

# (1,1-Dichloro-2,2,2-trifluoroethylimino)sulfur dichloride, $\text{CF}_3\text{CCl}_2\text{N}=\text{SCl}_2$ : Vibrational spectra and quantum chemical calculations

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## ABSTRACT

The vibrational spectra of (1,1-dichloro-2,2,2-trifluoroethylimino)sulfur dichloride,  $\text{CF}_3\text{CCl}_2\text{N}=\text{SCl}_2$ , were recorded in the gas phase with IR spectroscopy and in the liquid state with Raman spectroscopy. Quantum chemical calculations at the HF, B3LYP (6-311+G(d) and 6-311+G(2df) basis sets) and MP2 levels of theory (6-31+G(d) and 6-311+G(df) basis sets) were performed. According to all calculations the lowest energy conformer possesses  $C_1$  symmetry with *syn* orientation of the  $\text{SCl}_2$  group relative to the N–C bond and near-trans orientation of the  $\text{CF}_3$  group relative to the N=S bond. Calculations predict the presence of a second stable conformer with *anticlinal* orientation of the  $\text{SCl}_2$  group which, however, possesses considerably higher energy and is therefore not observed in the analysis of the experimental vibrational spectra. The vibrational spectra were assigned for a single conformer in accordance with these calculations.

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## 1. Introduction

Only a limited number of structural, conformational, and configurational studies of iminosulfur molecules  $\text{R}=\text{N}=\text{SX}_2$  have been reported in the literature and little is known about the factors which affect these properties. In principle, depending on the orientation of the R–N bond with respect to the X–S–X bisector two molecular forms, *syn* and *anti*, can be expected (See Scheme 1).

Vibrational spectroscopy, gas electron diffraction (GED), X-ray crystallography, and quantum chemical calculations have been shown to be powerful tools to determine the structural properties of this class of molecules. Thus, for systems of the type  $\text{R}=\text{N}=\text{SF}_2$ ,  $\text{R}=\text{CF}_3$  [1],  $\text{FC}(\text{O})$  [2],  $\text{CF}_3\text{C}(\text{O})$  [3],  $\text{CF}_3\text{CF}_2$  [4],  $\text{FSO}_2$  [5], and of the type  $\text{R}=\text{N}=\text{SCl}_2$ ,  $\text{R}=\text{CF}_3$  [6],  $\text{FC}(\text{O})$  [7],  $\text{CF}_3\text{CF}_2$  [8],  $\text{ClC}(\text{O})$  [9] it could be demonstrated that the *syn* configuration (*syn* of the R–N bond with respect to the X–S–X bisector) is the most stable structure, although it is sterically rather unfavorable. It is interesting to note that in molecules with different substituents attached to the sulfur atom, i.e. molecules of the type  $\text{R}=\text{N}=\text{SXY}$ , such as  $\text{FC}(\text{O})\text{N}=\text{S}(\text{F})\text{CF}_3$  [10] and  $\text{CF}_3\text{C}(\text{O})\text{N}=\text{S}(\text{F})\text{CF}_3$  [11], the most stable form turns out to be *anti* (R–N bond *anti* with respect to the X–S–Y bisector).

The preference of the *syn* configuration in molecules with symmetrical substitution at the sulfur atom can be explained by orbital interactions of the electron lone pairs at S and N with antibonding orbitals of vicinal N–R and S–X bonds, respectively. These an-

omeric effects strongly stabilize the sterically unfavorable *syn* structure. Numerical values for these interaction energies have been reported for  $\text{ClC}(\text{O})\text{N}=\text{SCl}_2$  [9]. Nevertheless, the effect of various substituents at nitrogen has not yet been fully understood.

In order to obtain additional experimental and theoretical information about the effects of such substituents on structural, conformational and vibrational properties of sulfur imides, we report in the present study results for  $\text{CF}_3\text{CCl}_2\text{N}=\text{SCl}_2$ . This compound allows for the first time to analyze the influence of an alkyl group with fluorine and chlorine substituents at the carbon atoms on the molecular properties.

