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4,4′-Di(N)Hexoxybenzalazine: Crystal and Molecular Structure and Phase Characterization of the Liquid Crystalline Compound

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The crystal and molecular structure of the mesogenic title compound (HBA) is described. Lattice parameters are: space group $P\bar{1}$, a = 9.003(2) Å, b = 8.850(2) Å, c = 8.510(2) Å, α = 79.63(1) °, β = 65.04(1) °, γ = 87.41(1) ° (at T = 299 K). The molecules contain a centre of symmetry and the phenyl rings are coplanar. In order to obtain better structural data for a comparison with its methoxy derivative (MBA) a redetermination of this structure was carried out using a new data set. The melting enthalpy of HBA is 45(2) kJmol^{-1} (127.8(5) °C) its clearing enthalpy is 1.5(4) kJmol^{-1} (153.2(5) °C). The fluctuation wave-length $2\pi/q_{\parallel}$ of 27(2) Å in the nematic state can be compared with the molecular length of 31.63 Å.

†Listings of observed and calculated structure factors for HBA and MBA as well as atomic and thermal parameters for MBA are available from the authors on request.

INTRODUCTION

Syntheses and transition temperatures of some mesogenic 4,4'-di(N)alkoxybenzalazines had been reported by Shaw and Brown.[1] Galiqué and Falgueirettes[2] determined the crystal structure of the methoxy compound (MBA) and found the two benzene rings to be nearly coplanar.

The influence of chemical changes on the geometry of the central core on the liquid crystalline properties of these compounds has been recently described.[3] Intramolecular hydrogen bonds of the type O—H-----N in one hydroxy-substituted benzalazine are thought to be responsible for the planarity of the molecules in 4,4'-di(N)ethoxy-2,2'-dihydroxy-α,α'-dimethylbenzalazine,[4,5] whereas in 4,4'-di(N)hydroxy-α,α'-dimethylbenzalazine monohydrate a dihedral angle between the two benzene rings of 32° was found.[6]

The object of this investigation was to gain an understanding of the molecular conformation within the benzalazines and the particular compound 4,4'-di(N)hexoxybenzalazine (HBA) was selected for detailed study.

EXPERIMENTAL

Substances

HBA was prepared according reference 1, MBA was obtained from Eastman Kodak Co., New York. No further purification was carried out.

Crystal data

Crystals suitable for X-ray structure analysis were obtained by slow evaporation of benzene solutions. These were needles in the case of HBA and short prisms, with point group symmetry m in the case of MBA.

Structure determination and refinement for HBA

The data collection was performed on a four-circle-diffractometer, STOE-Stadi 4 (CuK_α, λ = 1.54178 Å, graphite monochromated). The lattice dimensions were obtained, by least-squares refinement, from 32 strong reflections. The basic crystal data are given in Table I. No absorption correction was applied.

TABLE I

The basic crystal data

Formula weight	408.59
Space group	$P\bar{1}$
a = 9.003(2), b = 8.850(2), c = 8.510(2)Å, α = 79.63(1), β = 65.04(1), γ = 87.41(1)° at 26°C V = 603.74 Å^3	
Z = 1	
D_c = 1.12 Mg m^{-3}	
μ(Cu K_α) = 0.48 mm^{-1}	
F(000) = 222	
Number of measured reflections	3387
Number of independent reflections	1780
Number of unobserved reflections	53 (for $F_o < 2\,\sigma(F_o)$)
R = 0.057, R_w = 0.069	

$$R_w = \frac{\Sigma||F_o| - |F_c|| \cdot w^{1/2}}{\Sigma|F_o| \cdot w^{1/2}}$$

with

$$w = \frac{1}{[\sigma(F_o)]^2}$$

Because the solution of the phase problem by direct methods[7] failed, the structure was solved by a trial and error approach. This was done in the following way. Assuming space group $P\bar{1}$, since Z = 1 the molecule itself must contain a centre of symmetry and this must lie at the centre of the N—N-bond.

