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Non-mutagenic organic pigment intermediates. II. Isomorphous 2,2′-dichloro-5,5′-dipropoxybenzidine and 2,2′-dimethyl-5,5′-dipropoxybenzidine

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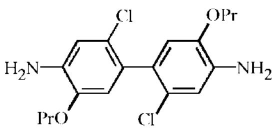
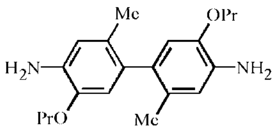
The title compounds, $C_{18}H_{22}Cl_2N_2O_2$ and $C_{20}H_{28}N_2O_2$, respectively, are isomorphous. The molecules lie at general positions in the unit cell. In each structure, chemically equivalent but crystallographically inequivalent amine N atoms exhibit different degrees of pyramidalization. The structures exhibit weak N—H···N hydrogen bonding, which is influenced by the differences in hybridization around the amine N atoms. The torsion angles across the biphenyl linkage for the two compounds are 67.2 (2) and 68.3 (3)°.

Comment

Colorants based on non-mutagenic highly twisted benzidine congeners are expected to be more soluble in organic solvents than the planar derivatives, and produce different color gamuts (Hinks *et al.*, 2000, 2001; Sokolowska *et al.*, 2001). The variety of colors obtained is due to varying degrees of delocalization in the conjugated π system and can be of considerable commercial importance. We have previously reported the structure of 3,3′-dipropoxybenzidene (El-Shafei *et al.*, 2003), which has a negligible twist about the biphenyl linkage. We undertook the X-ray structural investigation of two 2,2′-substituted dipropoxybenzidines to investigate the structural changes induced by the steric hindrance caused by the substituted *ortho* positions. In this paper, we report the structures of two isomorphous 2,2′-substituted benzidines, namely 2,2′-dichloro-5,5′-dipropoxybenzidine, (I), and 2,2′-dimethyl-5,5′-dipropoxybenzidine, (II).



(I)



(II)

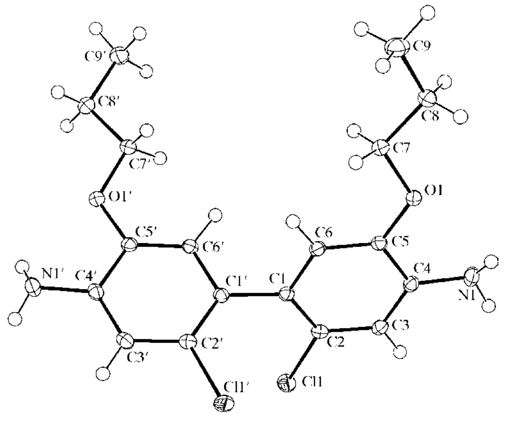


Figure 1
A view of the structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

The molecules of (I) and (II) (Figs. 1 and 2) lie on general positions in the unit cell. As expected, both diamines show appreciable twist across the biphenyl linkage. The C2—C1—C1′—C2′ torsion angle is 67.2 (2)° in (I) and 68.3 (3)° in (II). According to the rules stated by Kitaigorodskii (1965, 1973), chloro–methyl exchange does not change the crystal structure, since the two substituents have nearly the same volume (Cl 20 Å^3 and Me 24 Å^3). As this exchange rule appears to be active in the structures of (I) and (II), it is not surprising that the values of the torsion angles across the biphenyl linkage are similar. In addition, because (I) and (II) are isomorphous, the 'chloro effect' cannot be considered an important packing interaction in (I). It is interesting to note, however, that 2,2′-dichlorobenzidine (Smare, 1948) and 2,2′-dimethylbenzidine (Fowweather, 1952) are not isomorphous, crystallize with different site symmetries and have appreciably different torsion angles across the biphenyl linkage.

In (I), the C4—N1 bond is significantly shorter than the C4′—N1′ bond and this is consistent with delocalization of the lone pair on N1 into the aromatic π system. The same numeric trend is observed in (II), but the greater standard uncertainties associated with those bond lengths preclude making a definitive statement. It is interesting to note that the difference in hybridization between atoms N1 and N1′ is also manifest in their respective hydrogen-bonding properties (see below).

