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N-(3-Chlorophenyl)-2-hydroxy-1-naphthaldimine at 200 K

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Key indicators

Single-crystal X-ray study
T = 200 K
Mean σ(C–C) = 0.002 Å
R factor = 0.041
wR factor = 0.109
Data-to-parameter ratio = 16.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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The title compound, $C_{17}H_{12}ClNO$, (I), exists as the enol–imino tautomer [Csp^2—O 1.333 (2) Å] in the solid state at 200 K, while NMR spectroscopy reveals the ketoamino form in dimethyl sulfoxide solution. The orientation of the Csp^2—O (for the OH tautomer) and the Csp^2═O bond (for the NH tautomer) towards the *N*-3-chlorophenyl substituent shows that both tautomers are *E* isomers with respect to the imino N═C bond. The solid-state OH tautomer is benzenoid, forming the very short resonance-assisted O—H···N intramolecular hydrogen bond [N···O 2.537 (2) Å]. The molecules are assembled using only van der Waals contacts. The packing of the molecules within the unit cell implies π–π interactions of adjacent naphthalene and phenyl rings, respectively. The energetically more favourable non-planar geometry [the dihedral angle between the naphthalene and 3-chlorophenyl rings is 17.2 (1)°] is in accordance with the absence of intermolecular hydrogen bonding that could compensate the formation of a less energetically favourable planar molecule.

Comment

The design and synthesis of organic compounds with desired physical properties, by methods of crystal engineering, based on molecular recognition and self-organization, are under development for many applications (non-linear optics, organic superconductors, optical sensors, *etc.*) (Feringa *et al.*, 1993). The Schiff bases derived from *o*-hydroxy aromatic aldehydes with various alkyl or aryl *N*-substituents [Ar—C═N—Ar(*R*)] exhibit interesting photo- and thermochromic features. The salicylaldimine Schiff bases have been investigated more than naphthaldimines over the last 40 years (Cohen & Schmidt, 1962; Carles *et al.*, 1987; Inabe, 1991; Rontoyianni *et al.*, 1994; Hadjoudis, 1994, 1995; Ogawa & Fujiwara, 1999; Ogawa, 1999, 2000; Ogawa *et al.*, 2000, 2001; Pizzala *et al.*, 2000). Chromic behaviour is strongly related to the tautomerization between the O—H···N═C—C═C (enolimino) and —C═O···H—N—C═C— (ketoamino) tautomeric forms. The tautomerization induced by intramolecular proton transfer is accompanied by a π-electron configurational change in the central heterodiene moiety of the molecule (the two tautomers have different π-electron distributions). The presence of the particular tautomer in the crystal depends on the type of parent *o*-hydroxy aromatic aldehyde and the type of *N*-substituent (*i.e.* the type of amine used), implying that there is no simple correlation between the type of aldehyde and the molecular structure (*i.e.* tautomer) of the derived Schiff base. In other words, the electron withdrawing or donating ability of substituents and their position on the aromatic core, as well as hydrogen bonding donor–acceptor properties, can stabilize one or other tautomer in the crystal.

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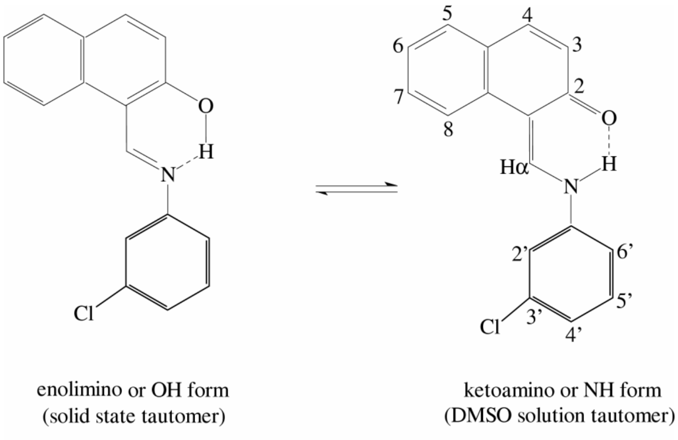

(I)

Photochromy and thermochromy are mutually exclusive properties in crystalline Schiff bases. The existence of one particular Schiff base compound in the NH form in one crystal and the OH form in another leads to polymorphism of Schiff bases, establishing that the crystal structure is responsible for the chromic behaviour of the Schiff base.

