This article was downloaded by: [Tomsk State University of Control Systems and Radio]
On: 23 February 2013, At: 03:48
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Molecular and Crystal Structure of P-Ethoxybenzylidene-P-N-Butylaniline (EBBA): Preliminary Data on P-Methoxybenzylidene-Cyanoaniline (MBCA)

Jak Howard [a] , Aj Leadbetter [b] & M Sherwood [a]
[a] Inorganic Chemistry Department, The University, Bristol, BS8 1TS
[b] Department of Chemistry, The University, Exeter, EX4 4QD
Version of record first published: 20 Apr 2011.

To cite this article: Jak Howard , Aj Leadbetter & M Sherwood (1980): Molecular and Crystal Structure of P-Ethoxybenzylidene-P-N-Butylaniline (EBBA): Preliminary Data on P-Methoxybenzylidene-Cyanoaniline (MBCA), Molecular Crystals and Liquid Crystals, 56:9, 271-277

To link to this article: http://dx.doi.org/10.1080/01406568008069808

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.tandfonline.com/page/terms-and-conditions

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Mol. Cryst. Liq. Cryst. Vol. 56 (Letters), pp. 271-277
0140-6566/80/5609-0271$04.50/0
© 1980, Gordon and Breach, Science Publishers, Inc.
Printed in the United States of America

Downloaded by [Tomsk State University of Control Systems and Radio] at 03:48 23 February 2013

MOLECULAR AND CRYSTAL STRUCTURE OF *p*-ETHOXYBENZYLIDENE-*p*-n-BUTYLANILINE (EBBA)
PRELIMINARY DATA ON *p*-METHOXYBENZYLIDENE-CYANOANILINE (MBCA)

JAK HOWARD,* AJ LEADBETTER,† and M SHERWOOD*

* Inorganic Chemistry Department, The University, Bristol, BS8 1TS

† Department of Chemistry, The University, Exeter, EX4 4QD

(Submitted for publication 13th February, 1980)

Abstract: Single crystal X-ray diffraction studies have revealed the detailed molecular structure of EBBA, whilst giving some insight into the packing of MBCA. The molecules lie in long chains with their long axes parallel, and pack together as in the ideal nematic mesophase.

Crystals of EBBA are Monoclinic, Space Group $P2_1/c$. $a = 7.943(1)$, $b = 5.623(4)$, $c = 37.376(19)$Å, $\beta = 92.20(4)^\circ$, $z = 4$. $R(R') = 0.082(0.060)$ for 951 data, $I > 2\sigma(I)$.

Crystals of MBCA are Triclinic, Space Group $P\bar{1}$, $a = 11.575(5)$, $b = 5.036(4)$, $c = 11.338(5)$Å, $\alpha = 89.79(6)$, $\beta = 108.14(4)$, $\gamma = 95.82(5)^\circ$, $z = 2$.

Few single crystal investigations of the liquid crystalline state had been completed when this study was begun, thus more information was sought with a view to correlating properties of the nematic mesophase with molecular packing.

Suitable crystals of EBBA were grown from 60/40 petroleum ether as translucent plates which for data collection were sealed into Lindemann glass capillaries. Intensity data were collected on a Syntex $P2_1$ 4-circle

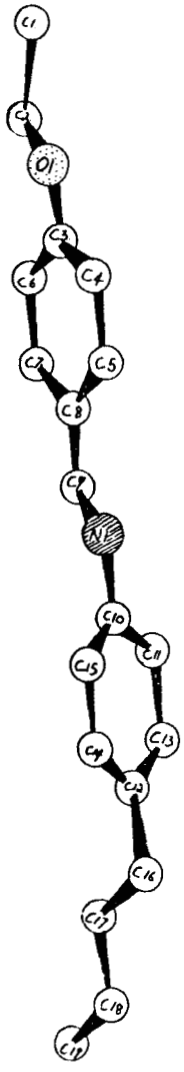
automated diffractometer, in the range $2.9 < 2\theta < 50^{o}$ using Mo-K_{α} monochromatised X-radiation and a variable scan mode. Of the total 1389 intensities recorded 951 data were deemed observable according to the criterion $I > 2\sigma(I)$ and only these were used in the final stages of refinement, during which all non-hydrogen atoms were refined with anisotropic thermal parameters and the hydrogen atoms isotropically (Table 1). In the last four cycles of refinement, the mean shift to error ratio was 0.2, with a maximum of 1.5 and the residual electron density difference synthesis showed no peaks >0.2 or <-0.2 eA^{-3}. The structure factor listing is deposited together with the anisotropic thermal parameters.

