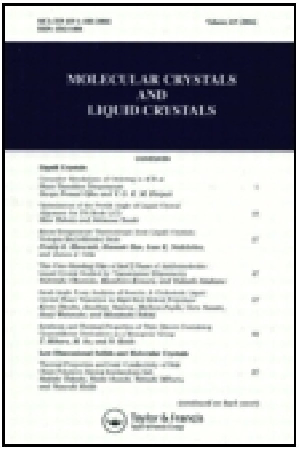

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Structure of 2′,3′′-dimethyl-p-sexiphenyl by X-ray and Semiempirical Methods

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Structure of 2′,3′′′′-dimethyl-*p*-sexiphenyl by X-ray and Semiempirical Methods

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A model is proposed in terms of possible packing and conformations of molecules to explain the different mesogenic behavior of *p*-sexiphenyl 1 and its 2,3′′′′-dimethyl derivative 2. Single crystal x-ray structure determination and semiempirical calculations of these compounds lend support to the proposed model.

INTRODUCTION

The synthesis and liquid crystalline properties of 2′,3′′′′-dimethyl-*p*-sexiphenyl 1, have been reported recently.[1,2] This dimethyl derivative differs from its parent *p*-sexiphenyl 2 in having a very low nematic onset temperature with complete absence of a smectic mesophase. To account for this unusually large decrease in nematic transition temperature, a lock-key model was proposed. The basic assumption of this model was a noncoplanar orientation for phenyl rings in both these compounds. To verify this assumption as well as to test this model, semiempirical calculations and an x-ray structure determination were carried out. This paper describes a comparative evaluation of the results from x-ray and those from the three semiempirical approaches *viz* MNDO, AM1, PM3.

RESULTS AND DISCUSSION

Geometry optimizations of both 1 and 2 by semiempirical calculations were done to see whether the preferred low energy conformers have a non-planar orientation

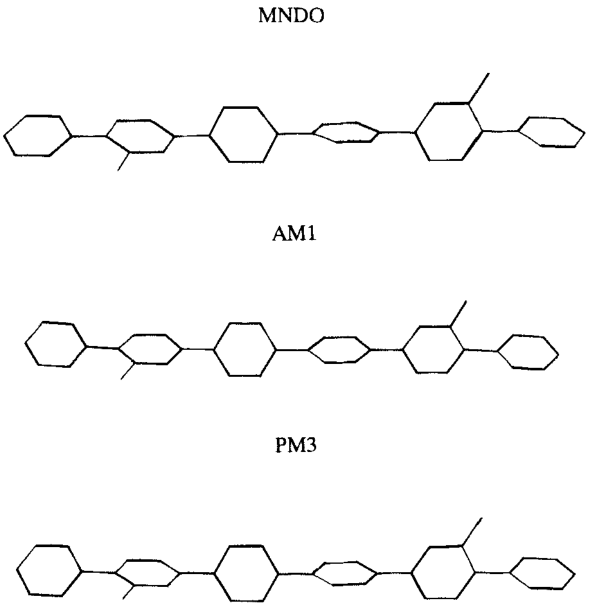


FIGURE 1 Optimized geometry of 1.

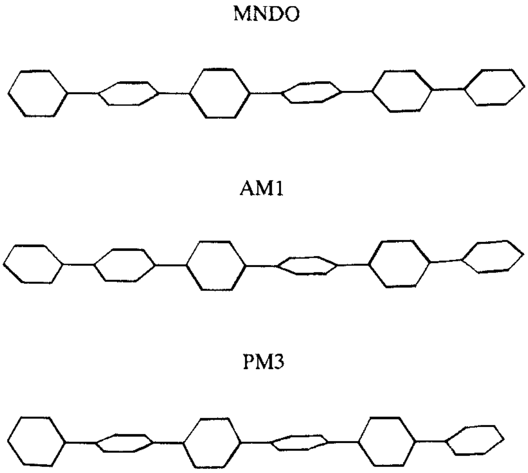


FIGURE 2 Optimized geometry of 2 views along perpendicular axes.

of phenyl rings as assumed. The optimized geometries of 1 and 2 as obtained from the three approaches are shown in Figures 1 and 2 respectively. Some of their calculated physical constants are shown in Table I. As the data indicate, the three methods agree fairly well in their predictions. The dipole moment seems to be an exception for it varies over a wide range among the three methods.

