

Structures of 3,6-Bis(3-chlorophenyl)pyrrolo[3,4-*c*]pyrrole-1,4-dione and 3,6-Bis(4-chlorophenyl)pyrrolo[3,4-*c*]pyrrole-1,4-dione

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Abstract

The crystal data of 3,6-bis(3-chlorophenyl)pyrrolo[3,4-*c*]pyrrole-1,4-dione (abbreviated to *m*-Cl-DPP) are: $C_{18}H_{10}Cl_2N_2O_2$, $M_r = 357.196$, triclinic, $P\bar{1}$, $a = 3.785$ (1), $b = 6.845$ (1), $c = 14.485$ (2) Å, $\alpha = 100.79$ (1), $\beta = 97.60$ (1), $\gamma = 80.91$ (1)°, $V = 362.0$ (2) Å³, $Z = 1$, $D_x = 1.638$, $D_m = 1.629$ Mg m⁻³, graphite-monochromated Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å, $T = 293$ K, $F(000) = 182$, $\mu = 0.460$ mm⁻¹, $R = 0.034$ for 1158 reflections. The crystal data of 3,6-bis(4-chlorophenyl)pyrrolo[3,4-*c*]pyrrole-1,4-dione (abbreviated to *p*-Cl-DPP) are: monoclinic, $P2_1/n$, $a = 5.658$ (1), $b = 23.099$ (3), $c = 5.585$ (1) Å, $\beta = 99.07$ (1)°, $V = 720.8$ (4) Å³, $Z = 2$, $D_x = 1.646$, $D_m = 1.630$ Mg m⁻³, graphite-monochromated Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å, $T = 298$ K, $F(000) = 364$, $\mu = 4.245$ mm⁻¹, $R = 0.08$ for 710 reflections. The molecule has C_i symmetry in both *m*-Cl-DPP and *p*-Cl-DPP. The phenyl rings are twisted, in the same direction, out of the plane of the heterocyclic system, by 10.3 (3)° in *m*-Cl-DPP and 3(2)° in *p*-Cl-DPP. The *m*-Cl-DPP molecules align, due to intermolecular hydrogen bonding, in nearly the same molecular plane and are parallel to each other. In contrast, the *p*-Cl-DPP molecules are arranged in a herringbone fashion. The π - π stacking overlap of adjacent molecules is significant in *m*-Cl-DPP whereas the overlap is quite insignificant in *p*-Cl-DPP. The difference in π - π overlap is well reflected in the optical absorption spectra in the solid state, whereas the solution spectra of these compounds are virtually the same.

Introduction

3,6-Bis(3-chlorophenyl)pyrrolo[3,4-*c*]pyrrole-1,4-dione (abbreviated to *m*-Cl-DPP; Fig. 1) and 3,6-bis(4-chlorophenyl)pyrrolo[3,4-*c*]pyrrole-1,4-dione (abbreviated to *p*-Cl-DPP; Fig. 2) are new heterocyclic pigments of orange-red and red colors, respectively. The latter has been on the market since 1986. These pigments are based on a completely new chromo-

phoric system of pyrrolo[3,4-*c*]pyrrole-1,4-dione (Iqbal, Cassar, Rochat, Pfenninger & Wallquist, 1988).

We have performed a series of investigations on the heterocyclic chromophore of 3,6-diphenylpyrrolo[3,4-*c*]pyrrole-1,4-dione (DPP) on the basis of the structure analysis (Mizuguchi & Wooden, 1991; Mizuguchi & Rihs, 1992; Mizuguchi, Grubenmann,

