

Crystal Structure Analysis of the Nematogenic Compound 2,2'-Dibromo-4,4'-bis-(*p*-methoxybenzylideneamino)biphenyl

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The crystal structure of 2,2'-dibromo-4,4'-bis-(*p*-methoxybenzylideneamino)biphenyl, $\text{CH}_3\text{-O-C}_6\text{H}_4\text{-CH=N-C}_6\text{H}_3\text{Br-C}_6\text{H}_3\text{Br-N=CH-C}_6\text{H}_4\text{-O-CH}_3$, has been determined by the heavy-atom method. It was refined by three-dimensional least-squares analysis (block-diagonal approximation) to an R of 0.046 for 3688 independent reflections. The crystal data are: space group $P\bar{1}$, $a=7.631$ (7), $b=11.55$ (2), $c=15.99$ (3) Å, $\alpha=114.39$ (4), $\beta=105.58$ (2), $\gamma=92.16$ (4)°, with two molecules per unit cell. $D_m=1.61$ g cm⁻³. The molecular axis is nearly parallel to the c axis and neighboring molecules are shifted with respect to each other, such that the middle of one molecule is near the end of its nearest neighbor. The angle between the two rings of the biphenyl segment is 80.1°, yielding a 'herringbone' packing in the plane perpendicular to the molecular axis.

Introduction

Studies of single crystals of nematogenic and smectogenic compounds (*i.e.*, compounds that exhibit a nematic liquid crystalline or a smectic liquid crystalline phase, respectively, with heating) show the nature of the packing of the molecules in the solid state and other molecular characteristics which could give insight into the nature of the nematic or smectic liquid crystal. The crystal structures determined to date with this primary objective are listed in Table 1.

Table 1. *Crystal structure determinations of mesogenic materials*

Compound	Phase ^a	Reference
<i>p</i> -Methoxybenzoic acid ^b	<i>I</i>	Bryan (1967)
Anisaldazine	<i>N</i>	Galigné & Falgueirettes (1968)
<i>p</i> -Azodiphenetole	<i>N</i> _{SC}	Galigné & Falgueirettes (1969)
Benzylideneaniline- <i>p</i> -carboxylic acid	<i>N</i>	Galigné (1970)
<i>p</i> -Azoxyanisole	<i>N</i>	Bürgi & Dunitz (1970)
Ethyl <i>p</i> -azoxybenzoate	<i>S</i> _A	Krigbaum, Chatani & Barber (1970)
2,2'-Dibromo-4,4'-bis-(<i>p</i> -methoxybenzylideneamino)biphenyl	<i>N</i>	Carlisle & Smith (1971)
		Krigbaum & Barber (1971)
		This paper

(*a*) The first phase obtained on heating the solid phase; *I*=isotropic, *N*=nematic, *N*_{SC}=skewed cybotactic nematic, *S*_A=smectic *A*. (*b*) Although this compound does not exhibit liquid crystallinity, higher homologs do.

The aim of the present study is to determine the crystal structure of the nematogenic compound 2,2'-dibromo-4,4'-bis-(*p*-methoxybenzylideneamino)biphenyl, $\text{CH}_3\text{-O-C}_6\text{H}_4\text{-CH=N-C}_6\text{H}_3\text{Br-C}_6\text{H}_3\text{Br-N=CH-C}_6\text{H}_4\text{-O-CH}_3$. The presence of the 2,2'-substituents

causes a large decrease in the liquid crystalline thermal stability relative to the unsubstituted compound. This decrease is attributed to the substituents causing an increased angle between the benzene rings of the biphenyl moiety of the molecule (Byron, Gray, Ibbotson & Worrall, 1963). The present study allows a determination of this angle, and an analysis of its possible influence on the stability of the nematic phase. The molecule contains two Schiff's base groupings, for which Bürgi & Dunitz (1970) found a large angle between the planes of the two benzene rings in a nematogenic compound. It has been suggested (*e.g.*, Bernal & Crowfoot, 1933; Gray, 1962) than an 'imbricated packing', *i.e.*, a molecular arrangement in which the end of one molecule is near the middle of its neighbor, is necessary for the formation of a nematic mesophase. Since the compound discussed in this paper is nematogenic, its crystal structure determination should be relevant to these questions.

