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Quantum Chemical Studies on Silacyclohexane-based Liquid Crystal Compounds – 4-(2-(4-isopropyl-4-silacyclohexyl)ethyl) Biphenyl Series

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AM1 and PM3 SCF-MO calculations have been performed to study the molecular geometries of five *trans*-silacyclohexane-based liquid crystal compounds by energy gradient completed optimizations. The stable configurations, electronic structures, heats of formation and dipole moments of titled compounds are first reported. The calculated results are discussed relating to the classical organic electronic theory.

Keywords: Silacyclohexane-based compounds; liquid crystal; AM1 method; PM3 method; molecular geometry; electronic structure

1. INTRODUCTION

Theoretical chemistry is widely used in many fields to study the relationship between molecular properties and structures of compounds, such as the medicine, biology and other kinds of compounds, including liquid crystals. Some semi-empirical molecular orbital (MO) methods have been employed to study the structures of some liquid crystal compounds, for example, the MNDO [1] method was used to study the structures of mesogenic *p*-alkoxybenzoic and pyrodinic acids [2]. As the improvement of the

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MNDO method, AM1 [3] and PM3 [4] methods are more advanced and are more suitable for calculating the molecular geometry, electronic structure and some properties of many kinds of compounds.

Silacyclohexane-based compound is a new kind of liquid crystal compounds which contains a silicon atom in the molecule so as to improve the characteristics for use as a liquid crystal substance [5]. To date, few experimental studies and theoretical researches have been performed on these compounds. In our opinion, the theoretical prediction of molecular structures is probably one of the most important subjects for understanding their properties. This paper deals with the molecular geometries, electronic structures, heats of formation and dipole moments of five *trans*-silacyclohexane-based compounds using the AM1 and PM3 self-consistent-field (SCF) MO methods. In addition, the ratios of molecular length to width required for the appearance of liquid crystalline phase are also obtained based on calculation results.

2. CALCULATION METHOD AND RESULTS

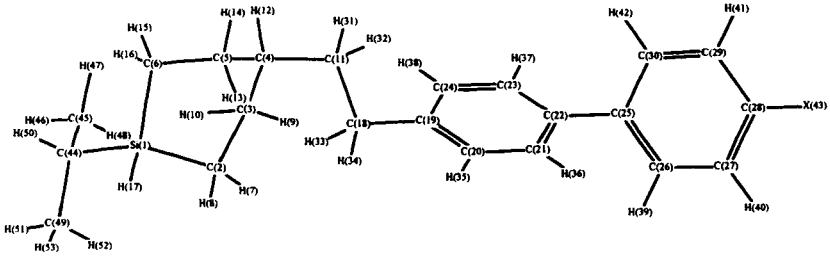
The SCF-MO AM1 and PM3 calculations were performed to study the electronic structures of titled compounds employing the MOPAC 6.0 program package. People's standard configuration data [6] were adopted as initial input of molecular geometry parameters. Their stable geometries at which the molecule has the minimum energy with respect to 3N-6 independent coordinate variables were obtained using an energy gradient method [7] through completed optimization calculations.

Figure 1 shows the order and atomic numbering of titled compounds. The fully optimized geometry of Compound (1) is given in Table I. The net charges on atoms and Wiberg bond orders between atoms in titled compounds are listed in Table II. Heats of formation and dipole moments of titled compounds are presented in Table III. Figure 2 shows the components of dipole moments obtained from AM1 calculations.

3. DISCUSSIONS

3.1. Molecular Geometry

In order to study the properties of a compound, its molecular structure should be understood initially. Because the five titled compounds have the



(1) X=F (2) X=Cl (3) X=CN (4) X=F, H(36)=CH_3 (5) X=F, H(40)=CH_3

FIGURE 1 The order and atomic numbering of titled compounds.

similar molecular structure, we use Compound (1) as an example to discuss the molecular geometries.