As the model assumed, the phenyl rings are lying in different planes both in 1 and in 2 with the interring plane angle changing between adjacent pairs. Table II and Table III list the interplanar angles for 1 and 2 respectively. Once again, a

TABLE I

Calculated physical data for 1 and 2

		MNDO	AM1	PM3
1	ΔH_f (kcal/mol)	136.2	140.8	132.1
	Dipole (D)	0.048	0.265	0.312
	I_0 (eV)	8.760	8.620	8.890
2	ΔH_f (kcal/mol)	145.5	153.7	148.3
	Dipole (D)	0.012	0.158	0.036
	I_0 (eV)	9.083	8.729	8.975

TABLE II

Interring-plane angle in 1

Ring No	X-Ray*	MNDO	AM1	PM3
1-2	41.6	84.4	83.9	84.2
2-3	30.6	93.2	93.9	93.8
3-4	0	60.4	46.8	51.1
4-5	31.9	55.0	34.2	48.7
5-6	44.4	93.6	106.9	95.1

*Note that 1–2 and 2–3 are from one molecule and 4–5 and 5–6 are from another.

close agreement can be noticed in the angle predicted by the three approaches with MNDO forming an exception, predicting an almost perpendicular orientation of rings in 2. These gas phase data cannot be taken as a strong support for the validity of the assumption. It is hard to say how far one is justified in extrapolating the gas phase geometries to solid or liquid crystalline phase geometries. The best evidence would be to know the actual structure and packing of these molecules in the solid state. A comparative analysis of the data will show then, the relative merits and/or drawbacks of these semiempirical approaches. This prompted the single crystal x-ray structure determination of 1. The ORTEP plots, two different views, as obtained from x-ray analysis are shown in Figure 3.

Clearly, the rings are different planes as predicted by semiempirical methods with obvious differences in the interplanar angles. The interring plane angles for the x-ray structure is listed in Table II along with calculated data (We note that the values are taken from two independent molecules in the unit cell, both of which lie on centers of symmetry.) Comparison of the data reveals that the semiempirical methods have overestimated the interplanar angle. This overestimation may be

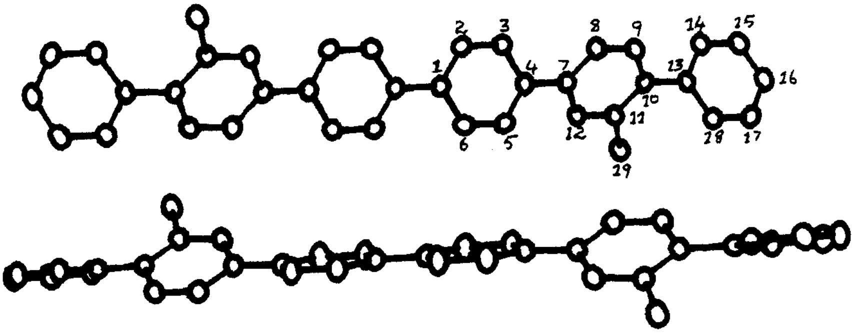


FIGURE 3 ORTEP plot of 1.

TABLE III

Interring-plane angle in 2

Ring No	MNDO	AM1	PM3
1-2	89.3	86.8	94.3
2-3	108.2	41.8	52.3
3-4	89.9	48.6	55.1
4-5	87.2	76.1	93.8
5-6	94.4	98.2	76.9

attributed to the fact that the semiempirical structure is that of a "free" molecule whereas the x-ray structure is that of a molecule with the maximum number of closest neighbors it can have and is subjected to the influence of packing forces. Even though the values do not agree numerically, one cannot fail to see the common trend of decreasing interring plane angle as one moves from the periphery towards the center of the molecule.

Another common and the most important similarity between the calculated and x-ray structure is the anti-orientation of the two methyl groups in 1. It is very likely that this orientation is the key reason for the observed, more than expected decrease in the transition temperature of 1 relative to 2. The current understanding of the structure-activity correlation is based on the fact that the addition of lateral substituents to a planar mesogen broadens the molecule, forcing the molecular axes apart, decreasing the intermolecular attraction and leads to a lower transition temperature. In biphenyl based mesogens, the lateral substituents may cause twisting of the rings in addition, causing poor packing and thus may lead to a low onset temperature. This argument holds good as long as the parent molecule is planar and addition of substituents introduces nonplanarity. In fact one can even predict the expected drop in temperature for a given substituent using additive principles.[3,4]