Experimental

Crystals of 2,2'-dibromo-4,4'-bis-(*p*-methoxybenzylideneamino)biphenyl, prepared by Lee (1967), were recrystallized from chlorobenzene by cooling. The crystal data are in Table 2. The unit-cell dimensions were obtained by least-squares refinement of 67 accurately centered reflections on an off-line Siemens four-circle single-crystal diffractometer (AED) using Ni-filtered Cu $K\alpha$ radiation.

Table 2. *Crystal data*

2,2'-Dibromo-4,4'-bis-(*p*-methoxybenzylideneamino)-biphenyl, $\text{C}_{28}\text{H}_{22}\text{N}_2\text{O}_2\text{Br}_2$, M.W. 578.32
Triclinic, $P\bar{1}$
 $a=7.631$ (7), $b=11.55$ (2), $c=15.99$ (3) Å
 $\alpha=114.39$ (4), $\beta=105.58$ (2), $\gamma=92.16$ (4)°, $V=1218.27$ Å³
 $D_{\text{obs}}=1.61$ g cm⁻³ ($n\text{-C}_6\text{H}_{14}$ and CCl_4), $D_{\text{calc}}=1.57$ g cm⁻³,
 $Z=2$, μ for Cu $K\alpha=52$ cm⁻¹
 $F(000)=580$, $(\sin \theta/\lambda)_{\text{max}}=0.610$ Å⁻¹

The intensities of 3688 independent reflections were collected in the range $0^\circ \leq \theta \leq 70^\circ$. The data were collected by the θ - 2θ coupled scan technique using the five-values measurement on the Siemens AED at an individually predetermined rate per reflection so that the statistical error for all reflections was approximately constant at about 1% (Killeen, 1967). The widths of the scans were calculated as a function θ , to accommodate the increase in the reflection width with θ .

The intensities of five reference reflections were measured every 100 reflections throughout the data collection to monitor the crystal stability. These reflections were also used to indicate the adjustments necessary to keep the crystal properly aligned during data collection. Plots of the intensities of the five reference reflections against time indicate a small, but definite, fall-off in intensity ($3.0 \pm 0.4\%$) over the time period of the data collection. The slopes of the five plots agree quite well with each other, and the average slope was used to correct the intensities of all the reflections with respect to the time of their measurement.

Reflections for which a negative net intensity was obtained were considered unobserved and given zero intensity. After correction for the intensity fall-off, the intensities were corrected with the Lorentz-polarization factor. The absorption correction ($\mu = 52 \text{ cm}^{-1}$) was made because of the 'plate' shape ($0.25 \times 0.20 \times 0.05 \text{ mm}$) of the crystal (de Meulenaer & Tompa-Alcock, 1969).

Determination and refinement of the structure

The structure was solved by the heavy-atom method in the assumed space group $P\bar{1}$. The positions of all atoms except hydrogen were refined with a modified version of the Oak Ridge least-squares program, *ORFLS*, with atomic scattering factors from *International Tables for X-ray Crystallography* (1962). The function minimized was $\sum w(|F_o| - |F_c|)^2$ and two R values were calculated: a conventional R , $R = (\sum |F_o| - |F_c|) / \sum |F_o|$ and a weighted R , $R' = \{[\sum w(|F_o| - |F_c|)^2] / [\sum w|F_c|^2]\}^{1/2}$. A full-matrix refinement with isotropic

temperature factors and $w=1$ for all reflections led to $R=22.1\%$ and $R'=18.4\%$. Several more cycles of refinement using anisotropic temperature factors in a block-diagonal least-squares approximation yielded $R=11.8\%$ and $R'=11.1\%$.

The initial weighting scheme of equal weights was then replaced with a set of calculated weights which were based on the estimates of the standard deviations derived from the counting statistics of each intensity measurement. The weights were calculated as the reciprocal of the square of the standard deviation in the structure factor, σ_F . This standard deviation was calculated with the following formula from Stout & Jensen (1968):

$$\sigma_F = \frac{1}{2} \frac{k}{\sqrt{Lp}} \sqrt{\frac{[\sigma^2(N) + (0.01I_{NET})^2]}{I_{NET}}}$$

where k = scale factor, Lp = Lorentz-polarization factor, $\sigma(N)$ = standard deviation in the count, I_{NET} = net observed intensity. The $(0.01I_{NET})^2$ term is an additional error included to allow for instrumental instability. Zero and negative net intensities were adjusted as follows for use in the determination of the weight: If the sum of the calculated intensity and observed intensity was greater than 1, I_{NET} was set equal to half of the sum. If the sum was less than 1, I_{NET} was set equal to $\frac{1}{2}$.

