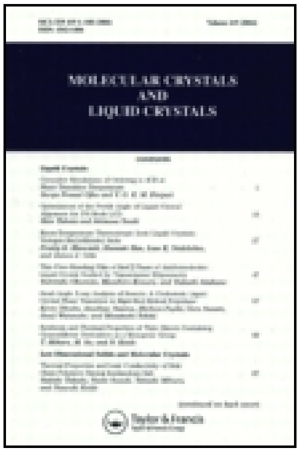

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A Structure Study of Sphere-like Mesogen Using PM3 Calculations

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In order to investigate the relation between molecular structure and liquid crystal properties, structural studies are carried out on sphere-like mesogen tetrasubstituted tribenzosilatrane using PM3 semi-empirical calculations. PM3 results show that the corresponding terminal cyano or chloro group compounds (alkyl R^2 replaced by CN or R^1 by Cl) have much bigger dipole moment or anisotropy of polarizability and like sphere much better than alkyl compounds. Cyano or chloro compounds are probably better candidates for sphere-like mesogens.

Keywords: Sphere-like mesogen; liquid crystal; tribenzosilatrane; PM3

INTRODUCTION

Liquid crystals of rod-like (one-dimensional) molecules were first discovered by Reinitzer in 1888 [1]. In 1977 mesophases of disc-like (two-dimensional) molecules were synthesized by Chandrasekhar *et al.* [2]. In 1985 bowl-like (three-dimensional) molecules were proved to form liquid crystal phases [3]. It is then natural to consider the case of (three-dimensional) sphere-like molecules. D. Wei *et al.* [4] used molecular-dynamics simulations to predict that dipole spheres can form a ferroelectric nematic phase in 1992. Recently [5] a sphere-like molecule, tetrasubstituted tribenzosilatrane (1), see Figure 1, has been synthesized, which forms mesophases at room temperature and 60°C. Spherical liquid cyrstal is a new type of material. It is physically very interesting and has potentially very important applications. In this paper we study the structure of (1) using PM3 method and try to

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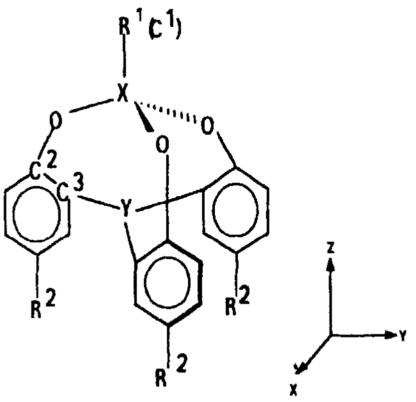

molecule	X	Y	R^1	R^2
(1)	Si	N	C_8H_{17}	$C_{12}H_{25}$
(2)	Si	N	CH_3	H
(3)	Si	N	CH_3	CH_3
(4)	Si	N	C_2H_5	CH_3
(5)	Si	N	C_3H_7	CH_3
(6)	Si	N	CH_3	C_2H_5
(7)	Si	P	CH_3	CH_3
(8)	Ge	N	CH_3	CH_3
(9)	Si	N	CH_3	CN
(10)	Si	P	CH_3	CN
(11)	Si	N	CN	CH_3
(12)	Si	N	Cl	CN
(13)	Si	N	C_6H_5	H

FIGURE 1 The molecular geometry, simplified nomenclature and various atomic index numbers of tetrasubstituted tribenzosilatrane and model molecules.

give some proposals for improving mesophase formation and stability of sphere-like mesogen.

METHOD OF CALCULATION

All calculations are made using PM3 method in program MOPAC 6.0 [6], and carried out on an IBM486 microcomputer. Because of the excessive demands of the calculation of (1) on computer time and memory resources, it is found necessary to use model molecules, which are shown with their simplified nomenclature in Figure 1. X atom is taken as orgin. The *z*-axis is defined as $X \rightarrow R^1$.