## 2. Experimental

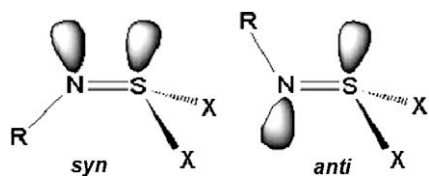
(1,1-Dichloro-2,2,2-trifluoroethylimino)sulfur dichloride was synthesized by the reaction of  $\text{CF}_3\text{CN}$  and  $\text{SCl}_2$ . The product was purified at reduced pressure by repeated trap-to-trap distillations [12]. A gas phase infrared spectrum at 5 mbar was recorded in the range  $4000\text{--}400\text{ cm}^{-1}$  with an FTIR Perkin Elmer 1600 spectrometer (resolution  $2\text{ cm}^{-1}$ ). Raman spectra of liquid  $\text{CF}_3\text{CCl}_2\text{N}=\text{SCl}_2$  between 2000 and  $50\text{ cm}^{-1}$  were obtained using a FT Bruker IFS 66v spectrometer (spectral resolution of  $4\text{ cm}^{-1}$ ) equipped with a Nd:YAG laser ( $1064\text{ nm}$ ). The liquid samples were handled in glass capillaries at room temperature.

## 3. Quantum chemical calculations

Calculations at different levels of theory (HF and B3LYP with 6-311+G(d) and 6-311+G(2df) basis sets and MP2 with 6-31+G(d)

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Scheme 1.

and 6-311+G(df) basis sets) were performed using the Gaussian 03 program package [13]. In the first step the potential functions for internal rotation around the N=S and N–C bonds were derived with the smaller basis sets. Fig. 1 shows the potential curves for internal rotation around the N=S bond.

The orientation of the SCl<sub>2</sub> group relative to the N–C bond is described by the dihedral angle between the N–C bond and the S–X direction with X being a dummy atom on the SCl<sub>2</sub> bisector. The potential curves were derived by structure optimizations at fixed dihedral angles  $\varphi(\text{C–N=S–X})$  in steps of 30°. With rotation around the N=S bond also the orientation of the CF<sub>3</sub> group ( $\varphi(\text{C–C–N=S})$ ) changes appreciably. To obtain the lowest-energy path for full rotation from 0° to 360° around the N=S bond which corresponds to a symmetrical potential function, the CF<sub>3</sub> group has to be forced to possess the same orientation for  $\varphi(\text{C–N=S–X}) = 180\text{--}360^\circ$  as for  $\varphi(\text{C–N=S–X}) = 0\text{--}180^\circ$ . Otherwise a higher-energy path is obtained. This potential curve demonstrates that the global minimum occurs for *syn* orientation with  $\varphi(\text{C–N=S–X}) \approx 10^\circ$ . Strong repulsion between the chlorine atoms bonded to the sulfur and carbon atoms causes distortion of this structure from C<sub>s</sub> to C<sub>1</sub> symmetry. The presence of a second stable form with near *anti* orientation of the SCl<sub>2</sub> group ( $\varphi(\text{C–C–N=S}) \approx 150^\circ$ ) and about 5–8 kcal/mol higher in energy is predicted. The potential function for internal rotation around the N–C bond was derived by geometry optimizations for fixed  $\varphi(\text{C–C–N=S})$  dihedral angles in steps of 20°. These potential functions (not shown) possess a double minimum shape near-*trans* orientation of the CF<sub>3</sub> group relative to the N=S bond with minima of  $\varphi(\text{C–C–N=S})$  between 150° and 160° (200° and 210°, respectively). The barrier between the two equivalent near-*trans* forms is predicted to be less than 0.5 kcal/mol. The MP2 method predicts an additional shallow minimum for a *gauche* orientation of the CF<sub>3</sub> group ( $\varphi(\text{C–C–N=S}) \approx 50^\circ$  and 310°) and about 2.5 kcal/mol higher in energy. On the other hand potential functions derived with HF and B3LYP approximations possess only

shoulders in this region. Additional calculations were performed for the barrier to internal rotation of the CF<sub>3</sub> group around the C–C bond. The values derived for this barrier (9.4, 7.2 and 9.2 kcal/mol according to HF, B3LYP and MP2 approximations) are much higher than usual. Intermediate barriers were predicted for CF<sub>3</sub>CF<sub>2</sub>N=SCl<sub>2</sub> [8].