Discussion: The overall molecular structure of EBBA, with the crystallographic numbering scheme, is shown in Figure 1 and the packing of these molecules in the unit cell in Figure 2. Selected bond lengths and angles are reported in Table 2. There are no unusually short intermolecular contacts and the aliphatic and aromatic carbon atoms show the expected tetrahedral and trigonal geometries, within experimental error. There are molecules stacked directly above and below those shown in Figure 2 and the molecular axes are slightly tilted relative to the ac plane. The molecules are arranged in head-to-tail rows with the terminal carbon atoms of each molecule eclipsed with respect to that of the next molecule in the row. The distance between lines representing adjacent rows in the ac plane is approximately 4.3Å. In the b direction, molecules in adjacent rows are stacked directly above each other to form columns, which are displaced relative to each other in the direction of the long molecular axes. Crystal structures in which the long axes have equal numbers of orientations differing by π appear to be common to all liquid crystal precursors so far determined consistent with the fact that no liquid crystal has yet been found to have ferroelectric properties conferred by preferred orientation of the long axes. The structure of EBBA is typical of nematic precursors[1] in having head-to-tail rows of molecules, sometimes staggered but always approximately parallel.

It is of considerable interest that the dipoles associated with both ether and Schiff's base linkages are nearly co-planar in planes parallel to (001) and that all the butyl groups overlap to form paraffinic sheets also parallel to (001). These two features appear therefore to combine to produce the observed crystal structure. In the nematic phase the same local structure is probably preserved but with a coherence length of only a few molecules in any direction.[2]

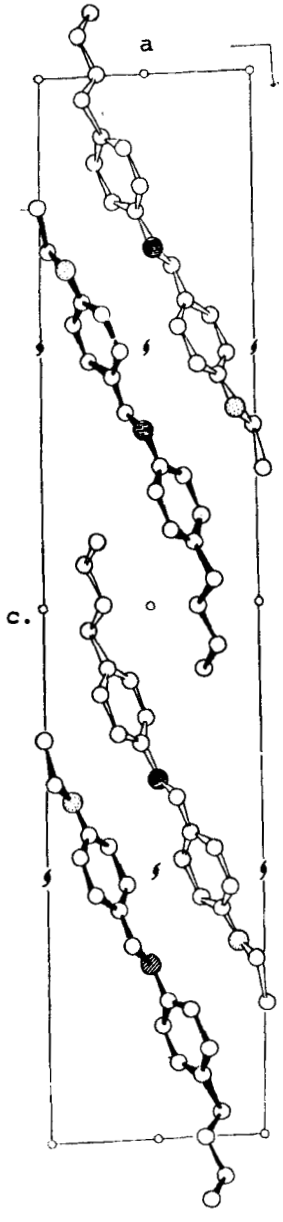
Downloaded by [Tomsk State University of Control Systems and Radio] at 03:48 23 February 2013

FIGURE 1



The molecular structure of EBBA

FIGURE 2



The molecular packing in a unit cell of EBBA, viewed down the b axis

Downloaded by [Tomsk State University of Control Systems and Radio] at 03:48 23 February 2013

TABLE 1

EBBA: Fractional atomic co-ordinates with standard deviations in parenthesis

ATOM	x/a	y/b	z/c
(i) *Ethoxy Group*			
C(1)	1.028(1)	0.117(2)	0.3695(3)
H(11)	1.122(9)	0.24(2)	0.368(2)
H(12)	0.909(8)	0.15(1)	0.386(2)
H(13)	1.123(9)	-0.03(2)	0.378(2)
C(2)	0.977(1)	0.050(2)	0.3316(3)
H(21)	1.090(8)	0.02(1)	0.316(2)
H(22)	0.931(8)	-0.09(1)	0.330(2)
O(1)	0.8760(8)	0.241(1)	0.3175(2)
(ii) *1st Phenyl Ring*			
C(3)	0.812(1)	0.218(2)	0.2831(3)
C(4)	0.712(1)	0.411(2)	0.2711(3)
H(41)	0.672(6)	0.54(1)	0.289(2)
C(5)	0.644(1)	0.413(2)	0.237
H(51)	0.558(7)	0.54(1)	0.230(2)
C(6)	0.846(1)	0.028(2)	0.2602(3)
H(61)	0.957(8)	-0.09(1)	0.267(2)
C(7)	0.774(1)	0.034(2)	0.2259(3)
H(71)	0.830(7)	-0.10(1)	0.208(2)
C(8)	0.674(1)	0.222(2)	0.2142(3)
(iii) *Anilinic Linkage*			
C(9)	0.596(1)	0.220(2)	0.1771(3)
H(91)	0.629(7)	0.09(1)	0.165(2)
N(1)	0.5228(9)	0.397(1)	0.1627(2)

