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Mesogenic Self-Assembly of Diamides. Crystal Structure of a 1,3-Diacylaminobenzene

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The crystal structure of a 1,3-diacylaminobenzene, quite close to mesogenic diamide analogues, is described. The compound crystallizes in the $P\bar{1}$ space group with two molecules per unit cell: $a = 11.007(2)$ Å, $b = 13.164(3)$ Å, $c = 8.806(3)$ Å, $\alpha = 93.40(3)°$, $\beta = 110.44(3)°$ and $\gamma = 101.03(1)°$. The final reliability R and wR factors were respectively equal to 0.065 and 0.078. The two antiparallel polar amide groups of each molecule are partly responsible, beside several weak van der Waals forces, of the crystal cohesion: the molecules are arranged in infinite parallel strands in which each amide group is connected to its two neighbors by four hydrogen bonds between CO and NH, as assumed in mesophases.

Keywords: liquid crystal; crystal structure; hydrogen bond; self-assembling

1. INTRODUCTION

From flexible and polar neat soaps, studied by Skoulios *et al.*[1] to partly rigid and apolar hydrocarbons such as cholestane **1**,[2] many thermotropic mesogens were synthesised.[3] Depending on the shape, rigidity and polarity of the core on which are skilfully grafted more or less numerous and more or less long paraffinic chains, the different parts of the mesogen segregate into distinct and contiguous stable structures consisting of parallel molecular stackings arranged in

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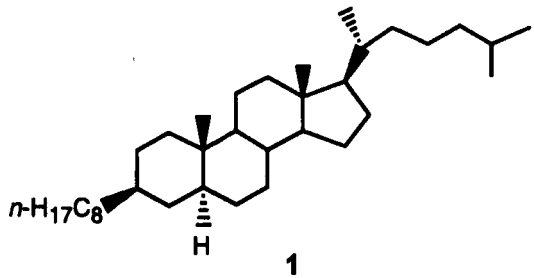
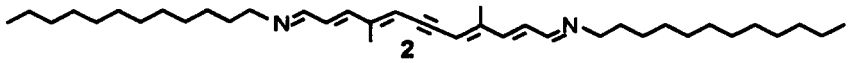
uncorrelated lamellae or columns. Besides these lamellar and columnar mesophases, there are nematic phases which only maintain parallelism between the main molecular axes and cubic mesophases which present a 3D order.



1

The low molecular weight mesogenic molecule is broadly rod-shaped, disc-shaped or with an intermediate structure like that of phasmids.[4] The rigid core itself can present a cyclic or – more rarely – an acyclic architecture such as that of the carotene derivative **2**,[5] and it only consists either of an entirely covalent unit or can be formed by metal complexation,[6] by charge transfer complexation[7] or by hydrogen bond assembling, from complementary components or by self-assembling.[8]



2

Mesogenic self-assembly was recently embodied with 1,3-diacylaminobenzenes **3a,b**[9a,b], **4a,b**[9b] and **5a,b**[10a-c], which showed nematic, lamello-columnar and columnar mesophases consisting of self-hydrogen bonded supramolecular wires, as postulated from X-ray diffraction measurements in mesophases (Fig.1). It was interesting to strengthen this assumption by knowing precisely the molecular arrangement in the crystalline phase, inasmuch the crystal structure indicates the favored interactions between different groups and foreshadows the molecular organization in the mesophase. [11a,b]

After many unsuccessful attempts with compounds **3–5** which unfortunately led to fluffy needles, we succeeded in producing exploitable crystals from the analogue **6**.

2. EXPERIMENTAL PART

Diamide **6** was prepared by the reaction (100°C, 30 min) of 2,4,6-trimethyl-1,3-phenylenediamine with two equivalents of 2-phenylpropionyl chloride