In the last step the structures of the two structures, *syn-trans* and *anti-trans* were optimized with the larger basis sets. The relative energy of the *anti-trans* form is calculated to be 4.9 (HF), 7.3 (B3LYP) and 8.0 kcal/mol (MP2). From these relative energies we conclude that only the *syn-trans* configuration shown in Fig. 2 is present at room temperature and it determines the experimental vibrational spectra. The structural parameters of this form are summarized in Table 1 and the vibrational frequencies in Table 2.

## 5. Vibrational spectra

Observed and calculated wavenumbers and approximate descriptions of the fundamental modes are listed in Table 2. For this molecule  $3N - 6 = 27$  normal modes of vibration are expected. The observed features in the IR and Raman spectra are consistent with the existence of a single conformer (see Figs. 3 and 4).

Calculations (MP2) predict a splitting of the N=S stretch of 24 cm<sup>-1</sup> between *syn* and *anti* conformers. No such splitting is observed in the experimental spectra. Thus, the *syn* structure possessing C<sub>1</sub> symmetry, as derived by theoretical calculations was used in the analysis of the vibrational spectra. The expected normal modes of vibration have been assigned on the basis of characteristic wavenumbers and taking into account the calculated vibrational frequencies and intensities for this compound. Furthermore, wavenumbers of related molecules, such as CF<sub>3</sub>N=SCl<sub>2</sub> [6], CF<sub>3</sub>CF<sub>2</sub>N=SCl<sub>2</sub> [8], CF<sub>3</sub>CF<sub>2</sub>N=SF<sub>2</sub> [4], CF<sub>3</sub>CF<sub>2</sub>N=S(F)CF<sub>3</sub> [14] and CF<sub>3</sub>CF<sub>2</sub>N=S(Cl)CF<sub>3</sub> [14], were used in the analysis of the fundamental modes.

In general, good agreement exists between the experimental and calculated values. Wavenumbers obtained with approximations including electron correlation (B3LYP/6-311+G(2df) and MP2/6-311+G(df)) reproduce experimental values slightly better than the scaled HF method. Some experimental wavenumbers are reproduced closer by the B3LYP method, others by the MP2 approximation.

According to reported data of most imidosulfur compound containing a CF<sub>3</sub> substituent, the region between 1400 and 900 cm<sup>-1</sup> contains the C–C, N=S, C–Cl and C–F stretching modes belonging to the CF<sub>3</sub> group. Thus, the presence of several intense and narrow bands in this region of the IR spectrum and weak and broad bands in the Raman spectrum is directly related to these vibrational modes. Considering that the C–C stretching mode of CF<sub>3</sub>CF<sub>2</sub>N=SF<sub>2</sub> and of CF<sub>3</sub>CF<sub>2</sub>N=SCl<sub>2</sub> (1410 and 1380 cm<sup>-1</sup> in the IR spectrum, respectively) was assigned to the signal of highest frequency in the vibrational spectra, the band of medium intensity located at

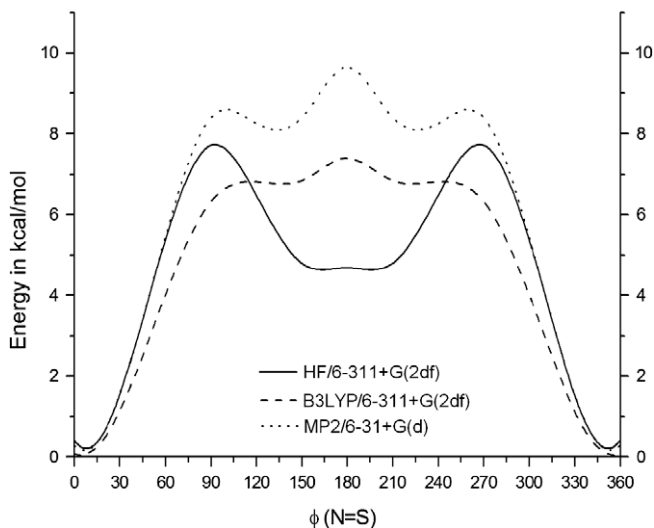
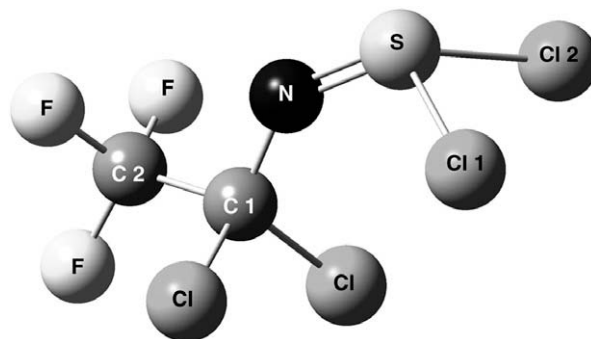


Fig. 1. Calculated potential functions for rotation around the N=S bond.