In the present case this general theory of reasoning is not applicable, for both the parent and its dimethyl derivatve have noncoplanar phenyl rings. No additional nonplanarity is introduced in molecule 1 by two methyl groups compared to 2. So twisting of the rings cannot be the main reason. As was proposed in our model, the head-tail packing or the lock-key fit packing seems to be the type of preferred packing even by the dimethyl derivative 1. The diagram in Figure 4 illustrates this packing. The fact that despite this best possible close packing, 1 does not show a smectic mesophase and has an extremely low nematic onset (200 deg. lower than that of 2) suggests a larger separation of molecules. This increase in intermolecular separation can only be due to the broadening of the molecule, and this broadening effect has to contribute 2–3 fold to cause the observed decrease of transition temperature. The multifold influence of two methyl groups is probably due to their anti-orientation. If this molecule were to have syn-orientation for the methyl groups, then the broadening of the molecule would equal the size of a single methyl group and the general theory would have been applicable. However this antiperiplanar orientation causes two fold broadening of the molecule and hence to greater separation of molecules. The intermolecular separation would be even greater and liquid crystallinity would have been completely lost if the methyl groups had an anti-clinal rather than the anti-periplanar arrangement. (The relation between the various arrangements is illustrated in Figure 5.) The anti-clinal arrangement would

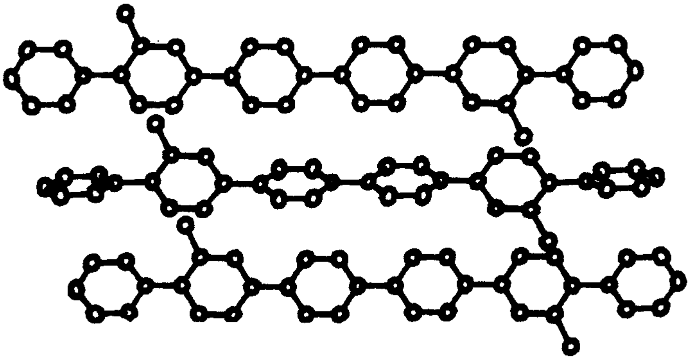
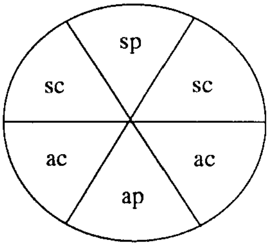


FIGURE 4 ORTEP plot of packing of 1.



s - syn

a - anti

p - periplanar

c - clinal

FIGURE 5 Various conformational arrangements.

increase the intermolecular separation in two dimensions and thus have a more deleterious effect for the same amount of broadening.

CONCLUSIONS

This study has clearly revealed an important point to be remembered when proposing qualitative models or explanations for the observed phenomenon, i.e., besides the nature and the number of substituents, the conformation of the groups should be taken into consideration. The term "conformation" may mean the orientation of lateral substituents as in the present case, but it may refer to the conformation of the whole molecule as well as the populations of various conformers in appropriate cases. A good example for the latter is a new model, proposed recently, for explaining the relation between molecular structure and spontaneous polarization of ferroelectric liquid crystals.[5,6]

EXPERIMENTAL SECTION

Semiempirical Calculations

All calculations were done using the MOPAC-5 package[7] on the Ohio Supercomputer center CRAY/Y-MP machine and using the Penn State University IBM ES/3090-600s computer.

X-ray Analysis

A colorless crystal of molecular formula $C_{38}H_{30}$ having approximate dimensions of 0.32 × 0.20 × 0.06 mm was mounted on a glass fiber in a random orientation. Data collection were performed with Mo Kα radiation (λ = 0.7101 Å) on a Enraf-Nonius computer controlled kappa axis diffractometer. The triclinic cell parameters are a = 8.882(2), b = 9.900(1), c = 15.703 (1) Å; α = 82.17(2), β = 79.82(2), γ = 76.44(1)°; V = 1314.7 Å^3. For Z = 2 and F.W = 486.66, the calculated density is 1.23 g/cm^3. The space group was determined to be P1.

The data were collected at a temp of 21 ± 1° using $\omega - 2\theta$ scan technique. Data were collected to a maximum of 2θ = 60.0°. A total of 8108 reflections were collected of which 7649 were unique. An anisotropic decay correction was applied ranging from 0.967 to 1.042 with an average value of 1.002. The linear absorption coefficient is 0.6 cm^{-1} for Mo Kα radiation. Relative transmission coefficient ranged from 0.977 to 0.999 with an average value of 0.989.