The structures of (I) and (II) show a number of intra- and intermolecular hydrogen bonds (Tables 2 and 4; the geometries are based on normalized N—H bond lengths of 1.01 Å[1]). As with the structure of 3,3′-dipropoxybenzidine, the present two structures show intramolecular hydrogen bonds between the *n*-propoxyl O atom and one of the amino H atoms. Unlike the structure of 3,3′-dipropoxybenzidine, these structures show no N—H···π interactions. However, (I) and (II) show a number of long-range intermolecular interactions involving the amino H atoms and N acceptor atoms. The individual N—

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[1] The normalized N—H length was obtained by searching the Cambridge Structural Database (Allen, 2002) for structures obtained by single-crystal neutron diffraction at 100 K or lower of compounds containing aryl-bound amine groups, and taking the mean of the N—H lengths.

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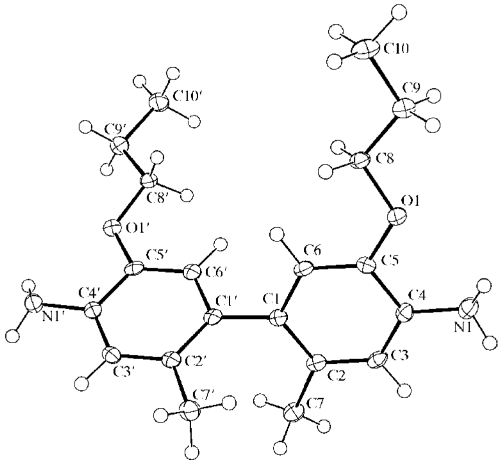

Figure 2
A drawing of the structure of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

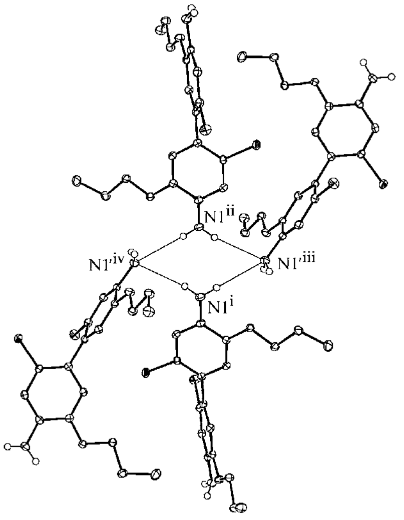

Figure 3
A diagram of the hydrogen-bonding pattern in (I). Displacement ellipsoids are drawn at the 50% probability level. H atoms bound to C atoms have been omitted for clarity, and the remaining H atoms are shown as small spheres of arbitrary radii [symmetry codes: (i) x, y, z; (ii) $1 - x, -y, 1 - z$; (iii) $\frac{3}{2} - x, y - \frac{1}{2}, \frac{3}{2} - z$; (iv) $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$].

H···N motifs form an $R_4^2(8)$ ring, which lies across a crystallographic center of symmetry (Fig. 3). The $R_4^2(8)$ pattern acts as a linkage between molecules, forming an extended two-dimensional network parallel to $(\bar{1}01)$.

A structural correlation study (Allen *et al.*, 1995) has indicated that N—H···N contacts with H···N $\leq$ 2.75 Å, which have $\chi_N \geq 35°$ and the N—H···N donor angle > 130°, can be considered true hydrogen bonds. These criteria were used to assess the long-range N—H···N interactions in (I) and (II). The values of χ_N and τ (χ_N measures the degree of pyramidalization around the amine N atom and τ measures the rotation of the NH_2 plane relative to the aryl plane) for (I) and (II), as well as those for 3,3′-dipropoxybenzidene, are listed in Table 5. As can be seen from Table 5, the N—H···N interactions for (I) and (II) fulfill these criteria. The more highly pyramidalized amine groups (N1′) act as hydrogen-bond acceptors, whereas the less pyramidal amine groups (N1) act as hydrogen-bond donors. Both H atoms on N1 participate in the hydrogen bonding. This is an interesting instance where chemically equivalent amine groups differ in their degree of pyramidalization and adopt different crystallographic functions in the structure.

Finally, it is worth pointing out that the structures of (I) and (II), as well as that of 3,3′-dipropoxybenzidine, highlight the competition between N—H···π and long-range (weak) N—H···N hydrogen bonds. Slight changes in the pyramidalization of the N atoms, as evidenced in the χ_N values, lead to completely different types of intermolecular hydrogen-bonding interactions. The χ_N values listed in Table 5 vary from a minimum of 36.9° in 3,3′-dipropoxybenzidine to a maximum of 53.4° in (II). The N atoms in 3,3′-dipropoxybenzidine are ineffective as hydrogen-bond acceptors, due to their relatively small degree of pyramidalization, and consequently the N—H donors use the aromatic π clouds as acceptors. In contrast, the more highly pyramidalized N atoms in (I) and (II) make marginally acceptable hydrogen-bond acceptors, and the crystal packing takes advantage of this greater basicity.