Fig. 2. Molecular model for the *syn* conformer of CF<sub>3</sub>CCl<sub>2</sub>N=SCl<sub>2</sub>.

**Table 1**  
Calculated geometric parameters for the *syn* conformer of  $\text{CF}_3\text{CCl}_2\text{N}=\text{SCL}_2$ .<sup>a</sup>

	HF 6-311+G(2df)	B3LYP 6-311+G(2df)	MP2 6-311+G(df)
<i>Bond lengths</i>			
C1–F <sup>b</sup>	1.304	1.334	1.322
C1–C2	1.549	1.565	1.552
C2–Cl <sup>b</sup>	1.782	1.806	1.768
C2–N	1.401	1.403	1.417
N=S	1.481	1.504	1.509
S–Cl <sup>b</sup>	2.063	2.144	2.108
<i>Angles</i>			
C1–C2–N	106.8	107.3	105.7
C2–N=S	137.1	138.7	134.0
N=S–Cl <sup>b</sup>	111.7	112.1	112.3
Cl1–S–Cl2	96.4	96.4	96.4
$\varphi(\text{C1–C2–N=S})$	–154.4	–160.1	–147.7
$\varphi(\text{C2–N=S–X})$	11.6	10.5	10.0

<sup>a</sup> Bond lengths in Å and angles in degrees. For atom numbering, see Fig. 2.

<sup>b</sup> For parameters that are not unique, average values are given.

1395  $\text{cm}^{-1}$  in the infrared spectrum and at 1410  $\text{cm}^{-1}$  in the Raman spectrum of  $\text{CF}_3\text{CCl}_2\text{N}=\text{SCL}_2$  is also assigned to this fundamental mode.

The frequency of the N=S stretching vibration has been shown to be directly related to the electron withdrawing properties of the substituents attached to nitrogen and sulfur atoms [15]. Increasing electron withdrawing properties of the substituents attached to any of these atoms strengthens this bond. Taking into account that the N=S stretch of  $\text{CF}_3\text{N}=\text{SCL}_2$  [6] (1314  $\text{cm}^{-1}$  IR and 1300  $\text{cm}^{-1}$  Raman) and of  $\text{CF}_3\text{CF}_2\text{N}=\text{SCL}_2$  [8] (1292  $\text{cm}^{-1}$  IR and 1286  $\text{cm}^{-1}$  Raman) and that group electronegativities of  $\text{CF}_3$ ,  $\text{CF}_3\text{CF}_2$  and  $\text{CF}_3\text{CCl}_2$  are similar, the band placed at 1303  $\text{cm}^{-1}$  (1304  $\text{cm}^{-1}$  Raman) was assigned to the N=S stretching vibration of this compound.

The symmetric and antisymmetric stretching modes belonging to the  $\text{CF}_3$  group were assigned to the bands localized at 1250 and 1238  $\text{cm}^{-1}$  in the infrared spectrum. This assignment is differ-

ent from that reported for  $\text{CF}_3\text{CF}_2\text{N}=\text{SCL}_2$ , where both stretching modes were assigned to a band at 1235  $\text{cm}^{-1}$  in the infrared spectrum (1218  $\text{cm}^{-1}$  Raman). Possibly the presence of the  $\text{CCl}_2$  group causes a splitting of these stretching modes of the  $\text{CF}_3$  group. The totally symmetric mode was assigned to the band located at 948  $\text{cm}^{-1}$  in the infrared spectrum, in agreement with the theoretical frequencies obtained by different approaches (950, 957 and 985  $\text{cm}^{-1}$ , according to methods HF, B3LYP and MP2, respectively). With respect to the  $\text{CCl}_2$  group, all quantum chemical calculations predict strong coupling of the totally symmetric stretching modes of the  $\text{CF}_3$  and  $\text{CCl}_2$  groups. Antisymmetric and symmetric stretching modes belonging to the  $\text{CCl}_2$  group were assigned to the bands centred at 915 and 833  $\text{cm}^{-1}$  (909 and 837  $\text{cm}^{-1}$ , Raman), respectively. All these modes were described considering local  $\text{C}_s$  symmetry of the  $\text{CF}_3\text{CCl}_2\text{N}$  moiety (see Fig. 2).

