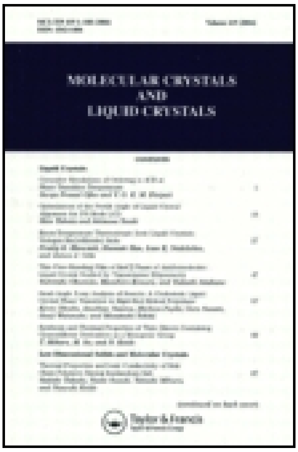

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Crystallography of 4,4 – Bis-(n-Propylamino) – Biphenyl [$C_{18}N_2H_{24}$]

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4,4 – bis-(n-propylamino)-biphenyl, $C_{18}N_2H_{24}$, $M_r = 268$, monoclinic, Cc, a = 6.381 (1) Å, b = 14.153 (3) Å, c = 17.730 (3) Å, $\beta = 81.80$ (2)°, v = 1584.83 Å^3, z = 4, $D_x = 1.125$ mg/m^3, $\mu = 0.659\text{cm}^{-1}$, F (000) = 584.0, λ (Mo Kα) = 0.71073 Å, final R and wR are 0.0499 and 0.1438 respectively using 1386 reflections.

Keywords: X-ray crystallography; crystal structure; biphenyl; liquid crystal

INTRODUCTION

There is substantial literature on the studies of Biphenyl and its derivatives. 2,3,4 – monosubstituted biphenyls have been studied extensively by various workers$^{(1-8)}$ for their molecular geometry, crystallization behaviour, crystal packing and thermal motion while literature on growth and structural aspects of linearly chained biphenyls (liquid crystals) is quite insufficient.

The range of conditions for crystallization reported so far indicated to us that liquid crystalline materials would be good subjects for a systematic analysis of growth conditions and morphology modifiers for the preparation of organic crystals from organic solvents. The first stage in this work concerns the crystallization of 4,4′- bis – (n-propylamino) – biphenyl from non-aqueous solutions. The

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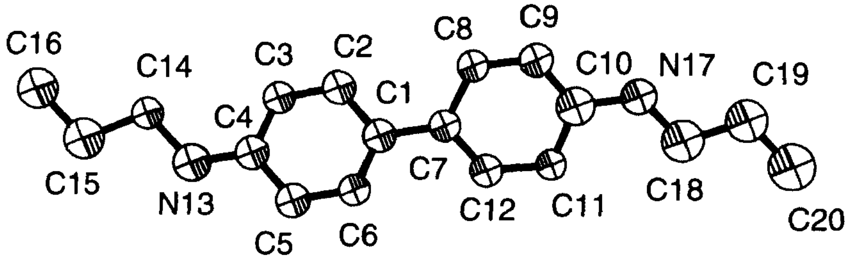

FIGURE 1 General View of the molecule indicating numbering scheme

present work reports the molecular & crystal structure of the title compound synthesized in the laboratory by the standard procedure.(9–10)

EXPERIMENTAL

Golden brown rectangular shaped platy crystals suitable for X-ray data collection were grown by slow evaporation technique using acetone as the solvent. Quality crystallization of this compound could not be achieved with other solvent systems. X-ray diffraction intensity data were collected from a single crystal of approximate dimensions 0.50 × 0.30 × 0.20mm on an Enraf-Nonius CAD-4 diffractometer using MoKα radiation. The accurate cell dimensions and orientation matrix were obtained by a least squares fit to the setting angles of 25 reflections. Intensities were collected by $\omega - 2\theta$ scan. 1604 unique reflections were measured in the range $2 < \theta < 25°, 0 < h < 7, 0 < k < 16, -20 < l < 20$. Two reflections measured every one hour showed no deterioration of the crystal. Lorentz and polarization corrections were applied. The crystal structure was solved by SHELXS – 86 (11) & refined by SHELXL-93)(12) Hydrogen atoms were placed at calculated positions (C-H= 0.93Å) and assigned isotropic thermal parameters equivalent to those of the atoms to which they are bonded. In the final cycle of refinement, 189 parameters were refined using 1402 unique reflections with $R = 0.0499$, $wR = 0.1438$, {where $w = k/[\sigma(F)^2 + P^*F^2]$ with $k = 1.000$, $P = 0.04$}. The maximum electron density in final electron density map is $(\Delta\rho)_{max} = 0.12e\text{Å}^{-3}$, and minimum is $(\Delta\rho)_{min} = -0.13e\text{Å}^{-3}$. $(\Delta/\sigma)_{max} = 0.484$. All calculations were performed on a PC/AT 486 computer.

