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NMR/IGLO/*Ab initio* Study of the 1,3-Dithiolanium Cation*[1]

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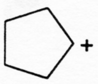
1,3-Dithiolanium cation was synthesized and characterized by ^{1}H and ^{13}C NMR spectroscopy. *Ab initio*/IGLO calculations were carried out for C_{2v} and C_2 conformers of the cation, and the calculated ^{13}C NMR chemical shifts are in reasonable agreement with the observed values. The slight deviations are attributed to the limitations of the IGLO method for the sulfur-containing compounds.

INTRODUCTION

Structures of small ring carbocations have increasingly been probed at high-level theoretical calculations.[2] Schleyer, Koch and coworkers calculated the structure of the cyclopentyl cation (**1**) at MP2(FU)6-31G* level of theory and found the twisted (C_2) cation as the global minimum.[3] By the comparison of IGLO (Individual Gauge for Localized Orbitals) calculated chemical shifts with the experimentally determined values, they ruled out C_s and C_{2v} structures, and arrived at the C_2 structure as the most stable structure for the cyclopentyl cation, **1**. The 1,3-dithiolanium ion, **2**, a synthetic formyl equivalent, deserves a similar careful study of its structure. It also allows in extending the applicability of IGLO calculations to heterocyclic cations, hitherto unexplored. We report here our initial calculations in this area on 1,3-dithiolanium cation.



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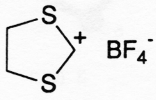

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* Dedicated to Professor Dionis E. Sunko on the occasion of his seventieth birthday.

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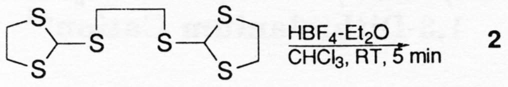
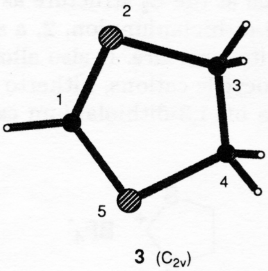
RESULTS AND DISCUSSION

We prepared the crystalline 1,3-dithiolanium tetrafluoroborate by reacting tetrafluoroboric acid-etherate with bis(1,3-dithiolane) in chloroform at room temperature, and obtained its ^{1}H and ^{13}C NMR spectra in CD_3NO_2 solution. The cation has ^{1}H NMR absorptions at δ 4.46 (CH_2) and 11.3 (CH), and ^{13}C NMR absorptions at δ 45.9 (CH_2), and 221.1 (CH). The ^{1}H NMR data are in agreement with those reported earlier for the corresponding perchlorate salt.[4]

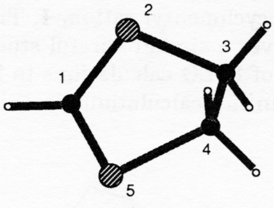


The relatively high stability of cation **2**, even at room temperature, shows the extraordinary stabilization of the cationic center by the sulfur atoms, which is also reflected in the relatively modest deshielding of the ^{13}C NMR chemical shift for the cationic center ($\delta^{13}C$ 221). The static cyclopentyl cation, on the other hand, obtained at 70 K, shows the corresponding cationic center's chemical shift at $\delta^{13}C$ 320.[5]

We have fully optimized the structures of planar (**3**, C_{2v}) and twisted (**4**, C_2) 1,3-dithiolanium cations at HF/6-31G* level, and found the latter to be more stable than the planar structure by 1.4 kcal/mol, similar in trend with that of the cyclopentyl cation. Inclusion of correlation at MP2/6-31G*//HF/6-31G* resulted in their energy difference as 2 kcal/mol. The envelope (C_s) structure was found to be not a minimum and collapsed to the C_{2v} structure without any activation barrier. Harmonic frequency calculations at HF/6-31G*//HF/6-31G* level showed that C_{2v} structure is a transition state whereas C_2 structure is a minimum, as the former has one imaginary frequency and the latter has no imaginary frequencies. The various bond lengths and angles are essentially the same in both the structures (Table I). The atomic charge on sulfur in structure **3** (0.496) is, however, more positive than that for structure **4** (0.487), reflecting more charge delocalization in the C_{2v} structure. In line, with this, the calculated electron density of the carbocationic center for **3** is also more than that for **4**.



