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Photoelectron Spectroscopy, Photoionization Mass Spectroscopy, and Theoretical Study on CCl$_3$SSCN

Lin Du[a,b], Li Yao[a,b], Mao-fa Ge[a]*

a. Beijing National Laboratory for Molecular Sciences, State Key Laboratory for Structural Chemistry of Unstable and Stable Species, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China;
b. Graduate School of Chinese Academy of Sciences, Beijing 100039, China

Trichloromethanesulfenyl thiocyanate, CCl$_3$SSCN, was generated and studied by photoelectron spectroscopy (PES), photoionization mass spectroscopy (PIMS), and theoretical calculations. This molecule exhibits a gauche conformation, and the torsional angle around S−S bond is 91.4° due to the sulfur-sulfur lone pair interactions. After ionization, the ground-state cationic-radical form of CCl$_3$SSCN$^{.+}$ adopts a trans planar main-atom structure with C$_s$ symmetry. The highest occupied molecular orbital (HOMO) of CCl$_3$SSCN corresponds to the electrons mainly localized on the sulfur 3p lone pair MO. The first ionization energy is determined to be 10.40 eV.

Key words: Photoelectron spectroscopy, Photoionization mass spectroscopy, Electronic structure

I. INTRODUCTION

Disulfides play an important role in living organisms. In the formation of the tertiary structure of proteins, covalent disulfide bonds are known to ensure the formation of cross-links, which are much stronger than hydrophobic interactions and hydrogen bonds [1]. The biochemical importance of the disulfide bond is also determined by the uniqueness of the nature of the thiol-disulfide system, in which the S−S bond can be formed under conditions appropriate for biological processes [1]. Considerable attention has been paid to the structure and conformational preferences of simple disulfides [2-7]. It is well-known that noncyclic disulfides XSSX prefer gauche structures around the S−S bond, with the dihedral angles δ_{XSSX} close to 90°. The dihedral angle of HSSH was determined to be 90.76(6)° [8] or 90.34° [9]. The reported torsional angles of several simple disulfides of FSSF [10], ClSSCl [11], ClSSCN [7], CH$_3$SSCH$_3$ [12], and CF$_3$SSCF$_3$ [13] are 87.7(4)°, 85.2(2)°, 86.92° (B3LYP/6-311+G(3df)), 85.3(37)°, and 104.4(40)°, respectively. The smallest dihedral angle around the S−S bond measured for noncyclic disulfides in the gas phase is that of FC(O)SSC(O)CF$_3$ (77.7(21)°) [6].

Experimental and theoretical studies on substituted disulfide ions are of great importance, because results from these studies can provide a sound basis for understanding the complexity of sulfur-sulfur bonding interactions [5,14]. Dimethyl disulfide, CH$_3$SSCH$_3$ [12], possesses a gauche structure, while the lowest energy structure of the radical ion, CH$_3$SSCH$_3$$^{.+}$, ex-

hibits a planar CSSC chain with a dihedral angle of 180°, which is explained by the formation of a three-electron π-bond [15,16]. Zeng *et al.* found that the most stable conformer of CF$_3$C(O)OSSOC(O)CF$_3$ shows a gauche conformation with both C=O groups *cis* to the S−S bond [17]. However, after ionization, the ground-state cationic-radical form of CF$_3$C(O)OSSOC(O)CF$_3$$^{.+}$ adopts a trans planar main-atom structure (δ_{OSSO}=180° and δ_{OCOS}=0°) with C$_{2h}$ symmetry. Besides, similar dramatic changes in geometry after ionization also have been observed in other fluorocarbonyl (di- and tri-) sulfur compounds FC(O)SSCH$_3$ and FC(O)SSSC(O)F [5,18].

However, structural studies of nonsymmetrical substituted disulfides of the type XSSY are less common, both experimental and theoretical data being scarce for these systems. In the present work, we report a combined experimental and theoretical investigation on trichloromethanesulfenyl thiocyanate, CCl$_3$SSCN. Quantum chemical calculations were performed to study the structural properties of the title compound, together with its ground-state cationic-radical form of CCl$_3$SSCN$^{.+}$. The electronic structure was investigated by means of photoelectron spectroscopy (PES). Photoionization mass spectroscopy (PIMS) was used to obtain some information about the ionization and dissociation of CCl$_3$SSCN. The first vertical ionization energy of CCl$_3$SSCN was determined by PES for the first time.

