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Comparative Crystallographic Analysis Of Some Mono And Linearly Chained Biphenyls

Kamni and Rajnikant

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Abstract:

Biphenyls is a state of matter which is sometimes observed intermediate between a solid crystal and an isotropic liquid. Biphenyls are of various kinds but we are concerned with only two types i.e., 2,3,4-mono-substituted biphenyls and 4,4'-substituted biphenyls. In view of the varied possible importance in case of both kinds of biphenyls, a comprehensive study has been carried out on the preparation of X-ray diffraction quality crystals, investigation of polymorphism and three-dimensional X-ray determination using crystallographic and computational techniques.

KEYWORDS:

Biphenyls, X-ray Diffraction, Crystal Structure.

INTRODUCTION:

Biphenyl molecule is a combination of two phenyl moieties joined together by a common single bond along the main molecular axis. Broadly, this type of material is classified into two categories:

- (i) mono-substituted biphenyls (in which mono-substituents occupy ortho, para or meta (2,3,4) positions of the biphenyl moiety)
- (ii) linearly chained biphenyls (in which a linear chain of hydrocarbons is located at 4 or 4' position of the biphenyl moiety) - also known as Liquid Crystals.

Biphenyl is a state of matter that is sometimes observed intermediate between a solid crystal and an isotropic liquid. Hundreds of organic compounds are known now to exist as liquid crystals [1]. When a substance showing a crystalline phase is heated at a particular temperature, the solid changes into a rather turbid liquid. When observed between cross polarizers, this fluid phase is found to be strongly birefringent. Upon further heating a second transition point is reached where the turbid liquid becomes isotropic and consequently optically clear. The melting point and the clearing point define the temperature range in which the mesophase becomes thermodynamically stable.

At the clearing point, however, these quantities are usually an order of magnitude smaller than those at the melting point.

The liquid crystals have often been classified into various categories but most important from the crystallography point of view are the Thermotropic (in which change in phase takes place due to variation in temperature) and Lyotropic liquid crystals (in which change in phase takes place due to the influence of crystallization solvent).

Biphenyls and its derivatives had been a subject of immense interest to researchers in various fields over the years. The earliest mention of biphenyl investigation dates back to 1929 when its molecular configuration in the solid state was first established [2-5]. By the early sixties, the structure of biphenyl was

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investigated thoroughly by X-ray crystallographic, gas phase electron diffraction and spectroscopic techniques and it was observed that the phenyl rings are co-planar in solid-state [6-8], unlike the gas phase where it shows a dihedral twist of 42° [9-11]. The structure of biphenyl was verified by further complete X-ray studies at 110 and 293K [12-13].

There have long been questions about the possibility of disorder in the structures of nearly planar biphenyls. Repulsions between ortho H atoms lead to a maximum in the potential energy surface for the isolated molecule at a twist angle ψ about the central C-C bond of 0° but crystal packing effects often favour a nearly planar conformation. At 295K biphenyl itself is apparently planar in the solid state (as evidenced by the location of the molecule on a crystallographic inversion center). At temperatures below 100K the biphenyls goes through a complicated series of phase change which ultimately leads to a final phase containing molecules with $\psi \sim 10^\circ$. Low-temperature phases containing twisted molecules have also been found for the related p-terphenyl and p-quaterphenyl molecules [14].

Biphenyls and its derivatives have been studied extensively in the past because of the difference found in the inter-ring torsion angles in the solid state [8,12-13] and in the gas phase [11,15]. This has entailed extended studies of the molecular geometry, crystal packing and thermal motion effects [14,16-18].

Biphenyls are of interest because of their importance in photophysics. They show strong absorption in the UV range but weak fluorescence. Steric fixing of biphenyls results in a bathochromic shift [19]. High photostability and good laser quality required maximum delocalization of π -electrons, which is achieved by a coplanar arrangement of biphenyl unit [20]. The role of liquid crystals in living systems appears to be very important one. Slight changes in composition and in physical and chemical properties can materially affect the formation, continuation or cessation of the liquid crystalline state, a delicate balance characteristic also of many biological processes. Catalytic processes in biological systems could readily find a favourable environment in the liquid crystalline structure [21].

