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He I Photoelectron Spectroscopy and Theoretical Investigation on Diaceto Disulfide, $CH_3C(O)OSSOC(O)CH_3$

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A novel species, diaceto disulfide ($CH_3C(O)OSSOC(O)CH_3$), has been generated through the heterogeneous reaction between sulfur monochloride (S_2Cl_2) and silver acetate ($AgOC(O)CH_3$). Photoelectron spectroscopy (PES) and theoretical calculations are performed to investigate its electronic and geometric structures. This molecule exhibits gauche conformation with both C═O groups syn to the S−O bond. The dihedral angle around the S−S bond is calculated to be −93.1° at the B3LYP/6-311++G(3df,3pd) level. After structural optimizations of the most stable conformer, a theoretical study involving the calculation of the ionization energies using orbital valence Green's functional (OVGF) was performed. The ionization energies of different bands in the photoelectron spectrum are in good agreement with the calculated values from the OVGF method. The first vertical ionization energy of $CH_3C(O)OSSOC(O)CH_3$ is determined to be 9.83 eV by photoelectron spectroscopy, which corresponds to the ionization of an electron mainly localized on the sulfur 3p lone pair molecular orbital.

Introduction

The first dialkoxy disulfide with the general formula ROSSOR was obtained more than a century ago.[1] It is only recently that interest has grown concerning this class of compounds along with their structural thionosulfite isomers.[2−4] The simplest molecule of ROSSOR compounds is dihydroxy disulfane (HOSSOH), the chainlike isomer of thiosulfurous acid. This molecule has been detected in the gas phase by means of neutralization−reionization mass spectrometry, but the free acid is unstable and hence unknown in condensed phases.[5] The geometries and energies of seven isomeric structures of $H_2S_2O_2$ were calculated theoretically. And the chainlike isomer is one of the most stable.[6] Among the compounds of the ROSSOR type, a simple molecule, $CH_3OSSOCH_3$, was extensively studied, including electronic structure,[7] crystal structure,[8] gas-phase structure,[9] and vibrational spectra.[9] The molecule is chainlike and asymmetrical in the gas phase with the symmetry C_1.

The chalcogen−chalcogen bonds in bivalent compounds are known to prefer gauche conformations with typical dihedral angles of 80−90°, which is usually attributed to the lone-pair interactions.[9] There are many reports of dichalcogens of the type RSSR′[10−13] and RSOR′,[14−19] which exhibit gauche structure in the gas phase. Recently, many compounds with the OSSO moiety have been obtained by S_2Cl_2 coupling of alcohols.[3] These dialkoxy disulfides prefer acyclic unsymmetric hemolytic cleavage. Zeng et al.[20] studied $CF_3C(O)OSSOC(O)CF_3$, which is not strictly a dialkoxy disulfide, by Raman, photoelectron spectroscopy (PES), and theoretical calculations. They found that this molecule exhibits gauche conformation with both C═O groups syn to the S−S bond, and the structure of the OSSO moiety is characterized by dihedral angle $\delta_{OSSO} = -95.1°$ due to the sulfur−sulfur lone pair interactions. The rotational barrier of δ_{OSSO} is relatively high (19.29 kcal/mol at the B3LYP/6-31G(d) level), which indicates the partial resonance-induced double bond character in this molecule. The electronic structure of $CF_3C(O)OSSOC(O)CF_3$ was also discussed in detail in their work. In addition, reviews concerning the synthesis, physical properties, and chemistry of the highly chalcogenated dialkoxy disulfides (ROSSOR) have been published in 2004.[21,22] Recently, the isomeric preference between cyclic dialkoxy disulfides and thionosulfites has been reported.[23] Rings smaller than seven atoms prefer the thionosulfite connectivity, whereas larger rings or acyclic analogues favor the unbranched dialkoxy disulfide structure.

In the present work, a novel disulfide, $CH_3C(O)OSSOC(O)CH_3$, was generated and characterized by PES. With the help of quantum chemical calculations, the molecular structure of $CH_3C(O)OSSOC(O)CH_3$ was investigated theoretically. Its electronic structure was discussed with the combination of the experimental and theoretical results. The first vertical ionization energy of $CH_3C(O)OSSOC(O)CH_3$ was determined by PES for the first time.