II. EXPERIMENT AND THEORETICAL METHODS

A. Generation of CCl$_3$SSCN

Trichloromethanesulfenyl thiocyanate, CCl$_3$SSCN, was first synthesized by Senning in 1963 through the

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*Author to whom correspondence should be addressed. E-mail: gemaofa@iccas.ac.cn

reaction between CCl_3SCl and KSCN in benzene [19]. In this work, a modified method was used. CCl_3SSCN was heterogeneously generated at about 20 °C by passing CCl_3SCl vapor over finely powdered AgSCN, and photoelectron spectrum was recorded subsequently after generation. The reaction route is illustrated as below:

$$CCl_3SCl(g)+AgSCN(s)\rightarrow CCl_3SSCN(g)+AgCl(s)$$
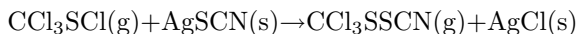
The precursor CCl_3SCl (from Alfa Aesar), which is widely used for preparation [20-22], was distilled in vacuum under room temperature to remove the slight impurities before use, and its purity was checked by photoionization mass spectroscopy. AgSCN was purchased from Alfa Aesar. It is also a common precursor to prepare thiocyanates [7,23,24]. Before reaction, it was dried in vacuum (13.3 mPa) for 2 h.

B. Instrumentation

The experimental apparatus used in this work has been described in detail previously [24]. Briefly, the photoelectron and photoionization mass spectrometer consists of two parts: the double-chamber UPS-II instrument and the time-of-flight mass spectrometer. The photoelectron spectrum was recorded on the double-chamber UPS-II instrument at a resolution of 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.

Experimental vertical ionization energies are calibrated by simultaneous addition of a small amount of argon and methyl iodide to the sample. Mass analysis of ions is achieved with the time-of-flight mass analyzer mounted directly to the photoionization point. The relatively soft ionization is provided by single-wavelength HeI radiation (58.4 nm). The PES and PIMS spectra can be recorded within seconds of each other under identical conditions.

C. Quantum chemistry calculations

Quantum chemistry calculations were performed for the title molecule using the Gaussian 03 program package [25]. The structure parameters of the neutral molecule and the cationic-radical form of $CCl_3SSCN^{\cdot+}$ were optimized with DFT methods. Relax scans were performed to search for other possible conformers of CCl_3SSCN at the $HF/6-31G^*$ and $B3LYP/6-31G^*$ levels. To interpret the photoelectron spectrum, Cederbaum's outer valence Green's function (OVGF) [26] method, which includes the effects of electron correlation and reorganization beyond the HF approximation, was used to obtain the theoretical vertical ionization energies of CCl_3SSCN.

III. RESULTS AND DISCUSSION

A. Geometry of CCl_3SSCN

The molecule of ClSSCN adopts a gauche conformation in the gas phase [7]. A similar gauche structure around the S−S bond of CCl_3SSCN was set as the starting geometry for quantum chemical calculations at different levels of theory. This conformer was found to be a stable conformer after vibrational analysis. Its molecular model and atom numbering is shown in Fig.1. To search for other possible conformers with different dihedral angle of δ_{CSSC}, the potential functions for internal rotation around the S−S bond in CCl_3SSCN were derived by structure optimizations at fixed dihedral angles between 0° and 360° using the HF and B3LYP method with the basis set of $6-31G^*$ (Fig.2). There is no other minimum except the expected minima for the gauche structure with the dihedral angles around 90° and 270° at both levels. The energy barrier for the S−S rotation is calculated to be 32.56 kJ/mol ($HF/6-31G^*$) and 29.97 kJ/mol ($B3LYP/6-31G^*$). This is caused by the S−S lone pair repulsion and steric interactions between CCl_3 and CN moieties. In comparison, 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 result of 23.8, 25.1, and