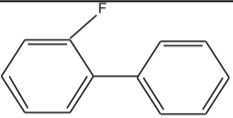
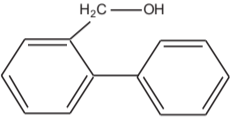
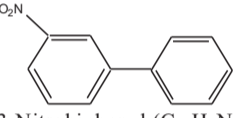
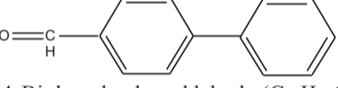
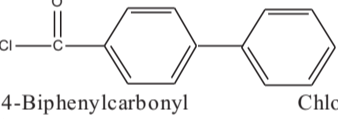
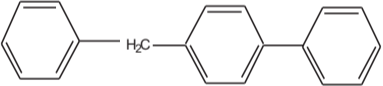
2. EXPERIMENTAL- SINGLE CRYSTAL GROWTH

The growth of single crystals i.e., production of X-ray diffraction quality crystals which could diffract the radiation at the desired resolution, is a phenomenon which involves the inter-play of many factors/variables. It has been said that number of variables which influence the crystallization of organic molecules is lengthy to say the least. Perhaps crystallization is a bit tricky and highly empirical but there are pathways and tools which allow a scientist to approach crystallization from a rational perspective.

Single crystal growth of some substituted biphenyls, as reported in this paper, have been prepared by using solvent-loss and vapour diffusion techniques. Solvent-loss crystallization provides a simple method for the investigation of the crystallization behaviour of a compound in a given range of solvents and solvent mixtures. It is wise not to allow the evaporation to proceed to completion to prevent the crystals from drying out and decomposing or becoming stuck to the walls of the container in which the crystallization is set-up. A modification that solves this problem is to use a solution containing a volatile solvent and a less volatile precipitant. Solvent-loss can also be controlled by putting a paraffin seal, sometimes pierced with a pin-hole, over the top of the crystallization vessel. The drawback of solvent-loss technique is that the reproducibility of the crystal is difficult. A more sophisticated technique, widely used and generally giving better results is vapour diffusion precipitation technique. In this technique the solution of the solvent and solute is kept around a solvent in which solute is insoluble. The container is sealed and the transport of vapours takes place which help the material to initiate nucleation, thus making the basis for lattice formation. The main advantage of this method is that only small volumes of materials are needed. Success rate in achieving quality single crystals using this technique is as good as solvent-loss technique.

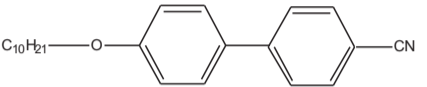
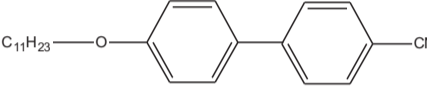
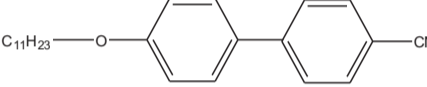
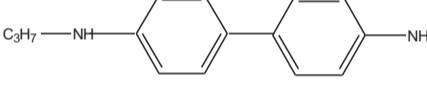
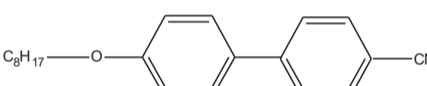
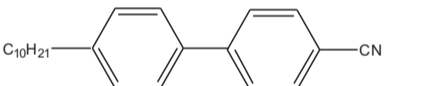
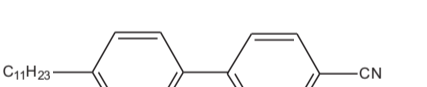
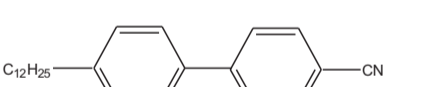
Table 1 and 2, presents the chemical structure, physical state, growth morphology and solvent system used for the preparation of X-ray diffraction quality crystals of mono-substituted and 4,4'-linearly chained biphenyls.

