

The Molecular Structure and Dihedral Angle and Effect on Some Liquid Crystal Phases using the Density-Functional Theory

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Abstract

Computer simulations provides a powerful tool for the investigation of liquid crystalline phases. In this work, the ability of simulations to accurately calculate the values of material parameters of liquid crystal molecules is investigated. A geometry optimization for liquid crystal molecules is performed using density functional theory DFT-B3LYP/6-311G (d,p) calculations on Schiff's bases substituted with polar groups Cl, Br, F, I, NO₂, CH₃, OCH₃ and COCH₃ in para position or aniline moiety molecules, which encompass key structural features of a range of common liquid crystalline molecules. Molecular quantum mechanical simulations of these 'fragment' molecules are carried out in the liquid crystal phase to investigate correlations between dihedral angles and liquid crystal's Smectic and Nematic phases. Density electronic distribution effect is also studied. The study of geometry and especially the value of the dihedral angle for core of molecule and phases showed the effect of the dihedral angle value to specify the type of the phase (Smectic or Nematic) for molecules in liquid crystals studied. Molecules that gave the Nematic phase had dihedral angle larger than those that showed Smectic phase for molecules in liquid crystals studied.

Key words: Dihedral Angle, Liquid Crystal Phases, Density Functional Theory.

الخلاصة

توفر المحاكاة الحاسوبية أداة قوية للبحث في الاطوار للبلورة السائلة. في هذا العمل والتحقيق في قدرة المحاكاة على حساب دقيق لقيم الابعاد الجزيئية من جزيئات البلورات السائلة. تم انجاز الموائمة الهندسية لجزيئات البلورات السائلة قيد الدراسة باستخدام اسلوب دالة الكثافة الالكترونية وطريقة B3LYP مع عناصر قاعدة 6-31G(d,p) وتمثل الجزيئات المدروسة قواعد شف المعوضة بمجاميع قطبية Cl, Br, F, I, NO₂, CH₃, OCH₃, COCH₃ في الموقع بارا لجزيئة الانلين الطرفية, التي تشمل الميزات الهيكلية الرئيسية لمجموعة من الجزيئات البلورية السائلة المشتركة. انجزت محاكاة الميكانيكية الكم الجزيئية من هذه ' جزء ' لجزيئات البلورات السائلة للبحث عن علاقة مشتركة بين زوايا ثنائي السطح و الطور السمكتي والنيماطي للبلورات السائلة. وتم دراسة تأثير كثافة التوزيع الإلكتروني أيضا. أظهرت دراسة الشكل الهندسة وخاصة قيمة زاوية ثنائي السطح للبلورات السائلة المدروسة تأثير قيمة زاوية ثنائي السطح على تحديد نوع الطور (سمكتي او نيماطي) لجزيئات البلورات السائلة المدروسة. الجزيئات التي أعطت الطور النيماطي لديها زاوية ثنائي السطح أكبر من تلك التي اعطت الطور السمكتي لجزيئات البلورات السائلة المدروسة.

الكلمات المفتاحية: زوايا ثنائي السطح، الاطوار للبلورة السائلة، دالة الكثافة الالكترونية.

Introduction

Oriented molecular fluids (liquid crystals) play a vital role in a wide variety of systems (e.g., computer and TV displays, biomembranes, and industrial applications) that affects our everyday lives. Liquid crystals form a fascinating array of macroscopic structures and are characterized predominantly by the long-range orientational (and in some cases positional) order of the component molecules. Liquid crystals in general consist of flexible molecules. The populations of various conformations form important property that is difficult to measure precisely, and the effect of the orientational (and possibly positional)

ordering on conformer populations poses a particularly interesting question (Adrian *et al.*, 2013).

The simplest liquid crystal phase is called the Nematic phase (N). It is characterized by a high degree of long range orientational order but no translational order. Molecules in a Nematic phase spontaneously order with their (for calamitic molecules) long axes roughly parallel. Smectic phases have further degrees of order compared to the nematic phase. In the simplest Smectic phase the molecules order into layers, with the layer normal paralleled to the director. Within the layers, liquid like structure remains closely related to the Smectic-A (SmA) phase is the Smectic-C (SmC) phase. Here, the molecules form a layer structure but the long axes of the molecules, and hence the director, lies at an angle to the layer normal (Sharon Ann Jewell, 2002; Salamon, *et al.*, 2010; Amelia Carolina Sparavigna, 2013).