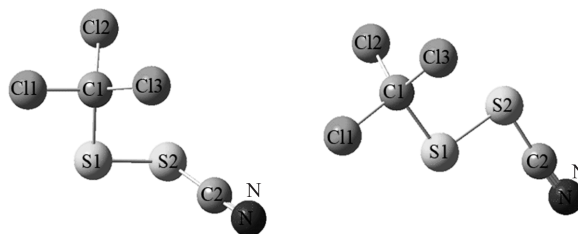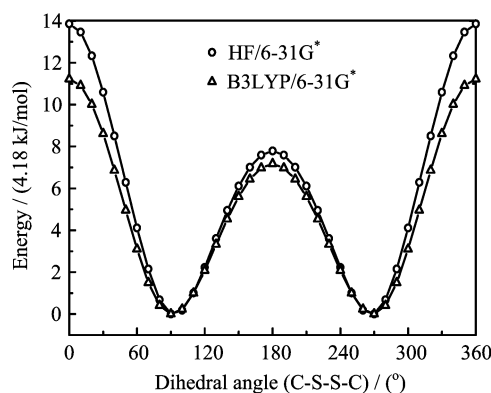FIG. 1 Schematic representation of the neutral molecule of CCl_3SSCN (left) and the cationic-radical form of $CCl_3SSCN^{\cdot+}$ (right).

FIG. 2 Conformational energy profile for CCl_3SSCN obtained using the relax scan of potential energy surface (rotating the CSSC dihedral angle in steps of 10°) at the $HF/6-31G^*$ and $B3LYP/6-31G^*$ levels.

TABLE I Optimized geometrical parameters for CCl_3SSCN and the cationic-radical form of $CCl_3SSCN^{\cdot +a}$

Parameters	CCl_3SSCN		$CCl_3SSCN^{\cdot +}$
	B3PW91/6-311+G(3df)	B3LYP/6-311+G(3df)	UB3LYP/6-311+G(3df)
r_{C1Cl1}	1.775	1.788	1.763
r_{C1Cl2}	1.767	1.780	1.753
r_{C1Cl3}	1.762	1.775	1.753
r_{C1S1}	1.835	1.847	1.907
r_{S1S2}	2.043	2.061	2.044
r_{S2C2}	1.693	1.699	1.679
r_{C2N}	1.156	1.155	1.158
$\alpha_{Cl1C1S1}$	101.5	101.8	99.3
$\alpha_{Cl2C1S1}$	112.5	112.6	109.7
$\alpha_{Cl3C1S1}$	112.5	112.6	109.7
α_{C1S1S2}	103.9	104.3	102.1
α_{S1S2C2}	103.3	103.4	98.7
$\delta_{Cl1C1S1S2}$	177.0	177.0	180.0
$\delta_{Cl2C1S1S2}$	59.2	59.3	62.0
$\delta_{Cl3C1S1S2}$	−64.9	−64.9	−62.0
$\delta_{C1S1S2C2}$	91.6	91.4	180.0
$\delta_{S1S2C2N}$	168.5	170.3	180.0

[a] Distances in Å, angles in (°). For atom numbering, see Fig.1.

21.7 kJ/mol, respectively [3]. The S−S torsional barriers for simple disulfides are within the range of 33.4-41.8 kJ/mol as measured in the solution [27]. But extremely high rotation barrier around S−S bond was found in $CF_3C(O)OSSOC(O)CF_3$, which was calculated to be 74.2 kJ/mol (HF/6-31G*) and 80.63 kJ/mol (B3LYP/6-31G*) [17].

The optimized structural parameters for CCl_3SSCN are given in Table I. The calculated S−S bond length of CCl_3SSCN is 2.061 Å, which is a bit longer than that of ClSSCN (2.039 Å) [7], as derived at the same theory level (B3LYP/6-311+G(3df)). The electrostatic model suggested by Oberhammer *et al.* can be used here to explain the difference in bond length [28]. Because the electronegativity of Cl atom is stronger than that of CCl_3 moiety, the polarity of the S−S bond in ClSSCN is larger and the bond length is shorter. However, a greater double-bond character is expected for dialkoxy disulfides. The experimentally determined S−S bond lengths of $CH_3OSSOCH_3$ (1.960(3) Å, GED) [29] and $ArCH_2OSSOCH_2Ar$ (1.957 Å, Ar=4-nitrophenyl, X-ray diffraction) [30] are much shorter than those of CCl_3SSCN and ClSSCN, which are determined theoretically.

