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

| D—H···A | D—H | H···A | D···A | D—H···A |
|---|---|---|---|---|
| O3—HO3···N2' | 0.76 (3) | 1.99 (3) | 2.744 (3) | 169 (3) |
| O4—HO4···O2" | 0.81 (3) | 1.70 (3) | 2.513 (2) | 175 (3) |
| N1—H1N1···O1'" | 0.91 (3) | 1.88 (3) | 2.784 (2) | 176 (2) |
| N1—H2N1···O2'ᵛ | 0.89 (3) | 1.85 (3) | 2.731 (2) | 178 (2) |
| N1—H3N1···O1 | 0.84 (3) | 1.97 (3) | 2.809 (3) | 176 (2) |
| N2—H1N2···O1'" | 0.85 (3) | 2.16 (3) | 2.972 (3) | 161 (2) |
| N2—H2N2···O3ᵛ | 0.87 (3) | 2.29 (3) | 3.051 (3) | 147 (2) |

Symmetry codes: (i) $-x, -y, 1 - z$; (ii) $1 + x, y, z$; (iii) $x - 1, y, z$; (iv) $-x, 1 - y, 1 - z$; (v) $-1 - x, -y, 1 - z$.

Data collection: *CAD-4 EXPRESS* (Duisenberg, 1992; Macíček & Yordanov, 1992). Cell refinement: *CAD-4 EXPRESS*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

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# trans-2,2'-Dichloro-4,4'-dimethylazobenzene

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## Abstract

The X-ray crystal structure of the title compound, $C_{14}H_{12}Cl_2N_2$, reveals a *trans* geometry of the two Cl atoms in the *ortho* position with respect to the azo

group. In the crystal packing the aromatic rings are stacked in a herring-bone mode along the *y* direction.

## Comment

Azobenzenes have been extensively used as ligands suitable for investigation on cyclometallated systems (Ryabov, 1990). In the course of our ongoing work on the synthesis and structural characterization studies of cyclopalladated mesogens containing azobenzene ligands (Crispini *et al.*, 1996), the title compound, (I), was synthesized and we report here its crystal structure. The compound was synthesized using 2-chloro-*p*-toluidine and following the synthetic routine recently reported in the literature (Bermídez *et al.*, 1994).



(I)
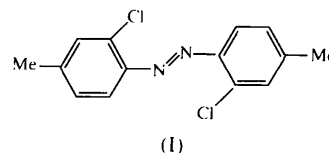
The molecule occupies a special position at an inversion centre and is essentially planar. The torsion angle about the central bond of 180° confirms a *trans* conformation with both aromatic rings in a parallel orientation, typical for stilbenes and diphenylazobenzenes (Bouwstra *et al.*, 1985; Klebe, 1994). Moreover, both these molecules diplay preferences for planarity of the entire Ph—X—X—Ph (X = C, N) fragment, with exceptions, due to the steric repulsion, in examples with non-H atoms at the *ortho* positions. The torsion angles about the N—C bond [N1'—N1—C1—C2 = −166.4 (2) and N1'—N1—C1—C6 = 14.4 (3)°] are comparable with the corresponding values of the related compound *trans*-2,2'-dichloroazobenzene [168.5 and −14.3°] (Komeyama *et al.*, 1973) and greater than values found for 4,4'-disubstituted azobenzenes like 4,4'-azodiphenetole (175.0, −171.7 and 7.7, −6.4°) (Galigne, 1970) and 4,4'-dibromoazobenzene (178.3 and −1.3°) (Howard *et al.*, 1994).
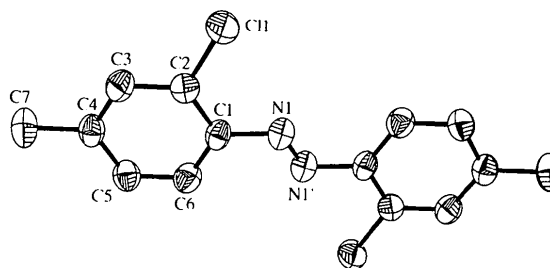


Fig. 1. Structure of the molecule showing 50% probability displacement ellipsoids. H atoms are omitted for clarity.