Table 1. 2,3,4 Mono-substituted biphenyls

Mol. No*.	IUPAC name of the Compound	Melting Point (°C)	Physical State	Growth Results	Solvent Used
I	 2-Fluorobiphenyl (C ₁₂ H ₉ F)	73-74	Small, equidimensional crystals, possibly XRD quality	Platey crystals	Toluene
II	 2-Methanolbiphenyl (C ₁₃ H ₁₂ O)	46-48	Very small crystalline particles stuck together in large lumps	Rectangular plates	Toluene
III	 3-Nitrobiphenyl (C ₁₂ H ₉ NO ₂)	not known	Small equidimensional crystals, few large ones, not XRD quality	Hexagonal shaped crystals	Methanol
IV	 4-Biphenylcarboxaldehyde (C ₁₃ H ₁₀ O)	57-59	Rounded lump made up of very small crystalline particles	Thin needles	Methanol
V	 4-Biphenylcarbonyl Chloride (C ₁₃ H ₁₀ O ₂)	not known	Some lumps consisting of very fine quality powdered particles	Thin needles	Methanol
VI	 4-Benzylbiphenyl (C ₁₉ H ₁₆)	85-87	Plate crystals, XRD quality	Rectangular plates	Ethanol

*Rajnikant *et al*, Acta Cryst, C51 (1995) 1452[I]; Rajnikant *et al*, Acta Cryst, C51 (1995) 2161[II]; Rajnikant *et al*, Acta Cryst, C51 (1995) 2071[III]; Rajnikant, Mol. Materials, 14 (2001) 165 [IV-V]; Rajnikant *et al*, Acta Cryst, C51 (1995) 2388[VI];

Table 2. Linearly chained biphenyls

Mol. No*.	IUPAC name of the Compound	Melting Point (°C)	Physical State	Growth Results	Solvent used
I	 4-Cyano-4'-N-Decyloxy-Biphenyl (C ₂₃ H ₂₉ NO)	59.5	Lumps of ice-like material	Colourless plate like	Dimethylformamide + cyclohexane
II	 4-Cyano-4'-N-Undecyloxy-biphenyl (C ₂₄ H ₃₁ NO)	71.5	Lumps of acrySTALLINE material	Pale yellow plate-like	Dimethylformamide + cyclohexane
III	 4-Cyano-4'-N-Dodecyloxybiphenyl (C ₂₅ H ₃₃ NO)	70.0	Lumps of acrySTALLINE material	White plate-like	Dimethylformamide + petrol ether
IV	 4,4'-Bis-(N-Propylamino)-Biphenyl (C ₁₈ H ₂₄ N ₂)	69.5	Lumps of acrySTALLINE material	Rectangular platey	Acetone
V	 4-Cyano-4'-N-Octyloxy-Biphenyl (C ₂₁ H ₂₅ NO)	54.5	Lump of very very small rectangular plates	White transparent needles	Acetic acid
VI	 4-Cyano-4'-N-Decylbiphenyl (C ₂₃ H ₂₉ N)	44.0	Fragile transparent rectangular crystals	White rectangular needles	Acetonitrile
VII	 4-Cyano-4'-N-Undecylbiphenyl (C ₂₄ H ₃₁ N)	53.0	Lump of very very small crystallites	White rectangular plates	Acetone
VIII	 4-Cyano-4'-N-Dodecylbiphenyl (C ₂₅ H ₃₃ N)	48.0	Transparent rectangular flakes	White transparent needles	Acetonitrile

*Rajnikant *et al.*, Mol. Cryst. Liq. Cryst., 383 (2002)99 [I,III]; Rajnikant *et al.*, Cryst. Rep., 48(2) (2003) 286[II]; Rajnikant *et al.*, Mol. Cryst. Liq. Cryst., 333 (1998)237 [IV]; Rajnikant *et al.*, Cryst. Rep., 45(1) (2000) 98 [V]; Rajnikant *et al.*, Asian J. of Physics, 81 (1999) 89 [VI, VII]; Rajnikant *et al.*, Mol. Materials, 1 (1999) 165 [VIII].

2.1. X-ray Structure Determination

The preliminary X-ray photographic techniques which are employed to ascertain the crystalline nature of any grown material provide a first hand information to a crystallographer to move ahead for the collection of X-ray diffraction data using a computer-controlled single crystal X-ray diffractometer. Three-

dimensional intensity data in case of crystals of both the classes of biphenyls was collected on a CAD-4 diffractometer by using either CuK α ($\lambda=1.5418\text{\AA}$) or MoK α ($\lambda=0.71069\text{\AA}$). ω - 2θ scan mode was employed for data collection. The cell parameters are usually refined from accurately determined 25 reflections in a given θ range. Two reference reflections were generally monitored every 100 reflections to check for crystal deterioration, if any, during beam exposure to the sample. The reflection data so obtained is usually raw in nature and is generally cleaned by applying various corrections.