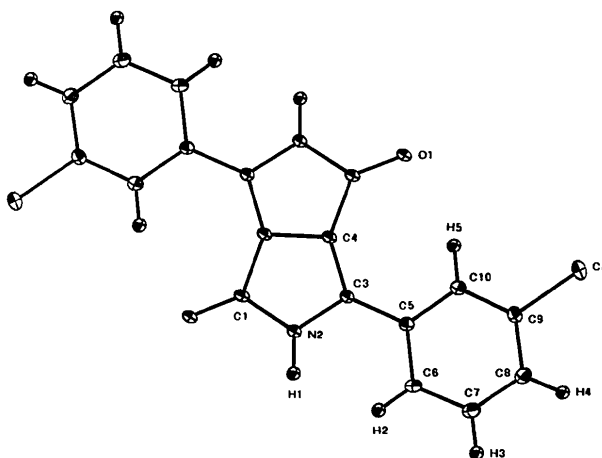


Fig. 1. Conformation of *m*-Cl-DPP.

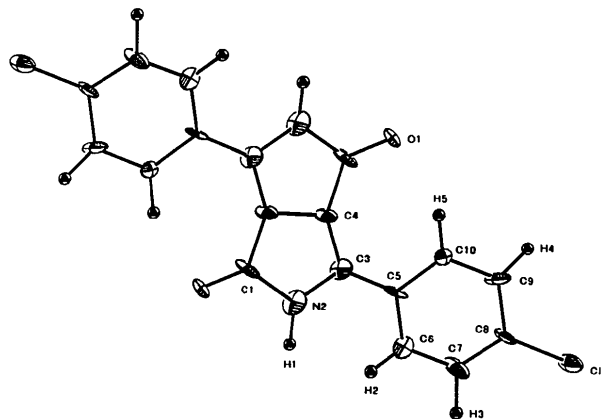


Fig. 2. Conformation of *p*-Cl-DPP. H atoms are not drawn.

Wooden & Rihs, 1992). Attention has been focused on why DPP only appears pale yellow in solution while it is an intense red pigment in the solid state. The optical absorption spectrum in the solid state is very similar in spectral shape to the molecular spectrum in solution, so that a large spectral shift (about 1400 cm^{-1}) is operative on going from solution to the solid state. We have interpreted the present spectral displacement as being due to intermolecular hydrogen bonding, in the solid state, between the NH group of one molecule and the oxygen of the neighboring molecule (Mizuguchi & Wooden, 1991).

The question arises as to why the color of *m*-Cl-DPP (orange-red) in the solid state is different from that of *p*-Cl-DPP (red), although the optical absorption spectra of these compounds look very similar in solution. This is obviously not explicable in terms of the intermolecular hydrogen bonding described above, and another intermolecular interaction must be taken into account. π - π interactions along the molecular stacking axis were therefore considered, thus requiring the present structural analyses. The results show that the strong π - π interaction in *m*-Cl-DPP perturbs the molecular-like spectrum of *p*-Cl-DPP and is responsible for the different color.

Experimental

m-Cl-DPP and *p*-Cl-DPP were synthesized from 3-chlorobenzonitrile and 4-chlorobenzonitrile, respectively, together with dimethyl succinate (Rochat, Cassar & Iqbal, 1986). Single crystals of *m*-Cl-DPP and *p*-Cl-DPP were grown from the vapor phase by means of a two-zone furnace (568/533 K) using argon as the gaseous carrier (Mizuguchi, 1981). The dimensions of the single crystals were: $0.6 \times 0.1 \times 0.005$ mm in *m*-Cl-DPP and $0.71 \times 0.43 \times 0.005$ mm in *p*-Cl-DPP.