The packing type can be easily identified as the simplest pattern observed for aromatic hydrocarbons: the herring-bone motif HB (Gavezzotti & Desiraju, 1988; Desiraju & Gavezzotti, 1989). As shown in Fig. 2,

the shortest distance between aromatic-ring centroids (5.10 Å) is for the non-parallel nearest neighbour molecules (interplanar angle of 65.3°) related by $\frac{3}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$.
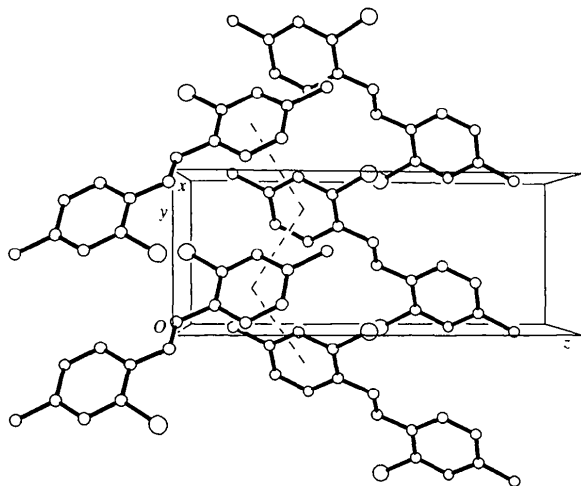


Fig. 2. Crystal packing of the molecules projected down the $a$ axis. Dashed lines show the shortest distances between aromatic-ring centroids.

The shortest intermolecular non-bonded distances C⋯Cl, C⋯C and C⋯H of 3.559 (2), 3.542 (2) and 2.96 Å are all near to the sum of the van der Waals radii. The presence of forces more dominant than Cl⋯Cl interactions [shortest intermolecular non-bonded distance Cl⋯Cl of 3.938 (2) Å] is one of the features which favour the adoption of non-$\beta$-(herring-bone) structures for chloro-aromatic compounds (Sarma & Desiraju, 1985; Desiraju, 1989).

## Experimental

Crystals were obtained by slow evaporation of a $CH_2Cl_2/Et_2O$ solution.

### Crystal data

| | |
|---|---|
| $C_{14}H_{12}Cl_2N_2$ | Mo $K\alpha$ radiation |
| $M_r = 279.16$ | $\lambda = 0.71073$ Å |
| Monoclinic | Cell parameters from 25 |
| $P2_1/n$ | reflections |
| $a = 8.103 (4)$ Å | $\theta = 7.7-14.8°$ |
| $b = 5.686 (3)$ Å | $\mu = 0.478$ mm$^{-1}$ |
| $c = 14.270 (8)$ Å | $T = 293 (2)$ K |
| $\beta = 95.94 (4)°$ | Parallelepiped |
| $V = 653.9 (6)$ Å$^3$ | $0.30 \times 0.22 \times 0.14$ mm |
| $Z = 2$ | Dark orange |
| $D_x = 1.418$ Mg m$^{-3}$ | |
| $D_m$ not measured | |

### Data collection

| | |
|---|---|
| Siemens $R3m/V$ diffractom- | $\theta_{max} = 25.05°$ |
| eter | $h = 0 \rightarrow 9$ |
| $\theta$–$2\theta$ scans | $k = -6 \rightarrow 6$ |
| Absorption correction: none | $l = -17 \rightarrow 16$ |

| | |
|---|---|
| 2349 measured reflections | 2 standard reflections |
| 1162 independent reflections | frequency: 98 min |
| 957 reflections with | intensity decay: not |
| $I > 2\sigma(I)$ | measured |
| $R_{int} = 0.045$ | |

### Refinement

| | |
|---|---|
| Refinement on $F^2$ | $w = 1/[\sigma^2(F_o^2) + (0.0685P)^2$ |
| $R[F^2 > 2\sigma(F^2)] = 0.042$ | $+ 0.1607P]$ |
| $wR(F^2) = 0.117$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 1.062$ | $(\Delta/\sigma)_{max} = -0.002$ |
| 1162 reflections | $\Delta\rho_{max} = 0.289$ e Å$^{-3}$ |
| 82 parameters | $\Delta\rho_{min} = -0.358$ e Å$^{-3}$ |
| H atoms riding, with fixed | Extinction correction: none |
| isotropic $U$ | Scattering factors from |
| | International Tables for |
| | Crystallography (Vol. C) |

Table 1. *Selected geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| Cl1—C2 | 1.737 (2) | N1—C1 | 1.425 (3) |
| N1—N1$^i$ | 1.250 (3) | | |
| N1$^i$—N1—C1 | 113.7 (2) | C2—C1—N1 | 118.0 (2) |
| C2—C1—C6 | 118.1 (2) | C6—C1—N1 | 123.8 (2) |

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

Data collection: *P3/V* (Siemens, 1990a). Cell Refinement: *P3/V*. Data reduction: *SHELXTL-Plus*, 1990). Program(s) used to solve structure: *SHELXTL-Plus*. Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *XP* (Siemens, 1990b). Software used to prepare material for publication: *SHELXL93*.