It has been established, thus far, that Schiff bases of the naphthaldimine type can exist in both the NH and OH forms. The NH form (for those derived only from primary amines) has been established by X-ray single-crystal diffraction in the structures of *N*-*n*-propyl-2-oxo-1-naphthylidenemethylamine (Kaitner & Pavlović, 1996), *N*-(α-naphthyl)- and *N*-(β-naphthyl)-2-oxo-1-naphthaldimines (Gavranić *et al.*, 1996), an *N*-4-methyl-2-pyridyl derivative (Elerman *et al.*, 1998), *N*-(2-hydroxyethyl)-2-oxo-1-naphthaldimine (Kaitner & Pavlović, 1999), *N*-(3-carboxy-phenyl)-2-hydroxy-1-naphthaldimine (Pavlović & Matijević-Sosa, 2000) and 1-[*N*-(2-pyridyl)-aminomethylidene]-2-naphthalenone (Hökelek *et al.*, 2000), while the OH tautomer (for those derived only from primary amines) has been found in the structures of *N*-*o*-tolyl-2-hydroxy-1-naphthaldimine (Kaitner *et al.*, 1998), *N*-(2-bromo-4-methylphenyl)naphthaldimine (Elmali, Elerman & Kendi, 1998), *N*-(3,5-dichlorophenyl)naphthaldimine (Elmali, Elerman, Svoboda *et al.*, 1998), 1-[(3-nitrophenylimino)methyl]-2-naphthol (Yeap *et al.*, 1998) and *N*-(2-aminophenyl)-naphthaldimine (Govindasamy *et al.*, 1999). The dynamic disorder of the hydrogen position between the oxygen and the nitrogen site, as in the structure of *N*-(2-hydroxy-1-naphthyl-methylene)-1-pyrenamine (Inabe *et al.*, 1994), reveals the possibility that both tautomeric forms are present in the crystal [N$\cdots$O hydrogen bond distances are 2.530 (6) and 2.551 (5) Å at 295 and 120 K, respectively].

It should be stressed that there is no simple relation between molecular conformation and the type of tautomer present in the crystalline state. In other words, the previously established well known fact that the NH tautomers are planar and the OH tautomers are non-planar is no longer accepted. There are ketoamino (NH) naphthaldimines of the Ar—C═N—*R* type with non-planar *N*-alkyl substituents such as *N*-*n*-propyl-2-oxo-1-naphthylidenemethylamine (Kaitner & Pavlović, 1996) and *N*-(2-hydroxyethyl)-2-oxo-1-naphthaldimine (Kaitner & Pavlović, 1999), while in the ketoamino Ar—C═N—Ar naphthaldimines, the naphthaldiminate moiety and the *N*-aryl substituent are inclined to each other at angles in the range 4.41 (7) (Pavlović & Matijević-Sosa, 2000) to 6.95 (5)° (Hökelek *et al.*, 2000). On the other hand, enolimino (OH) naphthaldimines with *N*-aryl substituents are in planar (Elmali, Elerman, Svoboda *et al.*, 1998; Yeap *et al.*, 1998), as well as in non-planar conformation in crystals (Elmali, Elerman & Kendi, 1998; Govindasamy *et al.*, 1999; Kaitner *et al.*, 1998). Obviously, the planarity and/or non-planarity is not an exclusive feature of the OH or NH tautomers.