In principle, the relationship between molecular structure and macroscopic properties can be investigated through the synthesis of series of similar mesogenic compounds. This however can be time consuming and may involve many difficult and expensive syntheses. Thus, the ability to determine the properties of a molecular structure before synthesis would be desirable. It is here that simulations can play an important role. Simulations on general molecular models can be used to find features that can lead to a particular property or phase (Zannoni, 2001). Atomistic simulations can be used to determine material properties of a particular molecular structure.

The aim of an electronic structure calculation is to calculate properties of a system from only the knowledge of the constituent atoms. When done without explicit recourse to experimental data (with the exception of the use of fundamental constants and comparison with experimental results), these can be termed *ab initio* calculations. Most properties of interest can be related to changes in energy of the system of interest. For example, the ground state geometry of a molecule is found from considering the change in energy of a molecule with regard to the change in the positions of the atomic nuclei. Traditionally electronic structure calculations, using methods such as the wave function based Hartree-Fock method (Szabo and Ostlund, 1982; Jensen, 1999), have found the energy of a system by solving the time-independent Schrodinger equation:

$$\left[\sum_{i=1}^N -\frac{\hbar^2}{2m_i} \nabla_i^2 + V(\mathbf{r}_1, \dots, \mathbf{r}_N) \right] \Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) = E \Psi(\mathbf{r}_1, \dots, \mathbf{r}_N),$$

where N is the number of particles (electrons and nuclei) with position vectors $\mathbf{r}_i$, or symbolically

$$\mathcal{H}(\mathbf{r}_1, \dots, \mathbf{r}_N) \Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) = E \Psi(\mathbf{r}_1, \dots, \mathbf{r}_N),$$

where it is the Hamiltonian given by

$$\mathcal{H}(\mathbf{r}_1, \dots, \mathbf{r}_N) = \left[\sum_{i=1}^N -\frac{\hbar^2}{2m_i} \nabla_i^2 + V(\mathbf{r}_1, \dots, \mathbf{r}_N) \right].$$

Electronic structure calculations have been proved in many areas of condensed matter of physics and chemistry, especially with the rapid growth in computer power. An alternative to wavefunction based methods, Density Functional Theory (DFT) has, over the past 20 years become widely used. DFT provides an (in principle) exact method for calculating the energy of a system of interacting electrons in terms of a set of single electron equations. In certain cases the accuracy of DFT calculations rival those of more computationally demanding quantum chemical calculations (Alain St-Amant *et al.*, 1995) and this has seen it become widely used in physics and chemistry. The motivation of Density Functional Theory (DFT) (Hohenberg and Kohn, 1964; Kohn and Sham, 1965) is that the ground state properties of a system can be described by considering the ground state charge density. The density can be found from the electronic wavefunction $\psi(r_1, r_2, \dots, r_n)$ by

$$\rho(r_1) = \int \Psi^*(r_1, r_2, \dots, r_n) \Psi(r_1, r_2, \dots, r_n) dr_2 \dots dr_n.$$

This has an obvious advantage over the wavefunction approach; for a N electron system, the wavefunction is a complex function of 3N variables (4N if spin is included), while the charge density is a function of 3 (4) variables. The usefulness of DFT arises as the ground state properties of a system are determined by the ground state density, which for a given number of electrons is a unique function of the potential.

Density Functional Theory calculations.

The quantum mechanical calculations of molecular properties in the gas phase were performed by using density functional theory (DFT) (Gaussian 09, Revision B.01, 2010) employing the combination of the Becke (3-parameter)–Lee–Yang–Parr (B3LYP) hybrid functional and the 6-31G (d,p) basis set using the Gaussian 09 package, to obtain the information related to molecular conformation, bend angle, dipole moment, molecular polarizability, and asymmetry parameter of all the compounds 1a–1f. Full geometry optimizations were carried out without imposing any constraints. Spin-restricted DFT calculations were carried out in the framework of the generalized gradient approximation (GGA) by using the B3LYP hybrid functional, exchange-correlation functional and the 6-31G(d,p) standard basis set (Kim and Jordan, 1994; Stephens *et al.*, 1994) due to its successful application to larger organic molecules, as well as hydrogen-bonded systems in the past (Leach, 2001; March, 1992; Kryachko and Ludeña, 1990) and bent-core molecules (Seltmann *et al.*, 2011; Selvaraj *et al.*, 2007) recently.