AM1 and PM3 calculation results show that both of the two benzene rings in the Compound (1) have planar geometries, since the dihedral angles between the carbon atoms on the benzene ring are all about 0° (or 180°), for example, C(24)—C(23)—C(22)—C(21) is 0°. However, the included angle between the two benzene rings is −40.4° (AM1) and −47.6° (PM3), showing that the two benzenes are not in the same plane. The dihedral angle of C(19)—C(18)—C(11)—C(4) is −177.8° (AM1) and −179.0° (PM3), very near to 180°, implying that the ethyl group is in a staggered conformation.

The change of the terminal substituent *X* has little effect on the bond lengths between the atoms which are far from the substituent. This is confirmed by the fact that the corresponding Si—C bond lengths of the five titled compounds are the same. However, it has influence on the C(28)—*X*(43) bond, the order of decreasing bond length of C(28)—*X*(43) is: C(28)—Cl > C(28)—CN > C(28)—F.

Due to the steric effect of methyl group, the bond lengths of C(22)—C(21) and C(22)—C(25) in Compound (4) are longer than that in Compound (1), the bond angle C(25)—C(22)—C(21) increases from 120.5° to 122.4° (AM1) and from 120.3° to 122.8° (PM3). Similarly, the bond length of C(27)—C(28) in Compound (5) is longer than that in Compound (1).

As stated above, the ratio of molecular length to width *L*/*W* is a basic factor which is required by rod-shaped liquid crystal compounds. According to the computational results, the longest interatomic distance of these molecules is between *X*(43) and H(51) or H(46), and the widest interatomic distance is between H(8) and H(16). Thus the ratio *L*/*W* which is

TABLE I The fully optimized geometry of Compound (1) Bond length (Å), Angle (°)