The crystal structures were analyzed at 293 K by means of a Philips PW1100 four-circle diffractometer: with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71069\text{ \AA}$) for *m*-Cl-DPP and with graphite-monochromated Cu $K\alpha$ radiation ($\lambda = 1.54178\text{ \AA}$) for *p*-Cl-DPP. θ - 2θ scans. Unit-cell dimensions: *m*-Cl-DPP, from 25 reflections ($15 < \theta < 22^\circ$); *p*-Cl-DPP, from 25 reflections ($20 < \theta < 30^\circ$). 2221 independent reflections were obtained for *m*-Cl-DPP in the range $6 < 2\theta < 60^\circ$ and 1126 independent reflections in the range $6 < 2\theta < 123^\circ$ for *p*-Cl-DPP. Among these 1158 and 710 reflections with $I > 3\sigma(I)$ were used for structure refinement for *m*-Cl-DPP and *p*-Cl-DPP, respectively. Corrections for absorption and secondary extinction were not applied. Three standard reflections monitored every 2 h during data collection showed no significant change in intensity. The densities of the single crystals were measured by flotation in a mixture of chloroform and methylene

Table 1. *Positional and isotropic displacement parameters with e.s.d.'s in parentheses for m-Cl-DPP*

Starred atoms were refined isotropically. Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Cl1	0.0646 (2)	0.2898 (1)	0.41139 (6)	0.0451 (1)
O1	0.9164 (5)	-0.3628 (3)	-0.0991 (1)	0.0331 (1)
N2	0.7119 (6)	-0.2721 (3)	0.0490 (1)	0.0260 (1)
C1	0.7526 (7)	-0.2390 (3)	-0.0414 (2)	0.0251 (1)
C3	0.5228 (7)	-0.1070 (3)	0.1014 (2)	0.0232 (1)
C4	0.4333 (7)	0.0371 (3)	0.0447 (2)	0.0228 (1)
C5	0.4513 (7)	-0.1077 (4)	0.1973 (2)	0.0239 (1)
C6	0.5205 (7)	-0.2855 (4)	0.2354 (2)	0.0294 (1)
C7	0.4435 (8)	-0.2827 (4)	0.3267 (2)	0.0347 (1)
C8	0.3031 (7)	-0.1056 (4)	0.3824 (2)	0.0328 (1)
C9	0.2399 (7)	0.0673 (4)	0.3428 (2)	0.0295 (1)
C10	0.3076 (7)	0.0716 (4)	0.2519 (2)	0.0276 (1)
H1	0.801 (9)	-0.392 (5)	0.071 (3)	0.0514 (8)*
H2	0.617 (9)	-0.407 (5)	0.198 (3)	0.0491 (8)*
H3	0.48 (1)	-0.404 (5)	0.352 (3)	0.0592 (9)*
H4	0.251 (9)	-0.103 (5)	0.445 (3)	0.0541 (9)*
H5	0.259 (9)	0.192 (5)	0.227 (3)	0.0491 (8)*

Table 2. *Positional and isotropic displacement parameters with e.s.d.'s in parentheses for p-Cl-DPP*

Starred atoms were refined isotropically. Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Cl1	0.0325 (3)	0.2606 (2)	0.7481 (4)	0.089 (1)
O1	0.9668 (8)	0.5469 (3)	0.2314 (9)	0.042 (1)
N2	0.728 (1)	0.4726 (4)	0.335 (1)	0.089 (1)
C1	0.785 (1)	0.5174 (5)	0.178 (1)	0.065 (1)
C3	0.507 (1)	0.4487 (2)	0.233 (1)	0.073 (1)
C4	0.415 (1)	0.4779 (4)	0.024 (1)	0.033 (1)
C5	0.399 (1)	0.4028 (4)	0.354 (1)	0.049 (1)
C6	0.504 (2)	0.3833 (4)	0.579 (1)	0.049 (1)
C7	0.394 (2)	0.3386 (7)	0.688 (1)	0.090 (1)
C8	0.175 (1)	0.3118 (5)	0.594 (1)	0.060 (1)
C9	0.052 (1)	0.3357 (5)	0.372 (1)	0.073 (1)
C10	0.167 (1)	0.3803 (4)	0.251 (1)	0.037 (1)
H1	0.85 (2)	0.462 (5)	0.49 (2)	0.11 (1)*
H2	0.66 (2)	0.401 (4)	0.66 (2)	0.06 (1)*
H3	0.49 (2)	0.329 (5)	0.87 (2)	0.11 (1)*
H4	-0.12 (2)	0.325 (5)	0.28 (2)	0.09 (1)*
H5	0.07 (1)	0.397 (4)	0.09 (2)	0.05 (1)*

chloride. Crystallographic data are given in the *Abstract*.

