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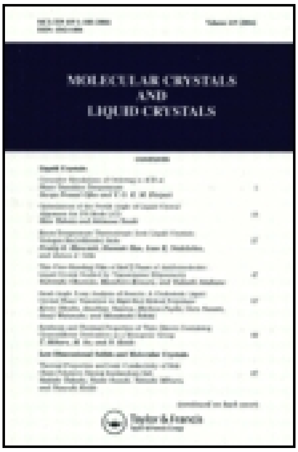

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
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Crystal Structure of 1,4-Bis(1-Naphthyl)-Buta-1,3-Diyne

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Version of record first published: 24 Sep 2006.

To cite this article: T. Manisekaran , A. Sarkar , L. P. Bhagwat , S. S. Talwar & J. Shashidhara Prasad (1995): Crystal Structure of 1,4-Bis(1-Naphthyl)- Buta-1,3-Diyne, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 268:1, 55-59

To link to this article: http://dx.doi.org/10.1080/10587259508030993

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Mol. Cryst. Liq. Cryst., 1995, Vol. 268, pp. 55–59
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Crystal Structure of 1,4-Bis(1-Naphthyl)-Buta-1,3-Diyne

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(Received April 15, 1994; in final form August 30, 1994)

1, 4-bis(1-naphthyl)-buta-1, 3-diyne, $C_{24}H_{14}$, $M_r = 302.38$, monoclinic, $P2_1/a$, $a = 7.534(1)$, $b = 6.012(1)$, $c = 17.969(3)$A, $\beta = 101.1(1)°$, $V = 798.67$ Å^3, $D_x = 1.257$ g/cc, F(000) = 316, λ(Mok)α = 0.71073Å, $T = 300$ K, final R and wR are 0.0389 and 0.0457 respectively using 1281 reflections taken in least squares calculations.

Keywords: Crystal structure, 1,4-bis(1-NAPHTHYL)-BUTA-1,3-DIYNE, nematic

1. INTRODUCTION

Diacetylenes (R—C≡C—C≡R′), where R and R′ are substitutent groups undergo polymerisation in solid state upon exposure to thermal stimulation, UV or γ-radiation. But not all the diacetylenes are reactive. The reactivity depends on the packing parameters of the diacetylene monomer crystals.[1,2,3] The substituents R and R′ in the diacetylene monomer influence the packing and thus reactivity through steric and electronic effects. Our research has been directed towards examining the reactivity of diacetylenes in which the substituents R and R′ are aromatic groups and which are in formal conjugation with the diacetylene unit.

Some of the diacetylene monomers studied in our laboratory show interesting thermotropic liquid crystalline behaviour.[4] Accordingly, our investigations have suitably diversified into the above area. Sustained interest in the study of liquid crystalline properties of diacetylene is due to their potential application is nonlinear optical materials.

We report here the structure of diacetylene, 1,4-bis(1-naphthyl)-buta-1,3-diyne (DNDA). It is observed that this compound which is a crystalline solid is not reactive in solid state. The title compound gives a nematic phase at 546.6 K and it polymerises in the liquid crystalline phase to yield a black intractable polymer which itself is not liquid crystalline.

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2. EXPERIMENTAL

The title compound was synthesised by coupling of 1-ethynylnaphthalene using the method of Frizche and Hunig.[5] Preliminary studies indicated that the diacetylene is almost unreactive in solid state upon exposure to heat, UV or γ-radiation. White crystals of dimensions 0.40 × 0.25 × 0.45 mm were obtained from a solution in cholorform and were used for intensity data collection on Enraf-Nonius CAD4 diffractometer employing Mokα radiation. Unit cell dimensions were determined from the angle settings of 25 randomly selected reflections and refined by least squares. Intensities were measured by the $\omega - 2\theta$ scan method. Lorentz and polarization corrections were applied. The crystal structure was determind by SHELXS 86[6] and was refined by full matrix least squares using the Enraf-Nonius structure determination package.[7] Hydrogen atoms, were included in calculated positions (C–H 0.95 Å) in the structure and given isotropic thermal parameters equivalent to those of the atoms to which they are attached. In the final refinement, 130 parameters were refined using 1281 unique reflections with $R = 0.0389$, $wR = 0.0457$, $\{$where $w = k/[\sigma(F)^2 + P^*F^2]$ with $k = 1.000$, $P = 0.04\}$, in the final difference map $(\Delta\rho)_{\max} = 0.115$, $(\Delta\rho)_{\min} = -0.205$ eÅ^{-3}, $(\Delta/\sigma)_{\max} = 0.028$. A Micro Vax 3100 was used for all the computations.

