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Non-mutagenic organic pigment intermediates. I. 3,3′-Dipropoxybenzidine

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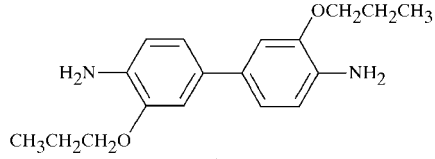
Crystals of the title compound, $C_{18}H_{24}N_2O_2$, were grown from ethanol by slow evaporation and the structure has been determined. The molecule resides on a crystallographic inversion center and the biphenyl moiety is essentially planar. The structure forms an infinite two-dimensional array of N—H···π(arene) interactions parallel to the (101) direction.

Comment

Colorants prepared from certain congeners of benzidine are manufactured on a large scale and are of significant commercial importance worldwide. Unfortunately, these benzidine congeners are genotoxic, and there are occupational and environmental risks associated with their synthesis and use (Freeman *et al.*, 1996). Hence, the development of new non-genotoxic analogs of benzidine-type intermediates of satisfactory technical performance is desirable. Recently, the design, synthesis and genotoxicity of non-mutagenic benzidine congeners (Hunger *et al.*, 1986; Hinks *et al.*, 2000), and their conversion to bis(azomethine) (Hinks *et al.*, 2001) and various bis(azo) pigments (Sokolowska *et al.*, 2001; Nakpathom *et al.*, 2001), have been reported. Efforts have focused toward the development of benzidine-type diamine intermediates that are not only non-mutagenic, but also provide a means of manipulating electronic absorption properties when converted to pigment.

A key factor in establishing structure–activity relationships of pigments and intermediates is the molecular geometry of the pure compound. This has been found to be an important factor when employing semi-empirical or *ab initio* theory to model colorant properties (Lye *et al.*, 1999). Therefore, as part of the study outlined above, we report here the crystal and molecular structure of 3,3′-dipropoxybenzidine, (I).

A view of (I) with the atom-labelling scheme is shown in Fig. 1. The structure contains two molecules in the unit cell. The molecules lie across a crystallographic inversion center which sits at the midpoint of the C1—C1^{i} biphenyl bond [symmetry code: (i) $1-x, -y, 1-z$]. The biphenyl moiety is essentially planar. There is no pronounced anisotropy in the aryl anisotropic displacement parameters, indicating that there is no disorder or dynamic twisting process to accommodate the steric crowding of the *ortho* H atoms of the biphenyl moiety.



(I)

The structure of (I) contains one N—H···O intramolecular hydrogen bond and no conventional intermolecular hydrogen bonds. The intramolecular hydrogen bond is formed between the N-bound H1*B* atom and the O atom of the *n*-propoxy group. The metrics for this interaction are N—H1*B* = 0.887 (19) Å, H1*B*···O = 2.287 (19) Å and N—H1*B*···O = 105.2 (14)°.

Primary amino groups exhibit double-donor–single-acceptor hydrogen-bond functionality. When a structure containing primary amino groups does not have sufficient conventional hydrogen-bond acceptor sites, there is a tendency to form N—H···π hydrogen bonds (Hanton *et al.*, 1992). The structure of (I) exhibits such a deficiency and forms a network of N—H···π(arene) hydrogen bonds. After normalizing the N—H bond lengths to 1.01 Å, the metrics for this interaction are H1*A*···π(arene)$_{cen}$ = 2.42 Å, N···π(arene)$_{cen}$ 3.41 Å and N—H···π(arene)$_{cen}$ = 169.4°. The distance of atom H1*A* from the aryl plane is 2.39 Å. The amino 'edge' of one molecule points to the aryl 'face' of an adjacent molecule to form the N—H···π(arene) interaction. The H···π(arene) vector forms an angle of 81.6° with the acceptor