Experimental

Benzidine analogs (I) and (II) were prepared as previously reported by Hinks *et al.* (2000). Suitable single crystals were produced by dissolving (I) (0.45 g) in ethanol (40 ml) and (II) (0.4 g) in methanol (40 ml), stirring at the boiling point for 2 min, filtering while hot into an Erlenmeyer flask and covering the neck of the flask with perforated Parafilm. The filtrates were then allowed to cool slowly and stand undisturbed for 5 d.

Compound (I)

Crystal data

$C_{18}H_{22}Cl_2N_2O_2$
$M_r = 369.29$
Monoclinic, $P2_1/n$
$a = 7.3054$ (4) Å
$b = 22.7966$ (11) Å
$c = 10.5956$ (8) Å
$\beta = 91.679$ (6)°
$V = 1763.82$ (19) Å^3
$Z = 4$

$D_x = 1.391$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 17.0–18.0°$
$\mu = 0.38$ mm^{-1}
$T = 148$ K
Prism, off-white
0.42 × 0.34 × 0.22 mm

Data collection

Enraf–Nonius CAD-4 MACH diffractometer
ω scans
5099 measured reflections
5089 independent reflections
4464 reflections with $I_{net} > \sigma(I_{net})$
$R_{int} = 0.035$

$\theta_{max} = 30.0°$
$h = -10 \rightarrow 10$
$k = 0 \rightarrow 31$
$l = 0 \rightarrow 14$
3 standard reflections
frequency: 80 min
intensity decay: 2.2%

Refinement

Refinement on F
$R = 0.030$
$wR = 0.039$
$S = 2.56$
4461 reflections
305 parameters

All H-atom parameters refined
$w = 1/[\sigma^2(F) + 0.00007F^2]$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.51$ e Å^{-3}
$\Delta\rho_{min} = -0.27$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

C1—C1′	1.4874 (15)	N1′—C4′	1.4117 (15)
N1—C4	1.3976 (15)	N1′—H1*A*′	0.853 (19)
N1—H1*A*	0.860 (18)	N1′—H1*B*′	0.833 (19)
N1—H1*B*	0.878 (18)		
C4—N1—H1*A*	114.8 (11)	C4′—N1′—H1*A*′	110.4 (12)
C4—N1—H1*B*	115.1 (11)	C4′—N1′—H1*B*′	114.6 (12)
H1*A*—N1—H1*B*	115.1 (16)	H1*A*′—N1′—H1*B*′	113.2 (17)
C2—C1—C1′—C2′	67.20 (16)	C2—C1—C1′—C6′	−115.7 (2)
C6—C1—C1′—C2′	−116.7 (2)	C6—C1—C1′—C6′	60.45 (15)

Table 2
Hydrogen-bonding geometry (Å, °) for (I).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···O1	1.01	2.39	2.6937 (13)	96
N1′—H1*A*′···O1′	1.01	2.30	2.6715 (14)	100
N1—H1*A*···N1′^{i}	1.01	2.59	3.5563 (15)	161
N1—H1*B*···N1′^{ii}	1.01	2.55	3.5492 (15)	169

Symmetry codes: (i) $\frac{3}{2} - x, y - \frac{1}{2}, \frac{3}{2} - z$; (ii) $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$.

Compound (II)

Crystal data

$C_{20}H_{28}N_2O_2$
$M_r = 328.45$
Monoclinic, $P2_1/n$
$a = 7.1703$ (3) Å
$b = 23.0083$ (9) Å
$c = 10.8483$ (6) Å
$\beta = 91.704$ (3)°
$V = 1788.92$ (14) Å^3
$Z = 4$

$D_x = 1.220$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 25 reflections
$\theta = 16.0$–18.0°
$\mu = 0.08$ mm^{-1}
$T = 148$ K
Cut sword, light amber
0.60 × 0.38 × 0.10 mm

Data collection

Enraf–Nonius CAD-4 MACH diffractometer
ω scans
3129 measured reflections
3129 independent reflections
2348 reflections with $I_{\rm net} > \sigma(I_{\rm net})$
$\theta_{\max} = 25.0°$