DISCUSSION

Fractional coordinates and equivalent isotropic temperature factors of the non-hydrogen atoms are given in Table I. Bond distances and angles are presented in Table II & III, respectively. A general view of the molecule with atomic numbering scheme is shown in Figure 1 (ORTEP)$^{(13)}$ and packing of the molecule is illustrated in Figure 2.

TABLE I Atomic coordinates and equivalent isotropic temperature factors (Å^2) with e.s.d.'s in parentheses, for the non hydrogen atoms

Atom	*x*	*y*	*z*	* *Ueq*
C1	0.206 (1)	0.613 (5)	0.053 (5)	0.060 (3)
C2	-0.006 (1)	0.635 (8)	0.079 (5)	0.070 (4)
C3	-0.090 (1)	0.636 (8)	0.156 (5)	0.069 (4)
C4	0.040 (1)	0.615 (8)	0.213 (6)	0.070 (4)
C5	0.251 (1)	0.594 (7)	0.186 (5)	0.066 (4)
C6	0.327 (1)	0.592 (8)	0.110 (6)	0.074 (4)
C7	0.288 (1)	0.613 (6)	-0.028 (6)	0.064 (4)
C8	0.160 (1)	0.593 (7)	-0.084 (5)	0.066 (4)
C9	0.243 (1)	0.595(8)	-0.160(5)	0.085(5)
C10	0.454 (1)	0.617 (7)	-0.185 (5)	0.064 (4)
C11	0.579 (1)	0.636 (8)	-0.130 (5)	0.077 (4)
C12	0.499 (1)	0.634 (8)	-0.055 (6)	0.071 (4)
N13	-0.038 (1)	0.618 (8)	0.289 (4)	0.083 (4)
C14	-0.252 (2)	0.633 (7)	0.318 (5)	0.075 (4)
C15	-0.298 (2)	0.633 (9)	0.403 (6)	0.088 (5)
C16	-0.517 (2)	0.644 (9)	0.436 (8)	0.112 (5)
N17	0.528 (1)	0.614 (7)	-0.262 (4)	0.083 (4)
C18	0.749 (1)	0.634 (7)	-0.292 (6)	0.080 (4)
C19	0.783 (2)	0.627 (9)	-0.377 (6)	0.086 (4)
C20	1.019(2)	0.641 (9)	-0.408(8)	0.102(5)

$$U_{eq.}=(1/3)\sum_i\sum_j U_{ij}\, a_i^* a_j^* a_i . a_j$$

TABLE II Bond Distances (Å) with e.s.d's in parentheses for non-hydrogen atoms

C1 – C2	1.398 (1)	C9 – C10	1.387 (1)
C1 – C6	1.394 (1)	C10 – C11	1.371 (1)
C1 – C7	1.466 (1)	C10 – N17	1.378 (1)
C2 – C3	1.398 (1)	C11 – C12	1.357 (1)
C3 – C4	1.425 (1)	N13 – C14	1.404 (1)

C4 - C5	1.398 (1)	C14 - C15	1.494 (1)
C4 - N13	1.361 (1)	C15 - C16	1.449 (1)
C5 - C6	1.363 (1)	N17 - C18	1.468 (1)
C7 - C8	1.397 (1)	C18 - C19	1.495 (1)
C7 - C12	1.390 (1)	C19 - C20	1.547 (1)
C8 - C9	1.374 (1)		