Experimental Section

We compared our theoretical results with experimental data of thermotropic liquid crystal that possess Nematic or Smectic phases, as a function of the dihedral angles of core in the molecules. Experimental data for nine different thermotropic liquid crystals have been obtained from another work (Ahmed AL-Hamdani *et al.*, 2010). A geometry optimization for liquid crystal molecules is performed using density functional theory DFT-B3LYP/6-311G (d,p) calculations on Schiff's bases substituted with polar groups Cl, Br, F, NO₂, CH₃, OCH₃ and COCH₃ in para position or aniline moiety molecules. The data base

provides observed phases and the transition temperatures: Isotropic $\rightarrow$ Nematic (N-I) and Isotropic $\rightarrow$ Smectic (Se-I). In Figure 1, the general patterns of structures for all molecules are shown. In Table 1 their liquid crystal properties are displayed (Ahood AL-Hamdani, *et al.*, 2010).

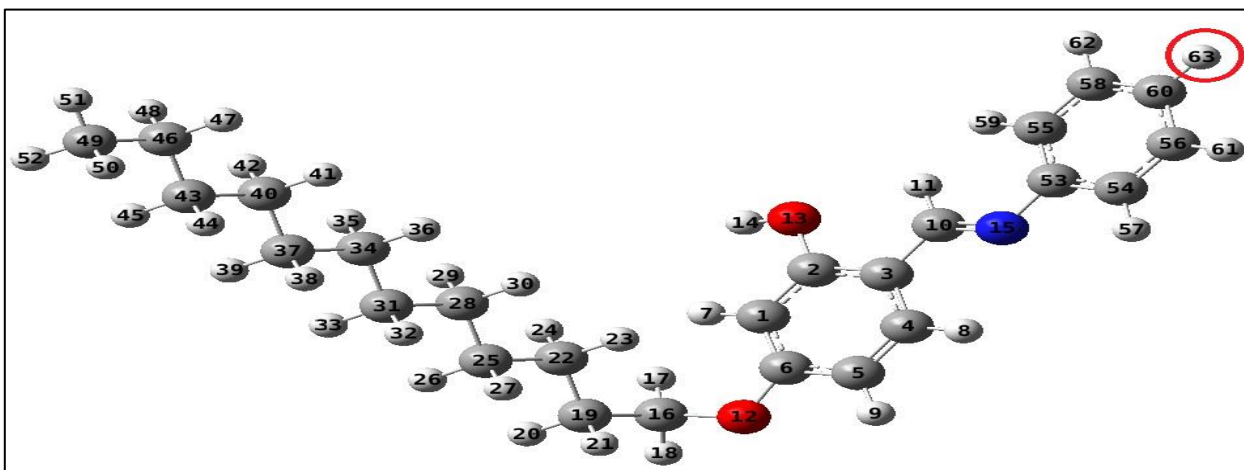


Figure 1. General structure and numbering system of the molecules studied. The atom No. 63 (which marked) is replaced by (Cl, Br, F, I, NO₂, CH₃, OCH₃ and COCH₃) in each time .

Table 1: The phase transition temperatures in °C for the molecules studied (Ahood AL-Hamdani *et al.*, 2010).

Compound	^a C-Se	C- ^b N	^c Se – I	N- ^d I	^e ΔT_S	^f ΔT_N
DNMO	-	84	-	130	-	25
DNM	-	79.38	-	99.01	-	19.7
DNBr	120	-	148	-	28	-
DNCl	98	-	120	-	22	-
DNF	80	-	95	-	15	-
DNI	105	-	124	-	19	-
DNNO ₂	123	-	132	-	9	-
DNAc	100.6	-	137.1	-	36.4	-
DNH	-	-	-	-	-	-

^aC: Solid , ^bN: Nematic , ^cS: Smectic , ^dI: Isotropic , ^e ΔT_S : Smectic thermal range ,
^f ΔT_N : Nematic thermal range

The dihedral angle for the nine liquid crystal molecules is studied using DFT-B3LYP hybrid function, exchange-correlation functional and the 6-31G(d,p) standard basis set calculation are reported in the table 2. Electronic density distribution across the core of the molecules are studied.