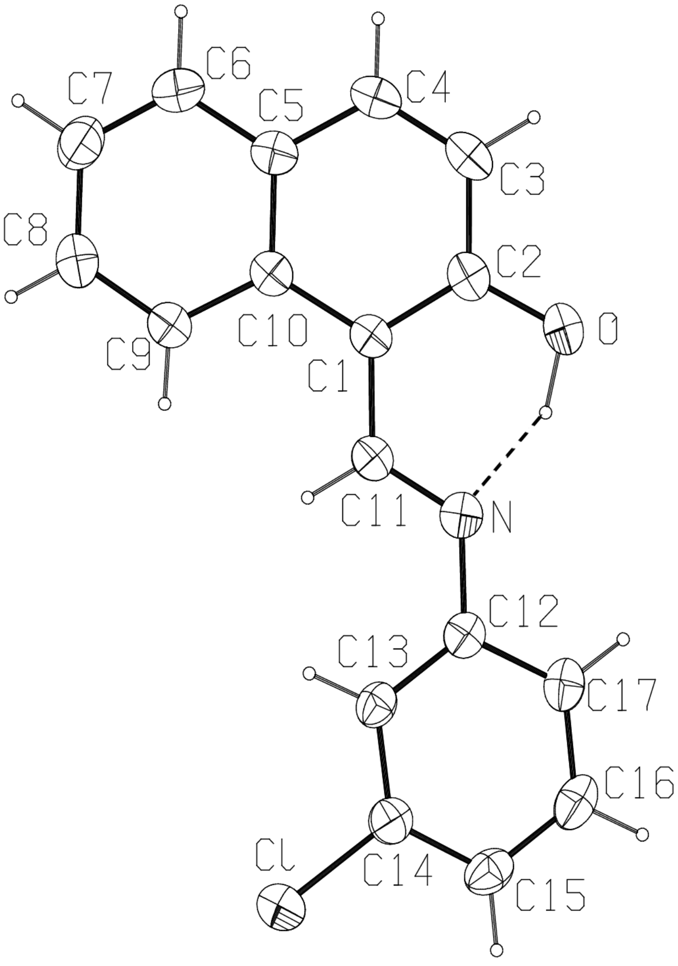

Figure 1
A perspective view of the molecule of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The intramolecular O—H$\cdots$N hydrogen bond is indicated by a dashed line.

The Csp^2—O and N═C bonds of the central part of the molecule are the most affected by the π-electron distribution within the Schiff base and thus are the most sensitive molecular geometry fragments in the determination of the ketoamino–enolimino tautomeric equilibrium shift. The O—C bond distances observed in ketoamino tautomers cited above