$h = -8 \rightarrow 8$
$k = 0 \rightarrow 27$
$l = 0 \rightarrow 12$
3 standard reflections
frequency: 80 min
intensity decay: 1.6%

Refinement

Refinement on *F*
$R = 0.051$
$wR = 0.056$
$S = 1.43$
2341 reflections
305 parameters

H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F) + 0.0007F^2]$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.22$ e Å^{-3}
$\Delta\rho_{\min} = -0.25$ e Å^{-3}

The positional and $U_{\rm iso}$ parameters of the N-bound H atoms were allowed to refine. The positional parameters of the C-bound H atoms were allowed to refine while the $U_{\rm iso}$ parameters were constrained to ride on the parent C atom [$U_{\rm iso}({\rm H}) = U_{\rm eq}({\rm C}) + 0.01$ Å^2].

For both compounds, data collection: *CAD*-4 *ARGUS* (Enraf–Nonius, 1994); cell refinement: *CAD*-4 *ARGUS*; data reduction: *DATRD*2 in *NRCVAX* (Gabe *et al.*, 1989); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *LSTSQ* in *NRCVAX*; molecular graphics: *NRCVAX* and *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *TABLES* in *NRCVAX* (January 1994 version).

Table 3
Selected geometric parameters (Å, °) for (II).

C1—C1′	1.497 (3)	C4′—N1′	1.408 (3)
C4—N1	1.397 (3)	N1′—H1*A*′	0.91 (3)
N1—H1*A*	0.95 (4)	N1′—H1*B*′	0.90 (3)
N1—H1*B*	0.90 (3)		
C4—N1—H1*A*	115 (2)	C4′—N1′—H1*A*′	116.6 (17)
C4—N1—H1*B*	116.2 (18)	C4′—N1′—H1*B*′	114.9 (17)
H1*A*—N1—H1*B*	111 (3)	H1*A*′—N1′—H1*B*′	107 (2)
C2—C1—C1′—C2′	68.3 (3)	C2—C1—C1′—C6′	−113.9 (4)
C6—C1—C1′—C2′	−115.0 (4)	C6—C1—C1′—C6′	62.8 (3)

Table 4
Hydrogen-bonding geometry (Å, °) for (II).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···O1	1.01	2.38	2.689 (3)	97
N1′—H1*A*′···O1′	1.01	2.37	2.677 (3)	96
N1—H1*A*···N1′^{i}	1.01	2.69	3.654 (3)	160
N1—H1*B*···N1′^{ii}	1.01	2.52	3.508 (3)	165

Symmetry codes: (i) $\frac{3}{2} - x, y - \frac{1}{2}, \frac{3}{2} - z$; (ii) $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$.

Table 5
Values of χ_N, τ and C—N for (I), (II) and 3,3-dipropoxybenzidine.

	χ_N (°)	τ (°)	C—N (Å)
N1 in (I)	42.8	22.6	1.3976 (15)
N1′ in (I)	50.8	26.9	1.4117 (15)
N1 in (II)	45.3	23.5	1.397 (3)
N1′ in (II)	53.4	28.2	1.408 (3)
3,3′-Dipropoxybenzidine	36.9	19.2	1.3934 (13)

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1327). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Allen, F. H., Bird, C. M., Rowland, R. S., Harris, S. E. & Schwalbe, C. H. (1995). *Acta Cryst.* B**51**, 1068–1081.
Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.
El-Shafei, A., Boyle, P. D., Hinks, D. & Freeman, H. S. (2003). *Acta Cryst.* C**59**, o71–o73.
Enraf–Nonius (1994). *CAD*-4 *ARGUS*. Version of 1994. Enraf–Nonius, Delft, The Netherlands.
Fowweather, F. (1952). *Acta Cryst.* **5**, 820–825.
Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.
Hinks, D., Freeman, H. S., Arai, Y. & Ando, H. (2001). *Dyes Pigm.* **48**, 7–13.
Hinks, D., Freeman, H. S., Nakpathom, M. & Sokolowska, J. (2000). *Dyes Pigm.* **44**, 199–207.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Kitaigorodskii, A. I. (1965). *Acta Cryst.* **18**, 585–590.
Kitaigorodskii, A. I. (1973). *Molecular Crystals and Molecules*. New York: Academic Press.
Smare, D. L. (1948). *Acta Cryst.* **1**, 150–154.
Sokolowska, J., Hinks, D. & Freeman, H. S. (2001). *Dyes Pigm.* **48**, 15–27.