Crystal structure of n–p–methoxybenzylidene–p–phenylazoaniline

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Abstract. The crystal structure of n–p–methoxybenzylidene–p–phenylazo-aniline, a nematogenic compound of positive dielectric anisotropy has been determined by x–ray diffraction methods using single crystals. It is established that the nearest neighbours are oriented antiparallel with respect to each other.

As part of a programme of x–ray investigations on mesogenic compounds the crystal structure analysis of n–p–methoxybenzylidene–p–phenylazoaniline
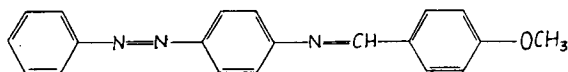
in its crystalline phase was undertaken. The compound forms a nematic mesophase at 149° C and becomes isotropic at 184° C.

Orange coloured needles of the compound were obtained by slow evaporation from a solution in toluene. The space group and unit cell dimensions were determined from oscillation and Weissenberg pictures and are given in table 1 along with other relevant crystal data. Three-dimensional intensity data were collected from reciprocal levels hko, Hkl, H = 0, 1, 2, 3, 4 and 5 using nickel filtered copper radiation. It must

Table 1

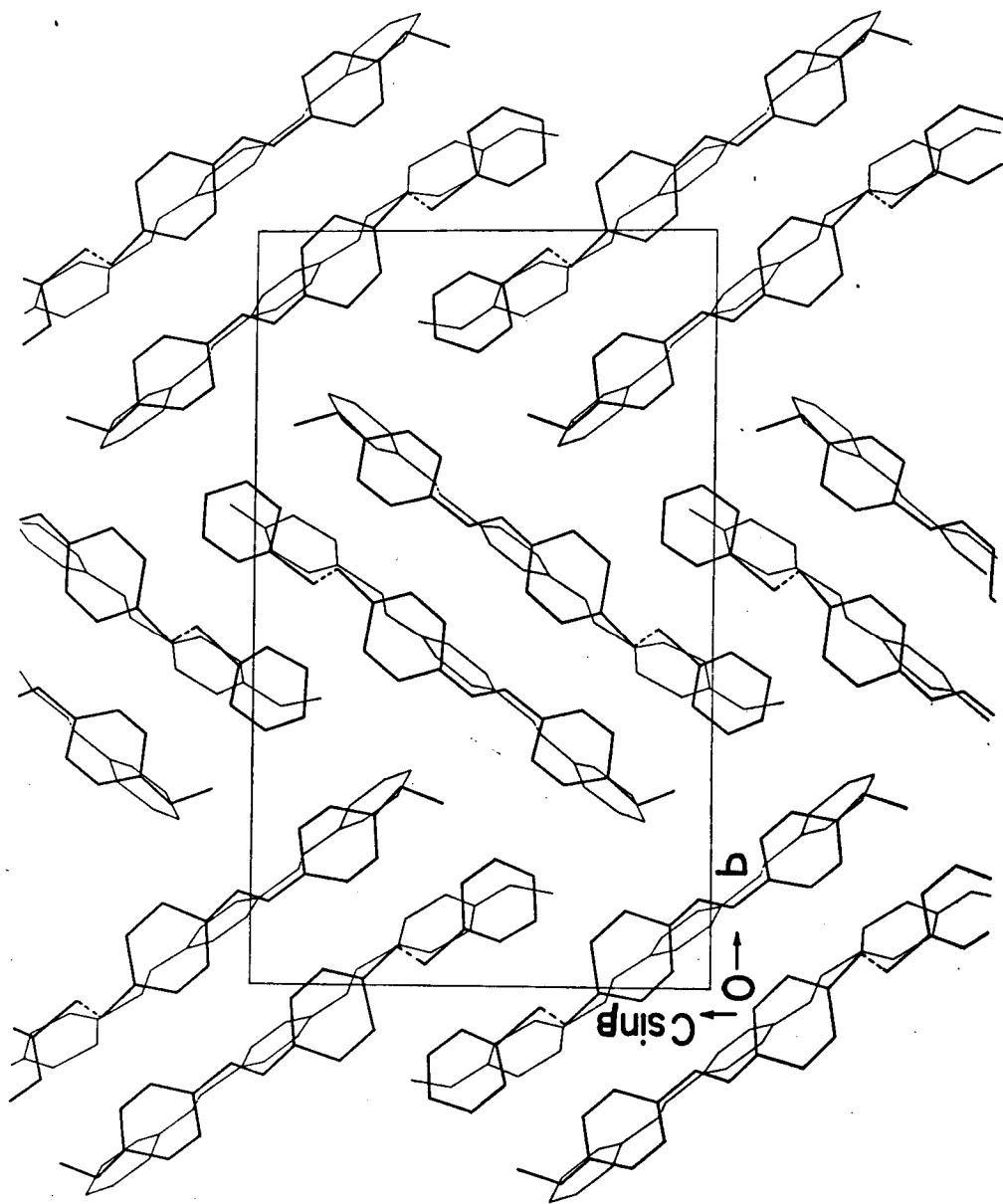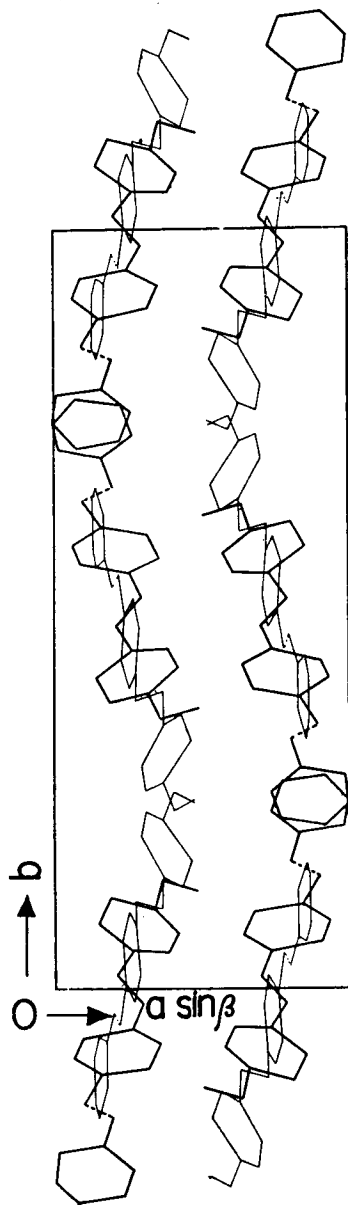| Molecular formula	$C_{20}H_{17}ON_3$
Space group	$P2_1/c$
$a = 9 \cdot 79 \pm 0 \cdot 04$ Å	
$b = 23 \cdot 75 \pm 0 \cdot 04$ Å	
$c = 15 \cdot 67 \pm 0 \cdot 03$ Å	
$\beta = 112° \; 26'$	
$Z = 8$	
$\mu = 6 \cdot 356$ cm^{-1}	
$\rho_{exp} = 1 \cdot 26$ gm cm^{-3}	
$\rho_{calc} = 1 \cdot 25$ gm cm^{-3}	