Structure determination and refinement

The structures of *m*-Cl-DPP and *p*-Cl-DPP were determined by direct methods using *MULTAN*82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) and *MULTAN*78 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), respectively. The structures were refined on $|F|$ by full-matrix least-squares calculations using the *SDP* package (B. A. Frenz & Associates Inc., 1985).

Refinement was made with anisotropic atomic displacement parameters, neglecting H atoms, up to $R = 0.056$ for *m*-Cl-DPP and $R = 0.081$ for *p*-Cl-DPP. In both structures, five H atoms were then located in difference electron density maps. Final $R = 0.034$,

$wR = 0.036$, $S = 0.40$ for *m*-Cl-DPP. Final $R = 0.080$, $wR = 0.087$, $S = 0.69$ for *p*-Cl-DPP. (The final R value for *p*-Cl-DPP is worse than that of *m*-Cl-DPP because of a relatively high concentration of crystal defects.) Weights of each reflection in refinement were $w = 1/\sigma^2(F_o)$, $\sigma(F_o)$ being the e.s.d. based on counting statistics. $(\Delta/\sigma)_{\max} = 0.01$ for *m*-Cl-DPP and 0.02 for *p*-Cl-DPP. Maximum heights in the final electron density maps were 0.133 for *m*-Cl-DPP and 0.412 e Å⁻³ for *p*-Cl-DPP. Atomic scattering factors for C, N and O were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Final atomic positional and equivalent isotropic displacement parameters appear in Tables 1 and 2.*

Discussion

Molecular geometry

The conformations of *m*-Cl-DPP and *p*-Cl-DPP are shown in Figs. 1 and 2, respectively, where the atoms are represented by displacement ellipsoids according to *ORTEP* (Johnson, 1971). Interatomic distances and bond angles together with their e.s.d.'s for *m*-Cl-DPP and *p*-Cl-DPP are listed in Table 3. The molecules of *m*-Cl-DPP and *p*-Cl-DPP, both of which belong to the point group C_{2v} , are not entirely planar. The phenyl rings are twisted, in the same direction, out of the plane of the heterocyclic system by 10.3 (3)° in *m*-Cl-DPP and by 3 (2)° in *p*-Cl-DPP.

In *m*-Cl-DPP, the interatomic distances H1—H2 and H5—O1 shown in Fig. 1 are 2.08 (6) and 2.34 (4) Å, respectively, and in *p*-Cl-DPP 2.1 (1) and 2.20 (7) Å. These distances are considerably shorter than the sum of the van der Waals radii of the corresponding atoms: 2.4 and 2.6 Å, respectively (Pauling, 1960). The C3—C5 distance of 1.451 (4) Å (Table 3) is considerably shorter than the value expected for a C—C single bond of 1.54 Å (Pauling, 1960). The observed value is even shorter than that of 1.496 (3) Å in biphenyl (Charbonneau & Delugeard, 1976). This indicates that the C3—C5 bond bears some double-bond character.

Arrangement of molecules

Figs. 3 and 4 show stereo diagrams of the crystal structures of *m*-Cl-DPP and *p*-Cl-DPP, respectively. In *m*-Cl-DPP, the molecules align in nearly the same plane and are parallel to each other. Along the $\langle 110 \rangle$ direction in the molecular plane, there are chains of

* Lists of structure factors, anisotropic thermal parameters, and bond lengths and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71295 (43 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SH0037]