Table 2 : Dihedral Angles according to DFT-B3LYP/6-311G calculation

Dihedral Angles	Compound								
	DNH	DNMO	DNM	DNBr	DNCl	DNF	DNI	DNNO ₂	DNAc
H11C10N15C53	-0.016	0.066	0.078	0.036	0.039	0.039	0.040	0.005	0.015
N15C53C55H59	-0.012	0.075	0.048	0.001	0.003	0.001	0.002	0.005	0.0301
N15C53C54H57	-0.004	-0.217	-0.037	0.002	0.002	0.003	0.002	0.007	-0.195
O13C2C3C10	-0.203	-0.209	-0.218	-0.112	-0.114	-0.116	-0.114	-0.001	0.058
H14O13C2C3	179.231	179.272	179.252	179.360	179.355	179.354	179.353	179.511	179.668
H14O13C2C10	179.129	179.166	179.112	179.303	179.970	179.296	179.295	179.510	179.697
C3C10N15C53	179.931	179.917	179.917	179.955	179.957	179.957	179.957	179.983	179.967

Results and Discussions

For all molecules studied, the most important differences are observed for the dihedral angle as a function of transition temperature in the liquid-crystal molecules are shown in Figure 2 and 3 for N(15)-C(53)-C(55)-H(59) and H(11)-C(10)-N(15)-C(53) Dihedral angle respectively, where transition temperatures are plotted against this dihedral angles values that's multiplication by 10^3 as a scale. From experimental results (Ahoud AL-Hamdani *et al.*, 2010) that's reported in Table 1. The molecules DNMO and DNM exhibited Nematic phase but the other molecules studied (DNBr, DNCl, DNF, DNI, DNNO₂ and DNAc) exhibited Smectic phase. While molecule DNH did not give a liquid crystalline behavior.

Figures 2 and 3 show that the values of dihedral angle for DNMO and DNM are bigger than values of dihedral angle for DNBr, DNCl, DNF, DNI, DNNO₂ and DNAc that's exhibited Smectic phase. While the dihedral angle of the molecule DNH was a negative value in the opposite direction to arrange the dihedral angle in the other molecules studied.

The study of geometry and especially the value of the dihedral angle for core of molecule and phase showed a relationship. Molecules that gave the Nematic phase have dihedral angle largest of those that showed Smectic phase for molecules in liquid crystals studied.