The molecular and crystal structures of 2,3,4-mono and 4,4'-substituted biphenyls have been solved by direct methods using SHELXS86 [22] software. Full-matrix least-squares refinement of organic structure is generally carried out by using CRYSTALS, SHELXL93 and SHELXL97 [23-24] softwares. The least-squares refinement of the positional (x,y,z) and thermal parameters (U_{eq} 's) provide precision in location of various atoms and their thermal amplitudes. All non-hydrogen atoms of the molecule are located from the E-map and all hydrogen atoms are either located or fixed stereo-chemically. Further refinement of the molecule with anisotropic thermal parameters provides the final yield of R-factor. Statistically, the refinement technique provides treatment to our data so that precision in the observed and calculated values for various structural and geometrical parameters is obtained. This treatment helps us in obtaining a good model of the structure where the level of confidence should be as close as 95-97% or in other words the reliability index i.e. R-factor, which is given by an expression,

$$R = \frac{F_o - F_c}{\sum F_o}$$

where F_o and F_c are the magnitudes of the observed and calculated structure factors and it should be between 3-6% for a well refined structure. Atomic scattering factors taken from international Tables for Crystallography (1992, Vol.C, Tables 4.2.6.8 and 6.1.1.4). Structural parameters such as bond distances, bond angles, torsion angles, dihedral angles between various planes of a given molecule etc. are obtained from the PARST [25] software and molecular modeling i.e. to obtain a general view of the molecule and plotting the molecules in the three dimensional environment in a unit cell is carried out with ORTEP [26] software.

Table 3. Comparative data of important parameters for mono-substituted biphenyls

S.No.	Bond Length C1-C7(?)	Bond Angle ($^{\circ}$)	Torsion Angle ψ ($^{\circ}$)	Dihedral Angle τ ($^{\circ}$)
I	1.483(4)	C2-C1-C6 = 117.2(2) C3-C4-C5 = 119.5(2) C8-C7-C12 = 117.2(2) C9-C10-C11 = 119.5(2)	-52.3(1)	54.0(3)
II	1.457(6)	C2-C1-C6 = 118.0(5)	55.1(1)	53.3(1)
	1.449(6)	C3-C4-C5 = 120.8(6)		
	1.460(6)	C8-C7-C12 = 115.7(5)		
	1.451(6)	C9-C10-C11 = 119.8(7)		
III		C2-C1-C6 = 117.3(5)	55.7(1)	58.9(1)
		C3-C4-C5 = 120.8(6)		
		C8-C7-C12 = 116.2(5)		
		C9-C10-C11 = 119.8(7)		
III		C2-C1-C6 = 117.6(6)	53.5(1)	52.6(1)
		C3-C4-C5 = 119.1(6)		
		C8-C7-C12 = 117.4(6)		
		C9-C10-C11 = 119.1(7)		
III		C2-C1-C6 = 116.9(6)	-61.9(1)	59.6(1)
		C3-C4-C5 = 117.4(7)		
		C8-C7-C12 = 117.6(5)		
		C9-C10-C11 = 117.5(7)		
III	1.502(9)	C2-C1-C6 = 118.1(7)	-26.0(1)	-----
	1.489(9)	C3-C4-C5 = 116.6(8)		
III		C8-C7-C12 = 117.9(7)		
		C9-C10-C11 = 119.5(8)		
		C2-C1-C6 = 115.9(7)	23.0(1)	-----
		C3-C4-C5 = 118.0(7)		
	C8-C7-C12 = 118.0(7)			
	C9-C10-C11 = 121.0(8)			