3. DISCUSSION

The final values of the atomic co-ordinates and equivalent temperature factors for non-hydrogen atoms of the asymmetric unit (half of the molecule) are given in Table 1, bond lengths in Table 2 and bond angles in Table 3. The ORTEP[8] and packing are given in Figure 1 and Figure 2 respectively. The two halves of the molecule are related by an

TABLE I

Positional and thermal parameters and their estimated standard deviations for the non-hydrogen atoms

Atom	X	Y	Z	BÅ^2 eq
C1	0.5001(3)	0.4266(4)	0.9706(1)	4.21(5)
C2	0.4988(3)	0.3010(3)	0.9192(1)	4.18(5)
C3	0.4978(3)	0.1583(4)	0.8554(1)	3.50(4)
C4	0.4241(2)	0.2329(3)	0.7839(1)	3.52(4)
C5	0.4301(2)	0.1007(3)	0.7198(1)	3.12(4)
C6	0.3575(3)	0.1740(4)	0.6453(1)	4.02(5)
C7	0.3705(3)	0.0440(4)	0.5846(1)	4.81(5)
C8	0.4544(3)	−0.1630(4)	0.5950(1)	4.86(5)
C9	0.5247(3)	−0.2394(4)	0.6654(1)	4.17(5)
C10	0.5138(2)	−0.1099(3)	0.7298(1)	3.29(4)
C11	0.5856(3)	−0.1849(3)	0.8042(1)	3.77(5)
C12	0.5764(3)	−0.0542(3)	0.8651(1)	3.84(5)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement Parameter defined as:

$(4/3)^*[a^{2*}B(1,1) + b^{2*}B(2,2) + c^{2*}B(3,3) + ab(\cos \text{gamma})^* B(1,2) + ac(\cos \text{beta})\, {}^*B(1,3) + bc(\cos \text{alpha})\, {}^*B(2,3)]$

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TABLE II

Bond Distances (Å) with e.s.d's in parentheses

C(5)–C(4)	1.407(3)	C(12)–C(11)	1.358(3)
C(5)–C(10)	1.410(3)	C(3)–C(2)	1.431(3)
C(5)–C(6)	1.415(3)	C(6)–C(7)	1.360(3)
C(4)–C(3)	1.374(3)	C(9)–C(8)	1.353(3)
C(10)–C(11)	1.416(3)	C(7)–C(8)	1.392(3)
C(10)–C(9)	1.410(3)	C(2)–C(1)	1.191(3)
C(12)–C(3)	1.405(3)		

TABLE III

Bond Angles (°) with e.s.d's in parentheses

C(4)–C(5)–C(10)	119.1(2)	C(4)–C(3)–C(2)	119.5(2)
C(4)–C(5)–C(6)	122.1(2)	C(12)–C(3)–C(2)	120.7(2)
C(10)–C(5)–C(6)	118.8(2)	C(10)–C(11)–C(12)	120.4(2)
C(5)–C(4)–C(3)	120.7(2)	C(5)–C(6)–C(7)	120.3(2)
C(5)–C(10)–C(11)	119.1(2)	C(10)–C(9)–C(8)	120.4(2)
C(5)–C(10)–C(9)	119.0(2)	C(6)–C(7)–C(8)	120.5(2)
C(11)–C(10)–C(9)	121.8(2)	C(3)–C(2)–C(1)	177.5(2)
C(3)–C(12)–C(11)	120.8(2)	C(9)–C(8)–C(7)	121.0(2)
C(4)–C(3)–C(12)	119.8(2)		

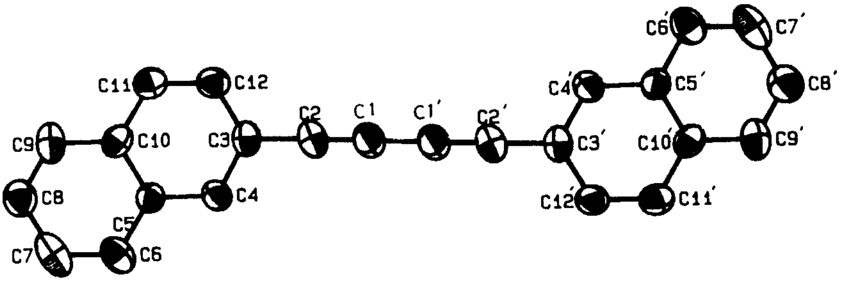

FIGURE 1 ORTEP plot of the molecule with thermal ellipsoids at 50% probability.

inversion symmetry. The molecules are stacked almost perpendicular to crystallographic a axis (Fig. 2). Also the rings on either of the two ends are coplanar. The bond lengths C(3)–C(2) = 1.431(3), C(2)–C(1) = 1.191(3), C(1)–C(1') = 1.377(3) C(3)–C(1) = 3.999(3) Å indicate that C(3)–C(2)–C(1)–C(1') is linear. The bond distances compare well with those reported for 1,4–diphenyl-1,3-butadiyne[9] and 1,4-bis(3-quinolyl)-1,3-butadiyne.[10] The aromatic groups, attached to the diacetylene rods, are almost parallel.