Anomalous dispersion corrections for the bromines were included using the data from *International Tables for X-ray Crystallography* (1962) and a program by Shiono (1970).

A difference Fourier map showed well defined electron density peaks in ten locations that agreed well with expected positions of hydrogen atoms. Only the hydrogen atom coordinates were refined, the temperature factors being held constant at the Wilson-plot value. Refinement of all parameters (excluding hydrogen temperature parameters) was continued until shifts were less than 0.1σ (σ = estimated error of each parameter). A final difference Fourier map yielded no other appreciable electron density.

The final R and R' values were 4.6% and 6.3%,

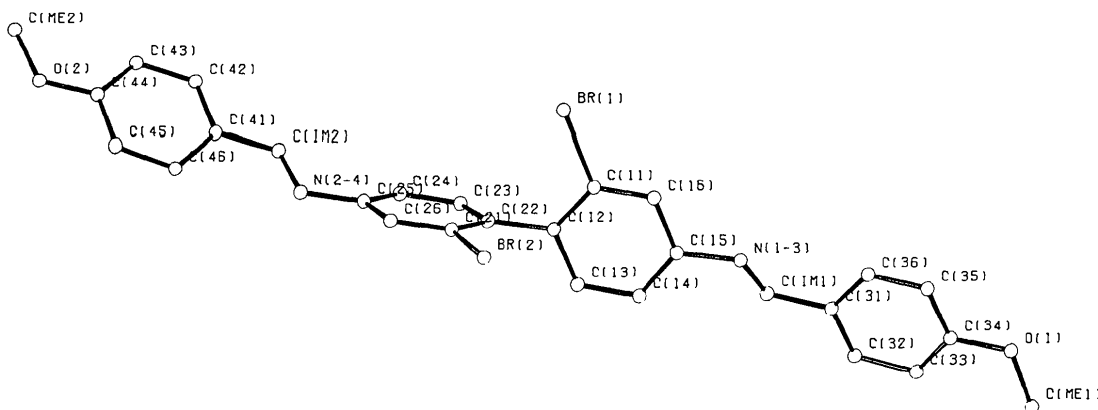


Fig. 1. Atomic nomenclature (hydrogen atoms are omitted for clarity).

Table 3. *Final atomic parameters*

Estimated standard deviations for last decimal given in parentheses.
(Coordinates $\times 10^4$; thermal parameters $\times 10^4$.)