Bond length	*AM*1	*PM*3	*Bond angle*	*AM*1	*PM*3	*Dihedral angle*	*AM*1	*PM*3
Si(1)—C(2)	1.837	1.899						
C(3)—C(2)	1.506	1.508	C(3)C(2)Si(1)	108.4	107.0			
C(4)—C(3)	1.527	1.535	C(4)C(3)C(2)	115.6	115.5	C(4)C(3)C(2)Si(1)	63.4	64.8
C(5)—C(4)	1.525	1.534	C(5)C(4)C(3)	113.5	115.1	C(5)C(4)C(3)C(2)	−28.2	−37.9
C(6)—C(5)	1.506	1.507	C(6)C(5)C(4)	113.2	114.1	C(6)C(5)C(4)C(3)	−45.3	−37.5
H(7)—C(2)	1.118	1.107	H(7)C(2)Si(1)	110.7	110.9	H(7)C(2)Si(1)C(3)	120.7	121.1
H(8)—C(2)	1.118	1.103	H(8)C(2)Si(1)	111.9	110.5	H(8)C(2)Si(1)C(3)	−120.4	−120.9
H(9)—C(3)	1.124	1.110	H(9)C(3)C(2)	109.6	109.7	H(9)C(3)C(2)C(4)	123.1	123.4
H(10)—C(3)	1.126	1.112	H(10)C(3)C(2)	108.1	108.4	H(10)C(3)C(2)C(4)	−121.3	−122.2
H(11)—C(4)	1.522	1.534	H(11)C(4)C(3)	112.6	111.9	H(11)C(4)C(3)C(5)	127.3	126.7
C(12)—C(4)	1.131	1.120	C(12)C(4)C(3)	106.4	105.6	C(12)C(4)C(3)C(5)	−117.1	−118.0
H(13)—C(5)	1.124	1.116	H(13)C(5)C(4)	109.7	109.4	H(13)C(5)C(4)C(6)	122.1	123.0
H(14)—C(5)	1.124	1.110	H(14)C(5)C(4)	108.1	108.4	H(14)C(5)C(4)C(6)	−121.9	−123.0
H(15)—C(6)	1.117	1.103	H(15)C(6)Si(1)	111.8	110.4	H(15)C(6)Si(1)C(5)	120.3	121.0
H(16)—C(6)	1.117	1.101	H(16)C(6)Si(1)	112.2	111.2	H(16)C(6)Si(1)C(5)	−119.9	−121.0
H(17)—Si(1)	1.466	1.502	H(17)Si(1)C(2)	108.6	109.7	H(17)Si(1)C(2)C(6)	−115.2	−116.8
C(18)—C(11)	1.517	1.524	C(18)C(11)C(4)	114.6	113.6	C(18)C(11)C(4)H(12)	−172.6	175.3
C(19)—C(18)	1.489	1.492	C(19)C(18)C(11)	111.4	111.3	C(19)C(18)C(11)C(4)	−177.8	−179.0
C(20)—C(19)	1.399	1.395	C(20)C(19)C(18)	120.7	120.4	C(20)C(19)C(18)C(11)	−108.1	−100.1
C(21)—C(20)	1.393	1.389	C(21)C(20)C(19)	120.6	120.3	C(21)C(20)C(19)C(18)	−179.5	−179.8
C(22)—C(21)	1.402	1.397	C(22)C(21)C(20)	120.4	120.2	C(22)C(21)C(20)C(19)	−0.14	−0.3
C(22)—C(21)[a]	1.405	1.403	C(28)—C(27)[b]	1.413	1.406			
C(23)—C(22)	1.403	1.397	C(23)C(22)C(21)	119.0	119.5	C(23)C(22)C(21)C(20)	0.16	0.1
C(24)—C(23)	1.391	1.389	C(24)C(23)C(22)	120.4	120.2	C(24)C(23)C(22)C(21)	0.00	0.2
C(25)—C(22)	1.461	1.469	C(25)C(22)C(21)	120.5	120.3	C(25)C(22)C(21)C(23)	180.0	180.0
C(25)—C(22)[b]	1.464	1.472	C(25)C(22)C(21)[b]	122.4	122.8			
C(26)—C(25)	1.402	1.398	C(26)C(25)C(22)	120.4	120.1	C(26)C(25)C(22)C(21)	−40.4	−47.6
C(27)—C(26)	1.390	1.389	C(27)C(26)C(25)	120.8	120.5	C(27)C(26)C(25)C(22)	180.0	−179.9
C(28)—C(27)	1.407	1.400	C(28)C(27)C(26)	119.5	119.0	C(28)C(27)C(26)C(25)	−0.1	−0.2
C(29)—C(28)	1.407	1.400	C(29)C(28)C(27)	120.1	121.1	C(29)C(28)C(27)C(26)	0.1	0.1
C(30)—C(29)	1.390	1.389	C(30)C(29)C(28)	119.5	119.0	C(30)C(29)C(28)C(27)	0.1	0.1
H(31)—C(11)	1.123	1.109	H(31)C(11)C(4)	108.6	109.1	H(31)C(11)C(4)C(18)	−122.1	−122.8