Another important feature for CCl_3SSCN is the dihedral angle of δ_{CSSC}, which can influence the overall structure of the molecule greatly. This torsional angle is calculated to be 91.4° according to the values derived at the B3LYP/6-311+G(3df) level. It is quite close to the ideal value (90°) of noncyclic disulfides. The gauche structure in disulfides can be interpreted in

two ways [18,31]. One is related to the barrier formed by the repulsion of the $3p\pi$ atomic orbital (AO) lone pairs. When these AOs are oriented orthogonal to each other, the repulsion is minimized. Another argument is based on a hyperconjugative mechanism, where the π-character of the S−S bond is enhanced, when S−C bonds in CCl_3SSCN are aligned for maximum transfer of electron density through the $3p\pi$ AOs to the C atom.

B. Geometry of CCl₃SSCN·⁺

After ionization, the CSSC dihedral angle in CH_3SSCH_3 [15,16] and $FC(O)SSCH_3$ [5] is expected to change to 180° in the ground-state of $CH_3SSCH_3^{\cdot +}$ and $FC(O)SSCH_3^{\cdot +}$. As for $CCl_3SSCN^{\cdot +}$, structure optimization was performed based on the structural parameters of the molecule CCl_3SSCN. The resulting structure is shown in Fig.1. The calculated geometric parameters (UB3LYP/6-311+G(3df)) for the ground-state cational-radical form $CCl_3SSCN^{\cdot +}$ are given in Table I for comparison with those of the corresponding neutral molecule.

As seen from Table I and Fig.1, the changes between the neutral and the ground-state cational-radical form are mainly in the molecular symmetry. CCl_3SSCN shows a symmetry of C_1, while the structure of $CCl_3SSCN^{\cdot +}$ exhibits C_s symmetry. The S−S bond shortens 0.017 Å after ionization, while the C−S bond between CCl_3 and SS moieties elongates 0.16 Å to 1.907 Å. It can be deduced that the S−S bond of

TABLE II Atomic charge for the neutral and cationic-radical form of CCl_3SSCN as obtained by the UB3LYP/6-311+G(3df) approximation

Atoms	CCl_3SSCN	$CCl_3SSCN^{\cdot+}$	$\triangle q^{a}$
Cl1	−0.344	−0.208	0.136
Cl2	−0.511	−0.296	0.215
Cl3	−0.514	−0.296	0.218
C1	1.787	1.427	−0.360
S1	−0.340	0.011	0.351
S2	0.030	0.383	0.353
C2	0.726	0.696	−0.030
N	−0.834	−0.719	0.115
TAC^{b}	0	1	1

^{a} $\triangle q = q(CCl_3SSCN^{\cdot+}) - q(CCl_3SSCN)$.
^{b} Total atomic charge.

$CCl_3SSCN^{\cdot+}$ is difficult to dissociate, while the C−S bond is probably the opposite. The Mulliken population analysis of the charges for both neutral and cational-radical forms is given in Table II. The results show that the atomic charges are delocalized all over the molecule, with an appreciable fraction localized on the sulfur atoms. It can be easily deduced that the first ionization occurs primarily on the electrons of the sulfur atoms, which are the sulfur 3p lone pair electrons. In general, the decrease of the sulfur-sulfur lone pair repulsion after ionization makes a stable planar structure possible for $CCl_3SSCN^{\cdot+}$.

C. Photoionization mass spectroscopy

The photoionization mass spectrum (PIMS) of CCl_3SSCN is presented in Fig.3. The peaks in the spectrum are assigned left-to-right as $CSCl^+$, CCl_3^+, and $NCSSCCl_2^+$. The peaks of $CSCl^+$ and CCl_3^+ also exist in the mass spectrum of the precursor CCl_3SCl, in which the strongest peak is CCl_3S^+ [32]. The appear-