The structure was solved by direct methods and refined in full matrix least-squares. Hydrogen atoms were included in the refinement with isotropic temperature factors. Only the 2727 reflections having intensities greater than 3.0× standard deviation were used in the refinement. The final cycle of refinement included

TABLE IV

Positional parameters and their estimated standard deviations

Atom	x	y	z	B(Å^2)
C1	-0.4215(3)	0.4742(2)	0.4745(2)	2.56(5)
C2	-0.3999(3)	0.4726(3)	0.3851(2)	3.52(6)
C3	-0.2544(3)	0.4247(3)	0.3383(2)	3.67(6)
C4	-0.1226(3)	0.3730(2)	0.3785(2)	2.86(5)
C5	-0.1434(3)	0.3770(3)	0.4681(2)	3.21(6)
C6	-0.2882(3)	0.4257(3)	0.5147(2)	3.17(6)
C7	0.0316(3)	0.3148(2)	0.3290(2)	2.88(5)
C8	0.0413(3)	0.2466(3)	0.2553(2)	3.03(5)
C9	0.1822(3)	0.1905(2)	0.2060(2)	2.90(5)
C10	0.3222(3)	0.2047(2)	0.2305(2)	2.78(5)
C11	0.3133(3)	0.2696(3)	0.3049(2)	3.35(6)
C12	0.1711(3)	0.3232(3)	0.3539(2)	3.50(6)
C13	0.4797(3)	0.1567(2)	0.1783(2)	2.80(5)
C14	0.5056(3)	0.1842(3)	0.0884(2)	3.31(6)
C15	0.6528(3)	0.1388(3)	0.0418(2)	3.83(6)
C16	0.7762(3)	0.0695(3)	0.0833(2)	3.94(6)
C17	0.7525(3)	0.0447(3)	0.1726(2)	3.94(7)
C18	0.6056(3)	0.0870(3)	0.2202(2)	3.42(6)
C19	0.1788(3)	0.1087(3)	0.1324(2)	4.23(6)
C20	1.4210(3)	0.0270(3)	0.5246(2)	2.80(5)
C21	1.3822(3)	0.1581(3)	0.5550(2)	3.82(6)
C22	1.2375(3)	0.2081(3)	0.6023(2)	3.95(7)
C23	1.1226(3)	0.1296(2)	0.6213(2)	2.88(5)
C24	1.1600(3)	-0.0003(3)	0.5890(2)	3.62(6)
C25	1.3053(3)	-0.0503(3)	0.5426(2)	3.56(6)
C26	0.9693(3)	0.1807(2)	0.6748(2)	2.82(5)
C27	0.9568(3)	0.2680(3)	0.7389(2)	3.20(6)
C28	0.8163(3)	0.3197(2)	0.7911(2)	2.96(5)
C29	0.6794(3)	0.2832(2)	0.7781(2)	2.70(5)
C30	0.6920(3)	0.1927(3)	0.7146(2)	3.21(6)
C31	0.8332(3)	0.1419(3)	0.6644(2)	3.13(5)
C32	0.5221(3)	0.3361(2)	0.8278(2)	2.72(5)
C33	0.4712(3)	0.4755(3)	0.8447(2)	3.44(6)
C34	0.3239(3)	0.5241(3)	0.8887(2)	4.03(6)
C35	0.2226(3)	0.4347(3)	0.9163(2)	4.40(7)
C36	0.2705(3)	0.2968(3)	0.8994(2)	4.24(7)
C37	0.4180(3)	0.2479(3)	0.8557(2)	3.41(6)
C38	0.8226(3)	0.4069(3)	0.8618(2)	4.05(6)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter

463 variable parameters and converged with unweighted and weighted agreement factors of

$$R_1 = \Sigma |F_0 - F_c| / \Sigma F_0 = 0.049$$

$$R_2 = \sqrt{\Sigma} W(F_0 - F_c)^2 / \Sigma WF_0^2 = 0.057$$

The standard deviation of an observation of unit weight was 1.62. The atomic positions are given in Table IV. All calculations were performed on a VAX 11/750 computer using SDP/VAX.

Supplementary Materials

Table of experimental details, observed and calculated structure factors, bond distances, bond angles, general displacement parameters of 1 are available.

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