	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br(1)	1703 (1)	1489 (1)	63 (1)	223 (1)	162 (1)	47 (1)	-6 (1)	40 (1)	37 (1)
Br(2)	4619 (1)	5012 (1)	1335 (1)	281 (1)	101 (1)	47 (1)	58 (1)	17 (1)	31 (1)
N(1-3)	7336 (5)	3897 (4)	4208 (2)	220 (9)	88 (5)	34 (2)	8 (5)	17 (3)	24 (2)
N(2-4)	3720 (5)	958 (4)	7094 (2)	182 (8)	96 (5)	32 (2)	16 (5)	24 (3)	18 (2)
C(Im1)	8619 (6)	3509 (5)	4664 (3)	184 (10)	93 (6)	37 (2)	-10 (6)	11 (4)	25 (3)
C(Im2)	4511 (6)	1532 (5)	6730 (3)	174 (9)	90 (5)	36 (2)	27 (6)	31 (6)	20 (3)
O(1)	21 (5)	4788 (4)	8596 (2)	282 (9)	158 (5)	40 (2)	78 (6)	33 (3)	42 (3)
O(2)	1577 (5)	502 (4)	2831 (2)	271 (9)	151 (5)	44 (2)	-17 (5)	17 (3)	47 (3)
C(Me1)	862 (8)	3939 (7)	8979 (4)	302 (15)	208 (10)	60 (3)	96 (10)	38 (6)	83 (5)
C(Me2)	2267 (10)	1279 (7)	2443 (4)	448 (20)	171 (9)	58 (3)	-15 (11)	48 (7)	70 (5)
C(11)	5683 (6)	3866 (4)	1827 (3)	158 (9)	82 (5)	37 (2)	25 (5)	19 (4)	25 (3)
C(12)	5940 (6)	2671 (5)	1192 (3)	165 (9)	85 (5)	32 (2)	20 (5)	18 (4)	20 (3)
C(13)	6754 (7)	1876 (5)	1591 (3)	294 (13)	85 (6)	40 (2)	49 (7)	20 (5)	25 (3)
C(14)	7243 (8)	2244 (5)	2584 (3)	294 (13)	86 (6)	40 (2)	34 (7)	8 (5)	24 (3)
C(15)	6956 (6)	3451 (5)	3194 (3)	173 (9)	87 (5)	33 (2)	6 (6)	15 (4)	23 (3)
C(16)	6154 (6)	4265 (5)	2817 (3)	153 (9)	88 (5)	36 (2)	5 (5)	13 (4)	23 (3)
C(21)	3559 (6)	1687 (4)	9525 (3)	160 (9)	77 (5)	37 (2)	18 (5)	27 (4)	23 (3)
C(22)	5375 (6)	2223 (4)	127 (3)	183 (10)	69 (5)	34 (2)	25 (5)	19 (4)	17 (3)
C(23)	6706 (6)	2296 (5)	9680 (3)	177 (10)	120 (6)	39 (2)	31 (6)	23 (4)	25 (3)
C(24)	6225 (6)	1873 (5)	8678 (3)	175 (10)	120 (7)	42 (2)	21 (6)	25 (4)	26 (3)
C(25)	4359 (6)	1379 (4)	8111 (3)	188 (9)	74 (5)	30 (2)	18 (5)	21 (4)	15 (3)
C(26)	3047 (6)	1258 (4)	8532 (3)	179 (9)	71 (5)	37 (2)	25 (5)	26 (4)	20 (3)
C(31)	9013 (6)	3878 (6)	5706 (3)	149 (9)	83 (5)	37 (2)	6 (5)	11 (4)	22 (3)
C(32)	144 (6)	3201 (5)	6100 (3)	165 (9)	91 (6)	43 (2)	8 (6)	8 (4)	22 (3)
C(33)	510 (6)	3465 (5)	7073 (3)	168 (9)	96 (6)	42 (2)	12 (6)	13 (4)	26 (3)
C(34)	9745 (6)	4435 (5)	7635 (3)	177 (9)	100 (6)	36 (2)	17 (6)	15 (4)	30 (3)
C(35)	8625 (7)	5157 (5)	7258 (3)	207 (11)	98 (6)	47 (3)	27 (6)	20 (4)	34 (3)
C(36)	8255 (6)	4867 (5)	6285 (3)	207 (10)	90 (6)	41 (2)	23 (6)	25 (4)	31 (3)
C(41)	3811 (6)	1224 (4)	5698 (3)	143 (8)	78 (5)	36 (2)	15 (5)	28 (3)	17 (3)
C(42)	4558 (6)	2015 (5)	5370 (3)	196 (10)	90 (6)	47 (2)	5 (6)	36 (4)	26 (3)
C(43)	3852 (7)	1813 (5)	4399 (3)	210 (11)	101 (6)	51 (3)	10 (6)	42 (4)	36 (3)
C(44)	2399 (6)	803 (5)	3787 (3)	175 (9)	105 (6)	37 (2)	26 (6)	28 (4)	32 (3)
C(45)	1654 (6)	9997 (5)	4096 (3)	195 (10)	110 (6)	42 (2)	-5 (6)	23 (4)	31 (3)
C(46)	2364 (6)	209 (5)	5057 (3)	187 (10)	85 (5)	37 (2)	4 (6)	27 (4)	22 (3)

Table 3 (cont.)

The numbers are those of the carbon atoms to which the hydrogens are attached (all quantities $\times 10^2$).