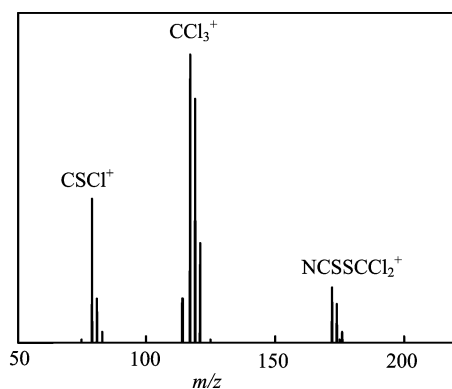ance of the $NCSSCCl_2^+$ and the disappearance of the peak of $CCl_3SCl^{\cdot+}$ confirms the generation and identification of the product. Normally, HeI photoionization produces a fragment distribution similar to that of electron-impact ionization [7]. Similar to the generation of $NCSSCCl_2^+$, the fragment of $CH_3CCl_2^+$ is also found in the electron-impact spectrum of CH_3CCl_3 [32], both of which result from the direct dissociation of the Cl−C bond of CCl_3 moiety. However, because of the instability, no parent ion is found in the mass spectrum of CCl_3SSCN.

Furthermore, the isotopic distribution patterns in the mass spectrum fit the theoretically calculated patterns of Cl-containing fragments. In a word, the results of the mass spectrum can confirm the generation of CCl_3SSCN under our experimental conditions. The dominant fragment of CCl_3^+ indicates that the $CCl_3SSCN^{\cdot+}$ ion prefers the dissociation of the C−S bond between CCl_3 and SS moieties. This result is consistent with the obvious change in the length of the C−S bond between the neutral and cationic-radical forms.

D. Photoelectron spectroscopy

Photoelectron spectroscopy (PES) with a HeI resonance source is an effective method to investigate electronic structures of unstable compounds in combination with *ab initio* calculations [33]. The valence shell structure of gas-phase molecules can be readily obtained by HeI photoelectron energy analysis. The HeI photoelectron spectrum of CCl_3SSCN is shown in Fig.4. Before assigning the spectrum, OVGF calculations were carried out to obtain the ionization energies for CCl_3SSCN. The experimental vertical ionization potentials, theoretical vertical ionization energies, molecular orbitals, and corresponding characters of outer valence shells for CCl_3SSCN are listed in Table III. The OVGF results are in general in good agreement with the experimental data. Drawings of nine molecular orbitals (MOs) for CCl_3SSCN are given in Fig.5.

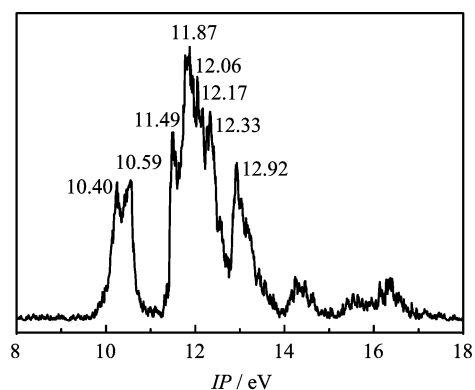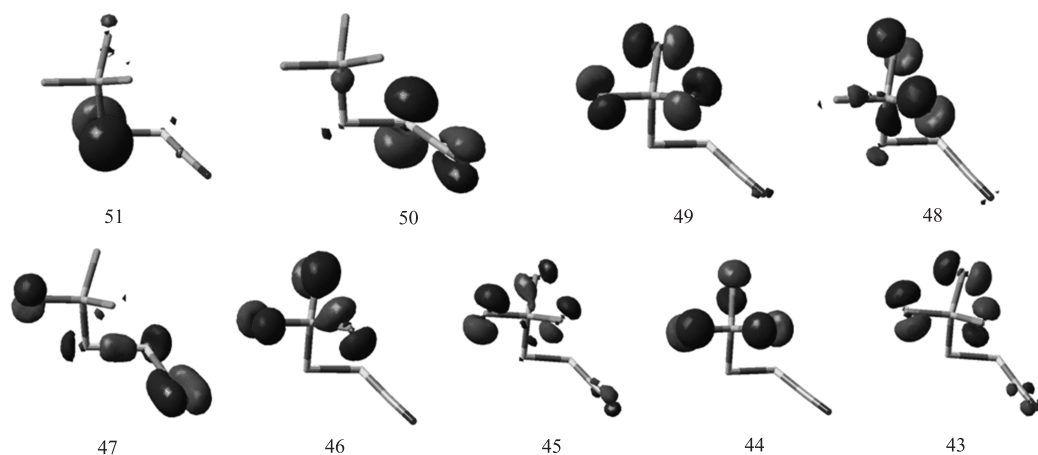FIG. 3 Photoionization mass spectrum of CCl_3SSCN.