Figure 1(i)

Figure 1 (ii)

Figure 1   View of the structure as seen perpendicular to the (i) *a*-axis and (ii) *c*-axis. The thick and the thin lines denote the crystallographically independent molecules in the unit cell. The broken lines denote the –N = N- bond.

be mentioned that even with optically clear single crystals the diffraction pattern was not of high quality and moreover they did not extend to the high angle region. The photographically recorded intensities were estimated visually and were corrected for Lorentz–polarisation factors, absorption and spot shape effects.

The solution of the structure was initiated by computing a three-dimensional Patterson map. The continuous distribution of vector density in the Patterson map indicated only the possible orientations of the molecules in the unit cell. Trial calculations were, however, carried out on the basis of molecular models fixed by examining a few intense low angle reflections. The solution of the structure was simultaneously attempted by the direct methods[1] also. The MULTAN computer programme of Germain et al.[2], as modified by Ramakumar and Murthy for the IBM 360/44 computer, was used for generating the signs of reflections. From the E–map corresponding to the best solution of the MULTAN, a few atoms of one of the molecules in the asymmetric part could be identified; but, there was no indication of the atomic positions of the other crystallographically independent molecule in this map. Using the set of atomic positions obtained from the E–map as the starting point and employing packing considerations and trial calculations the complete structure was derived in several stages. The initial R–factor for the correct model was 51·9% for 1074 observed reflections. The positional and thermal parameters of the atoms have been refined to R = 17·3% by leastsquares method. Further refinement of the structure is in progress.

Figures 1(i) and 1(ii) show the arrangement of molecules in the planes perpendicular to the *a*– and the *c*–axes respectively. The two crystallographically independent molecules in the unit cell are oriented antiparallel to each other and are nearly one above the other, separated by a distance of about 5Å along the *a*–direction. The planes of the benzene rings in the two molecules are not parallel, the maximum tilt between them being about 90° near the molecular centres. Also, in each molecule, the benzene ring to which the methoxy group is attached is tilted with respect to the plane of the other two rings. Detailed description of the molecular geometry and other structural features will be discussed elsewhere.

References

1 KARLE I L and KARLE J *Acta Cryst.* **21** 849 (1966)
2 GERMAIN G, MAIN P and WOOLFSON M M *Acta Cryst.* **A27** 368 (1971)