Experimental Section

Generation of $CH_3C(O)OSSOC(O)CH_3$. Sulfur monochloride (S_2Cl_2) was found to be an ideal precursor for the preparation of dialkoxy disulfides (ROSSOR).[3,20] $CH_3C(O)OSSOC(O)CH_3$ was generated through gas−solid reaction by passing S_2Cl_2 vapor over finely powdered $AgOC(O)CH_3$ at room temperature of about 20 °C. The photoelectron spectrum and the photoionization mass spectrum of the gas-phase product were recorded in situ. S_2Cl_2 (98%) was purchased from Aldrich, and

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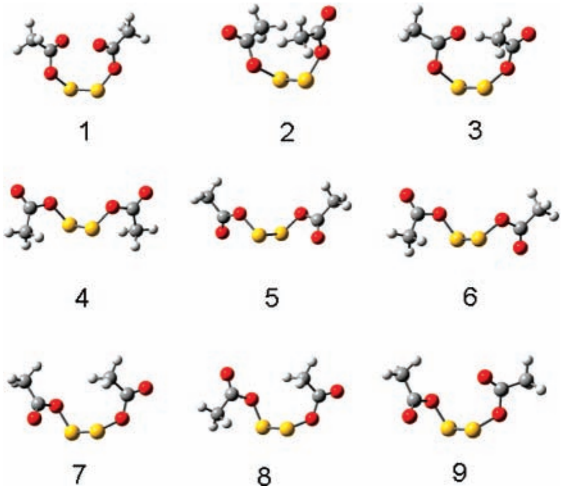

Figure 1. Schematic representation of nine conformers (1−9) of $CH_3C(O)OSSOC(O)CH_3$.

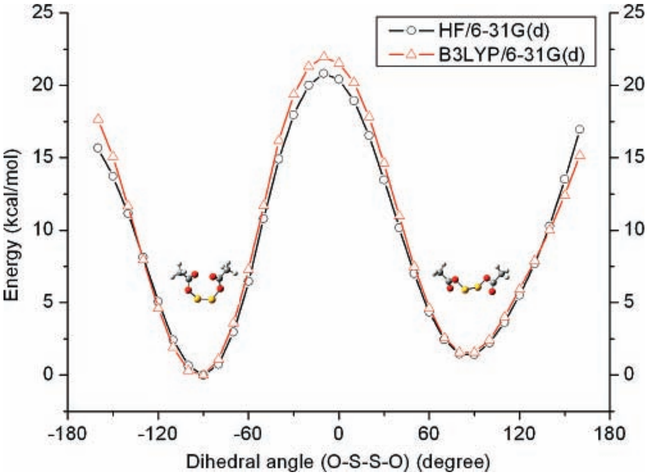

Figure 2. Conformational energy profile for $CH_3C(O)OSSOC(O)CH_3$ obtained using the relax scan of the potential energy surface (rotating the OSSO dihedral angle in steps of 10°) at the HF/6-31G(d) and B3LYP/6-31G(d) levels.

its purity was checked by photoionization mass spectroscopy. $AgOC(O)CH_3$ (99%) was purchased from Alfa Aesar, and it was dried in a vacuum at 50 °C before experiment. The reaction pathway is similar to the generation of $CF_3C(O)OSSOC(O)CF_3$.[20]

Photoelectron Spectroscopy. As previously reported,[12,17] the photoelectron spectrum was recorded on a double-chamber UPS-II instrument, which was specially designed for detecting unstable species. The spectral resolution of He I spectrum is about 30 meV, when measured as the full width at half-maximum (fwhm) of the $3p^{-1}\ {}^2P_{2/3}\ Ar^+ \leftarrow Ar\ ({}^1S_0)$ line. During the experiments, a small amount of Ar gas and CH_3I were added to the sample flow to calibrate the experimental vertical ionization potentials. As for the mass spectrum, it was recorded by a time-of-flight mass spectrometer, which was connected to the double-chamber UPS-II instrument. The apparatus was described in detail in the previous work.[24] Briefly, mass analysis of ions is achieved with the time-of-flight mass analyzer mounted directly to the photoionization point. The ionization is provided by single-wavelength He I radiation. The photoelectron spectrum and photoionization mass spectrum can be recorded within seconds of each other under identical conditions. In the mass spectrum of $CH_3C(O)OSSOC(O)CH_3$, the strongest ion fragment is $CH_3C(O)^+$ ($m/z = 43$). Together with the weaker fragment of $CH_3C(O)OSS^+$ ($m/z = 123$), they can confirm the generation of the title compound. However, no parent ion of the product was found in the mass spectrum. Furthermore, $CH_3C(O)OSSOC(O)CH_3$ was prepared in a way similar to that of $CF_3C(O)OSSOC(O)CF_3$.[20] Its liquid Raman spectrum was recorded, which could also confirm the identity of the product. The experimental and calculated Raman spectra are given in the Supporting Information.

