Journal of Molecular Liquids 214 (2016) 128–135

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Comparative computational analysis of electronic structure, MEP surface and vibrational assignments of a nematic liquid crystal: 4-n-methyl-4´-cyanobiphenyl

Dipendra Sharma *, S.N. Tiwari

Department of Physics, D.D.U. Gorakhpur University, Gorakhpur 273009, India

ARTICLE INFO

Article history:
Received 19 September 2015
Accepted 17 November 2015
Available online 17 December 2015

Keywords:
Liquid crystal
GAMESS
MEP
HOMO
LUMO
Vibrational assignment

ABSTRACT

The homologues of 4-n-alkyl-4´-cyanobiphenyl liquid crystal series constitute an important class of materials because of their technology development applications. The first member of this series namely, 4-n-methyl-4´-cyanobiphenyl is reported to be a pure nematic liquid crystal. The molecular geometry of this nematogen has been optimized by ab-initio HF/6–31G(d, p) as well as DFT B3LYP/6–31G(d, p) methods using GAMESS programme. The molecular electrostatic potential surface has been scanned with 0.001 electron/bohr^3. Molecular and thermodynamic properties such as total energy, dipole moment, entropy, enthalpy, Gibbs free energy, HOMO and LUMO energies have been calculated. Further, vibrational assignments of 4-n-methyl-4´-cyanobiphenyl molecule have been carried out. A computational analysis of results obtained by ab-initio and DFT techniques has been discussed in the light of experimental observations available in literature.

1. Introduction

The liquid crystalline state, lying between the crystalline and the isotropic liquid states of matter, offers a broad range of applications where its anisotropic but liquid properties can be explained. Although liquid crystalline materials were observed for over a century in 1888 but were recognized as such in 1980's. Presently, liquid crystals have emerged as beautiful, mysterious and soft condensed materials. Due to widespread use in the development of technology, industry and biomedical applications, scientists from almost all the disciplines have focused their attention on liquid crystal science [1–5].

Certain type of molecules form LC phases when heated above their melting points. However they all are anisotropic and differ either in their shape or solubility properties. Derived from the shape of constituting molecules, LCs are differentiated into three main categories: calamatic, discotic and banana shaped liquid crystals. The most common type of molecules of LCs are rod shaped molecules (i.e. one molecular axis is larger than the other two axes) forming calamatic liquid crystal. Calamatic liquid crystals may be considered as the classical liquid crystals. Because of their elongated shape, under appropriate conditions, molecules exhibit orientational and/or positional order; accordingly they are categorized as nematic, smectic etc. [6–8]. The molecular structure of a typical rod-like liquid crystal molecule consists of two or more benzene rings connected by a central linkage group and alkyl or alkoxy chain at the terminals. It is the nature and strength of various types of molecular interactions operating between sides, planes and ends of a pair of molecules, which are solely responsible for the liquid crystalline behaviour of molecules [6]. In view of the key role of molecular interactions in mesogenic compounds, semi-empirical and quantum mechanical studies have been reported [9–16]. Further, availability of high speed computers have facilitated the understanding of liquid crystallinity based upon the computer simulation, modelling and quantum chemical techniques [17–27]. The maps of molecular electrostatic potential (MEP) are being systematically used in scientific research for over fifty years [28]. Advances in the graphic and computational devices have increased the use of MEP surfaces, HOMO and LUMO as tools for studying molecular reactivity, charge transfer, interactions and other molecular properties [29–33]. However, to correlate the molecular structure with liquid crystalline properties at the molecular level still remains an elusive goal.

In view of the above facts, molecular structure, molecular electrostatic potential surface, HOMO and LUMO studies and vibrational assignments of 4-n-methyl-4′-cyanobiphenyl (1CB) molecule have been carried out using ab-initio HF/6–31G(d,p) and DFT B3LYP/6–31G(d,p) techniques with GAMESS programme [34,35].

2. Method of calculation

The molecular structure of 4-n- methyl-4´-cyanobiphenyl (1CB) molecule has been optimized by both ab-initio (RHF) and density

---

* Corresponding author.
E-mail addresses: d_11sharma@rediffmail.com (D. Sharma), sntiwari123@rediffmail.com (S.N. Tiwari).

http://dx.doi.org/10.1016/j.molliq.2015.11.045
0167-7322/

Table 1
Comparison of bond lengths (Å) and bond angles (°) calculated using GAMESS with HF/6–31G(d,p) and B3LYP/6–31G(d,p) basis sets.