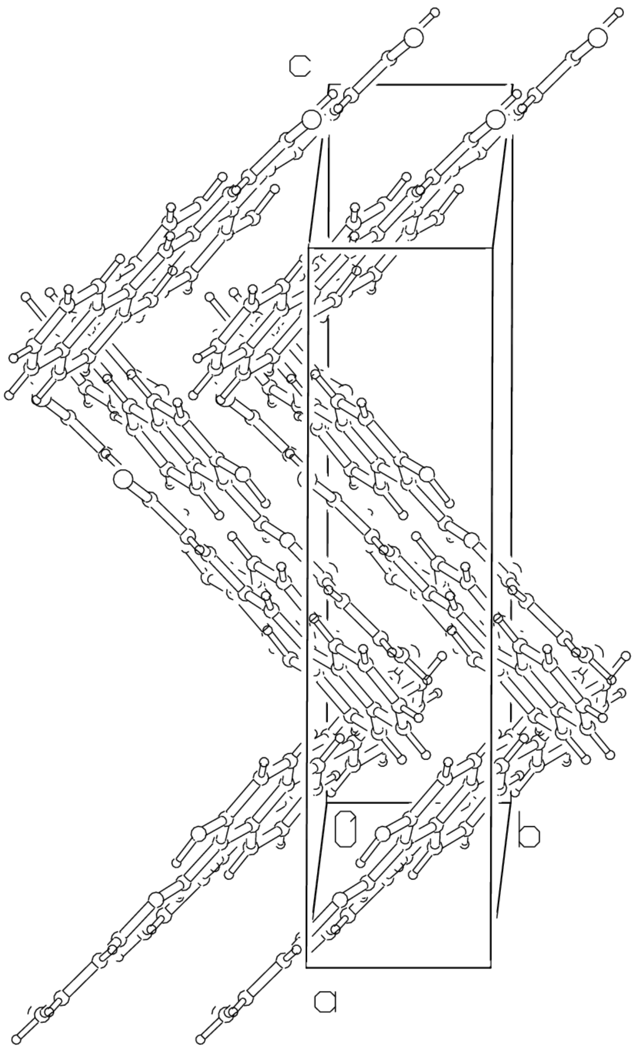

Figure 2
The crystal structure of (I), showing the herring-bone type of molecular packing. The π–π interactions appear along the short b axis.

are 1.274 (4)–1.302 (3) Å, and those in enol tautomers 1.320 (3)–1.323 (3) Å. The imino N═C bond distances observed in the crystals of NH tautomers are 1.294 (5)–1.345 (4) Å, longer than those in OH tautomers, 1.290 (3)–1.291 (4) Å. The C2—O and N═C11 bond distance values in the title Schiff base are 1.333 (2) and 1.294 (2) Å, respectively. The H atom belonging to the oxygen site was found in an electron-density map at a distance O—H1O of 1.01 (3) Å; together with the C2—O—H1O bond angle value of 105 (2)°, this confirms the sp^3 hybridization of the O atom. The single Cl—C14 bond distance value is normal, 1.745 (2) Å (Allen *et al.*, 1987). The bond distances within the phenyl and naphthyl rings are normal (Allen *et al.*, 1987). The torsion angle around the single N—C12 bond is 13.7 (2)°, revealing molecular non-planarity, which is accompanied by involvement of the N lone electron pair in resonance with the π-electron system of the *N*-phenyl ring. The only known crystal structure of naphthaldimine with the *N*-group substituted by chlorine is the nearly planar structure of N-(3,5-dichlorophenyl)naphthaldimine (Elmali, Elerman, Svoboda *et al.*, 1998), with an O—H···N intramolecular hydrogen bond of 2.570 (3) Å.

The hydrogen-bond distances of the above-mentioned naphthaldimine Schiff bases are in the range 2.503 (3)–2.570 (3) Å for OH tautomers and 2.531 (3)–2.578 (2) Å for NH tautomers and they belong to the RAHB (resonance-assisted hydrogen bond) type of hydrogen bond (Bertolasi *et al.*, 1993; Dziembowska, 1994, 1998; Bertolasi *et al.*, 1999; Krygowski *et al.*, 1999; Gilli *et al.*, 2000). The π-electron delocalization is spread out over the central part of the molecule formed by the pseudo-aromatic six-membered chelate ring. The hydrogen bond length in the title Schiff base is among the shorter ones in naphthaldimines [O···N 2.537 (2) Å, O—H 1.01 (3) Å, H···N 1.60 (3) Å and O—H···N angle 152 (3)°)]. The IR spectral data confirm the enol tautomer in the solid state (Yuzawa *et al.*, 1993). ^{1}H and ^{13}C NMR spectra reveal the ketoamino form of the Schiff base in dimethyl sulfoxide solution. The *syn* orientation of *meta*-Cl towards the C-α proton was deduced from the NOE contacts in ^{1}H spectra. Variable temperature measurements showed that the large downfield chemical shift of NH arises from intramolecular hydrogen bonding.

