474.996608	1.065	1.234	1.674		180	
XIII	474.927024	1.086	1.306	1.82		91.3	
III	482.514926	1.069	1.240	1.673	2.341	163.9	57.6
IV	637.278619	1.069	1.238	1.678	2.653	169.6	62.1
V	1074.894325	1.069	1.239	1.671	3.032	170.5	64.9
IX[a]	514.315415	1.461	1.232	1.682		180	
X[b,c]	706.082113	1.409	1.240	1.656		180	
	(703.352102)	(1.426)	(1.207)	(1.679)		(180)	
XI[b,d]	1305.737725	1.423	1.237	1.663	3.032	172.8	64.39
	(1302.504513)	(1.441)	(1.207)	(1.693)	(3.031)	(174.2)	(67.80)
XII[b,e]	785.21806	1.424	1.218	1.689		178.1	
	(781.972479)	(1.431)	(1.185)	(1.677)		(179.1)	

[a] $d(H–C)$ 1.105 Å. [b] Parenthesized are the HF/6-31+G(d) calculation results. [c] $d(H–C)$ 1.088, $d(C_i–C_o)$ 1.426, $d(C_o–C_m)$ 1.393, $d(C_m–C_p)$ 1.403 Å. [d] $d(H–C)$ 1.088, $d(C_i–C_o)$ 1.414, $d(C_o–C_m)$ 1.392, $d(C_m–C_p)$ 1.397 Å. [e] $d(H–C)$ 1.087, $d(C_i–C_o)$ 1.408, $d(C_o–C_m)$ 1.392, $d(C_m–C_p)$ 1.396, $d(S–CH_2)$ 1.840 Å, $\angle CH_2SC^1$ 101.6°.

(ethylsulfanyl)phenylethyne (**XII**) at the HF/6-31+G(d) level under the assumption of C1 symmetry [22]. The results of the traditional HF quantum-chemical calculations and those based on DFT, compared in Tables 1 and 2, are consistent with the above conclusions.

Even though acetylenic thiolates are unstable compounds, we could isolate potassium phenylethynethiolate (**XI**) [23]. It was characterized by means of ^{13}C NMR and IR spectroscopy. The experimental spectra compare with those resulting from DFT calculations. The IR spectra of salt **XI** were calculated at the B3LYP/6-31G(d) level; the scaling factor for calculated frequencies was 0.9613 [24]. The latter method provides a better fit of calculated values to experimental [25]. The experimental frequency of the strong C≡C absorption band in the spectrum of potassium phenylethynethiolate (**XI**) (2089.7 cm^{-1}) is consistent with that resulting from DFT calculations (2089.9 cm^{-1}).

The ^{13}C NMR spectra of compounds **X** and **XI** were calculated by the DFT/IGLO method [26]. Table 3 compares the calculated and experimental carbon chemical shifts of these compounds.

Previously we showed that potassium phenylethynethiolate (**XI**) is weakly dissociated in aprotic solvents [27]. Comparison of the chemical shifts of the C1S and C^{2}CS carbons (109.9 and 69.1 ppm) in the experimental ^{13}C NMR spectra with calculation for compound **X** (C^{1}S 128.8 and C^{2}CS 60.4 ppm) and compound **XI** (C^{1}S 115.4 and C^{2}CS 63.3 ppm) provides evidence for the structure of the latter and its weak dissociation in DMSO. From a comparison of the calculated chemical shifts of phenylethynethiolate (**X**) (C^{1}S 128.8 and C^{2}CS 60.4 ppm) and potassium phenylethynethiolate (**XI**) (C^{1}S 115.4 and C^{2}CS 63.3 ppm), as well as of the experimental data one can also reveal an upfield shift of the C^{1}S signal and a small downfield shift of the C^{2}CS signal. As known, ^{13}C NMR chemical shifts correlate with the electron density on the corresponding carbon atoms [28]. Therefore, it is safe to state that the above findings are evidence favor of increasing contribution of the PhC$^-$=C$^+$–S$^-$ structure in going from the uncharged (ethylsulfanyl)phenylethyne (**XII**) to potassium phenylethynethiolate (**XI**) and especially to ion **X**.

EXPERIMENTAL

The IR spectrum was registered on a Shimadzu FTIR–8400 instrument in KBr. The ^{13}C NMR spectra were measured on a Bruker AMX-400 instrument (100 MHz) using as internal reference ^{13}C NMR signals of DMSO-d_6.

Table 2. Natural atomic charges (q, $\bar{e}$) in acetylenic thiolates RC^2≡C^{1}SM (M = Li, Na, K) and PhC^2≡C^{1}SEt

Comp. no.	q(*H*–C^2≡, *C*–C^2≡)	q(C^2)	q(C^1)	q(S)	q(M)
I	0.213	–0.541	–0.219	–0.453	
III	0.258	–0.529	–0.324	–0.342	0.937
IV	0.251	–0.526	–0.299	–0.381	0.956
V	0.245	–0.554	–0.277	–0.390	0.976
IX^a	–0.714	–0.270	–0.201	–0.476	
X^{b,c}	–0.075	–0.238	–0.165	–0.356	
	(–0.022)	(–0.299)	(–0.079)	(–0.501)	
XI^{b,d}	–0.106	–0.254	–0.253	–0.366	0.974
	(–0.078)	(–0.263)	(–0.18)	(–0.501)	(0.982)
XII^{b,e}	–0.116	–0.007	–0.254	0.329	
	(–0.122)	(–0.046)	(–0.225)	0.302	

[a] q(H) 0.221 $\bar{e}$. [b] Parenthesized are the HF/6-31+G(d) calculation results. [c] Σq(H)/5 0.227, $\Sigma q(C_o)/2$ –0.242, $\Sigma q(C_m)/2$ –0.257, $q(C_p)$ –0.304 $\bar{e}$. [d] Σq(H)/5 0.249, $\Sigma q(C_o)/2$ –0.235, $\Sigma q(C_m)/2$ –0.249, $q(C_p)$ –0.267 $\bar{e}$. [e] Σq(H)/5 0.24, $\Sigma q(C_o)/2$ –0.203, $\Sigma q(C_m)/2$ –0.232, $q(C_p)$ –0.235 $\bar{e}$.

Table 3. Calculated and experimental chemical shifts (δ_C, ppm) in the ^{13}C NMR spectra (DMSO-d_6) of phenylethynetiolate (**X**), potassium phenylethynethiolate PhC^2–C^{1}S$^-$ (**XI**), and (ethylsulfanyl)phenylethyne PhC^2≡C^{1}SEt (**XII**)

Comp. no.	C^1	C^2	C$_i$	$\Sigma\sigma(C_o)/2$	$\Sigma\delta(C_m)/2$	C$_p$
X	128.8	60.4	131.3	125.8	120.4	105.3
XI	115.4	63.3	123.8	123.3	123.1	116.4
XI (exp.)	109.9	69.1	130.8	130.3	127.8	122.2
XII^a	82.7	97.4	119.9	126.1	122.8	121.3
XII^b (exp.)	79.9	93.7	123.8	131.3	128.3	127.9

[a] δ_C, ppm: 35.4 (CH$_2$) and 16.5 (CH$_3$). [b] δ_C, ppm: 29.9 (CH$_2$) and 14.8 (CH$_3$).

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