The C–N stretching mode was assigned to the medium intensity bands placed at 725 and 722  $\text{cm}^{-1}$  in the IR and Raman spectra, respectively. Theoretical values for this mode (HF 719  $\text{cm}^{-1}$ ; B3LYP 719  $\text{cm}^{-1}$  and MP2 746  $\text{cm}^{-1}$ ) together with reported frequencies for related molecules support this assignment.

According to theoretical wavenumbers, the band observed at 567  $\text{cm}^{-1}$  in the IR spectrum and at 556  $\text{cm}^{-1}$  in the Raman spectrum can be assigned to the symmetric deformation of the  $\text{CF}_3$  group. This band has a lower wavenumber with respect to the observed signals for  $\text{CF}_3\text{CF}_2\text{N}=\text{SCL}_2$  (709  $\text{cm}^{-1}$  IR) [8] and  $\text{CF}_3\text{CF}_2\text{N}=\text{SF}_2$  (732  $\text{cm}^{-1}$  [4]). The presence of the  $\text{CCl}_2$  group may modify considerably the vibrational properties of the  $\text{CF}_3$  group.

The  $\text{SCL}_2$  antisymmetric and symmetric stretching modes appear in the 500–400  $\text{cm}^{-1}$  region of the vibrational spectra. By comparison with  $\text{CF}_3\text{N}=\text{SCL}_2$  [6] and  $\text{CF}_3\text{CF}_2\text{N}=\text{SCL}_2$  [8] and taking into account the results obtained from theoretical calculations, the band observed at 469  $\text{cm}^{-1}$  in the infrared spectra (446  $\text{cm}^{-1}$  shoulder, Raman) can be assigned to the symmetric stretching of the  $\text{SCL}_2$  group. The antisymmetric stretching, displaced to lower frequencies in both reference molecules, is assigned to the band located in 428  $\text{cm}^{-1}$  in the IR spectra (430  $\text{cm}^{-1}$  Raman) of

**Table 2**  
Experimental and calculated wavenumbers ( $\text{cm}^{-1}$ ) of the *syn* conformer and tentative assignment.

Approximate description <sup>a</sup>	IR (gas)	Raman (liquid)	HF <sup>b</sup> 6-311+G(2df)	B3LYP 6-311+G(2df)	MP2 6-311+G(df)
C2–C1 stretch.	1395	1410	1330	1345	1391
N=S stretch.	1303	1304	1270	1239	1314
$\text{CF}_3$ sym. stretch.	1250	1250	1256	1207	1291
$\text{CF}_3$ asym. stretch.	1238	1204	1245	1190	1285
$\text{CF}_3$ sym. stretch.	948	–	950	957	985
$\text{CCl}_2$ sym. stretch.	915	909	914	893	962
$\text{CCl}_2$ asym. stretch.	833	837	844	794	912
C1–N stretch.	725	722	719	719	746
$\text{CF}_3$ sym. def.	579	–	565	563	586
$\text{CF}_3$ sym. def.	567	556	554	549	576
$\text{CF}_3$ asym. def.	537	538	529	525	556
$\text{SCL}_2$ sym. stretch.	469	446 sh	470	453	466
$\text{SCL}_2$ asym. stretch.	428	430	452	422	433
$\text{CCl}_2$ asym. def.	–	–	419	393	410
$\text{SCL}_2$ sym. def.	–	384	390	381	393
$\text{CF}_3$ sym. def.	–	–	362	355	381
$\text{CF}_3$ asym. def.	–	349	350	342	363
$\text{CCl}_2$ sym. def.	–	261	259	257	275
$\text{CF}_3\text{CCl}_2$ sym. def.	–	243	244	238	250
$\text{SCL}_2$ asym. def.	–	212	217	203	217
$\text{SCL}_2$ sym. def.	–	197	198	187	195
$\text{CF}_3\text{CCl}_2$ asym. def.	–	166	166	160	167
C1–C2–N def.	–	147	144	138	145
C2–N=S def.	–	114	113	104	118
$\text{CF}_3$ torsion	–	85	81	77	86
$\text{SCL}_2$ torsion	–	–	66	63	66
C2–N torsion	–	–	23	14	20