The necessary monomer packing condition (Wegner, 1977; Bloor, 1982) required for the solid state polymerisation reaction (given in square brackets) is not satisfied in case of DNDA (Fig. 3) as mentioned below:

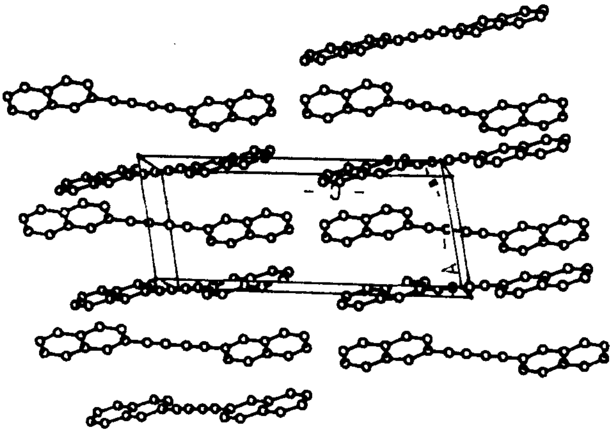

FIGURE 2 Packing of the molecules. Projection of the unit cell down *b* axis.

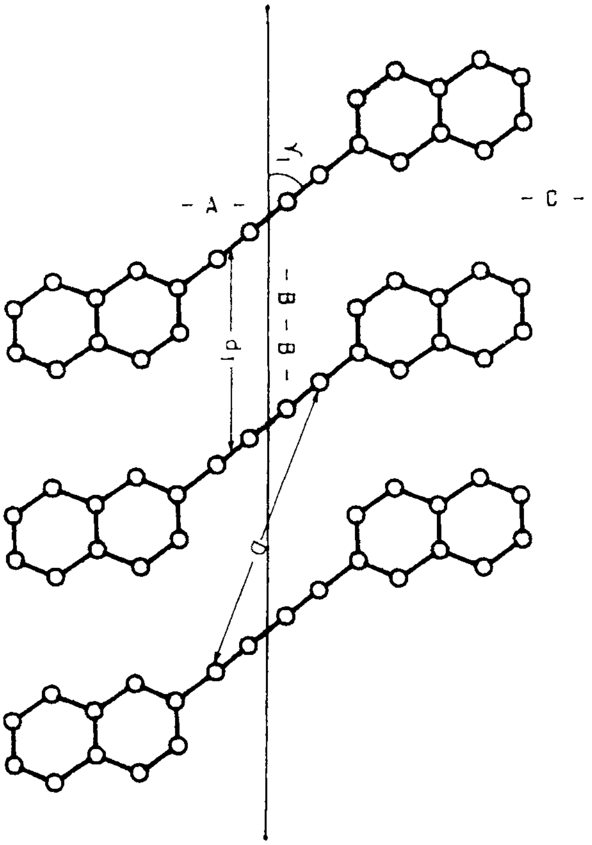

FIGURE 3 Stacking of the molecules along *b* axis.

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(i) The distance between C(2) and C(2′) of adjacent molecules is 6.074(8) Å [$D < 4.0$ Å].
(ii) The separation between the successive diacetylene molecules along the axis of polymerisation (ie. the b-axis) is $d_1[\equiv b] = 6.011(8)$ Å.
(iii) $\gamma_1 = 21.77°$ [$\gamma_1 \cong 45°$]
(iv) $S_1 = d_1 \sin(\gamma_1)$, $S_1 = 2.2297$ Å [$3.4 \leq S_1 \leq 4.0$ Å]

Accordingly, DNDA monomer packing is not favorable for solid state polymerisation. In view of this, it does not show reactivity in solid sate.

Interestingly, the diacetylene, 1,4-bis(3-quinolyl)-1,3-butadiyene (DQ), which has quinolyl as substituent group in contrast to naphthalene in DNDA, satisfies the packing parameter for solid state reactivity [$d_1 = 4.807$ Å, $\gamma_1 = 47.5°$, $S_1 = 3.45$ and $D = 3.603$ Å] (Das, 1990) and accordingly this monomer shows significant reactivity. The point to be appreciated in this context is that by changing the one C–atom of naphthalene by N-atom in quinoline, the packing parameter of the diacetylene gets favourably altered towards reactive arrangement. Thus, it can be suggested that the N-atom is the controlling factor in the packing arrangement, providing for closer packed system in the present case. The comparison of DNDA with DQ is quite significant, in that it throws light upon the influence of different groups on the reactivity of diacetylene.

Acknowledgements

TMS, would like to express his thanks to the Head, RSIC, IIT Madras for the facilities provided. AS, is grateful to CSIR, New Delhi, for providing research fellowship. JSP, would like to thank DST for the award of project No. SP/S2/M-34/86.

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