Experimental

The title compound was prepared by adding 3-chloroaniline (127 mg, 1 mmol) to a solution of 2-hydroxynaphthaldehyde (172 mg, 1 mmol) in methanol (approximately 10 ml). After stirring the reaction mixture for 3 h at room temperature, a yellow precipitate was formed. The crude yellow product, obtained from the reaction mixture by cooling, was separated under vacuum and washed with water (196 mg, yield 70%; m.p. 384–386 K; literature m.p. 389–390 K; Beilstein 12EI302). Recrystallization from toluene by slow evaporation gave single crystals of good diffraction quality. IR spectral data were recorded with a Paragon 500 FT–IR Perkin–Elmer spectrophotometer. IR (KBr, cm^{-1}): 1619 and 1569 (C═N), 1318 (Csp^2—O). One- and two dimensional NMR spectra (COSY, NOESY, HETCOR and HMBC) were recorded with Gemini 300 and Unity Inova 300 Varian spectrometers. The samples were dissolved in dimethyl sulfoxide and examined at 293 K in 5 mm NMR tubes. The concentration was 7 mg ml^{-1} for ^{1}H and 15 mg ml^{-1} for ^{13}C measurements. Chemical shifts are referred to TMS. ^{1}H NMR shifts (p.p.m.): NH 15.48 (*d*), Hα 9.69 (*d*), H8 8.55 (*d*), H4 7.96 (*d*), H2′ 7.86 (*s*), H5 7.81 (*d*), H7 7.56 (*t*), H5′ 7.50 (*t*), H6′ 7.54 (*d*), H4′ 7.36 (*d*), H6 7.37 (*t*) and H3 7.04 (*d*). ^{13}C NMR shifts (p.p.m.): C═0 169.58 (*s*), Cα 157.16 (*d*), C1′ 146.12 (*s*), C4 137.12 (*d*), C3′ 134.21 (*s*), C9 133.12 (*s*), C5′ 131.11 (*d*), C5 129.04 (*d*), C7 128.18 (*d*), C10 126.89 (*s*), C4′ 126.19 (*d*), C6 123.73 (*d*), C3 121.71 (*d*), C8 120.74 (*d*), C6′ 120.20 (*d*), C2′ 120.08 (*d*), C1 108.86 (*s*). The multiplicity of signals is denoted within parentheses: *s* = singlet, *d* = doublet and *t* = triplet. The atom-numbering scheme is shown in the Scheme.

Crystal data

$C_{17}H_{12}ClNO$
$M_r = 281.73$
Monoclinic, $C2/c$
$a = 30.706$ (1) Å
$b = 4.7860$ (1) Å
$c = 18.9937$ (5) Å
$\beta = 108.133$ (1)°
$V = 2652.69$ (10) Å^3
$Z = 8$

$D_x = 1.411$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2100 reflections
$\theta = 1$–27.5°
$\mu = 0.28$ mm^{-1}
$T = 200$ (2) K
Prism, pale yellow
0.15 × 0.13 × 0.08 mm

Data collection

Nonius KappaCCD area-detector diffractometer
ω scans
Absorption correction: none
4881 measured reflections
2954 independent reflections
2387 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.020$
$\theta_{\rm max} = 27.5°$
$h = -39 \rightarrow 39$
$k = -4 \rightarrow 6$
$l = -24 \rightarrow 24$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.109$
$S = 1.04$
2954 reflections
185 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0456P)^2 + 2.5286P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.27$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.33$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N—C11	1.294 (2)	O—C2	1.3330 (19)
N—C12	1.413 (2)		
C11—N—C12	122.77 (13)	C2—O—H1O	104.9 (16)

Diffraction data were collected on a Nonius KappaCCD diffractometer (capillary optics) at 200 K. 385 frames were collected at the crystal-detector distance of 35 mm, 10 s/°, 8 sets of ω scans, 1° per frame. All H atoms were included in calculated positions as riding atoms, with *SHELXL*97 (Sheldrick, 1997) default parameters, except for atom H1O which was found in an electron-density Fourier map, at a distance O—H1O of 1.01 (3) Å, and refined freely.

Data collection: *DENZO* and *COLLECT* (Otwinowski & Minor, 1997); cell refinement: *DENZO* and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON*98 (Spek, 1998); software used to prepare material for publication: *SHELXL*97.

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References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–19.

Bertolasi, V., Ferretti, V., Gilli, P., Gilli, G., Issa, Y. M. & Sherif, O. E. (1993). *J. Chem. Soc. Perkin Trans.* 2, pp. 2223–2228.