S.No.	Bond Length C1-C7(?)	Bond Angle ($^{\circ}$)	Torsion Angle ψ ($^{\circ}$)	Dihedral Angle τ ($^{\circ}$)
IV	1.477(3)	C2-C1-C6 = 117.2(2)	-----	29.1(1)
	1.470(2)	C3-C4-C5 = 118.6(2)		
	1.472(3)	C8-C7-C12 = 117.1(2) C9-C10-C11 = 119.0(2)		
V	1.481(7)	C2-C1-C6 = 116.9(2)	-----	32.2(1)
		C3-C4-C5 = 118.8(2)		
		C8-C7-C12 = 117.3(2) C9-C10-C11 = 119.5(2)		
V	1.475(7)	C2-C1-C6 = 117.1(2)	-----	35.4(1)
		C3-C4-C5 = 118.9(2)		
		C8-C7-C12 = 117.6(2) C9-C10-C11 = 119.5(2)		
V	1.487(7)	C2-C1-C6 = 120.9(5)	-----	-----
		C3-C4-C5 = 121.9(5)		
		C8-C7-C12 = 117.9(5) C9-C10-C11 = 119.7(6)		
V	1.485(7)	C2-C1-C6 = 121.0(5)	-----	-----
		C3-C4-C5 = 121.4(5)		
		C8-C7-C12 = 117.8(5) C9-C10-C11 = 119.8(5)		
V	1.487(7)	C2-C1-C6 = 120.1(6)	-----	-----
		C3-C4-C5 = 121.1(5)		
		C8-C7-C12 = 117.6(5) C9-C10-C11 = 119.8(6)		
VI	1.485(4)	C2-C1-C6 = 117.3(2) C3-C4-C5 = 117.4(2) C8-C7-C12 = 117.5(3) C9-C10-C11 = 119.6(3)	-41.57(1)	106.35(1)

“-----“ stands for planar structures

Table 4. Comparative data of important parameters for linearly chained biphenyls

S.No.	Bond Length C1-C7(?)	Bond Angle(°)	Torsion Angle ψ (°)	Dihedral Angle τ (°)
I	1.471(1)	C2-C1-C6 = 116.9(1) C3-C4-C5 = 117.9(1) C8-C7-C12=115.9(1) C9-C10-C11=118.1(1)	32.2(3)	31.2(7)
II	1.479(2)	C2-C1-C6 = 117.4(2) C3-C4-C5 = 117.4(1) C8-C7-C12=116.0(1) C9-C10-C11=118.9(1)	32.2(1)	31.5(6)
III	1.427(2)	C2-C1-C6 = 114.9(2) C3-C4-C5 = 117.9(2) C8-C7-C12=115.6(3) C9-C10-C11=116.9(3)	30.8(9)	31.0(2)
IV	1.466(1)	C2-C1-C6 = 114.6(1) C3-C4-C5 = 115.6(1) C8-C7-C12=115.9(1) C9-C10-C11=116.9(1)	-29.7(1)	29.14(3)
V	Mol I = 1.474(3) Mol II = 1.478(3)	C2-C1-C6 = 116.9(2) C3-C4-C5 = 119.4(2) C8-C7-C12=117.6(2) C9-C10-C11=119.9(2)	-37.3(3)	$\tau_{1-3} = 37.79(7)$ $\tau_{2-4} = 38.67(8)$
		C2'-C1'-C6' = 117.3(2) C3'-C4'-C5' = 117.4(2) C8'-C7'-C12'=117.5(3) C9'-C10'-C11'=119.6(3)	38.4(2)	
VI	1.483(3)	C2-C1-C6 = 115.5(2) C3-C4-C5 = 116.5(3) C8-C7-C12=115.3(2) C9-C10-C11=118.4(3)	-0.0(4)	2.37(1)
VII	Mol I = 1.480(3) Mol II = 1.478(3)	C2-C1-C6 = 116.9(2) C3-C4-C5 = 116.6(2) C8-C7-C12=117.3(2) C9-C10-C11=119.5(2)	35.0(4)	$\tau_{1-3} = 35.63(9)$ $\tau_{2-4} = 30.43(8)$
		C2'-C1'-C6' = 116.4(3) C3'-C4'-C5' = 116.3(3) C8'-C7'-C12'=116.9(3) C9'-C10'-C11'=118.9(3)	-29.2(4)	
VIII	1.479(4)	C2-C1-C6 = 117.1(3) C3-C4-C5 = 116.7(3) C8-C7-C12=117.2(2) C9-C10-C11=118.9(3)	29.7(3)	31.7(1)