Table 3. Bond lengths (Å) and angles (°) with e.s.d.'s in parentheses

			<i>m</i> -Cl-DPP	<i>p</i> -Cl-DPP
C11	C8			1.73 (1)
C11	C9		1.742 (2)	
O1	C1		1.227 (3)	1.23 (1)
N2	C1		1.403 (3)	1.42 (1)
N2	C3		1.390 (3)	1.40 (1)
C1	C4		1.455 (3)	1.47 (1)
C3	C4		1.374 (3)	1.38 (1)
C3	C5		1.451 (4)	1.45 (1)
C4	C4'		1.425 (3)	1.45 (1)
C5	C6		1.403 (4)	1.38 (1)
C5	C10		1.402 (3)	1.44 (1)
C6	C7		1.387 (4)	1.39 (1)
C7	C8		1.394 (4)	1.41 (1)
C8	C9		1.384 (4)	1.43 (1)
C9	C10		1.381 (4)	1.44 (1)
C1	N2	C3	112.3 (2)	108.2 (6)
O1	C1	N2	123.6 (2)	121.1 (6)
O1	C1	C4	132.4 (2)	131.1 (9)
N2	C1	C4	104.0 (1)	107.6 (8)
N2	C3	C4	106.8 (2)	110.0 (6)
N2	C3	C5	121.7 (2)	121.2 (6)
C4	C3	C5	131.5 (2)	128.7 (6)
C1	C4	C3	143.2 (3)	145.8 (8)
C1	C4'	C4	107.3 (2)	105.0 (7)
C3	C4	C4'	109.5 (2)	109.1 (6)
C3	C5	C6	120.8 (2)	120.8 (7)
C3	C5	C10	119.4 (2)	120.3 (6)
C6	C5	C10	119.8 (2)	118.7 (7)
C5	C6	C7	119.6 (2)	118.9 (8)
C6	C7	C8	121.4 (3)	126.0 (8)
C11	C8	C7		124.4 (7)
C11	C8	C9		119.6 (6)
C7	C8	C9	117.5 (3)	115.4 (9)
C11	C9	C8	118.1 (2)	
C11	C9	C10	118.7 (2)	
C8	C9	C10	123.2 (2)	119.2 (7)
C5	C10	C9	118.4 (2)	121.4 (7)

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

intermolecular hydrogen bonds between the NH group of one molecule and the O atom of the neighboring molecule and there are van der Waals contacts along the c axis. In *p*-Cl-DPP, by contrast, the molecules are arranged in a herringbone fashion and are either parallel or almost at right angles along the stacking c axis and there are chains of intermolecular hydrogen bonds along the $\langle 101 \rangle$ direction.

Overlap of the two molecules along the stacking axis is shown in Figs. 5(a) and 5(b) for *m*-Cl-DPP and *p*-Cl-DPP, respectively. Atoms which interact are shown by dotted ellipses. One immediately recognizes a striking difference in the π - π overlap between *m*-Cl-DPP and *p*-Cl-DPP.

Hydrogen bonding

Figs. 3 and 4 show the intermolecular hydrogen bonds between the NH group and the O atom. In the hydrogen bond in *m*-Cl-DPP, the angle NH...O is 166 (2)° and the distances between O/H, N/H and N/O are 1.92 (4), 0.93 (4) and 2.837 (3) Å, respectively. The values for *p*-Cl-DPP are: NH...O = 172 (5)°, and O/H = 1.76 (8), N/H = 1.0 (1) and N/O

= 2.78 (1) Å. It is expected that hydrogen bonding in *p*-Cl-DPP is slightly stronger than in *m*-Cl-DPP, because the N, H and O atoms align more linearly and the N/O distance is shorter in *p*-Cl-DPP than in *m*-Cl-DPP.

A strong intermolecular NH...O bond is generally linear (to within 10°) and the nitrogen/oxygen distance is about 2.8 Å (Pauling, 1960). The hydrogen-bond parameters of *m*-Cl-DPP and *p*-Cl-DPP satisfy these conditions for a strong hydrogen bond. Strong intermolecular hydrogen bonding blocks invasion of solvent between the pigment molecules. In fact, *m*-Cl-DPP and *p*-Cl-DPP are highly insoluble in organic solvents.