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
H(13)	68 (1)	9 (1)	11 (1)	5.3
H(14)	80 (1)	15 (1)	28 (1)	5.3
H(16)	59 (1)	53 (1)	34 (1)	5.3
H(23)	83 (1)	29 (1)	2 (1)	5.3
H(Im1)	94 (1)	30 (1)	43 (1)	5.3
H(43)	42 (1)	24 (1)	42 (1)	5.3
H(45)	7 (1)	92 (1)	36 (1)	5.3
H(46)	18 (1)	97 (1)	53 (1)	5.3
H(Me2)	36 (1)	12 (1)	25 (1)	5.3
H(Me2)	20 (1)	22 (1)	28 (1)	5.3

respectively, for all reflections (4.0% and 5.7%, respectively, for observed reflections).*

Final parameters are given in Table 3. The nomenclature for the atoms of the asymmetric unit is given in Fig. 1. Calculated bond lengths and angles are given in Tables 4 and 5.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30711 (26 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Discussion

As can be seen in Fig. 2, the molecules of 2,2'-dibromo-4,4'-bis-(*p*-methoxybenzylideneamino)biphenyl crystallize in an imbricated arrangement with one asymmetric unit consisting of the 'half'* portions of two different molecules. The other asymmetric unit is related to the first by a center of symmetry at the center of the unit cell. The molecular axis is very nearly parallel to the *c* axis of the unit cell.

The relationship between the bromine atoms within the molecule is *cis*. The planes containing bromine and its corresponding phenyl ring form an angle of 80.1° with each other, which agrees well with the value of 75.0° found for 2,2'-dibromobiphenyl by Bastiansen (1950), using gas-phase electron-diffraction measurements. The Br-Br distance of 3.961 ± 0.01 Å agrees well with twice the van der Waals radius of Pauling (1960), 3.90 Å.

The benzene rings on either side of the imidazole linkage are *trans* as would be expected from steric considerations. The two imidazole bond lengths are

* Each molecule can be divided into two halves at the biphenyl bond; however, the two halves are not identical crystallographically.

Table 4. Bond lengths (Å)

Estimated standard deviations for last decimal given in parentheses.

Br(1)—C(11)	1.904 (6)	Br(2)—C(21)	1.894 (5)
C(11)—C(12)	1.394 (8)	C(21)—C(22)	1.399 (7)
C(12)—C(13)	1.396 (7)	C(22)—C(23)	1.407 (7)
C(13)—C(14)	1.398 (7)	C(23)—C(24)	1.402 (7)
C(14)—C(15)	1.399 (8)	C(24)—C(25)	1.412 (7)
C(15)—C(16)	1.391 (7)	C(25)—C(26)	1.380 (6)
C(16)—C(11)	1.389 (7)	C(26)—C(21)	1.387 (7)
C(15)—N(1-3)	1.423 (6)	C(25)—N(2-4)	1.421 (6)
N(1-3)—C(Im1)	1.269 (6)	N(2-4)—C(Im2)	1.273 (6)
C(Im1)—C(31)	1.478 (7)	C(Im2)—C(41)	1.470 (7)
C(31)—C(32)	1.385 (7)	C(41)—C(42)	1.397 (7)
C(32)—C(33)	1.399 (7)	C(42)—C(43)	1.412 (7)
C(33)—C(34)	1.379 (8)	C(43)—C(44)	1.387 (8)
C(34)—C(35)	1.407 (7)	C(44)—C(45)	1.386 (7)
C(35)—C(36)	1.393 (7)	C(45)—C(46)	1.396 (7)
C(36)—C(31)	1.400 (8)	C(46)—C(41)	1.395 (8)
C(34)—O(1)	1.370 (6)	C(44)—O(2)	1.372 (6)
O(1)—C(Me1)	1.442 (7)	O(2)—C(Me2)	1.437 (7)
C(12)—C(22)	1.489 (7)		

equal, 1.269 and 1.273 Å, and agree well with the values obtained for the same bond in benzylideneaniline-*p*-carboxylic acid and *p*-methylbenzylidene-*p*-nitroaniline (Bürgi & Dunitz, 1970), 1.281 and 1.269 Å respectively. A value of 1.237 Å is reported for this bond in benzylideneaniline (Bürgi & Dunitz, 1970). This low value may be the result of the absence of substituents on the rings. The angle between the normals to the planes of the benzene rings is 16.6° in one half of the asymmetric unit (between ring 1 and ring 3) and 39.1° in the other half (between ring 2 and ring 4; for ring numbering see Fig. 3). These angles are less than the values for the compounds discussed above, 54.8, 58.3 and 65.5°, respectively. The effect of these smaller angles is to give each half of the molecule approximate planarity. The plane of one half of the molecule is nearly perpendicular to the plane of the other half. This, coupled with the imbrication of the molecules, causes each half portion of one molecule to be

Table 5. Bond angles (°)

Estimated standard deviations for last decimal given in parentheses.