There is a similar compound phenyl(2,2′,2″-nitrilotriphenoxy)silane (13), also see Figure 1, whose crystal structure was determined from three-dimensional X-ray diffraction data [7]. In order to exam the reliability of PM3 method for this system, full geometry optimizations were performed on (13) using PM3. The comparison of PM3 calculation for (13) with the X-ray data was given in Table I. In this paper, bond lengths are in angstrons, angles in degrees, dipole moments in Dedye, polarizabilities in $Å^3$. Our calculated results for (13) are in good agreement with experimental data. Therefore PM3 method can be applied to this system.

TABLE I A comparison of PM3 calculations for (13) with the X-ray data (in parentheses)

Bond Length		*Angle*
Si—R^1	1.874(1.853)	R^1—Si—N 179.72(179.40)
Si—O	1.714(1.650)	R^1—Si—O 99.56(99.84)
O—C^2	1.343(1.387)	Si—O—C^2 123.81(125.40)
C^2—C^3	1.414(1.362)	O—C^2—C^3 121.41(118.63)
C^3—N	1.455(1.434)	Dihedral angle between R^1(benzene) and SiNC^3 plane
Si—N	2.415(2.344)	91.07(90.00)

RESULTS AND DISCUSSIONS

All internal coordinates were optimised without symmetry constraint for model molecules (2)–(6). The optimisation of (2), (3) and (6) leads to the C_{3v} configurations within calculational error. The three dihedral angles between R^{1}SiO planes are very close to 120°. (4) and (5) have C_s symmetry, a little distortion from C_{3v} because R^1 has C_s symmetry. The conformation on adjacent Si and C atoms are staggered, like staggered ethane. The optimized geometrical data also show that the bond lengths and angles in alkyl groups and benzene rings are very close to standard values [8]. To confirm that these structures are true energy minima, we calculated the vibrational frequencies of (2), which are all real.

The optimized geometries and properties of model molecules (2)–(6) are listed in Table II. Table II indicates that the different chain lengths of alkyl groups have little effect on the geometry, charge distribution and bond order of tribenzosilatrane core. Thus we can prodict reliably the situation of the core of real molecule (1) according to those of model molecules (2)–(6). The geometry at the silicon atom can be described as a distorted trigonal bypyramid, in which the three equatorial oxygen atoms are bent away from the R^1 substituent toward the nitrogen atom. The R^1-Si-O angle is close to 100°, halfway between the 90° of an ideal trigonal bipyramid and the tetrahedral angle of 109.5°. Table II also indicates that bond lengths of Si-N of (2)–(6) are about 2.37 Å. They are longer than sum of covalent radii 1.87 Å, but much shorter than the sum of the respective van der Waals radii 3.5 Å. The bond orders of Si-N are about 0.23. These molecular parameters indicate that the strength of Si$\leftarrow$N interaction is substantially less than a real chemical bond. The bond order of N-C [3] is 0.97, which is a real covalent bond.

The dipole moment of (1) is generally considered to be N$\leftarrow$Si [5] because the electronegativity of N is larger than Si. But the calculation result $\mu_z < 0$,

TABLE II The optimised geometries and properties of model molecules (2)–(6)