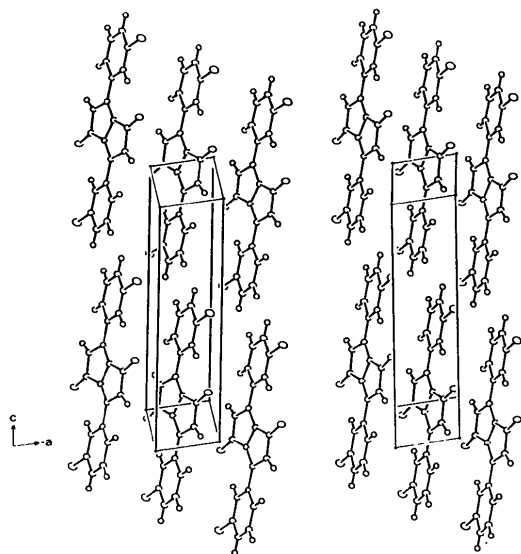


Fig. 3. Stereoview of the crystal structure of *m*-Cl-DPP (triclinic).

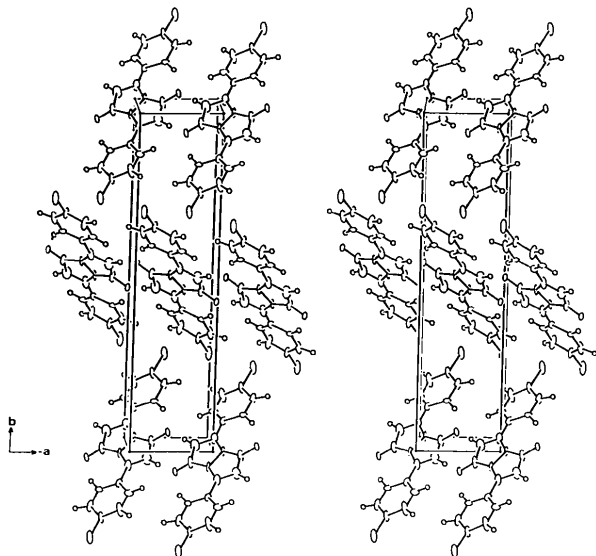


Fig. 4. Stereoview of the crystal structure of *p*-Cl-DPP (monoclinic).

Correlation between π - π interactions and optical absorption spectra in the solid state

The optical absorption spectra of *m*-Cl-DPP and *p*-Cl-DPP in solution look very similar, although the former occurs at slightly shorter wavelengths than the latter by about 5 nm. In the solid state, however, the spectra are different in optical absorption intensities while the peak positions are virtually the same.