TABLE III Bond Angles (°) with e.s.d's in parentheses for non-hydrogen atoms

C6 - C1 - C7	124.0 (1)	C7 - C8 - C9	120.2 (1)
C2 - C1 - C7	121.4 (1)	C8 - C9 - C10	122.7 (1)
C2 - C1 - C6	114.6 (1)	C9 - C10 - N17	119.4 (1)
C1 - C2 - C3	123.0 (1)	C9 - C10 - C11	116.9 (1)
C2 - C3 - C4	120.7 (1)	C11 - C10 - N17	123.6 (1)
C3 - C4 - N13	121.4 (1)	C10 - C11 - C12	120.9 (1)
C3 - C4 - C5	115.6 (1)	C7 - C12 - C11	123.4 (1)
C5 - C4 - N13	123.0 (1)	C4 - N13 - C14	124.7 (1)
C4 - C5 - C6	122.0 (1)	N13 - C14 - C15	114.4 (1)
C1 - C6 - C5	124.1 (1)	C14 - C15 - C16	116.7 (1)
C1 - C7 - C12	122.1 (1)	C10 - N17 - C18	122.4 (1)
C1 - C7 - C8	121.9 (1)	N17 - C18 - C19	110.5 (1)
C8 - C7 - C12	115.9 (1)	C18 - C19 - C20	109.5 (1)

The average bond distances for the C(1)-C(6) and C(7)–C(12)phenyl rings are in good agreement with some of the reported linearly chained biphenyls(14,15). The four internal ring bond angles at C(1) [114.59 (1)°], C(4) [115.62 (1)°], C(7) [115.9 (1)°] and C(10) [116.91 (1)°] are significantly smaller than the ideal angles of 120°, but similar to those found in some related compounds (14,15). The length of the bond joining two phenyl rings [C(1)-C(7)=1.466(1)A°] is quite close to the standard value for a single – bond length between trigonally linked carbon atoms (16). The magnitude of the torsion angle between the phenyl rings of the biphenyl moiety along C(1) -C(7) is –29.7 (1)°. The biphenyl fragment is planar, with N13(-0.086Å) and N17(0.010Å) deviating slightly from the main molecular axis. The molecule as such is flat and there appears to be no intra- or intermolecular interaction in the unit cell. The molecules appear to be extending along c-axis forming molecular stacks parallel to each other.

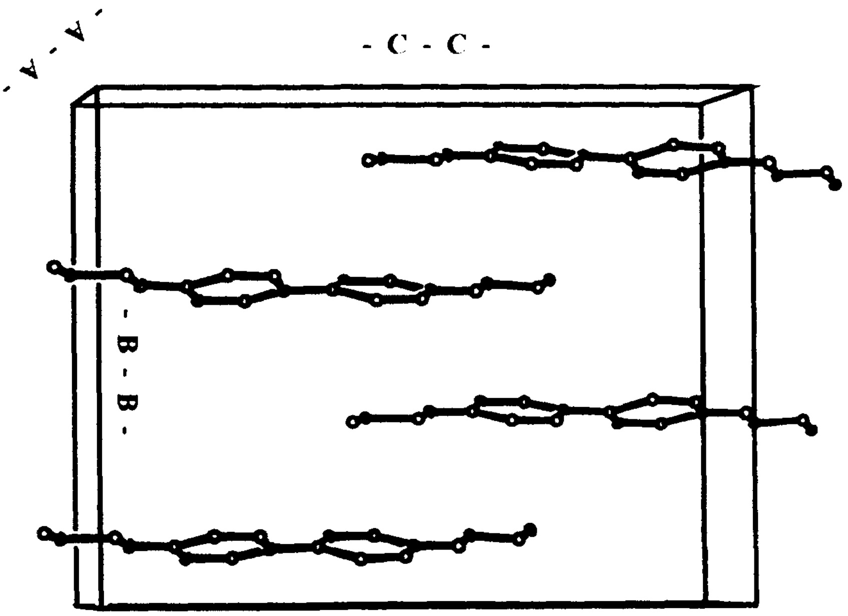

FIGURE 2 Packing of the molecule down a-axis

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