Downloaded by [Tomsk State University of Control Systems and Radio] at 03:48 23 February 2013

TABLE 1 (continued)

(iv) 2nd Phenyl Ring

C(10)	0.445(1)	0.368(2)	0.1278(3)
C(11)	0.342(1)	0.178(2)	0.1187(3)
H(111)	0.304(7)	0.06(1)	0.138(2)
C(13)	0.260(1)	0.175(2)	0.0852(3)
H(131)	0.180(7)	0.05(1)	0.079(2)
C(14)	0.389(1)	0.537(2)	0.0700(3)
H(141)	0.425(7)	0.67(1)	0.054(2)
C(15)	0.470(1)	0.554(2)	0.1034(3)
H(151)	0.542(7)	0.70(1)	0.110(2)
C(12)	0.286(1)	0.356(2)	0.0597(3)

(v) Butyl Group

C(16)	0.195(1)	0.342(2)	0.0230(3)
H(161)	0.050(9)	0.29(1)	0.025(2)
H(162)	0.189(7)	0.48(1)	0.013(2)
C(17)	0.271(1)	0.155(2)	-0.0009(3)
H(171)	0.424(9)	0.19(1)	-0.006(2)
H(172)	0.267(8)	0.02(1)	0.008(2)
C(18)	0.185(1)	0.139(2)	-0.0381(3)
H(181)	0.035(9)	0.13(1)	-0.037(2)
H(182)	0.220(8)	0.28(1)	-0.048(2)
C(19)	0.250(1)	-0.066(2)	-0.0603(3)
H(191)	0.378(8)	-0.06(1)	0.008(2)
H(192)	0.23(1)	-0.22	-0.048
H(193)	0.220(8)	-0.06(1)	-0.084(2)

Downloaded by [Tomsk State University of Control Systems and Radio] at 03:48 23 February 2013

Downloaded by [Tomsk State University of Control Systems and Radio] at 03:48 23 February 2013

TABLE 2

Selected bond lengths

ATOM	Distance /A°	ATOM	Distance /A°
C(1) - C(2)	1.51(1)	N(1) - C(10)	1.43(1)
C(2) - O(1)	1.43(1)	C(10) - C(11)	1.38(2)
O(1) - C(3)	1.37(1)	C(11) - C(13)	1.39(1)
C(3) - C(4)	1.41(2)	C(13) - C(12)	1.40(2)
C(4) - C(5)	1.36(3)	C(10) - C(15)	1.40(2)
C(5) - C(8)	1.40(1)	C(15) - C(14)	1.39(1)
C(3) - C(6)	1.40(2)	C(12) - C(16)	1.52(2)
C(6) - C(7)	1.38(1)	C(16) - C(17)	1.52(2)
C(7) - C(8)	1.38(1)	C(17) - C(18)	1.53(1)
C(8) - C(9)	1.50(1)	C(18) - C(19)	1.52(1)
C(9) - N(1)	1.26(1)		

Selected bond angles

ATOM	Angle/degrees
C(2) - O(1) - C(3)	117.1(8)°
C(8) - C(9) - N(1)	123.9(8)°
C(9) - N(1) - C(10)	118.4(8)°

The aliphatic and aromatic carbons show typical tetrahedral and trigonal angles.

The angle between the two phenyl rings is 57.6°.

We report here also the crystallographic data for MBCA. The translucent crystals grown from diethyl ether have the triclinic dimensions given in the abstract, with two molecules per unit cell. This suggests that the molecules lie diagonally across the cell, related to one another by an inversion centre and all our preliminary direct method results support this hypothesis. It is also in accord with the solution found for EBBA, but unfortunately a complete solution has not yet been achieved.

References

[1] RF Bryan, Proc Pre-Congress Symposium on Organic Crystal Chemistry, Poznan-Dymaczewo, Poland, pp.105-154 (1979).

[2] AJ Leadbetter, RM Richardson, and CN Colling, *J de Physique*, *36*, C1-37 (1975).

NOTE: Structure factor listings and anisotropic thermal parameters may also be obtained on request from any of the authors.

Downloaded by [Tomsk State University of Control Systems and Radio] at 03:48 23 February 2013