3. DISCUSSION

Though there are various common structural features which need explanation but a comparative analysis of some general features of the biphenyl derivatives is based on the following parameters some of which are presented in Table 3 and Table 4:

- (i) The length of the central C-C bond.
- (ii) The magnitude of bond angle at C4, C1, C7, C10 which constitutes the main molecular axis of the moiety and atomic deviations, if any, in case of the substituents located at C4 or C10 are accounted for while performing Least-squares plane calculation for each structure.
- (iii) The value of inter ring torsion angle (ψ)
- (iv) The magnitude of dihedral angle (θ) between two phenyl rings

Mono-substituted biphenyls subjected to crystallization by using various solvents have shown that they can adopt various shapes with different solvent systems e.g., Toluene give plates, methanol give needles and ethanol gives rectangular plates. 4,4'-linearly chained biphenyls were also grown by using various solvents and some of them were grown by using various combinations of the solvent systems for e.g., combination of dimethyl formamide and cyclohexane give plate like crystals, acetone gives rectangular plates, acetonitrile and acetic acid gives needles. The variation in crystal habit is probably due to the influence of the solvent system used.

Average values of endocyclic bond angles at C1, C4, C7 and C10 in 2,3,4-monosubstituted biphenyls is $118.56(5)^\circ$ which is significantly smaller than the ideal value of 120° . The decrease in the value of bond angles at these four carbon positions has also been observed in the literature [27]. The average value of length of the bond joining two phenyl rings in monosubstituted at C1-C7 is $1.48(6)\text{\AA}$ which is very close to the standard value of 1.484\AA [28]. The average value of dihedral angle is 53.49° which is quite large than the value of 42° [29]. The average value of torsion angles i.e. $46.13(1)^\circ$.

Average values of endocyclic bond angles at C1, C4, C7 and C10 in 4,4'-linearly chained biphenyls is $117.34(2)^\circ$ which is significantly smaller than the ideal value of 120° . The average value of length of the bond joining two phenyl rings in linearly chained biphenyls at C1-C7 is $1.471(3)\text{\AA}$. This value is quite close to the standard value of a single bond between trigonally linked carbon atoms [30]. The average value of dihedral angle is $30(5)^\circ$ which is quite smaller than 42° [29]. Average value of torsion angles in the present study i.e. $32.7(3)^\circ$ and it supports strict planarity of the biphenyl moiety.

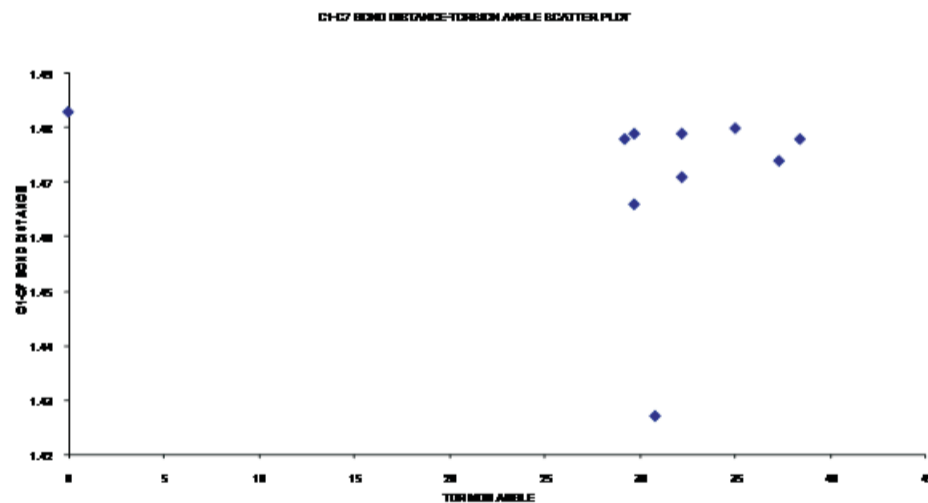


Fig. 1. Scatter plot of C1-C7 bond distance (\AA) and Torsion angle ψ ($^\circ$)