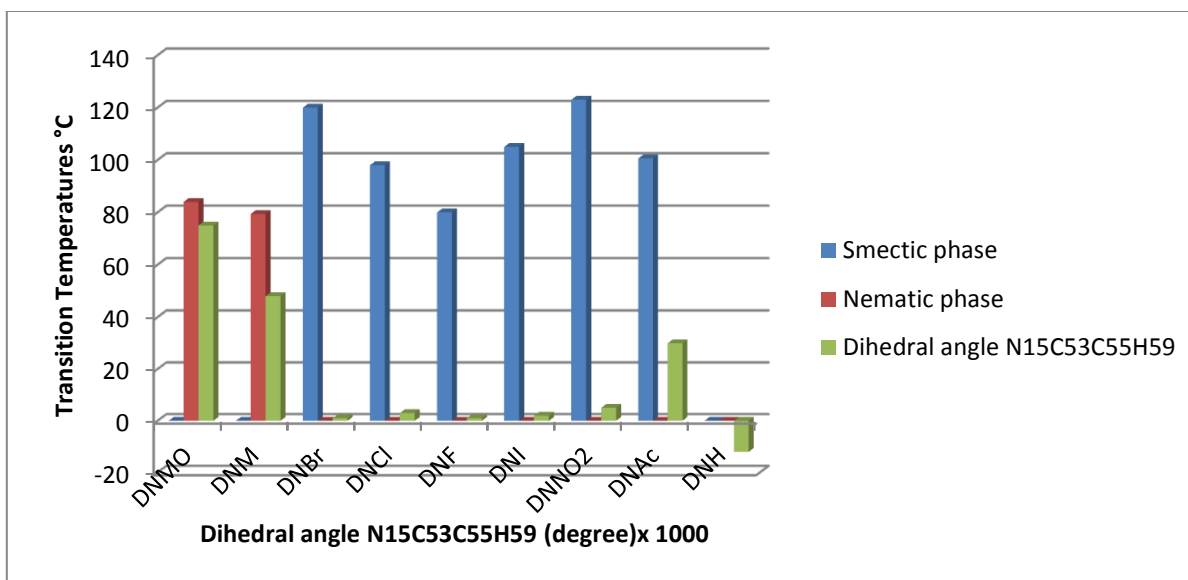


Figure 2. Dihedral angle N(15)-C(53)-C(55)-H(59) as a function of transition temperature and Smectic and Nematic phases in the liquid-crystal molecules studied.

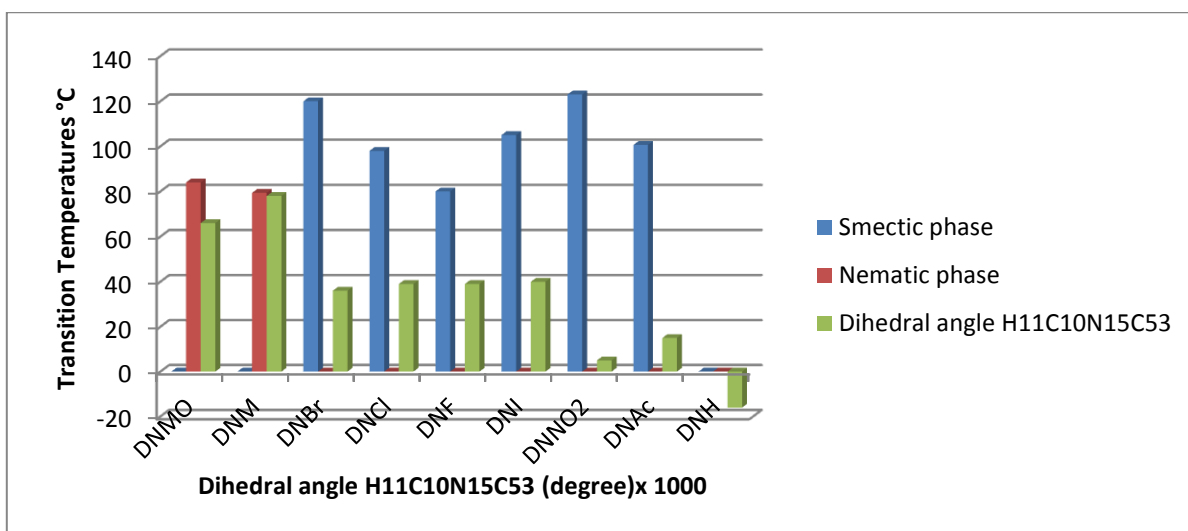


Figure 3. Dihedral angle H(11)-C(10)-N(15)-C(53) as a function of transition temperature and Smectic and Nematic phases in the liquid crystal molecules studied .

This means that Dihedral angle play an important role in the observations phases of liquid crystallinity of the studied molecules. In order to obtain more information about the structure and effect of electronic density distribution across the core of the molecules studied, we perform of a quantum mechanical geometry optimization and electron density from total SCF density (Warren Hehre, 2003) and generate contours for the planer grid

calculation by DFT –B3LYP/6-311G (d,p) methods to each molecules. The goal behind this step is to include the electronic contributions and electronic distribution of density and spread across the core of the molecule and the effect on the phase in liquid crystals for each molecules studied. Figure 4 shows that the concentration of electron density near the Nitrogen in the core of the molecule contributes to give the Nematic phase, as is the case for molecules DNM and DNMO. While the spread of electronic density near the Nitrogen contributed in giving Smectic phase of the liquid crystal molecules studied.