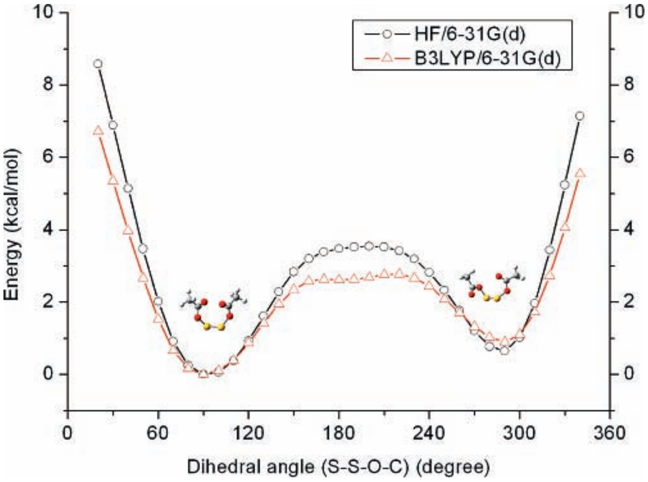

Figure 3. Conformational energy profile for $CH_3C(O)OSSOC(O)CH_3$ obtained using the relax scan of the potential energy surface (rotating the SSOC dihedral angle in steps of 10°) at the HF/6-31G(d) and B3LYP/6-31G(d) levels.

Quantum Chemical Calculations. The calculations were performed by using Gaussian 03[25] applied with the ab initio Hartree−Fock (HF) and the MP2 methods as well as the density function B3LYP approach, in which Beck's three-parameter hybrid functional,[26] representing the exchange term, is combined with the correlation functional of Lee, Yang, and Parr.[27] All the possible conformers of $CH_3C(O)OSSOC(O)CH_3$ were optimized with different methods and basis sets. Vibrational-frequency calculations have been carried out to verify stationary points. Higher levels of theory, including both ab initio and density functional theory (DFT) methods, were used to optimize the theoretically most stable conformer. The vertical ionization energies were calculated at the ab initio level according to Cederbaum's outer valence Green's function (OVGF)[28] method, which includes the effects of electron correlation and reorganization beyond the HF approximation. Three-dimensional molecular orbitals (MOs) were obtained with the GaussView program. Each orbital displayed with the 0.08 isodensity value was oriented in a way that allowed for the best view, which is similar to the work of Yao et al.[12]

Results and Discussion

Geometry of $CH_3C(O)OSSOC(O)CH_3$. As previously reported,[29] lone-pair interactions make compounds of the type RSOR′ and RSSR′ prefer gauche conformations around the S−O or S−S bond. Obviously, two rotamers are possible for each chalcogen−chalcogen bond, representing segments of right-hand or left-hand helices. The total number of conceivable rotamers grows with the chalcogen chain length. Dimethoxysulfane (CH_3OSOCH_3) has three possible rotamers. Electron diffraction[30] and X-ray diffraction[31] studies revealed that the molecule adopts a C_2 structure both in the gas phase and in the crystal. Ab initio and experimental studies on $CH_3OSSOCH_3$ indicated that three conformers resulting from the rotation of S−O and S−S bonds should be stable.[9] As for $CH_3C(O)OSSOC(O)CH_3$, the presence of a carbonyl group attached to the O−S bond, just as the S−S

TABLE 1: Calculated Relative Energies (kcal/mol) of Different Conformers of $CH_3C(O)OSSOC(O)CH_3$[a]

conformer	HF/6-31+G(d)	MP2/6-31+G(d)	B3PW91/6-311+G(d)	B3LYP/6-311+G(d)
1	0	0	0	0
2	15.15	12.98	11.16	11.57
3	8.99	7.97	6.56	6.58
4	16.62	16.48	12.36	12.89
5	0.99	2.89	0.62	0.80
6	8.27	9.32	6.13	6.49
7	8.50	8.14	6.07	6.29
8	14.84	13.67	10.78	11.13
9	0.65	1.55	0.40	0.54

[a] As for the structure of different conformers, see Figure 1.