If we have a close look at the chemical structure of all the six mono-substituted biphenyls, we find that it is always the 4 position which is carrying a chain of hydrocarbons of the kind C_nH_{2n+1} while the 4'

position is mostly occupied by cyanide group. It has also been observed from Table 2 that the linear chain of hydrocarbons, in most of the cases e.g., molecule I-V is connected to 4 position of the phenyl ring through an abridging atom. It is quite possible that the unusual value of the C-C bond length in case of molecule-III is due to the overall stretching in the C12-H25-O-C4 unit which might have led the data point to appear distinctly in the scatter plot (Fig 1). In case of molecule-VI, there appears to be no justifiable reason as to why the Torsion angle ψ (o) should have zero value whereas the values in the remaining molecules do have complete agreement.

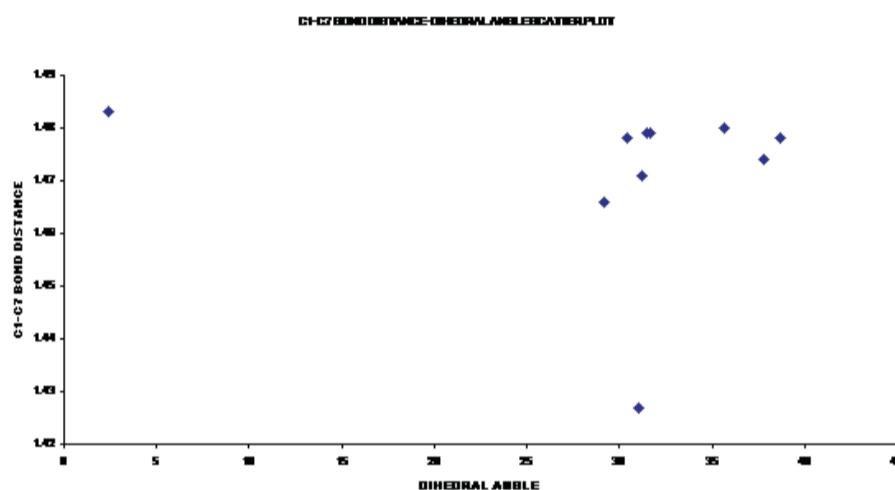


Fig. 2. Scatter plot of C1-C7 bond distance (Å) and Dihedral angle (o)

The argument regarding unusual value of the C-C bond length (in case of molecule-III) and zero value of the torsion angle (in case of molecule -VI) is further authenticated by the corresponding data points as reflected in the scatter-plot (Fig. 2). Except these two molecules, there appears to be an agreement between values as obtained for the remaining molecules.

Polymorphism and phase transformations in crystals have attracted the attention of solid-state scientists for nearly a century. Earlier investigations of the phenomena were based on the thermodynamical considerations which provided only a partial understanding. It is only after the development of X-ray diffraction methods of structure determination and the subsequent knowledge of atom i.e. groupings in crystals that a structural understanding of polymorphism has emerged, in the last 3-4 decades. Just as any substance or matter of a definite chemical composition, in general, can exist in the solid, liquid or the gaseous state depending upon the conditions of temperature and pressure, so also a solid formed from solution, melt or vapour phase can crystallize in more than one possible structure depending on the conditions of temperature and pressure prevailing at the time of crystallization. This phenomenon of the same chemical substance crystallizing in more than one crystalline form is known as polymorphism.

Biphenyls especially the mono-substituted ones are very good candidates for the study of their polymorphic modifications. A critical survey of the Cambridge Crystal Data Center (CCDC), U.K. reveals that there exists only one compound i.e. 4-hydroxy biphenyl having three polymorphic modifications [16]. In a series of experiments which have been conducted by us on the preparation of X-ray diffraction quality single crystals and X-ray structure analysis of mono - substituted biphenyls we have observed that 4-biphenylcarboxaldehyde exists in three polymorphic modifications when crystallized with different solvent systems. The indication for polymorphic modifications came after the application of preliminary X-ray photographic techniques. The visible difference in the recorded diffraction pattern indicated that the parent material has underwent some kind of structural modification and this made us interested in taking up the crystallographic analysis of each polymorphic form.