Br(1)—C(11)—C(12)	119.6 (3)	Br(2)—C(21)—C(22)	119.8 (3)
Br(1)—C(11)—C(16)	117.6 (4)	Br(2)—C(21)—C(26)	117.6 (4)
C(11)—C(12)—C(13)	117.3 (4)	C(21)—C(22)—C(23)	117.1 (4)
C(12)—C(13)—C(14)	121.5 (5)	C(22)—C(23)—C(24)	121.4 (4)
C(13)—C(14)—C(15)	119.2 (5)	C(23)—C(24)—C(25)	118.9 (4)
C(14)—C(15)—C(16)	120.6 (4)	C(24)—C(25)—C(26)	120.4 (4)
C(15)—C(16)—C(11)	118.6 (4)	C(25)—C(26)—C(21)	119.4 (4)
C(16)—C(11)—C(12)	122.8 (5)	C(26)—C(21)—C(22)	122.6 (4)
C(14)—C(15)—N(1-3)	123.7 (5)	C(24)—C(25)—N(2-4)	123.4 (4)
C(16)—C(15)—N(1-3)	115.6 (4)	C(26)—C(25)—N(2-4)	116.2 (4)
C(15)—N(1-3)—C(Im1)	119.3 (4)	C(25)—N(2-4)—C(Im2)	118.7 (4)
N(1-3)—C(Im1)—C(31)	121.9 (5)	N(2-4)—C(Im2)—C(41)	121.4 (4)
C(Im1)—C(31)—C(32)	118.0 (4)	C(Im2)—C(41)—C(42)	118.7 (5)
C(Im1)—C(31)—C(36)	121.6 (4)	C(Im2)—C(41)—C(46)	121.5 (4)
C(31)—C(32)—C(33)	120.9 (5)	C(41)—C(42)—C(43)	120.9 (5)
C(32)—C(33)—C(34)	118.3 (5)	C(42)—C(43)—C(44)	117.6 (5)
C(33)—C(34)—C(35)	121.9 (4)	C(43)—C(44)—C(45)	122.3 (4)
C(34)—C(35)—C(36)	118.9 (5)	C(44)—C(45)—C(46)	119.4 (5)
C(35)—C(36)—C(31)	119.6 (5)	C(45)—C(46)—C(41)	120.0 (5)
C(36)—C(31)—C(32)	120.3 (4)	C(46)—C(41)—C(42)	119.7 (4)
C(35)—C(34)—O(1)	114.5 (4)	C(45)—C(44)—O(2)	113.9 (5)
C(33)—C(34)—O(1)	123.5 (4)	C(43)—C(44)—O(2)	123.8 (5)
C(34)—O(1)—C(Me1)	116.9 (4)	C(44)—O(2)—C(Me2)	118.0 (5)
C(11)—C(12)—C(22)	112.9 (4)	C(21)—C(22)—C(12)	122.9 (4)
C(13)—C(12)—C(22)	119.8 (4)	C(23)—C(22)—C(12)	119.9 (4)

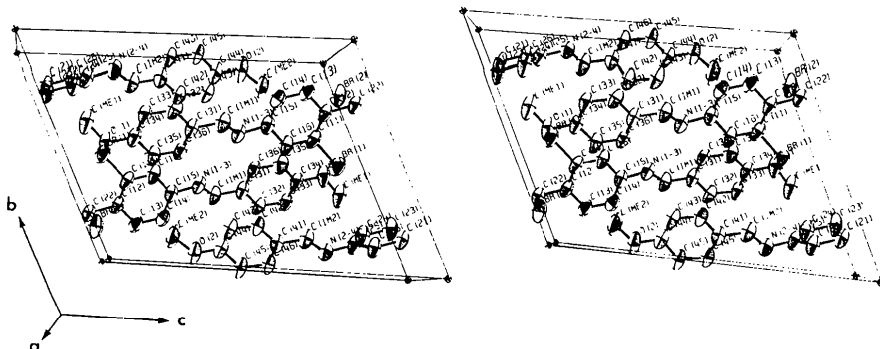


Fig. 2. Stereoscopic drawing of the unit cell (hydrogen atoms are omitted for clarity).

approximately perpendicular to the corresponding half portion of its neighbor molecule. The resultant effect is a 'herringbone' packing of the benzene rings in planes perpendicular to the molecular axes, with the principal intermolecular van der Waals contacts between the hydrogens of the benzene rings of one molecule and the π -electron clouds of the benzene rings of the neighbor molecules. All intermolecular contacts (excluding hydrogens) are greater than 3.5 Å.