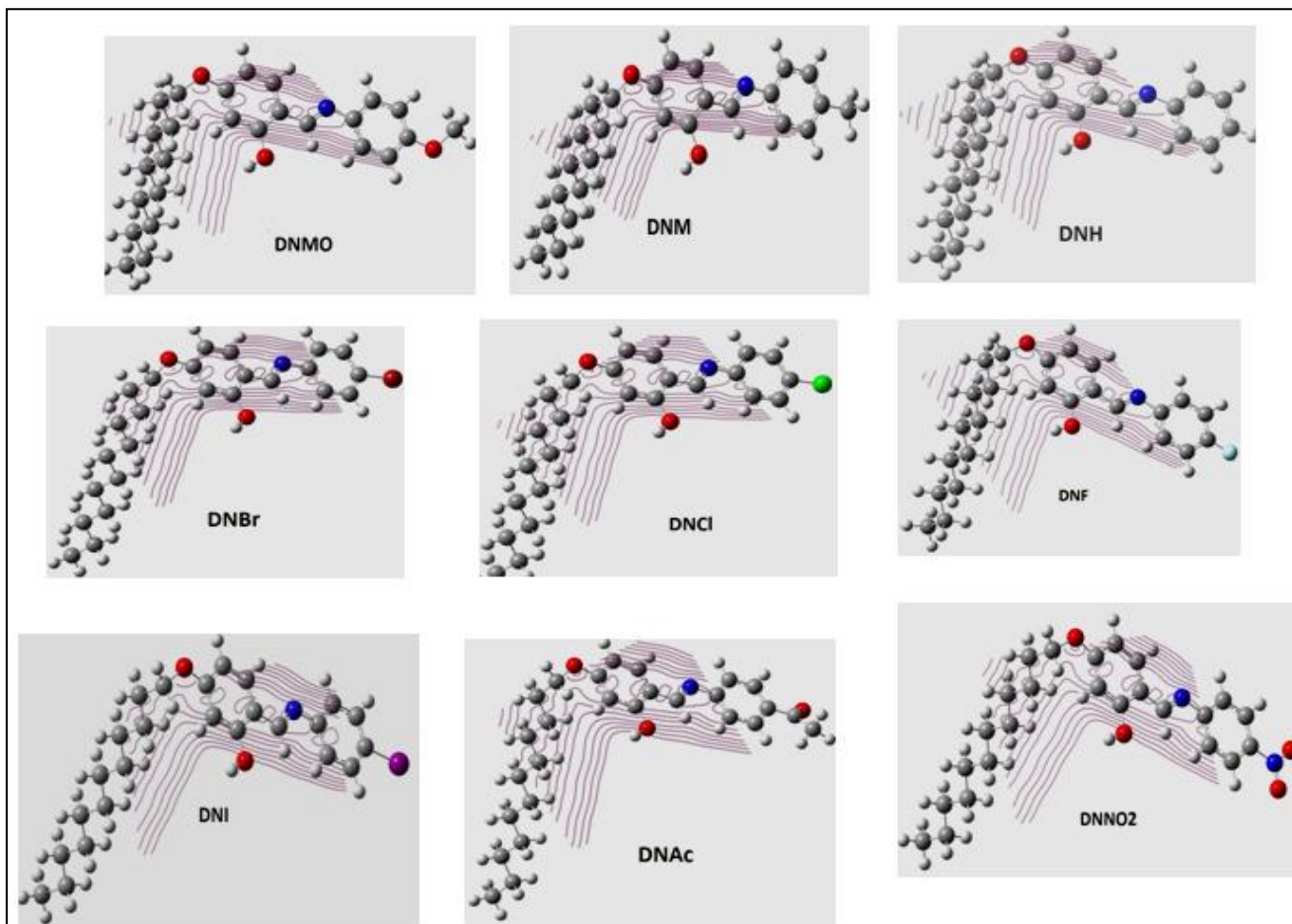


Figure 4. Electron density from total SCF density and generate contours for the planer grid calculation by DFT –B3LYP/6-311G (d,p) methods.

Conclusions

We have presented a theoretical study of torsional barriers and electron density from total SCF density and generate contours for the planer grid calculation by DFT –B3LYP/6-311G (d,p) methods. Our torsional barrier and electron density results are in good agreement with experimental studies. We have also observed that the thermotropic liquid crystals that possess Nematic or Smectic phase are heavily dependent on the dihedral angle. However, Nematic or Smectic phase depends slightly on the electron density from total

SCF density distribution and spread across the core of the molecule near Nitrogen in the core of thermotropic liquid crystals for molecules studied.

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