H(32)—C(11)	1.123	1.108	H(32)C(11)C(4)	108.5	109.6	H(32)C(11)C(4)C(18)	121.6	122.9
H(33)—C(18)	1.124	1.115	H(33)C(18)C(19)	109.0	110.4	H(33)C(18)C(19)C(11)	− 121.3	− 121.4
H(34)—C(18)	1.123	1.114	H(34)C(18)C(19)	110.0	111.0	H(34)C(18)C(19)C(11)	121.5	122.7
H(35)—C(20)	1.100	1.096	H(35)C(20)C(21)	119.6	119.8	H(35)C(20)C(21)C(19)	179.9	− 180.0
H(36)—C(21)	1.100	1.096	H(36)C(21)C(22)	119.8	119.8	H(36)C(21)C(22)C(20)	179.5	179.8
H(37)—C(23)	1.101	1.096	H(37)C(23)C(24)	119.8	120.0	H(37)C(23)C(24)C(22)	− 179.5	− 180.0
H(38)—C(24)	1.100	1.096	H(38)C(24)C(23)	119.9	120.0	H(38)C(24)C(23)C(19)	179.9	− 179.9
H(39)—C(26)	1.101	1.096	H(39)C(26)C(27)	119.5	119.7	H(39)C(26)C(27)C(25)	− 179.5	− 179.9
H(40)—C(27)	1.099	1.095	H(40)C(27)C(26)	120.8	120.6	H(40)C(27)C(26)C(28)	179.9	180.0
H(41)—C(29)	1.099	1.095	H(41)C(29)C(28)	119.7	120.4	H(41)C(29)C(28)C(30)	− 179.9	− 180.0
H(42)—C(30)	1.101	1.096	H(42)C(30)C(29)	119.5	119.7	H(42)C(30)C(29)C(25)	− 179.5	− 179.9
F(43)—C(28)	1.355	1.344	F(43)C(28)C(27)	119.9	119.4	F(43)C(28)C(27)C(29)	180.0	180.0
Cl(43)—C(28)[c]	1.700	1.686	C(43)—C(28)[d]	1.421	1.424			
C(44)—Si(1)	1.833	1.910	C(44)Si(1)C(2)	114.3	112.8	C(44)Si(1)C(2)C(6)	125.1	122.6
C(45)—C(44)	1.503	1.505	C(45)C(44)Si(1)	110.2	109.5	C(45)C(44)Si(1)C(6)	67.1	64.1
H(46)—C(45)	1.118	1.009	H(46)C(45)C(44)	110.9	111.7	H(46)C(45)C(44)Si(1)	− 117.1	− 177.1
H(47)—C(45)	1.118	1.099	H(47)C(45)H(46)	108.1	107.5	H(47)C(45)H(46)C(44)	− 121.4	− 122.4
H(48)—C(45)	1.119	1.100	H(48)C(45)H(46)	107.8	107.2	H(48)C(45)H(46)C(44)	121.5	122.5
C(49)—C(44)	1.504	1.506	C(49)C(44)C(45)	111.6	112.1	C(49)C(44)C(45)Si(1)	− 120.6	− 120.2
H(50)—C(44)	1.123	1.112	H(50)C(44)C(45)	108.4	109.7	H(50)C(44)C(45)Si(1)	119.9	117.5
H(51)—C(49)	1.118	1.099	H(51)C(49)C(44)	110.9	111.7	H(51)C(49)C(44)Si(1)	− 179.2	179.4
H(52)—C(49)	1.119	1.100	H(52)C(49)C(44)	110.8	111.6	H(52)C(49)C(44)H(51)	119.6	119.9
H(53)—C(49)	1.118	1.098	H(53)C(49)C(44)	110.6	111.3	H(53)C(49)C(44)H(51)	− 119.9	− 120.1

[a] Compound 4; [b] Compound 5; [c] Compound 2; [d] Compound 3.

TABLE II Net charges on atoms and Wiberg bond orders between atoms in titled compounds

	(1)		(2)		(3)		(4)		(5)	
	*AM*1	*PM*3	*AM*1	*PM*3	*AM*1	*PM*3	*AM*1	*PM*3	*AM*1	*PM*3
Si(1)	1.093	0.384	1.093	0.384	1.093	0.385	1.093	0.384	1.093	0.384
C(2)	−0.484	−0.257	−0.484	−0.257	−0.484	−0.258	−0.484	−0.257	−0.484	−0.258
H(17)	−0.228	−0.098	−0.228	−0.098	−0.228	−0.098	−0.228	−0.098	−0.228	−0.098
C(21)	−0.116	−0.090	−0.115	−0.090	−0.112	−0.086	−0.050	−0.052	−0.116	−0.090
C(28)	0.090	0.063	−0.061	−0.126	−0.018	0.024	0.089	0.062	0.086	0.060
C(6)—Si(1)	0.895	0.964	0.895	0.964	0.895	0.964	0.896	0.964	0.895	0.964
C(3)—C(2)	0.997	0.998	0.997	0.998	0.997	0.998	0.997	0.998	0.997	0.998
H(14)—C(5)	0.966	0.976	0.966	0.976	0.966	0.976	0.966	0.976	0.966	0.976
C(22)—C(21)	1.383	1.394	1.383	1.393	1.382	1.392	1.375	1.379	1.384	1.392
F(43)—C(28)	1.017	1.003					1.017	1.002	1.017	1.002
Cl(43)—C(28)			0.997	1.009						
N(54)—C(43)					2.886	2.886				