model molecules	*(2)*	*(3)*	*(4)*	*(5)*	*(6)*
bond length					
Si—C^1	1.912	1.912	1.927	1.927	1.912
Si—O	1.717	1.717	1.718	1.718	1.718
Si—N	2.370	2.372	2.373	2.373	2.372
O—C^2	1.345	1.345	1.345	1.345	1.346
N—C^3	1.457	1.457	1.456	1.456	1.455
bond angle					
$<C^1SiO$	95.56	99.55	99.59	99.59	99.60
$<SiOC^2$	123.69	123.66	123.57	123.88	123.83
bond order					
Si—C^1	0.9322	0.9320	0.9154	0.9149	0.9322
Si—O	0.7918	0.7929	0.7950	0.7952	0.7931
Si—N	0.2302	0.2291	0.2287	0.2287	0.2293
O—C^2	1.1004	1.0987	1.0983	1.0980	1.0983
N—C^3	0.9707	0.9706	0.9709	0.9709	0.9710
net charge					
Si	1.0144	1.0133	1.0014	1.0009	1.0041
C^1	−0.2491	−0.2496	−0.2259	−0.2257	−0.2443
O	−0.3526	−0.3516	−0.3538	−0.3551	−0.3565
C^2	−0.2403	−0.2320	−0.2361	−0.2360	−0.2347
C^3	−0.2403	−0.2320	−0.2361	−0.2360	−0.2347
N	0.2552	0.2495	0.2595	0.2595	0.2609
dipole moment					
point charge	0.669	−0.063	−0.154	−0.237	−0.301
hybrid	−1.685	−1.544	−1.587	−1.559	−1.483
sum	−1.015	−1.607	−1.741	−1.796	−1.784
polarizability					
α	29.145	32.895	34.119	35.267	36.112
$\Delta\alpha$	7.911	9.600	8.816	10.523	9.590

i.e. the dipole moment of the whole molecule is in minus direction of *z* axis. The first reason is that O atoms have large electronegativity and make nitrogen electronic positive through benzene rings. The second reason is the hydridization moment contribution [9]. For model molecules (2)–(6), the hybrid parts have large minus contribution to the whole dipole moment.

For dipole moment we only discuss μ_z component since μ_x and μ_y are very small or being zero because of the molecular symmetry. μ_z is a increasing function of the chain length of R^1 and R^2, but μ_z increases less and less when chain of R^1 and R^2 being longer and longer. We may predict the μ_z component of the real molecule (1) is about 2.0 D according to the trend of increase of dipole moment with the carbon atom number of R^1 and R^2. The experimental value of dipole moment of (1) is 4.9 D in benzene and 4.6 D in $CHCl_3$. The calculated value is about its half. This is not a great surprise because of the complication of the system and the approximation of the model and the calculation method.

The mean polarizabilities α of melocules increase directly proportional to the carbon atom number of R^1 and R^2. α increases $1.186\,\text{Å}^3$ per every carbon atom of R^1 and $3.484\,\text{Å}^3$ per every carbon atom of R^2. Thus we may expect that the α of (1) is about $32.895 + 1.186 \times 7 + 3.484 \times 11 = 79.5\,\text{Å}^3$. In contract to α, the anisotropy of polarizability $\Delta\alpha = \alpha_{//} - \alpha_{\perp}$ shows odd-even rule with R^1, that is, $\Delta\alpha$ is larger when carbon atom number of R^1 is odd than when it is even. It does not show odd-even rule with R^2 because R^2 is not along with z axis.

On the basis of above calculations, we have further studied some assumed molecules (7)–(12). They are obtained by replacing some atoms or groups of (3) with P, Ge, CN or Cl respectively. The results are listed in Table III.

When N replaces by P or Si replaced by Ge, molecular dipole moments and polarizabilities have no big changes as compared with (3).

TABLE III The optimised geometries and properties of model molecules (7)–(12)