In view of the characteristic pattern of growth in terms of morphology with different solvent systems for 4-biphenylcarboxaldehyde, the three-dimensional intensity data for all the four crystals of this material (grown from different solvents) were undertaken for X-rays investigations. The reliability index (R-factor) in case of structures grown from ethanol dichloromethane (with petrol ether as precipitant) and methanol (with cyclohexane as precipitant) did not converge below 20%, whereas the refinement of the data for 4-biphenylcarboxaldehyde grown from methanol (as solvent and cyclohexane as precipitant) converged to a sufficiently low value of R = 5.9% with three crystallographically independent molecules

adopting herringbone configuration in the unit cell.

During the course of structure solution and refinement, it was noticed that the structure partially look like that of 4-biphenylcarboxylic acid as reported by Brock and Haller [16]. In order to ensure the right chemical composition in the structure, the mass spectral data for the pure 4-biphenylcarboxaldehyde, 4-biphenylcarboxylic acid, and that of the crystals we had obtained from methanol (with cyclohexane as precipitant) were recorded. A comparative but precise data for all the four polymorphic forms with that of 4-biphenylcarboxylic acid is presented in Table 5.

Table 5. Precise crystal data of four forms of 4-biphenyl carboxaldehyde and 4-biphenyl carboxylic acid

Crystal data	4-biphenyl carboxyldehyde grown from				4-biphenyl carboxylic acid
	Ethanol	Dichloromethane (pet. Ether as precipitant)	Dichloromethane (cyclohexane as precipitant)	Methanol (cyclohexane as precipitant)	Ethanol
a(Å)	6.902	9.086	9.088	7.421	7.438
b(Å)	9.084	13.796	13.800	26.933	26.907
c(Å)	15.619	15.626	31.244	15.782	15.776
α ($^\circ$)	90	90	90	90	90
β ($^\circ$)	90	90	90	102.86	102.93
γ ($^\circ$)	90	90	90	90	90
Cell Volume(Å ³)	979.3	1958.9	3916.5	3077.3	3075.3
No. of reflections	1635	1690	970	3253	5379
R-factor	23%	25%	21%	5.9%	3.8%

The existence of three crystallographic forms of this material leads us to believe that crystallization of pure aldehyde is very unfavourable (in the solvents we examined). There is no evidence about the distribution of aldehyde with respect to its position relative to the nucleus of the crystal i.e., whether an acid-rich nucleus can give rise to an aldehyde-rich surface. However, this phenomenon has not been discovered so far in linearly chained biphenyls through a process of crystallization using a variety of polar and non-polar solvent systems, though it is an established fact that liquid crystals undergo phase transitions at varied temperatures. Therefore, polymorphism in mono-substituted biphenyls is a rare property which has been investigated by us and the structural correlations have also been established and published.

An extraordinary thing observed in case of packing of these six materials is that 4-benzyl has one molecule in the asymmetric unit, 2-fluoro has half molecule, 3-nitro has two molecules and the mixture of aldehyde and acid has three molecules. The observation of multiple molecules in the asymmetric unit is also uncommon for simple biphenyls, especially if the molecules are arranged so that their long molecular axes are approximately parallel. Some examples wherein this phenomenon of multimolecules has been observed are the low-temperature phases of biphenyl [32] i.e., p-terphenyl [14], p-quarterphenyl [14], 4-bromobiphenyl [29], one polymorph of 4-hydroxybiphenyl [16] and 4-biphenylferrocene [33]. In the present study, most of the mono-substituted biphenyls show a tendency to exist as crystallographically independent multiple molecules in the asymmetric unit whereas in linearly chained biphenyls, only two molecules exist as crystallographically independent in the asymmetric unit.

So far as the packing of molecules in the unit cell is concerned the molecule I, IV and VI exhibit herringbone kind of packing, whereas molecules are held in layers stacked one above the other in case of molecule -III. The molecule -II depicts slight overlap of the phenyl rings and molecules in the unit cell are arranged along the same orientation when viewed along the a-axis. This indicates that though structurally similar, mono-substituted biphenyls do exhibit variation when their placement in the unit cell is plotted.

Molecule I-III exhibit ladder type of molecular packing and this kind of packing appears to be quite useful in case of synthesis of nanotubes. The remaining molecules show the packing arrangement characteristic to their usual patterns, depending upon the crystal symmetry and the crystal system.

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