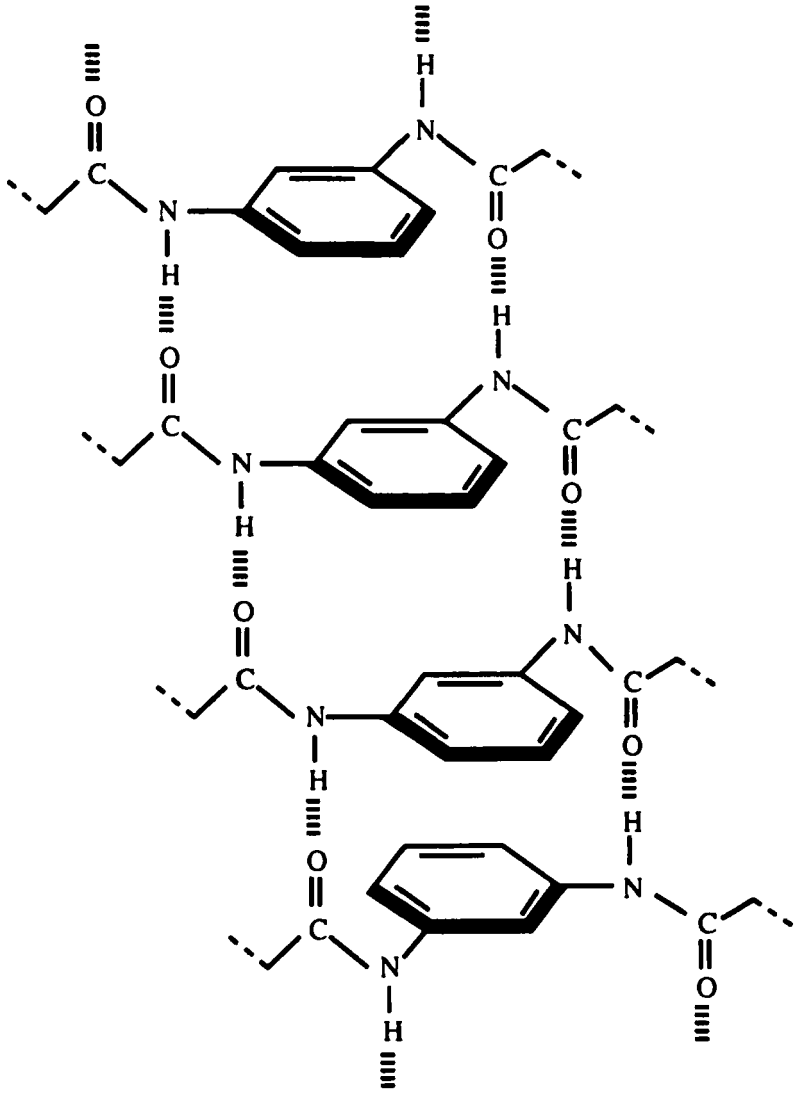
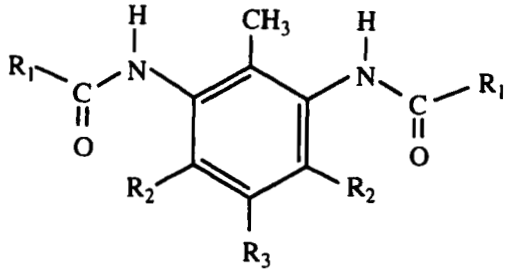


FIGURE 1 Schematic representation of the possible supramolecular hydrogen-bonded self-association of diamides **3–5** in the mesomorphic state

in dry dimethylacetamide (40 mL for 10 mmol of diamine) in the presence of two equivalents of 4-(dimethylamino)pyridine. Water was added and the precipitate (in quantitative amount) was separated and purified by recrystallization from a CCl_4-xylene mixture; mp 250°C (white crystals). ^1H NMR (250 MHz,



3 a $R_1 = n\text{-}C_nH_{2n+1}$-; R_2 = -CH_3; R_3 = -H

b $R_1 = n\text{-}C_nH_{2n+1}$-; R_2 = -H; R_3 = *tert*-butyl-

4 a R_1 = 3,5-($n\text{-}C_nH_{2n+1}O)_2C_6H_3$-; R_2 = -CH_3; R_3 = -H

b R_1 = 3,5-($n\text{-}C_nH_{2n+1}O)_2C_6H_3$-; R_2 = -H; R_3 = *tert*-butyl-

5 a $R_1 = n\text{-}C_nH_{2n+1}$-; R_2 = -H; R_3 = -CO_2Y

b R_1 = 3,5-($n\text{-}C_nH_{2n+1}O)_2C_6H_3$-; R_2 = -H; R_3 = -CO_2Y

(Y = alkyl, alkenyl chains or aromatic groups)

6 $R_1 = C_6H_5\text{-}CH_2\text{-}CH_2$-; R_2 = -CH_3; R_3 = -H

DMSO-d_6, 297 K) δ 1.71 (3H, s, $ArCH_3$), 1.95 (6H, s, $ArCH_3$), 2.62 (2H, t, J = 7.5 Hz, $ArCH_2$-), 2.91 (2H, t, J= 7.5 Hz, -CH_2-CO-), 6.86 (1H, s, ArH), 7.27 (10H, m, -C_6H_5).