TABLE 2: Optimized Geometrical Parameters for Conformer 1 of $CH_3C(O)OSSOC(O)CH_3$[a]

param	MP2[b]	B3PW91[b]	B3LYP[b]	B3LYP[c]
r_{C1H}[d]	1.091	1.091	1.090	1.088
r_{C1C2}	1.501	1.499	1.505	1.502
r_{C2O1}	1.204	1.196	1.198	1.195
r_{C2O2}	1.386	1.376	1.381	1.378
r_{O2S1}	1.721	1.725	1.737	1.710
r_{S1S2}	1.979	1.977	1.995	1.959
α_{HC1H}[d]	109.7	109.4	109.4	109.4
α_{HC1C2}[d]	109.2	109.6	109.5	109.6
α_{C1C2O1}	127.0	126.8	126.8	126.6
α_{C1C2O2}	108.8	109.3	109.3	109.7
α_{C2O2S1}	116.2	117.4	117.8	117.7
α_{O2S1S2}	104.5	106.6	106.4	107.0
$\delta_{H1C1C2O1}$	22.1	13.2	13.6	11.1
$\delta_{H2C1C2O1}$	145.2	135.7	136.1	133.5
$\delta_{H3C1C2O1}$	−96.3	−106.0	−105.5	−108.4
$\delta_{C1C2O2S1}$	−173.8	−178.9	−178.4	−178.4
$\delta_{O1C2O2S1}$	3.9	0.2	0.6	0.7
$\delta_{C2O2S1S2}$	88.7	93.3	92.3	92.3
$\delta_{O2S1S2O3}$	−89.5	−93.7	−93.3	−93.1

[a] Distances in angstroms; angles in degrees. For atom numbering, see Figure 4. [b] At the 6-311++G(d,p) level. [c] At the 6-311++G(3df,3pd) level. [d] Average.

bond in $FC(O)SSC(O)CF_2Cl$,[32] may promote a conformational equilibrium, but this depends on the relative orientation of the C═O and O−S bonds. Besides the different conformation around the chalcogen−chalcogen bonds, the C═O bonds of both $CH_3C(O)$ moieties can be anti- or synperiplanar to the S−O bond. After referring to the stable conformers of $CH_3OSSOCH_3$, nine stable conformers (1−9) of $CH_3C(O)OSSOC(O)CH_3$ were found after preliminary structure optimization with the B3LYP/6-31G(d) method. A scheme of all these conformers (1−9) is presented in Figure 1.