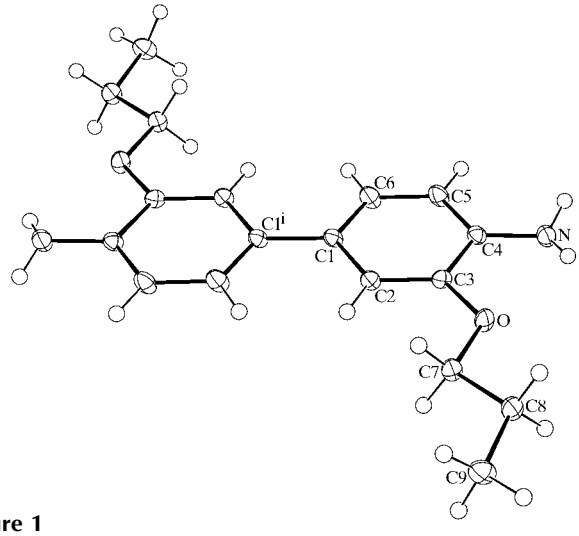


Figure 1
A view of the molecule of (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii [symmetry code: (i) $1-x, -y, 1-z$].

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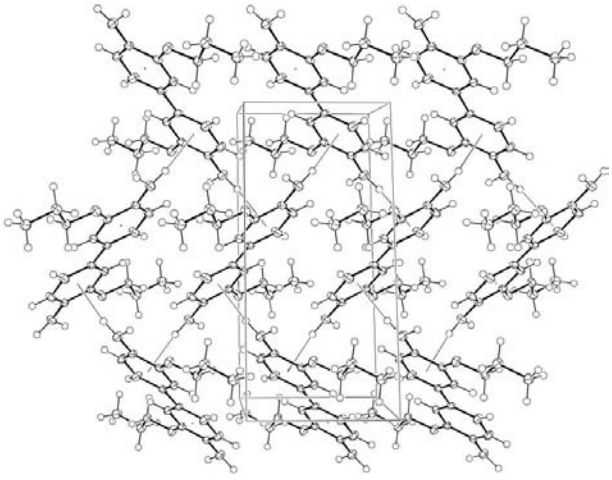

Figure 2
A view of the extended two-dimensional network of N—H···π(arene) hydrogen bonds in (I). The view is approximately down the *a* axis, with *c* running vertically and *b* horizontally to the right. Displacement ellipsoids are shown at the 50% probability level.

aryl plane. These N—H···π(arene) hydrogen bonds form an infinite two-dimensional array of macrocyclic aggregates parallel to the (101) set of planes (Fig. 2). The aryl groups involved in the hydrogen bonding act as single hydrogen-bond acceptors. Considering the centroid to be one 'ring-equivalent' atom, the graph-set designation (Etter *et al.*, 1990; Bernstein *et al.*, 1995) for the macrocyclic system is $R_1^1(20)$.

In the light of these N—H···π(arene) interactions, it is interesting to note that the geometry around the amino N atom in (I), although somewhat pyramidal, is close to sp^2 hybridization. As pointed out by Hanton *et al.* (1992), sp^2 hybridization of such an N atom makes both the amino group a better hydrogen donor and the aryl group a better hydrogen acceptor, because the delocalization of the N-atom lone pair into the aromatic ring system makes it more electron rich. Thus, the structure of (I) seems to be optimized to maximize N—H···π(arene) interactions.

Experimental

Compound (I) was prepared as previously reported by Hinks *et al.* (2000). Suitable single crystals were obtained by dissolving (I) (0.4 g) in ethanol (40 ml), stirring at the boiling point for 2 min, filtering while hot into an Erlenmeyer flask and covering with perforated Parafilm, and then allowing the filtrate to cool slowly and stand undisturbed for 5 d. The solution was checked after 3 d to monitor crystal growth. Appropriate single crystals of (I) were selected for X-ray analysis by examining them under a microscope.