The average bond length and angle for each of the benzene rings are given below:

- Ring 1 C(11) through C(16) 1.394 (4) Å; 120.0 (2.0)°
 Ring 2 C(21) through C(26) 1.397 (12); 120.0 (1.9)°
 Ring 3 C(31) through C(36) 1.393 (10); 120.0 (1.1)°
 Ring 4 C(41) through C(46) 1.395 (9); 120.0 (1.6)°

The range of individual bond lengths (1.379–1.412; Table 4) is within experimental error, but does not rule out a possible systematic relationship indicated by the good agreement between corresponding bond lengths in the two halves of the molecule. For the individual bond angles, the range (117.1–122.8; Table 5) is twice the experimental error and again the corresponding angles in the two halves of the molecule agree quite well.

Table 6 lists the deviations in Å from several least-squares planes [calculated according to Schomaker, Waser, Marsh & Bergman (1959)], and also the equations of these planes.

Each of the four benzene rings is planar with no significant deviations; the deviations found are comparable to those for the benzene rings in the nematic compound benzylideneaniline-*p*-carboxylic acid.

Other least-squares planes were also calculated. The atoms included in these planes are identified by the circles in Fig. 3. The imidazole linkages form planes *B* and *E*. The deviations from these two planes are consistent within each plane and seem to indicate, in addition to the twist of the two adjacent benzene rings, that there are bends in the molecule at these points. The planes *A*, *F* and *C*, *D* are the benzene rings 3, 4 and 1, 2 with the methoxy groups and the bromine atoms added, respectively. The 'bromine' planes are found to be approximately planar, with Br(2) being farther from ring 2 than Br(1) is from ring 1.

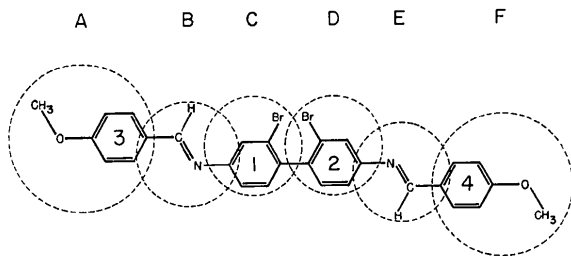


Fig. 3. Least-squares planes. The circles indicate which atoms are used to determine best-fit planes. (Most hydrogen atoms are omitted for clarity.)

Table 6. *Least-squares planes*

Deviations in Å for planes 2, <i>A</i> , <i>B</i> , <i>D</i> , <i>E</i>						
Plane	Atoms included	Deviation from plane	Plane	Atoms included	Deviation from plane	
2	C(21)	+0.003	<i>D</i>	Br(2)	+0.018	
	C(22)	-0.012		C(21)	-0.014	
	C(23)	+0.006		C(22)	-0.022	
	C(24)	+0.009		C(23)	+0.010	
	C(25)	-0.019		C(24)	+0.021	
	C(26)	+0.012		C(25)	-0.015	
<i>B</i>	C(15)	+0.019	<i>E</i>	C(25)	-0.031	
	N(1-3)	-0.018		N(2-4)	+0.029	
	C(Im1)	-0.020		C(Im2)	+0.033	
	C(31)	+0.019		C(41)	-0.031	
<i>A</i>	C(31)	+0.045				
	C(32)	-0.021				
	C(33)	-0.053				
	C(34)	-0.043				
	C(35)	-0.006				
	C(36)	+0.045				
	O(1)	-0.085				
	C(Mel)	+0.125				

Ring 1: $0.9207x + 0.3744y + 0.1101z = 4.6562$
 Ring 2: $0.2239x - 0.9672y - 0.1198z = 2.3546$
 Ring 3: $0.7689x + 0.5936y + 0.2377z = 5.4410$
 Ring 4: $-0.7697x + 0.5904y + 0.2428z = 0.2144$