All the conformers were then further optimized at different levels, including HF/6-31+G(d), MP2/6-31+G(d), B3PW91/6-311+G(d), and B3LYP/6-311+G(d). The calculated relative energies of different conformers of $CH_3C(O)OSSOC(O)CH_3$ are listed in Table 1. It can be clearly seen that conformer 1 should be the most stable conformer in view of relative energy. Conformer 1 exhibits 0.54 kcal/mol in energy lower than the second stable conformer 9 at the B3LYP/6-311+G(d) level. To better understand the difference between the conformers, a relax scan of the potential energy surface was performed by rotating the torsional angle δ_{OSSO} in steps of 10° at the HF/6-31G(d) and B3LYP/6-31G(d) levels, respectively, while keeping the structures of $CH_3C(O)O$ moieties optimized. The resulting potential curves for dihedral angle from $-160°$ to $+160°$ are shown in Figure 2. The curves display two minima at $-90°$ and $+90°$ (δ_{OSSO}) at both levels. As for the minimum at about $-90°$, the molecular structure has the skeleton of conformer 1, as shown in Figure 1. The minimum at about 90° is an enanthiomer of conformer 5, whose relative energy is 1.40 (HF/6-31G(d)) or 1.55 kcal/mol (B3LYP/6-31G(d)) higher than the minimum at $-90°$. The enanthiomers have the same energy. The calculations with B3LYP/6-311+G(d) predict the energy difference between conformers 5 and 1 is 0.80 kcal/mol (Table 1). The potential curve further shows that conformer 1 is more stable than conformer 5. The energy barrier for the S−S rotation is calculated to be about 20 kcal/mol at both levels. The extremely high rotation barrier around the S−S bond was also found in a similar molecule $CF_3C(O)OSSOC(O)CF_3$, which was calculated to be 17.75 (HF/6-31G(d)) and 19.29 kcal/mol (B3LYP/6-31G(d)).[20] Barrier calculations for the full symmetrical disulfides (R−S−S−R, R = Me, *t*-Bu, C_8H_7) at the B3LYP/6-31G(d) level provide the results of 5.7, 6.0, and 5.2 kcal/mol, respectively.[33] The replacement of electronegative oxygen in dialkoxy disulfide moiety OSSO to carbon in disulfides with the moiety CSSC raises the energy barrier, as reported recently.[2,34,35] After NBO analysis, Harpp et al.[33] pointed out that ROSSOR exhibited high S−S barriers by stabilizing the ground state, while RSSR sustains a low barrier by stabilizing the transition state. Restricted rotation about a single bond is not usually influenced solely through stereoelectronic interactions; the S−S lone pair repulsion and steric interactions between two $CH_3C(O)$ moieties should also be taken into account.[20] Besides, a relax scan around the S−O bond was also performed, as shown in Figure 3. There are two minima in the potential curve derived at the HF/6-31G(d) level. They are located at about 90 and 290°, which possess the structure of conformer 1 and an enanthiomer of conformer 9, respectively. In the potential curve at the B3LYP/6-31G(d) level, besides the two expected minima at about 90 and 290°, there is a third shallow minimum at 180°. This curve also shows that conformer 1 is more stable than conformer 9.

As seen from Table 1, the conformers with the C═O bonds of both $CH_3C(O)$ moieties antiperiplanar to the S−O bond (conformers 2, 4, and 8 in Figure 1) generally have higher energies. When C═O bonds are syn to the S−O bond, the corresponding conformers are more stable. Among them, conformer 1 is theoretically determined to be the most stable one. The preferred syn structure can be rationalized by the aromaticity and the anomeric effect.[36] The stabilization of the conformer is accounted for by the attractive π nonbonded interactions. Moreover, the instability of the anti conformers can be understood on the basis of the aromaticity. Generally, if one of the central atoms in an A−B−C−D chain possesses one or more lone pairs, the anomeric effect may influence the conformational properties of the compound greatly.[37] This effect contributes to the preference of the syn form for the conformation of −C(O)O-containing compounds.[38] To obtain more accurate structural parameters of the most stable conformer of $CH_3C(O)OSSOC(O)CH_3$, the structure of conformer 1 was then optimized with larger basis sets, the results of which are listed in Table 2. As for the atom numbering, it is clearly shown in

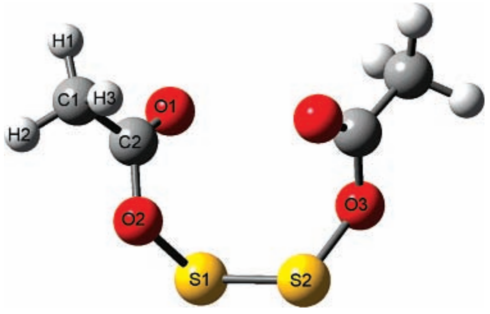

Figure 4. Schematic representation for conformer 1 of $CH_3C(O)OSSOC(O)CH_3$.

Figure 4. Our discussion of the structural feature of $CH_3C(O)OSSOC(O)CH_3$ is mainly focused on the optimized results of conformer 1.

The calculated S−S bond length of $CH_3C(O)OSSOC(O)CH_3$ is 1.959 Å (B3LYP/6-311++G(3df,3pd)), which is quite close to those of $CH_3OSSOCH_3$ (1.960(3) Å, GED)[9] and $ArCH_2OSSOCH_2Ar$ (1.957 Å, Ar = 4-nitrophenyl, X-ray diffraction).[2] However, it is much shorter than those of disulfides, for example, CH_3SSCH_3 (2.031(3) Å),[39] $FC(O)SSCF_3$ (2.027(4) Å),[40] $FC(O)SSC(O)CF_2Cl$ (2.029(1) Å),[32] and $FC(O)SSC(O)CF_3$ (2.023(3) Å).[11] As a consequence, a somewhat greater double-bond character is expected for dialkoxy disulfides, which would thus account for their larger free energy of activation for the S−S rotation with respect to that of disulfides.[2] The bond shortening could be possibly explained in two ways. One explanation is that one of the unpaired electrons in the antibonding molecular orbital of the SS moiety might be available for establishing a bond with one electron of the oxygen atom. The resulting three-center bond would thus account for the reduction of the S−S bond length.[41] Another explanation is that an n−σ* interaction occurs between the sulfur lone pairs and the rear lobes of the antibonding polar S−O σ bond orbital.[2] There would be a double n−σ* interaction from each S to the respective S−O σ* orbital in the gauche conformation. This effect also explains the high torsional barrier of ROSSOR relative to dialkyl disulfides that do not have significantly polar S−X bonds.