3 (C_{2v})



4 (C_2)

It is known that the IGLO-calculated chemical shifts are very sensitive to the subtle changes in structural geometries.[6] Such calculations for sulfur-stabilized cations, however, were lacking. We carried out IGLO calculations for these structures employing IGLO basis sets DZ and II on 6-31G* optimized structures (Table II). It is evident from Table II that as the IGLO basis set is increased from DZ to II, there is an im-

TABLE I

*Atomic charges and selected bond-lengths (Å) and angles (deg) for structures **3** (C_{2v}) and **4** (C_2) at 6-31G*//6-31G*.*

structure (energy, -au)	atomic charge		bond length		bond angle	
3	C1	−0.401	C1S2	1.656	SCS	122.7
(911.27266)	S2	0.496	S2C3	1.834	CSC	96.8
	C3	−0.545	C3C4	1.543	SCC	111.8
4	C1	−0.397	C1S2	1.663	SCS	121.6
(911.27487)	S2	0.487	S2C3	1.834	CSC	95.0
	C3	−0.540	C3C4	1.524	SCC	108.7
					S5C1S2C3	−9.0
					C1S2C3C4	27.0
					C2C3C4S5	−35.5
					C3C4S5C1	−27.0

provement in approaching the observed chemical shifts. At basis set II, the planar (C_{2v}) cation shows a cationic center's chemical shift of $\delta^{13}C$ 260.6 ppm, 6 ppm less than that for the C_2 structure. This value, although relatively higher than the experimental value (by 34.5 ppm), more closely resembles it. Using geometries obtained at correlated levels, and at higher levels of basis sets in IGLO calculations, it is expected to show closer to experimental values. However, it was not possible for us to calculate these structures at MP2/6-31G* level, because of the enormous computer time and disc space requirements.

TABLE II

*IGLO-calculated chemical shifts for structures **3** and **4***

Structure		^{13}C		^{1}H	
		DZ//6-31G*	II//6-31G*	DZ//6-31G*	II//6-31G*
3 (C_{2v})	CH	307.3	260.6	16.91	11.17
	CH_2	37.5	34.4	3.78	3.00
4 (C_2)	CH	313.7	266.8	17.74	11.71
	CH_2	39.9	36.8	3.94	3.18
				3.16	2.61
Experimental:[a]		CH 221.1	CH_2 45.9	CH 11.3	CH_2 4.46

[a] in CD_3NO_2 solution.

In order to see the applicability of the IGLO calculations to sulfur-containing organic compounds, we carried out the IGLO calculations of CS_2 at II//6-31G* level of theory as a model. The calculated ^{13}C chemical shift of $\delta^{13}C$ 233.3 differs from the experimental value of $\delta^{13}C$ 192.8 ppm by 40.5. A similar difference (39.5 ppm) in the chemical shifts (between calculated and experimental shifts of the cationic center) for the dithiolanium cation reflects the extent of accuracy of the IGLO calculations for sulfur-containing organic compounds. The calculated IGLO ^1H NMR chemical shifts at II/6-31G* level are also in reasonable agreement with the experimental results (Table II).

The extremely small difference in the energies of structures **3** and **4** at 6-31G* level of theory may change in magnitude with inclusion of correlation at even higher basis sets, but the difference appears not to change significantly as single-point MP2 calculations raised the energy by only 0.6 kcal/mol. The present *ab initio* calculations show that structures **3** and **4** are nearly equal in energy, and the C_{2v} structure **3** is a saddle point and the C_2 structure **4** a minimum. The present IGLO calculations show reasonably close agreement with experimental values for both the structures, but cannot distinguish between structures **3** and **4**. Based on the harmonic frequency calculations at HF/6-31G*//HF/6-31G* level, however, it appears that the C_2 conformer **4** is the favored structure for the 1,3-dithiolanium cation.

EXPERIMENTAL

Dithiolanium Tetrafluoroborate (**2**).

Dithiolane, 1,[7] (15 g, 0.049 mol) dissolved in 100 mL of anhydrous chloroform was placed in a 250-mL round bottom flask equipped with a magnetic stirrer, a nitrogen inlet and serum cap. Tetrafluoroboric acid-diethyl etherate (24.1 g, 0.15 mol) was then added to the contents through a hypodermic syringe. The reaction was instantaneous, and the dithiolanium tetrafluoroborate appeared as a white precipitate. The precipitate was filtered under a nitrogen atmosphere, washed with copious amounts of chloroform, ether, and dried under nitrogen. The salt (14.9 g, 98%) was stored in a flask under nitrogen atmosphere. The salt was very hygroscopic, but is stable under nitrogen atmosphere for several days. ^{13}C NMR (CD_3NO_2): δ 45.9 (t, $J=151$ Hz, CH_2), 221.1 (d, $J=194$ Hz, CH). ^{1}H NMR (CD_3NO_2): δ 4.46 (CH_2), 11.3 (CH).

Ab initio calculations were performed on an Alliant FX/40 computer using Gaussian-86 series of programs.[8] Full geometry optimizations were performed for the selected point groups. IGLO calculations were done according the reported method of Schindler.[6]

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SAŽETAK

NMR/IGLO/*Ab Initio* proučavanje 1,3-ditiolanijeva kationa

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Opisana je priprava 1,3-ditiolanijeva tetrafluoborata i njegovi ^1H i ^{13}C NMR spektri. Izmjereni kemijski pomaci uspoređeni su s kemijskim pomacima izračunanima primjenom IGLO i *ab initio* računa. *Ab initio* računi provedeni su uporabom 6-31G baznog skupa, uz uključenje korelacije MP2.