<sup>a</sup> stretch., stretching; def., deformation; sym., symmetric; asym., antisymmetric; sh., shoulder. For atom numbering, see Fig. 2.

<sup>b</sup> Scaled by the factor 0.9.

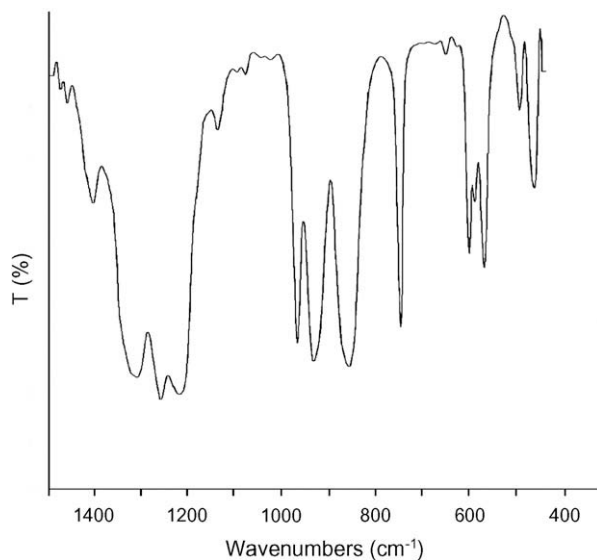


Fig. 3. Gas phase infrared spectrum of  $\text{CF}_3\text{CCl}_2\text{N}=\text{SCl}_2$  ( $P = 5$  mbar).

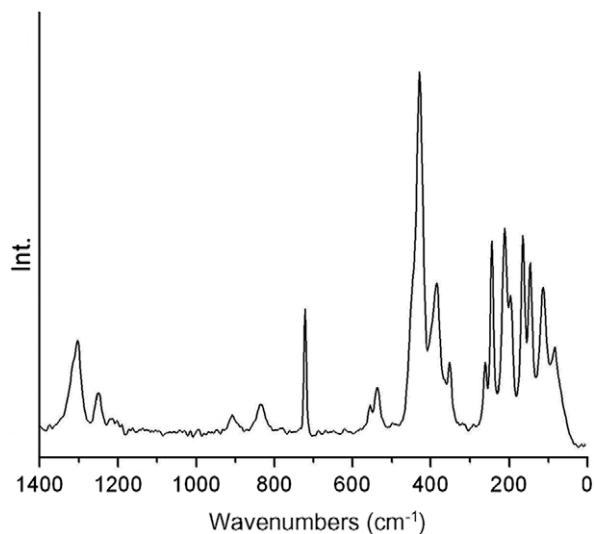


Fig. 4. Liquid phase Raman spectrum of  $\text{CF}_3\text{CCl}_2\text{N}=\text{SCl}_2$ .

$\text{CF}_3\text{CCl}_2\text{N}=\text{SCl}_2$ . Both experimental wavenumbers are in good agreement with calculated values.

## 6. Conclusions

The applied quantum chemical methods demonstrate to be a powerful tool for the determination of the structural and conformational properties of this kind of molecules. Although these

calculations predict the presence of two stable conformers for  $\text{CF}_3\text{CCl}_2\text{N}=\text{SCl}_2$ , *syn* and *anti* configuration of the  $\text{C}=\text{N}=\text{SCl}_2$  moiety and *trans* orientation of the  $\text{CF}_3$  group, only the *syn* configuration has to be considered in the interpretation of the experimental vibrational spectra. The *anti* conformer is predicted to be considerably higher in energy. The number of bands observed in the spectra confirms the presence of single species. The theoretical vibrational modes agree very well with the observed ones. This agreement together with the reported data for analogous molecules confirms the assignment of the 27 fundamental modes of the title compound.

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