The S−O bond length of $CH_3C(O)OSSOC(O)CH_3$ is calculated to be 1.710 Å (B3LYP/6-311++G(3df,3pd)). It is longer than the experimentally determined S−O bond lengths of $CH_3OSSOCH_3$ (1.653(3) Å)[9] and $CF_3SOC(O)CF_3$ (1.663(5) Å).[15] When calculated at the same theory level (B3LYP/6-311++G(3df,3pd)), CF_3SOCF_3 has much shorter S−O bond length (1.677 Å)[42] than that of $CH_3C(O)OSSOC(O)CH_3$. However, $CF_3C(O)OSSOC(O)CF_3$ has a longer S−O bond length (1.755 Å),[20] which was obtained at the B3LYP/6-311G(d) level. The trends of S−O bond length in thioperoxides (RSOR′) can be rationalized with the electrostatic model suggested by Oberhammer et al.[15] When the electronegativity of substitute R′ at the O atom increases, the polarity of the S−O bond is decreased and the bond lengthens. The electronegativity of the $CF_3C(O)$ moiety is larger than that of $CH_3C(O)$, so the corresponding S−O bond length in $CF_3C(O)OSSOC(O)CF_3$ is longer.

The torisonal angle around the S−S bond in dialkoxy disulfides is of great concern when studying such compounds. This dihedral angle in $CH_3C(O)OSSOC(O)CH_3$ is calculated to be −93.1° according to the values derived at the B3LYP/6-311++G(3df,3pd) level. It is near the angle of $CF_3C(O)OSSOC(O)CF_3$ (−95.1°)[20] and quite close to the ideal value of noncyclic disulfides. The corresponding dihedral angles in $CH_3OSSOCH_3$ [9] and $ArCH_2OSSOCH_2Ar$ (Ar = 4-nitrophenyl)[2] are determined to be 91(4) and 85.4°, respectively. The gauche structure in disulfides can be interpreted in two ways.[43] One is related to the barrier formed by the repulsion of the pπ atomic orbital (AO) lone pairs. When these AOs are oriented orthogonal to each other, the repulsion is minimized. The second is based on a hyperconjugative mechanism, where the π-character of the S−S bond is enhanced, when S−O bonds in $CH_3C(O)OSSOC(O)CH_3$ are aligned for maximum transfer of electron density through the 3pπ AOs to the O atom. This feature is consistent with the anomeric effects at OSSO moiety in dialkoxy disulfides. The torisonal angle around the S−O bond in $CH_3C(O)OSSOC(O)CH_3$ is calculated to be 92.3° (B3LYP/6-311++G(3df,3pd)), which can also be interpreted with the effects mentioned above for that of S−S bond.

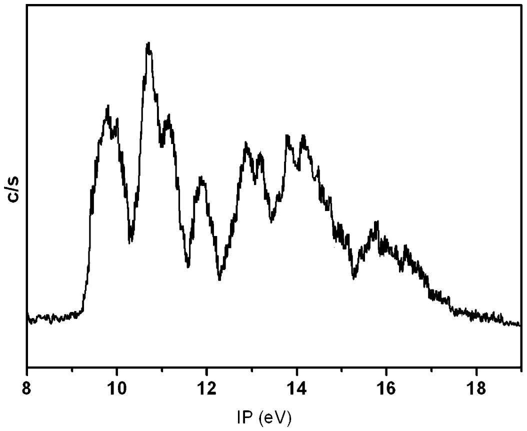

Figure 5. He I photoelectron spectrum of $CH_3C(O)OSSOC(O)CH_3$.