Assuming a N—N bond length of 1.4 Å one N-atom must be positioned on a hemisphere, centered on $\bar{1}$, of radius 0.7 Å. 50 grid points of this surface were calculated and for every point a Fourier synthesis was caluculated. The synthesis with the lowest R_M value[7] showed some peaks roughly compatible with the molecular structure (N at −0.0392, 0.0568, 0.0501). Subsequent Fourier maps revealed all other non-hydrogen atoms. Refinement using anisotropic thermal parameters converged at R = 0.17.

From ΔF syntheses all H atoms were located. Refinement with fixed isotropic thermal parameters for the hydrogen atoms, converged at R = 0.057 (R_w = 0.069). In the last least-squares refinement cycle the shift/esd ratio was considerably smaller than 0.05 for all parameters. A final difference Fourier synthesis showed no peaks higher

TABLE II

Atomic coordinates ($\times 10^4$, for H $\times 10^3$) and isotropic thermal parameters with e.s.d.'s in parentheses. <U> defined as $(U_{11} + U_{22} + U_{33})/3Å^2$

	x	y	z	<U>
O	−2819(2)	6312(2)	4303(2)	.072(2)
N	−514(2)	518(2)	508(2)	.060(9)
C1	321(2)	1616(2)	591(2)	.056(5)
C2	−484(2)	2832(2)	1570(2)	.052(8)
C3	451(2)	3959(2)	1723(2)	.057(7)
C4	−277(2)	5136(2)	2635(2)	.058(9)
C5	−1959(2)	5206(2)	3399(2)	.056(8)
C6	−2915(2)	4088(2)	3251(3)	.063(1)
C7	−2189(2)	2922(2)	2364(3)	.061(1)
C8	−1943(2)	7486(2)	4576(3)	.061(7)
C9	−3219(3)	8471(3)	5689(3)	.070(1)
C10	−2480(2)	9749(2)	6144(3)	.063(7)
C11	−3755(3)	10784(2)	7196(3)	.065(9)
C12	−3052(3)	12047(3)	7691(3)	.080(2)
C13	−4312(4)	13119(3)	8679(5)	.106(3)
H1	150(3)	164(2)	0(2)	.06
H3	167(3)	392(2)	113(2)	.06
H4	344(3)	587(2)	276(2)	.06
H6	−401(3)	414(2)	376(2)	.06
H7	−289(3)	218(2)	233(2)	.06
H81	−134(2)	696(2)	517(2)	.06
H82	−117(2)	804(2)	342(3)	.06
H91	−395(3)	779(2)	681(3)	.07
H92	−390(3)	894(2)	511(3)	.07
H101	−168(3)	1036(2)	511(3)	.07
H102	−195(3)	927(2)	692(3)	.07
H111	−430(3)	1126(2)	646(3)	.07
H112	−453(3)	1017(2)	823(3)	.07
H121	−207(3)	1261(3)	654(3)	.08
H122	−238(3)	1158(2)	828(3)	.08
H131	−538(4)	1261(3)	981(4)	.11
H132	−412(4)	1391(4)	923(4)	.11
H133	−504(4)	1353(3)	814(4)	.11

than 0.18 e $Å^{-3}$. The final atomic parameters are given in Table II.† For a better comparison of this structure with that of MBA the crystal and molecular structure of the latter were redetermined using a new data set. Lattice parameters are a = 17.404(3) Å, b = 10.706(2) Å, c = 8.420(2) Å, β = 113.76(1) °. The structure was refined to R = 0.046 (R_w = 0.037) using 2504 independent reflections. The resulting molecular data are used in the following discussion.

†Listings of observed and calculated structure factors for HBA and MBA as well as atomic and thermal parameters for MBA are available from the authors on request.

All calculations were performed using an IBM 3083 E computer of the Technische Hochschule Darmstadt.

X-ray investigations on the liquid crystalline phase

For the X-ray examination of the liquid crystalline state the samples were contained in Lindemann glass capillaries. An oven, especially constructed for X-ray investigations, allowed measurements to be made in the temperature range 20–200°C. The camera used was of the flat plate type. The quoted values are mean values of at least three measurements with estimated standard deviation given in parentheses.

Thermodynamic investigations

The thermal and calorimetric investigations were performed using a Du Pont 990 Thermal Analyzer in conjunction with the Differential Scanning Calorimeter Cell. The samples were encapsulated in hermetically sealed aluminium sample pans. The mass of the samples used was about 2 mg. The DSC measurements were performed in the heating mode with a rate of 2 K min^{-1}. The integration of the endothermic maxima was accomplished with a Haff-Planimeter.