Colorless prismatic crystals were grown by slow evaporation of 50:50 $CHCl_3$/EtOH solutions. Compound **6** ($C_{27}H_{30}N_2O_2$, M_x = 414,55 g mol^{-1}) crystallizes in the triclinic system with a $P\bar{1}$ space group (Z = 2). The unit-cell parameters were obtained by a least-square fit of the setting angles of 25 reflections with θ between 25 and 42°: a = 11.007(2) Å, b = 13.164(3) Å and c = 8.806(3) Å and α = 93.40(3)°, β = 110.44(3)°, γ= 101.03(1)° (V = 1155 $Å^3$). The calculated density (d_x = 1.192 $g.cm^{-3}$) is rather low. The linear absorption coefficient is μ = 0.60 mm^{-1} for the CuKα radiation (1.54178 Å). The diffracted intensities were collected on a CAD-4 Enraf-Nonius four-circle diffractometer equipped with a graphite monochromator for θ_{max}= 60°: $-10 \leq h \leq 10$;

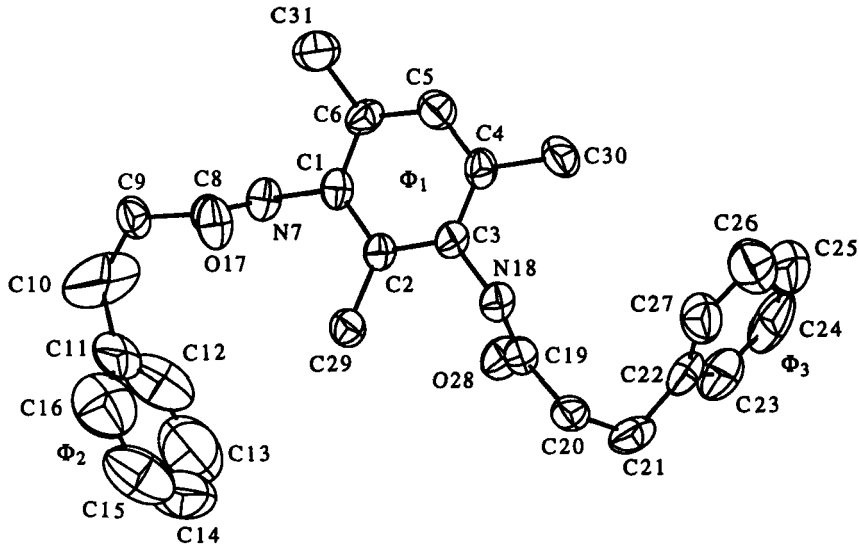


FIGURE 2 SNOOPI drawing of the molecule and atomic labelling (thermal ellipsoids are represented at the 50% probability level)

$-13 \leq k \leq 13$; $0 \leq l \leq 8$. Three standard reflections were used to monitor the data collection and detect any decrease of intensity (1 8 –4, –6 –3 4, –7 –2 3); the transmission factor T(hkl) lies between 0.95 and 1.0. Nevertheless the crystal absorption correction was performed using the Ψ scan technique.[12] There were 2396 independent reflections of which 1304 were considered as observed [$I \geq 2\sigma(I)$ and Rint = 0.019].

The crystal structure was solved using the MITHRIL program[13] and refined with the local CRISAF program. The hydrogen atoms were located in their theoretical positions and following the atoms to which they are attached; the refinement was then resumed. The weight was taken equal to $1/\sigma^2$ (Fo). The final reliability R and wR factors were respectively equal to 0.065 and 0.078 and the goodness of fit S equal to 1.55.

3. RESULTS AND DISCUSSION

The fractional x,y,z coordinates and the equivalent Ueq thermal motion factors are listed in Table I. The SNOOPI[14] drawing of the molecule is presented along with the atom labelling in Fig. 2. The bond lengths are given in Table II.