TABLE III Heats of formation and dipole moments of titled compounds from AM1 and PM3 calculations

Compounds	*Heats of formation-ΔH_f(kJ/mol)*		*Dipole moments($10^{-30}C^*M$)*	
	AM1	*PM3*	*AM1*	*PM3*
(1)	251.14	236.21	7.459	7.299
(2)	91.71	81.97	6.703	4.974
(3)	−96.53	−113.61	14.432	14.892
(4)	274.52	266.99	7.196	6.946
(5)	279.40	273.20	6.699	6.480

approximately equal to the ratio of the longest to the widest distance is calculated and obtained results are in a range of 3.700–3.722 and 3.592–3.664 respectively for AM1 and PM3. Because the breadths of the five compounds are almost the same, but the lengths of these molecules are different depending on the differential terminal substituents, the order of decreasing of molecular length is: Cl > CN > F, thus, the ratio of length to width has the same order.

3.2. Electronic Structure

According to Mulliken population analysis [8], the net charges on some atoms and the Wiberg bond orders [9] between some atoms have been calculated. Table II shows the obtained electronic structure of titled compounds.

Since the electronegativity of Si is smaller than C, the net charge on Si is positive, the net charges on C(6), C(4) and C(34) are negative. Due to the polarization of Si, the net charge on H(17) is negative, making H(17) the only hydrogen atom whose net charge is negative among all hydrogen atoms in the molecules. When H(36) is substituted by methyl group, the net charge on C(21) decreases from −0.116 to −0.050(AM1) and from −0.090 to −0.052(PM3).

Because of the difference of electronegativity of terminal substituent *X*, the net charges on atom C(28) are different. The order of decreasing electronegativity is F > CN > Cl, thus, the net charges on atom C(28) change from positive to negative. For example, the calculation result of PM3 is: 0.063 (1) > 0.024 (3) > −0.126 (2).

The calculation results of bond orders of AM1 and PM3 are similar to each other, both are coincided basically with the ordinary estimation from organic electronic theory. The bond orders of single bond such as C(6)—Si(1), C(3)—C(2), C(5)—H(14), F(43)—C(28) and Cl(43)—C(28) *etc.*, are all