Crystal data

$C_{18}H_{24}N_2O_2$
M_r = 300.40
Monoclinic, $P2_1/n$
a = 9.2522 (6) Å
b = 6.4359 (3) Å
c = 14.0080 (11) Å
β = 105.175 (9)°
V = 805.04 (9) Å^3
Z = 2
D_x = 1.239 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 24 reflections
θ = 16.0–18.0°
μ = 0.08 mm^{-1}
T = 148 K
Prism, light yellow
0.40 × 0.30 × 0.16 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
2322 measured reflections
2319 independent reflections
1934 reflections with $I_{net} > \sigma(I_{net})$
R_{int} = 0.018
θ_{max} = 30°
$h = -12 \rightarrow 12$
$k = 0 \rightarrow 9$
$l = 0 \rightarrow 19$
3 standard reflections
frequency: 80 min
intensity decay: 2.1%

Refinement

Refinement on F
R = 0.039
wR = 0.051
S = 2.15
1928 reflections
149 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F) + 0.0002F^2]$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.37 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O—C3	1.3754 (11)	C2—C3	1.3881 (14)
O—C7	1.4396 (12)	C3—C4	1.4126 (14)
N—C4	1.3934 (13)	C4—C5	1.3921 (14)
C1—C1^{i}	1.4909 (18)	C5—C6	1.3945 (15)
C1—C2	1.4120 (13)	C7—C8	1.5124 (14)
C1—C6	1.3996 (14)	C8—C9	1.5250 (15)
C3—O—C7	117.68 (8)	C2—C3—C4	121.22 (9)
C1^{i}—C1—C2	121.15 (9)	N—C4—C3	119.67 (9)
C1^{i}—C1—C6	121.93 (9)	N—C4—C5	122.86 (9)
C2—C1—C6	116.92 (9)	C3—C4—C5	117.42 (9)
C1—C2—C3	121.35 (9)	C4—C5—C6	121.34 (9)
O—C3—C2	124.84 (9)	O—C7—C8	107.45 (8)
O—C3—C4	113.94 (8)	C7—C8—C9	111.01 (9)

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

H-atom positions were derived from difference Fourier maps, and the H-atom positional and isotropic displacement parameters were included in the refinement; refined distances involving H atoms were C—H = 0.962 (14)–1.013 (12) Å and N—H = 0.867 (17) and 0.884 (18) Å. The calculated structure factors included corrections for anomalous dispersion from the usual tabulation (*International Tables for X-ray Crystallography*, 1974, Vol. IV, Table 2.3.1). An extinction refinement was attempted, but the coefficient refined to within an s.u. of 0.0, and was subsequently removed from the final refinement model.

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: *ORTEP*II (Johnson, 1976) in *NRCVAX*; software used to prepare material for publication: *TABLES* in *NRCVAX*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ1002). Services for accessing these data are described at the back of the journal.

References

Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.

Bernstein, J., Davies, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Enraf–Nonius (1994). *CAD*-4-*ARGUS*. Enraf–Nonius, Delft, The Netherlands.
Etter, M. C., MacDonald, J. C. & Bernstein, J. (1990). *Acta Cryst.* B**46**, 256–262.
Freeman, H. S., Hinks, D. & Esancy, J. (1996). *Physico-Chemical Principles of Color Chemistry*, *Advances in Color Chemistry Series*, edited by A. T. Peter & H. S. Freeman, Vol. 4, pp. 254–292, *Genotoxicity of Azo Dyes: Bases and Implications*. London: Blackie Academic & Professional.
Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.
Hanton, L. R., Hunter, C. A. & Purvis, D. H. (1992). *J. Chem. Soc. Chem. Commun.* pp. 1134–1136.
Hinks, D., Freeman, H. S., Arai, Y. & Ando, H. (2001). *Dyes Pigm.* **48**, 7–13.
Hinks, D., Freeman, H. S. & Lye, J. (1995). American Association of Textile Chemists and Colorists International Conference and Exhibition, Atlanta, Georgia, USA, Book of Papers, pp. 74–85. Raleigh, NC: AATCC.
Hinks, D., Freeman, H. S., Nakpathom, M. & Sokolowska, J. (2000). *Dyes Pigm.* **44**, 199–207.
Hunger, K., Froelich, H., Hertel, H. & Habig, K. C. (1986). German Patent DE 3511544.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Lye, J., Freeman, H. S. & Hinks, D. (1999). *Text. Res. J.* **69**, 583.
Nakpathom, M., Hinks, D. & Freeman, H. S. (2001). *Dyes Pigm.* **48**, 93–106.
Sokolowska, J., Hinks, D. & Freeman, H. S. (2001). *Dyes Pigm.* **48**, 15–27.