B: $0.7000x - 0.6968y - 0.1563z = 0.7320$
E: $0.6214x + 0.7597y + 0.1917z = 4.5331$
A: $-0.7695x + 0.5896y + 0.2455z = 0.2351$
F: $0.7791x + 0.5681y + 0.2651z = 5.7273$
C: $0.2329x + 0.9646y - 0.1240z = 2.2897$
D: $0.9218x + 0.3714y + 0.1114z = 4.6595$

Interplanar angles (°)

1 \wedge 2	+80.1	2 \wedge 3	+64.7		
1 \wedge 3	-16.6	2 \wedge 4	+39.1		
1 \wedge 4	+62.3	3 \wedge 4	+78.8		
<i>A</i> \wedge <i>B</i>	+14.9	<i>B</i> \wedge <i>C</i>	-28.4	<i>C</i> \wedge <i>E</i>	+68.3
<i>A</i> \wedge <i>C</i>	+16.4	<i>B</i> \wedge <i>D</i>	+52.8	<i>C</i> \wedge <i>F</i>	+62.1
<i>A</i> \wedge <i>D</i>	-66.9	<i>B</i> \wedge <i>E</i>	+83.3	<i>D</i> \wedge <i>E</i>	+31.2
<i>A</i> \wedge <i>E</i>	+83.5	<i>B</i> \wedge <i>F</i>	-89.8	<i>D</i> \wedge <i>F</i>	+39.1
<i>A</i> \wedge <i>F</i>	+77.9	<i>C</i> \wedge <i>D</i>	+81.0	<i>E</i> \wedge <i>F</i>	+9.0

Deviations for planes 1, 3, 4, *C* and *F* were less than ± 0.010 Å.

50% probability thermal ellipsoids were calculated and plotted in a stereoscopic drawing, Fig. 2 (see also Fig. 1). The long axes of the thermal ellipsoids of nearly all the atoms are roughly perpendicular to the long axis of the molecule. Thus, on the average, the atoms in the molecule undergo greater transverse motion than along the molecular axis. The sizes of all the thermal ellipsoids are approximately the same.

The results of the present work are consistent with the view that imbricated packing condition is a necessary condition for a compound to form a nematic liquid crystal. The large interplanar angle is consistent with the explanation that it is an increased interplanar angle that causes the decrease in mesomorphic stability of the 2,2'-substituted derivative relative to the unsubstituted parent, which is believed to be parallel or nearly

so. No definite trends can be seen yet for the Schiff's base grouping since the angle values from the present work differ substantially from the previous work (Bürgi & Dunitz, 1970).

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The Structure of the Tripeptide L-Alanyl-L-alanyl-L-alanine

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The tripeptide L-alanyl-L-alanyl-L-alanine, a competitive inhibitor of the enzyme elastase, crystallizes from a water/dimethylformamide solution as a hemihydrate ($C_9H_{17}N_3O_4 \cdot \frac{1}{2}H_2O$). The unit-cell parameters are $a = 18.513$ (8), $b = 5.330$ (3), $c = 24.775$ (10) Å, $\beta = 98.64$ (4)°. The space group is $C2$ with $Z = 8$ (two molecules per asymmetric unit). The data were collected on a four-circle diffractometer and the structure was solved by direct methods and refined to $R = 0.031$. The tri-L-alanine molecules are packed in an anti-parallel pleated-sheet arrangement. Precise molecular and conformational parameters are given.

Introduction

The tripeptide L-alanyl-L-alanyl-L-alanine (AAA) has been found to be an effective competitive inhibitor of the esterolytic activity of the pancreatic enzyme elastase (Dzialoszynski & Hofmann, 1973). Shotton, White & Watson (1971) have studied the crystal structure of the tri-L-alanine–elastase complex at 3.5 Å

resolution. Their difference electron-density map shows firstly that tri-L-alanine binds with almost full occupancy near the catalytic site of elastase and, secondly, that there are no secondary binding sites. In this paper we present precise molecular and conformational parameters for tri-L-alanine which may be of use in interpreting substrate–enzyme interactions for the tri-L-alanine–elastase complex as well as furnishing