Bond length	HF/6–31G(d,p)	B3LYP/6–31G(d,p)	Bond angle	HF/6–31G(d,p)	B3LYP/6–31G(d,p)
C(15)–H(26)	1.083	1.093	C(12)–C(15)–H(24)	110.99	111.47
C(15)–H(25)	1.085	1.097	C(12)–C(15)–H(25)	110.98	111.44
C(15)–H(24)	1.085	1.097	C(12)–C(15)–H(26)	111.24	111.33
C(14)–H(23)	1.072	1.084	H(24)–C(15)–H(25)	107.55	106.98
C(13)–H(22)	1.077	1.088	H(24)–C(15)–H(26)	107.95	107.68
C(13)–C(14)	1.379	1.391	H(25)–C(15)–H(26)	107.95	107.69
C(12)–C(15)	1.509	1.509	H(23)–C(14)–C(9)	120.90	120.31
C(12)–C(13)	1.390	1.401	H(23)–C(14)–C(13)	117.42	117.83
C(11)–H(21)	1.076	1.088	C(9)–C(14)–C(13)	121.66	121.84
C(11)–C(12)	1.385	1.399	H(22)–C(13)–C(14)	118.96	118.80
C(10)–H(20)	1.072	1.084	H(22)–C(13)–C(12)	119.63	119.62
C(10)–C(11)	1.384	1.392	C(14)–C(13)–C(12)	121.39	121.57
C(9)–C(14)	1.397	1.408	C(15)–C(12)–C(13)	120.95	121.20
C(9)–C(10)	1.392	1.406	C(15)–C(12)–C(11)	121.75	121.87
C(7)–N(8)	1.136	1.163	C(13)–C(12)–C(11)	117.29	116.91
C(6)–C(7)	1.442	1.431	H(21)–C(11)–C(12)	119.71	119.70
C(5)–H(19)	1.074	1.085	H(21)–C(11)–C(10)	118.90	118.68
C(5)–C(6)	1.387	1.404	C(12)–C(11)–C(10)	121.38	121.60
C(4)–H(18)	1.070	1.084	H(20)–C(10)–C(11)	117.30	117.82
C(4)–C(5)	1.379	1.388	H(20)–C(10)–C(9)	120.99	120.30
C(3)–C(9)	1.497	1.488	C(11)–C(10)–C(9)	121.70	121.86
C(3)–C(4)	1.398	1.409	C(3)–C(9)–C(14)	121.70	121.86
C(2)–H(17)	1.071	1.083	C(3)–C(9)–C(10)	121.74	121.93
C(2)–C(3)	1.398	1.410	C(14)–C(9)–C(10)	116.55	116.19
C(1)–H(16)	1.074	1.085	C(6)–C(7)–N(8)	179.96	179.94
C(1)–C(6)	1.388	1.404	C(7)–C(6)–C(5)	120.43	120.66
C(1)–C(2)	1.379	1.388	C(7)–C(6)–C(1)	120.39	120.61
			C(5)–C(6)–C(1)	119.12	118.72
			H(19)–C(5)–C(6)	119.86	119.65
			H(19)–C(5)–C(4)	119.93	120.08
			C(6)–C(5)–C(4)	120.19	120.25
			H(18)–C(4)–C(5)	117.44	117.56
			H(18)–C(4)–C(3)	120.80	120.30
			C(5)–C(4)–C(3)	121.74	122.13
			C(9)–C(3)–C(4)	121.55	121.76
			C(9)–C(3)–C(2)	121.51	121.70
			C(4)–C(3)–C(2)	116.92	116.52
			H(17)–C(2)–C(3)	120.78	120.32
			H(17)–C(2)–C(1)	117.43	117.60
			C(3)–C(2)–C(1)	121.77	122.07
			H(16)–C(1)–C(6)	119.85	119.67
			H(16)–C(1)–C(2)	119.95	120.03
			C(6)–C(1)–C(2)	120.18	120.28

functional theory (B3LYP) methods with 6–31G(d,p) basis set. The exchange correlation energy used in density functional theory is of the following form:

$$E_{XC} = (1-a_0)E_X^{LSDA} + a_0E_X^{HF} + a_X\Delta E_X^{B88} + a_CE_C^{LYP} + (1-a_C)E_C^{VWN} \qquad (1)$$

Where the energy terms used are the Slater exchange, the Hartree–Fock exchange, Becke's exchange functional correction, the gradient corrected correlation functional of Lee, Parr, Yang and the local correlation functional of Vosco, Wilk and Nusair [36].

Density functional theory (DFT) [37] has now emerged as the most significant quantum mechanical technique in providing theoretical insights into the chemical reactivity and selectivity, in terms of popular

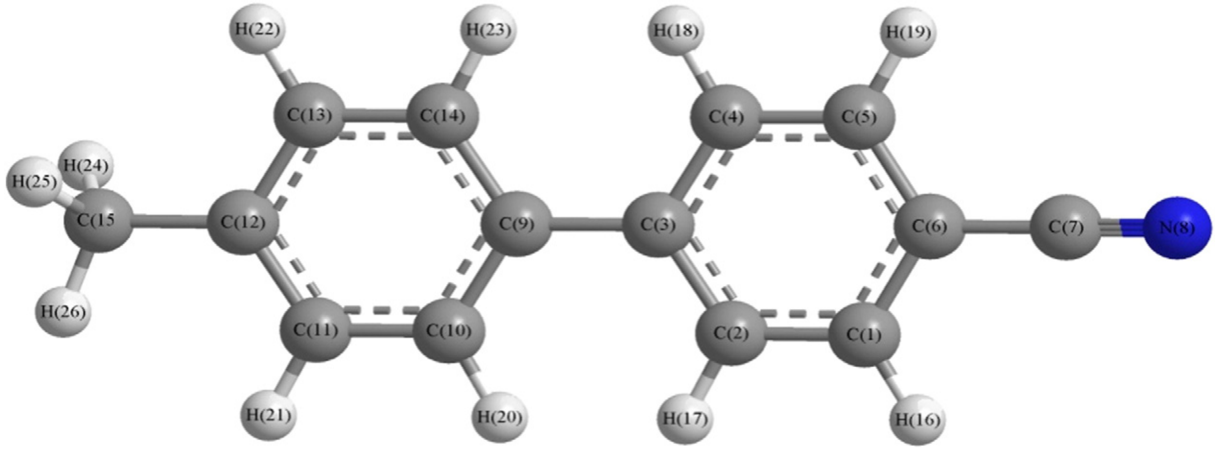

Fig. 1. Optimized molecular geometry of 4-n-methyl-4′-cyanobiphenyl (1CB).