FIG. 4 HeI photoelectron spectrum of CCl_3SSCN.

FIG. 5 Drawings of nine molecular orbitals (MOs) for CCl$_3$SSCN.

TABLE III Experimental vertical ionization energies, calculated vertical ionization energies (OVGF/6-311+G*), and molecular orbital characters for CCl$_3$SSCN

Experimental/eV	Calculated/eV	MO	Character
10.40	10.47	51	$n_{S(CCl_3S)}$
10.59	10.63	50	$n_{S(SCN)}, \pi_{CN}$
11.49	11.55	49	n_{Cl}
11.87	11.93	48	n_{Cl}
12.06	12.08	47	σ_{SS}, π_{CN}
12.17	12.09	46	n_{Cl}
12.33	12.32	45	n_{Cl}
12.92	12.91	44	n_{Cl}
	12.98	43	n_{Cl}

As pointed out by Baker *et al.* [34], the first two bands in the photoelectron spectra of disulfides correspond to the symmetric and antisymmetric linear combinations of the outermost p-atomic orbitals. The first two peaks in the photoelectron spectrum of CCl$_3$SSCN are centered at 10.40 and 10.59 eV. The main characters for the first two outmost orbitals are $\{51a(n_{S(CCl_3S)})\}^{-1}$ and $\{50a(n_{S(SCN)}, \pi_{CN})\}^{-1}$, and the theoretically predicted first two vertical ionization energies are 10.47 and 10.63 eV. The energy difference ΔE between the first two bands is 0.19 eV, which is slightly smaller than those of HSSH (ΔE=0.27 eV) [35] and FC(O)SSCH$_3$ (ΔE=0.3 eV) [5]. This difference originates from the interaction of the two lone pairs at the adjacent S atoms. The ionization from the orbital mainly localized at the σ bond of the SS moiety and the π orbital on the C≡N moiety causes the energy of 12.06 eV. It is smaller than the ionization energy from σ_{SS} orbital of its parent compound HSSH (12.62 eV) [35]. The difference is caused by the effect of the substituents on the S−S bond.

Another important functional group in CCl$_3$SSCN is the SCN moiety, which can influence the electronic structure of the whole molecule greatly. The electronic structure of the SCN moiety can be explained in the following way [36]. We can assume a single S−C bond and a triple C≡N bond, so two bands from the C≡N π bond are expected in the low-energy region of the spectrum. The corresponding bands in the photoelectron spectrum are located at 10.59 and 12.06 eV, which come from the ionization processes of $\{50a(n_{S(SCN)}, \pi_{CN})\}^{-1}$ and $\{47a(\sigma_{SS}, \pi_{CN})\}^{-1}$, respectively.

Similar to the molecular orbital characters of CCl$_3$SCl [33], many ionization processes of CCl$_3$SSCN come from the orbitals localized at the CCl$_3$ moiety (Fig.5). The assignments of the bands with the ionization energy lower than 13.0 eV are listed in Table III in detail. The remaining bands in the higher ionization region arising from inner molecular orbitals can not be assigned with certainty.

IV. CONCLUSION

A simple disulfide, CCl$_3$SSCN was generated and characterized by photoelectron spectroscopy and photoionization mass spectroscopy. Its first vertical ionization energy was determined to be 10.40 eV, which was caused by the ionization of the sulfur lone pair electron. The structures of the neutral molecule and the cationic-radical form of CCl$_3$SSCN$^{.+}$ were investigated theoretically by quantum chemical calculations. The neutral molecule shows a gauche structure with the dihedral angle around S−S bond of 91.4° (B3LYP/6-311+G(3df)). After ionization, the cationic-radical form of CCl$_3$SSCN$^{.+}$ adopts a planar main-atom structure with C$_s$ symmetry.

V. ACKNOWLEDGMENTS

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