TABLE I Fractional atomic coordinates and equivalent U_{eq} thermal motion factors

	x/a	*y/b*	*z/c*	U_{eq}
C(1)	0.5527(8)	− 0.0738(6)	0.3306(10)	0.040(4)
C(2)	0.4955(8)	0.0018(6)	0.2445(10)	0.036(4)
C(3)	0.5810(8)	0.0849(6)	0.2143(10)	0.040(4)
C(4)	0.7177(9)	0.0929(7)	0.2670(11)	0.045(4)
C(5)	0.7670(9)	0.0147(7)	0.3462(12)	0.053(5)
C(6)	0.6887(9)	− 0.0709(7)	0.3779(11)	0.046(5)
N(7)	0.4706(7)	− 0.1579(5)	0.3691(8)	0.043(4)
C(8)	0.3906(8)	− 0.2415(6)	0.2593(11)	0.039(4)
C(9)	0.3193(9)	− 0.3245(7)	0.3265(12)	0.052(5)
C(10)	0.1913(22)	− 0.3420(21)	0.2626(49)	0.144(34)
C(11)	0.0884(10)	− 0.2963(10)	0.1616(15)	0.088(7)
C(12)	0.0924(13)	− 0.2113(14)	0.2609(17)	0.125(10)
C(13)	0.0189(16)	− 0.1404(14)	0.2133(25)	0.169(13)
C(14)	− 0.0626(14)	− 0.1504(14)	0.0546(22)	0.147(12)
C(15)	− 0.0784(13)	− 0.2352(14)	− 0.0513(16)	0.127(10)
C(16)	− 0.0055(15)	− 0.3108(13)	0.0029(19)	0.127(10)
O(17)	0.3766(6)	− 0.2490(5)	0.1156(7)	0.056(3)
N(18)	0.5277(7)	0.1654(5)	0.1284(8)	0.041(3)
C(19)	0.4717(8)	0.2339(7)	0.1825(10)	0.042(4)
C(20)	0.4269(9)	0.3129(7)	0.0719(11)	0.049(5)
C(21)	0.4576(10)	0.4207(8)	0.1697(13)	0.064(6)
C(22)	0.6039(10)	0.4708(7)	0.2606(12)	0.056(5)
C(23)	0.6419(12)	0.5389(8)	0.3989(14)	0.078(6)
C(24)	0.7741(14)	0.5887(8)	0.4822(14)	0.099(7)
C(25)	0.8663(13)	0.5707(9)	0.4253(18)	0.110(8)
C(26)	0.8292(12)	0.5035(10)	0.2862(18)	0.101(8)
C(27)	0.6986(11)	0.4522(8)	0.2028(14)	0.074(6)
C(28)	0.4563(6)	0.2309(5)	0.3138(7)	0.054(3)
C(29)	0.3485(9)	− 0.0062(7)	0.1869(11)	0.048(4)
C(30)	0.8095(9)	0.1864(8)	0.2421(13)	0.063(5)
C(31)	0.7466(10)	− 0.1557(9)	0.4603(14)	0.074(6)

TABLE II Bond lengths in Å and standard-deviations

C(1) – C(2)	1.40(1)	C(11) – C(16)	1.44(2)
C(1) – C(6)	1.40(2)	C(12) – C(13)	1.34(3)
C(1) – N(7)	1.43(1)	C(13) – C(14)	1.35(3)
C(2) – C(3)	1.40(1)	C(14) – C(15)	1.36(3)
C(2) – C(29)	1.50(2)	C(15) – C(16)	1.39(3)
C(3) – C(4)	1.39(2)	N(18) – C(19)	1.34(1)
C(3) – N(18)	1.44(1)	C(19) – C(20)	1.50(2)
C(4) – C(5)	1.37(2)	C(19) – O(28)	1.22(1)
C(4) – C(30)	1.52(2)	C(20) – C(21)	1.53(2)
C(5) – C(6)	1.39(2)	C(21) – C(22)	1.51(2)
C(6) – C(31)	1.49(2)	C(22) – C(23)	1.35(2)
N(7) – C(8)	1.35(1)	C(22) – C(27)	1.37(2)
C(8) – C(9)	1.50(2)	C(23) – C(24)	1.38(2)
C(8) – O(17)	1.21(1)	C(24) – C(25)	1.33(2)
C(9) – C(10)	1.29(4)	C(25) – C(26)	1.35(2)
C(10) – C(11)	1.44(4)	C(26) – C(27)	1.37(2)
C(11) – C(12)	1.36(2)		

The significative torsion angles which entirely define the molecular conformation are as follow:

C(2)-C(1)-N(7)-C(8)	=	77(1)°
N(7)-C(8)-C(9)-C(10)	=	119(2)°
C(8)-C(9)-C(10)-C(11)	=	– 14(3)°
C(9)-C(10)-C(11)-C(12)	=	– 72(3)°
C(2)-C(3)-N(18)-C(19)	=	66(1)°
N(18)-C(19)-C(20)-C(21)	=	– 140(1)°
C(19)-C(20)-C(21)-C(22)	=	64(1)°
C(20)-C(21)-C(22)-C(23)	=	– 152(1)°

The phenyl rings Φ_1 [C(1) to C(6)], Φ_2 [C(11) to C(16)], Φ_3 [C(22) to C(27)] and the two amide groups are perfectly planar. The dihedral angles Φ_1/Φ_2, Φ_1/Φ_3 and Φ_2/Φ_3 are respectively equal to 77.3(5)°, 83.4(4)° and 57.7(6)°.

The crystal cohesion involves wires of weak intermolecular hydrogen bonds between the CO and NH of neighboring molecules, giving infinite ribbons parallel to the (xOz) plane (Fig. 3), each ribbon consisting of a tilted column of parallel benzene rings. Actually, the two antiparallel polar amide groups of each

molecule come out of the benzene plane so that they form four hydrogen bonds through the amide groups belonging to two adjacent molecules. Concomitantly, the two meta Ar-NHCO groups of each molecule are in the opposite side from those of the two neighboring molecules along the Oz axis.

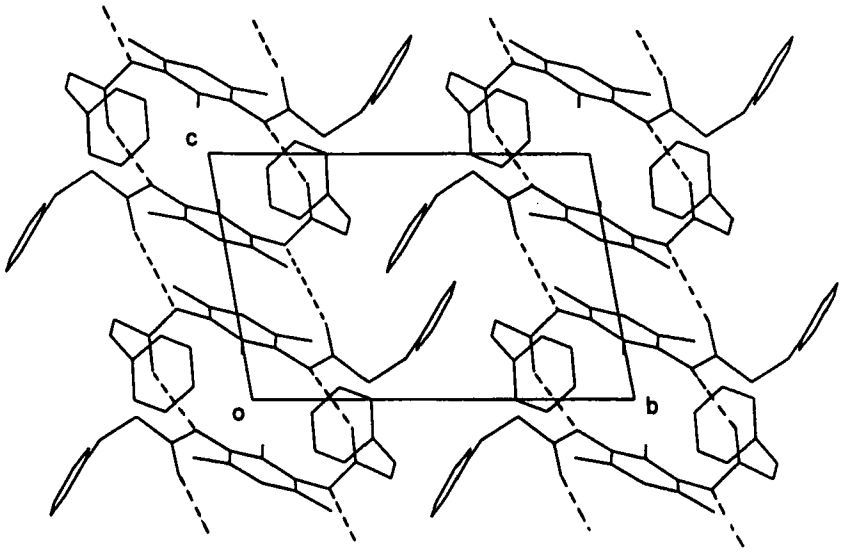


FIGURE 3 Projection of the structure on the (yOz) plane (dotted lines = hydrogen bonds)

The characteristics of hydrogen bonds are as follows:

N(7) – **H**(107) (x, y, z) •••• **O**(28) (1-x, -y, 1-z):

- length [**N**(7)-**O**(28)] = 2.90(1) Å
- length [**H**(107)-**O**(28)] = 2.19(2) Å
- angle [**N**(7)-**H**(107)-**O**(28)] = 140(2)°

O(17) (x,y,z) •••• **H**(118) – **N**(18) (1-x, -y, -z)

- length [**O**(17)-**N**(18)] = 2.89(1) Å
- length [**O**(17)-**H**(118)] = 2.13(2) Å
- angle [**O**(17)-**H**(118)-**N**(18)] = 149(2)°

The diamides ribbons resulting from the hydrogen bond network parallel to the (xOz) plane, interact through several weak van der Waals forces, essentially between phenyl rings at y = 0.5, and is in agreement with the quite low calculated density (d_x = 1.192 g.cm^{-3}). However there is no stacking, strictly speaking, between the aromatic planes.

4. CONCLUSION

The crystal structure of a mesogenic diamide analogue such as compound **6** corroborates what has been assumed in the mesomorphic state: the two antiparallel polar amide groups of each molecule give rise to intermolecular hydrogen bonds arranging the molecules in infinite parallel columns.

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