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# 1,2-Dimethylpyrido[1,2-a]benzimidazole-4-carbonitrile

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## Abstract

The title compound, $C_{14}H_{11}N_3$, is planar to within 0.030 Å (excluding H atoms). Wide bond angles are observed exocyclic to the five-membered ring [maximum 134.2 (2)°]. Molecules are connected into zigzag chains by hydrogen bonds of the form $C_{arom}$—H···N≡C, with an H···N distance of 2.47 Å.

## Comment

In the course of our preparative studies of fused heterocyclic nitrogen compounds utilizing readily obtainable nitrile intermediates (Elgemeie *et al.*, 1992, 1997; Elgemeie & Fathy, 1995), we have reported new approaches starting from 2-cyanomethylazolyl derivatives (Elgemeie & Elaal, 1986; Elgemeie & Fathy, 1988). We report here a novel synthesis of a benzo[g]-imidazo[1,2-a]pyridine derivative from the readily obtainable 2-cyanomethylbenzimidazole, (1). Compound (1) reacted with the sodium salt of 3-(hydroxymethylene)-2-butanone, (2), in the molar ratio 1:1 to give a product for which several possible isomeric structures [*cf.* (3)–(6) in Scheme] were considered. The spectral data were ambiguous; an X-ray structure determination indicated form (6) for the product in the solid state. The formation of (6) from the reaction of (1) and (2)

is assumed to proceed *via* initial addition of the active methylene-C atom of form (1b) to the formyl group of (2) to give the favoured kinetically and thermodynamically controlled product (6).
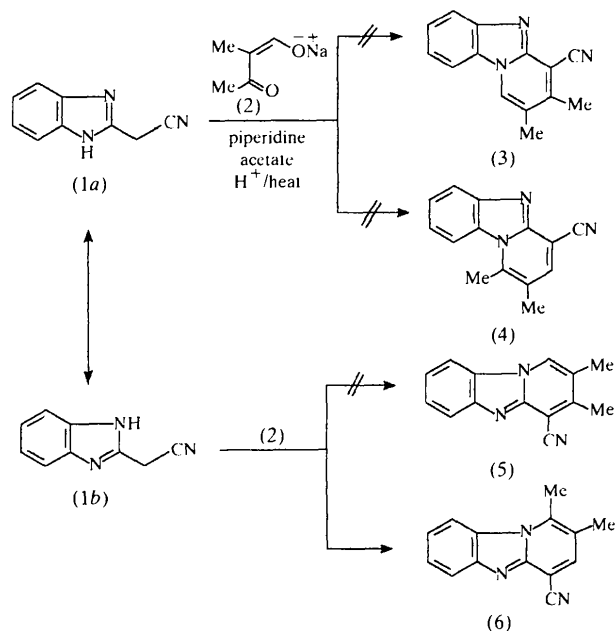


The molecule of (6) (Fig. 1) is planar, with an r.m.s. deviation of all non-H atoms from the least-squares plane of 0.030 Å. [The r.m.s. deviation is reduced to 0.014 Å on excluding atoms C14 and N3, which lie 0.109 (3) and 0.056 (3) Å, respectively, outside the improved plane.] The bond lengths and angles are closely similar to those of a benzimidazo[1,2-a]pyridine derivative with a further annelated seven-membered ring recently determined by us (Elgemeie *et al.*, 1998); in particular, wide angles are observed exocyclic to the five-membered ring [*e.g.* C1—N1—C9 132.41 (18) and C8—C9—N1 134.2 (2)°].
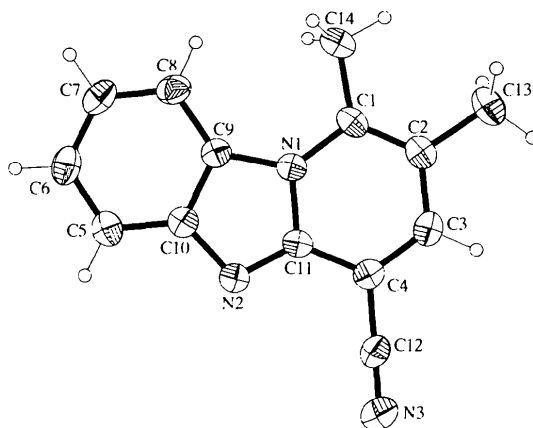


Fig. 1. The molecule of the title compound in the crystal. Ellipsoids are shown at 50% probability levels and H atoms are shown as circles of arbitrary radii.