Photoelectron Spectroscopy. Photoelectron spectroscopy with a He I resonance source (58.4 nm) is an effective method to investigate the electronic structure of unstable compounds and free radicals in combination with ab initio calculations. The valence shell structure of molecular vapors can be readily obtained by He I photoelectron energy analysis. The He I photoelectron spectrum of $CH_3C(O)OSSOC(O)CH_3$ is shown in Figure 5. Before assigning the spectrum, OVGF calculations were carried out to obtain the theoretical ionization energies of $CH_3C(O)OSSOC(O)CH_3$. Our discussion of the photoelectron spectrum is based on conformer 1, which is the most stable one, for simplification. OVGF calculations (OVGF/6-311++G(d,p)) were performed by using the structure parameters optimized at the B3LYP/6-311++G(d,p) level. The information obtained from several empirical and theoretical considerations should be used simultaneously to assign the spectrum. The experimental vertical ionization energies, calculated vertical ionization energies, and molecular orbital characters for conformer 1 of $CH_3C(O)OSSOC(O)CH_3$ are listed in Table 3. Drawings of ten molecular orbitals (MOs) for conformer 1 are shown in Figure 6. The molecular orbitals have C_2 symmetry, as shown in Table 3 and Figure 6.

As for the photoelectron spectrum of $CH_3C(O)OSSOC(O)CH_3$, its shape is quite similar to that of $CF_3C(O)OSSOC(O)CF_3$.[20] The ionization energies of different bands are in good agreement with the calculated values derived from the OVGF method. The molecular orbitals associated with each ionization band are assigned according to their atomic and bonding characters. The first band in the spectrum with high intensity can overlap two peaks at 9.83 and 9.95 eV. The main characters for the first two outermost orbitals are $\{24a(n_S)\}^{-1}$ and $\{23b(n_S, n_{O(C=O)})\}^{-1}$. For disulfides, the first two peaks in the photoelectron spectra correspond to the symmetric and antisymmetric linear combinations of the outermost p-atomic

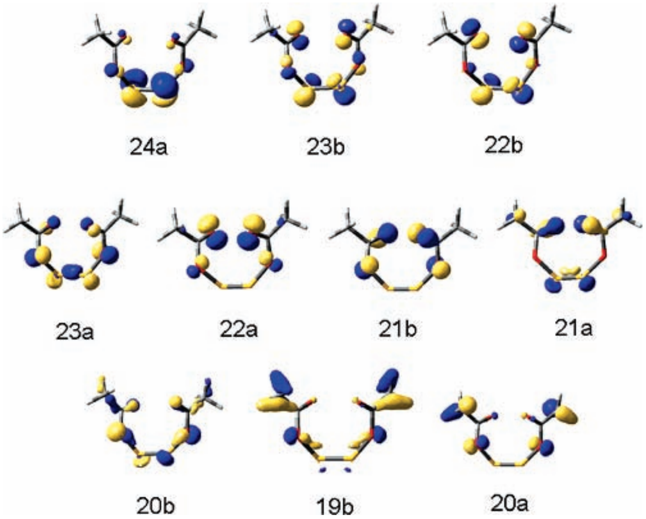

Figure 6. Drawings of the ten MOs for conformer 1 of $CH_3C(O)OSSOC(O)CH_3$.

TABLE 3: Experimental Vertical Ionization Energies (eV), Calculated Vertical Ionization Energies (eV, OVGF/6-311++G(d,p)), and Molecular Orbital Characters for Conformer 1 of $CH_3C(O)OSSOC(O)CH_3$

exp	calc[a]	MO	character
9.83	9.80 (0.89)	24a	n_S
9.95	10.21 (0.89)	23b	n_S, $n_{O(C=O)}$
10.69	10.84 (0.89)	22b	n_S, $n_{O(C=O)}$
11.15	11.01 (0.89)	23a	$n_{O(COS)}$, σ_{S-S}
	11.03 (0.89)	22a	$n_{O(C=O)}$
11.87	12.08 (0.88)	21b	$n_{O(COS)}$, $n_{O(C=O)}$
12.85	13.09 (0.89)	21a	$\pi_{C=O}$, σ_{S-S}
13.19	13.17 (0.89)	20b	$n_{O(COS)}$
13.79	13.99 (0.90)	19b	$n_{O(COS)}$, π_{CH_3}
14.15	14.11 (0.90)	20a	$n_{O(COS)}$, π_{CH_3}