model molecules	*(7)*	*(8)*	*(9)*	*(10)*	*(11)*	*(12)*
bond length						
$X—C^1$	1.912	1.994	1.897	1.903	1.903	2.078
X—O	1.730	1.818	1.717	1.732	1.717	1.710
X—Y	2.349	2.348	2.451	2.369	2.270	2.371
$O—C^2$	1.354	1.336	1.340	1.345	1.348	1.342
$Y—C^3$	1.779	1.459	1.455	1.776	1.460	1.458
bond angle						
$<C^1XO$	98.18	98.60	100.44	99.04	96.53	98.22
$<XOC^2$	127.12	121.29	123.99	128.33	120.55	121.82
bond order						
$X—C^1$	0.9234	0.9217	0.9422	0.9341	0.7397	0.9055
X—O	0.8007	0.8202	0.7928	0.7888	0.8122	0.7849
X—Y	0.2103	0.2535	0.1910	0.1995	0.2997	0.2445
$O—C^2$	1.0970	1.1079	1.1168	1.1156	1.0941	1.1080
$Y—C^3$	0.9049	0.9714	0.9715	0.9047	0.9689	0.9702
net charge						
X	1.0212	0.7594	1.0471	1.0593	1.2014	1.2016
C^1	−0.2332	−0.1395	−0.2492	−0.2320	−0.2762	−0.2614
O	−0.3517	−0.3287	−0.3483	−0.3538	−0.3338	−0.3575
C^2	0.2087	0.1842	0.2128	0.2401	0.1839	0.2145
C^3	−0.4073	−0.2401	−0.2436	−0.4337	−0.2550	−0.2580
Y	0.6621	0.2877	0.2293	0.6841	0.3050	0.2538
dipole moment						
point charge	1.758	0.042	8.939	10.021	−5.857	5.315
hybrid	−3.034	−1.829	0.776	−0.862	−1.415	0.608
sum	−1.276	−1.787	9.715	9.159	−7.272	5.923
polarizability						
α	36.778	34.451	37.611	41.688	33.709	38.036
$\Delta\alpha$	7.355	6.890	7.522	8.337	14.573	24.972

The most interesting results occur in model molecules (9) and (10), which are formed from (3) and (8) replaced R^2 by CN group. The dipole moments of (9) and (10) have big change as compared with (3) and (8). The dipole moments are changed to the positive direction of z axis and the values are increased to over 9.0 D. Molecular-dynamics simulations [4] show that strongly interacting dipolar sphere can form a nematic phase. However, (1) is not a good example for sphere-like mesogen because of its long alkyl chains. According to the optimized geometries of (2)–(6), we can put the value of length/breadth ratio of (1) at 2.7:1(30.01 Å/11.14 Å). It is almost same as para-azoxyanisole, a famous rod-like mesogen PAA, which has the ratio = 2.6:1 according to its crystallographic data [10]. Up to now there is no report for the mesomorphism of tetrasubstituted tribenzosilatrane with shorter alkyl chains, which has almost same dipole moment as long alkyl chain compound. This fact probably shows that the mesomorphism of molecule (1) is due to its steric anisotropy, not its dipole moment.

As R^1 of (3) replaced by CN group, (11) shows a bigger dipole moment, and has stronger dateve bond of $Si \leftarrow N$ (bigger bond order and shorter bond length) because of the stronger acceptor of CN. As R^1 replaced by Cl and R^2 by CN, (12) shows a very large anisotropy of polarizability $\Delta\alpha$. According to the mean field thoery of liquid crystal [11], the clear point of liquid crystal is directly proportional to $(\Delta\alpha)^2$. Therefore that model molecules (12) has also a tendency to form liquid crystal phase.

Rigorously speaking, all molecules in nature are of course three-dimensional. The "dimension" of molecules referred here really means the dimension of "molecules" in the physical model used in the description of the mesophases. In other word, it means the minimal (or important) character of the molecular shape when mesophases are formed. So molecule (1) may act as a rod-like mesogen because of its length/breath ratio although it has large breath about 11 Å. The molecules (9), (10) and (11) have large dipole moments and (12) has large anisotropy of polarizability, which presumably have strong tendency to form mesophases according to the molecular-dynamics simulation [4] and mean field theory [11]. Furthermore the length/breadth ratios of these melocules are about, 1:1. For example, the length/breadth ratio of molecule ($R^1{=}C_2H_5$, $R^2{=}CN, X{=}Si, Y{=}N$) is 10.96/11.16 = 0.98. Therefore, the cyano or chloro compounds, like (9)–(12) would be better candidates for sphere-like mesogens.

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