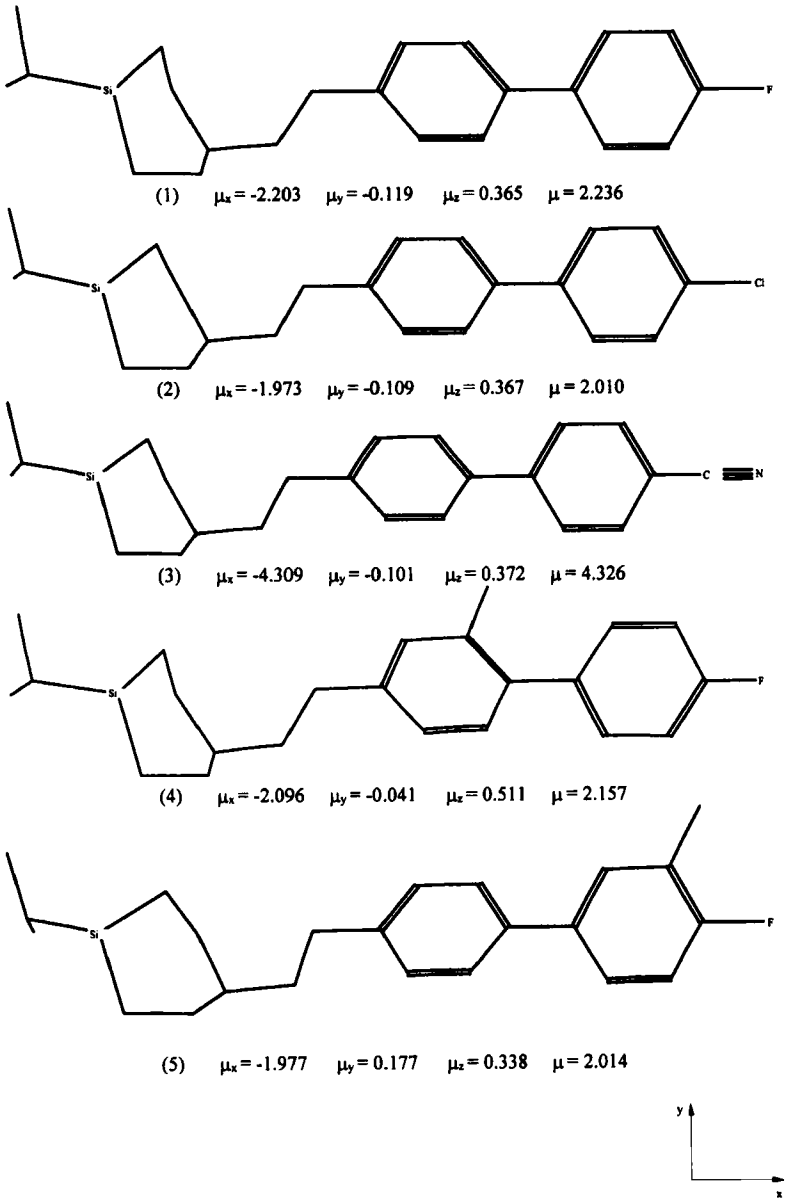


FIGURE 2 The magnitude and direction of dipole moments (in Debye) of titled compounds obtained by AM1 calculations.

about 1.0 and that of the conjugated double bond in the benzene rings such as C(22)—C(21) is about 1.4; the bond order of the cyano- N(54)—C(43) is 2.886.

3.3. Some Molecular Properties

Heat of formation is one of the basic thermochemical parameters. From the magnitude of heat of formation, the stability order of isomers is known immediately. However, the compounds under consideration are not isomers. But if we know the heat of formation of the substituent, then we can calculate the relative heat of formation of the titled compounds and assess the relative stability of them. According to calculation results, the order of magnitudes of heat of formation is the same given by AM1 and PM3 methods (see Tab. III). It can be illustrated by AM1 results(in kJ/mol): (5) 279.40 > (4) 274.52 > (1) 251.14 > (2) 91.97 > (3) −69.53. Thus Compound (4) is more stable than its isomer (5).

Dipole moments of titled compounds have also been obtained from AM1 and PM3 calculations. The results of total dipole moments are listed in Table III. The components of dipole moment (μ_x, μ_y, and μ_z) are shown in Figure 2. For the sake of brevity, only the AM1 results are shown. According to the equation of Maier and Meier [10], the dipole moment μ and the angle β between the vector of the dipole moment and the preffered long molecular axis have large effects on the dielectric anisotropy $\Delta\varepsilon(= \varepsilon_{//} - \varepsilon_{\perp})$ of liquid crystals. From computational results it is easy to see that the obtained dipole moments vary with the terminal substituents X, the decreasing order is: CN > F > Cl, however, the angle β between the dipole moment and the long molecular axis (5.1°, 9.8° and 11.0° for compounds (3), (1) and (2), respectively) increases. When X is F and H(36) or H(40) is substituted by methyl group (Compounds (4) or (5)), the dipole moment decreases compared with that of Compound (1) and the angle β increases, implying a decrease in dielectric anisotropy $\Delta\varepsilon$. Thus, the $\Delta\varepsilon$ of Compound (3) is the largest among the five titled compounds and that of Compound (5) is the smallest.

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