[a] Pole strength in parentheses.

orbitals.[44] Similar to $CF_3C(O)OSSOC(O)CF_3$, the antisymmetric linear combination of the sulfur 3p lone pair orbitals was influenced by the participation of the carbonyl oxygen lone pair. The energy difference ΔE between the first two peaks is 0.12 eV, which is slightly smaller than that of $CF_3C(O)OSSOC(O)CF_3$ ($\Delta E = 0.16$ eV, $\delta_{OSSO} = -95.1°$).[20] This difference is originated by the interaction of the two lone pairs at the adjacent S atoms, showing a clear dependence on the dihedral angle. Generally, it is to be expected that as the dihedral angle δ deviates from +90° (or −90°), the energy difference ΔE will increase; i.e., the 3p orbitals in parallel configuration ($\delta = 0°$, 180°) interact more strongly than in an orthogonal configuration ($\delta = 90°$).[45] The dihedral angle around the S−S bond in $CH_3C(O)OSSOC(O)CH_3$ is more close to 90° than that of $CF_3C(O)OSSOC(O)CF_3$, so the energy difference ΔE is smaller.

Besides, it should be addressed that the first vertical ionization energy of $CH_3C(O)OSSOC(O)CH_3$ (9.83 eV) is 0.98 eV lower than that of $CF_3C(O)OSSOC(O)CF_3$ (10.81 eV),[20] which means that the lone pair electron of the S atom tends to be more difficult to ionize in $CF_3C(O)OSSOC(O)CF_3$. This is probably caused by the electron-withdrawing effect of the $CF_3C(O)O$ moiety with high electronegativity. It is quite similar to the difference between the first vertical ionization energy of $CCl_3SOC(O)CH_3$ (9.67 eV) and $CCl_3SOC(O)CF_3$ (10.34 eV).[17]

The second band is composed of two peaks, which are localized at 10.69 and 11.15 eV, respectively. Three ionization processes happened in this ionization region, including $\{22b(n_S, n_{O(C=O)})\}^{-1}$, $\{23a(n_{O(COS)}, \sigma_{S-S})\}^{-1}$, and $\{22a(n_{O(C=O)})\}^{-1}$. As for the ionization process of the lone pair from the oxygen atom at the C=O moiety, it is similar to the first ionization process of $CH_3C(O)OH$ (10.87 eV).[46] However, such processes in $CH_3OC(O)SSCN$, $CH_3OC(O)Cl$, and $CH_3OC(O)CN$ cause the ionization energies of 11.32,[13] 11.36,[47] and 11.65 eV,[47] respectively, which are due to the inductive effect of the SSCN moiety, Cl atom, and CN moiety, respectively.

Among the assigned bands (Table 3), the ionization energy from the σ orbital at the S−S bond is also of great interest in disulfides. In $CH_3C(O)OSSOC(O)CH_3$, this process causes the ionization energy of 12.85 eV, as determined by photoelectron spectroscopy. It is slightly higher than the ionization energy from the σ_{S-S} orbital of its parent compound HSSH (12.62 eV).[48] As for the similar molecules, the corresponding bands in $CF_3C(O)OSSOC(O)CF_3$ and $CH_3OC(O)SSCN$ are localized at 12.16 [20] and 12.08 eV,[13] respectively. The differences are caused by the effect of different substituents on the S−S bond. All the assignments in the low-energy region (<14.5 eV) are given in Table 3, and the remaining bands in the high-energy region arising from the inner molecular orbitals cannot be assigned with certainty.

Conclusion

A novel disulfide, $CH_3C(O)OSSOC(O)CH_3$, was generated and characterized by photoelectron spectroscopy. The molecular structure was investigated with the help of quantum chemical calculations. This molecule prefers a gauche conformation with both C=O bonds cis to the S−O bonds, as predicted by structural optimization and vibrational analysis. The structure of the OSSO moiety is characterized by a gauche dihedral angle of −93.1° due to the sulfur−sulfur lone-pair interactions. The first vertical ionization energy of $CH_3C(O)OSSOC(O)CH_3$ is determined to be 9.83 eV, which corresponds to the ionization of the electron mainly localized on the sulfur 3p lone-pair molecular orbital.

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Supporting Information Available: Experimental and calculated Raman spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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