RESULTS AND DISCUSSION

Description of the structure HBA

Figure 1 shows a projection of the molecular structure on the plane defined by N, C1, and C2. Selected interatomic distances and angles are listed in Table III. The centrosymmetric molecule is fully elongated with the hexoxy group in an all *trans* conformation. The benzene rings are exactly coplanar. The non-zero dihedral angles between the best planes defined by the benzene rings (A), the C1—N—N^{i}—$C1^{i}$ fragment (B), and the hexoxy group (C) are ϕ (A,B) = 4.3°, ϕ (A,C) = 4.2°, and ϕ (B,C) = 8.3°. Consequently, the whole molecule is nearly coplanar and forms a rectangular prism 31.63 Å × 5.54 Å × 3.44 Å (H atom radius used = 0.55 Å). Bond lengths within the non-centrosymmetric MBA molecules resulting from our determination are presented in Figure 2.

Figure 3 shows the packing of the HBA molecules in the crystalline state. They are aligned along the crystallographic direction [−8, 2, 3].

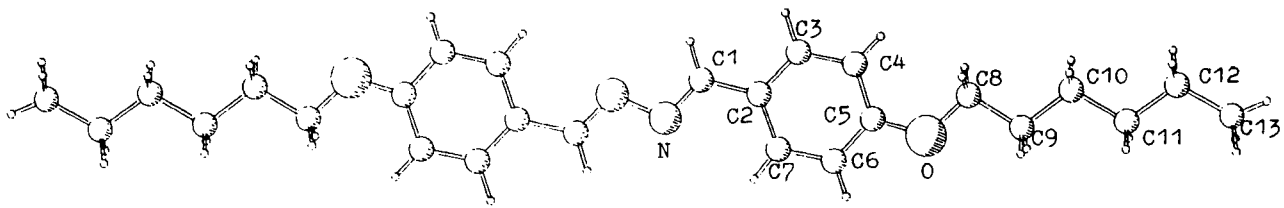

FIGURE 1 Molecular structure of HBA, projected onto the plane defined by N, C1, and C2.

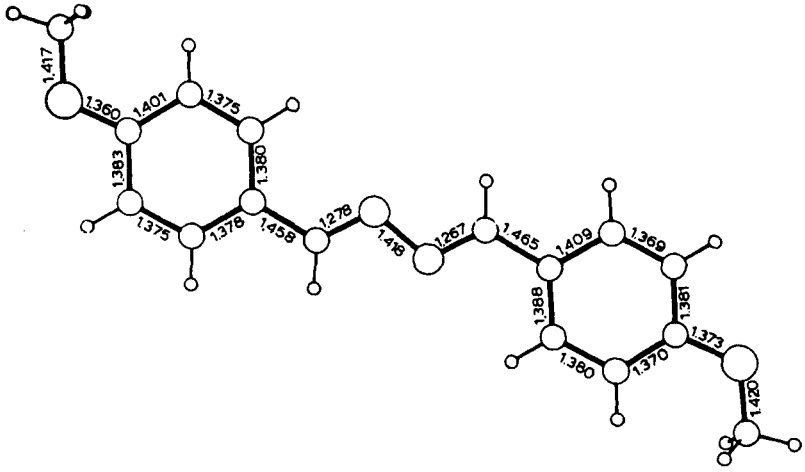

FIGURE 2 Molecular structure of MBA with bond lengths obtained from our redetermination; (e.s.d.'s are 0.003 Å) projected onto the plane defined by N1, N2, and C8.

In Table IV a comparison of some distances for the structurally investigated benzalazines[5,6] is given. While the distances for HBA, MBA, and $C_{20}H_{24}N_2O_4$ are nearly equivalent, small differences are found for $C_{16}H_{16}N_2O_2 \cdot H_2O$ for the C-C_{phenyl} distances.