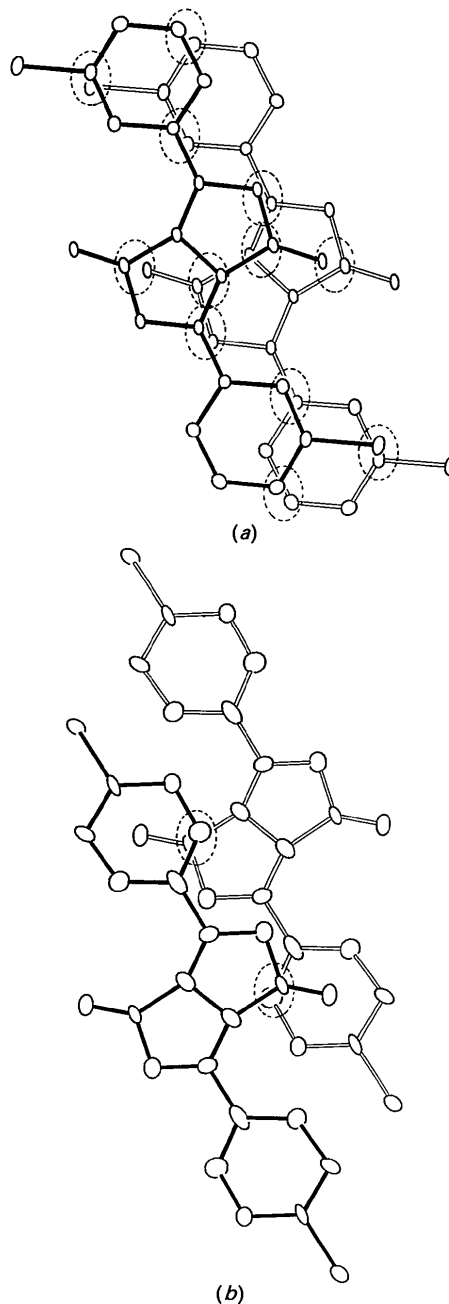


Fig. 5. Overlap of the two molecules: (a) *m*-Cl-DPP along the *a* axis, and (b) *p*-Cl-DPP along the *c* axis. H atoms are not drawn.

There is no significant difference in intermolecular hydrogen bonding between *m*-Cl-DPP and *p*-Cl-DPP as seen in the previous section. A striking difference is, however, found in the π - π overlap along the stacking axis of the molecules (Figs. 5a and 5b). The overlap is quite insignificant in *p*-Cl-DPP, so that the basic molecular absorption characteristics remain almost unchanged even in the solid state. By contrast, the molecular nature of *m*-Cl-DPP is appreciably perturbed by strong π - π interactions in the solid state so as to give a different optical absorption spectrum.

Further details on this subject are given in our previous report (Mizuguchi & Rihs, 1992).

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Structure of the Incommensurate Phase of 4,4'-Dichlorobiphenyl Sulfone at 90 K

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Abstract

The structure of the incommensurate phase of 4,4'-dichlorobiphenyl sulfone, (ClC₆H₄)₂SO₂, has been determined at 90 K using the superspace formalism. Refinement of the atomic modulation, which is of a displacive type, with wavevector $\mathbf{q} = 0.780(2)\mathbf{b}^*$, has been performed in the superspace group $P(I2/a)$: (*s*, -1), using main and first-order satellite reflections. A model of the distortion including zero, first- and second-order harmonics has been considered in the modulation. The final agreement factors are $R = 0.042$, $R_0 = 0.039$ and $R_1 = 0.044$ for all, main and first-order satellite reflections, respectively. Second-order harmonics are critical in the refinement as they decrease the R_1 factor from 0.12 down to 0.043. The primary distortion corresponds to a displacive mode of A_2 symmetry, with atomic displacements reaching up to 0.3 Å. It involves intermolecular librational and translational motions and a significant intra-

molecular twist of the phenyl groups. The secondary distortion given by the second harmonic in the modulation has a much smaller amplitude and includes a slight bending of the molecule. Crystal data of the average structure: $T = 90$ K, $M_r = 287.2$, monoclinic, $I2/a$, $a = 20.20(2)$, $b = 4.910(2)$, $c = 12.054(9)$ Å, $\beta = 90.02(4)$, $V = 1195(2)$ Å³, $Z = 4$, $D_x = 1.597$ Mg m⁻³, $\lambda(\text{Mo K}\alpha) = 0.7107$ Å, $\mu = 0.67$ mm⁻¹, $F(000) = 584$.

1. Introduction

The compound 4,4'-dichlorobiphenyl sulfone, (ClC₆H₄)₂SO₂ (hereafter DCBPS), is currently attracting great interest due to the stability of an incommensurate phase at low temperature. Pusiol, Wolfenson & Brunetti (1989), on the basis of ³⁵Cl NQR measurements, proposed for the first time the incommensurate nature of this phase, which is stable