The planarity of the molecule $C_{20}H_{24}N_2O_4$ has been explained as a consequence of intramolecular hydrogen bonding of the type O—H---N (O---N = 2.545(7) Å[5]) involving hydroxy groups in the 2 and 2′ positions. In HBA, MBA, and $C_{16}H_{16}N_2O_2 \cdot H_2O$ however, these positions are unoccupied and only in the case of $C_{16}H_{16}N_2O_2 \cdot H_2O$ is there a significant departure from planarity and this can be ascribed to interactions with solvent molecules within the crystal. In our opinion there is an intrinsic tendency for such molecules to be

TABLE III

Some interatomic distances (Å) and angles (°) with e.s.d.'s in parentheses

N-N^i	1.406(3)	N^i-N-C1	111.3(2)
N-C1	1.285(3)	N-C1-C2	121.1(2)
C1-C2	1.456(3)	C1-C2-C3	119.9(2)
C5-O	1.359(2)	C1-C2-C7	122.1(2)
O-C8	1.439(2)	C4-C5-O	125.4(2)
		C6-C5-O	114.9(2)
		C5-O-C8	119.0(1)
		O-C8-C9	106.4(2)

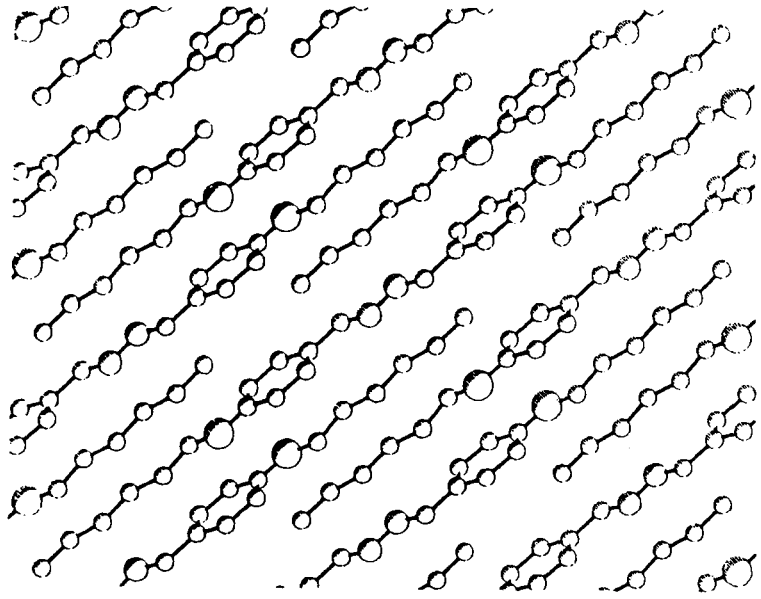

FIGURE 3 Crystal packing in HBA, projection onto the plane (100).

planar because of the conjugation of the unsaturated system. The presence of intramolecular hydrogen bonds has only a secondary effect.

Liquid crystalline properties

HBA melts at 127.8(5)°C giving a nematic phase with an enthalpy of fusion of 45(2) kJ mol^{-1}. The clearing point is at 153.2(9)°C with an

TABLE IV

Selected bond lengths (Å) in known benzalazines. The data for MBA are from our redetermination

	MBA	HBA	$C_{20}H_{24}N_2O_4$(5)	$C_{16}H_{16}N_2O_2 \cdot H_2O$(6)
N—N	1.418(3)	1.406(3)	1.390(7)	1.417(7)
N—C	1.267(3)	1.285(3)	1.293(7)	1.282(7)
	1.278(3)			1.278(7)
C—C_{phenyl}	1.465(3)	1.456(3)	1.459(7)	1.495(7)
	1.458(3)			1.499(7)
O—C_{phenyl}	1.373(2)	1.359(2)	1.365(7)	1.379(7)
	1.360(2)			1.379(7)
O—C_{alkox}	1.420(2)	1.439(2)	1.429(7)	
	1.417(3)			

enthalpy of 1.5(4) kJ mol^{-1}. The determined points of the phase transitions are in good agreement with the data given in reference 1.

The X-ray investigations of the nematic phase at 138.5(5)°C yielded the wave-lengths $2\pi/q_{\parallel}$ of 27(2) Å and 4.52(4) Å for $2\pi/q_{\perp}$. These data are comparable with the given molecular data and an order parameter S = 0.59 at 138.5°C.

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