Bertolasi, V., Gilli, P., Ferretti, V., Gilli, G. & Vaughan, K. (1999). *New J. Chem.* **23**, 1261–1267.

Carles, M., Eloy, D., Pujol, L. & Bodot, H. (1987). *J. Mol. Struct.* **156**, 43–58.

Cohen, M. D. & Schmidt, G. M. (1962). *J. Phys. Chem.* **66**, 2442–2446.

Dziembowska, T. (1994). *Pol. J. Chem.* **68**, 1455–1489.

Dziembowska, T. (1998). *Pol. J. Chem.* **72**, 193–209.

Elerman, Y., Kabak, M., Elmali, A. & Svoboda, I. (1998). *Acta Cryst.* C**54**, 128–130.

Elmali, A., Elerman, Y. & Kendi, E. (1998). *Acta Cryst.* C**54**, 1137–1139.

Elmali, A., Elerman, Y., Svoboda, I. & Fuess, H. (1998). *Acta Cryst.* C**54**, 974–976.

Feringa, B. L., Jager, W. F. & de Lange, B. (1993). *Tetrahedron*, **49**, 8267–8310.

Gavranić, M., Kaitner, B. & Meštrović, E. (1996). *J. Chem. Crystallogr.* **26**, 23–28.

Gilli, P., Bertolasi, V., Ferretti, V. & Gilli, G. (2000). *J. Am. Chem. Soc.* **122**, 10405–10417.

Govindasamy, L., Velmurugan, D. & Rajendran, T. M. (1999). *Acta Cryst.* C**55**, 1368–1369.

Hadjoudis, E. (1994). *Mol. Cryst. Liq. Cryst.* **246**, 127–134.

Hadjoudis, E. (1995). *Mol. Eng.* **5**, 301–337.

Hökelek, T., Kiliç, Z., Işiklan, M. & Toy, M. (2000). *J. Mol. Struct.* **523**, 61–69.

Inabe, T. (1991). *New J. Chem.* **15**, 129–136.

Inabe, T., Luneau, I., Mitani, T., Maruyama, Y. & Takeda, S. (1994). *Bull. Chem. Soc. Jpn*, **67**, 612–621.

Kaitner, B. & Pavlović, G. (1996). *Acta Cryst.* C**52**, 2573–2575.

Kaitner, B., Meštrović, E. & Pavlović, G. (1998). *J. Chem. Crystallogr.* **28**, 77–82.

Kaitner, B. & Pavlović, G. (1999). *Croat. Chem. Acta*, **72**, 607–620.

Krygowski, T. M., Stepien, B., Anulewicz-Ostrowska, R. & Dziembowska, T. (1999). *Tetrahedron*, **55**, 5457–5664.

Ogawa, K. & Fujiwara, T. (1999). *Chem. Lett.* pp. 657–658.

Ogawa, K. (1999). *Crystal Engineering: From Molecules and Crystals to Materials*, edited by D. Braga *et al.*, pp. 469–479. Dordrecht, The Netherlands: Kluwer Academic Publishers.

Ogawa, K. (2000). *Chem. Lett.* pp. 528–529.

Ogawa, K., Fujiwara, T. & Harada, J. (2000). *Mol. Cryst. Liq. Cryst.* **344**, 169–178.

Ogawa, K., Harada, J., Fujiwara, T. & Yoshida, S. (2001). *J. Phys. Chem. A*, **105**, 3425–3427.

Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter and R. M. Sweet, pp. 307–326. London: Academic Press.

Pavlović, G. & Matijević-Sosa, J. (2000). *Acta Cryst.* C**56**, 1117–1119.

Pizzala, H., Carles, M., Stone, W. E. E. & Thevand, A. (2000). *J. Chem. Soc. Perkin Trans.* 2, pp. 935–939.

Rontoyianni, A., Hadjoudis, E. & Mavridis, I. M. (1994). *Mol. Cryst. Liq. Cryst.* **242**, 221–226.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.

Spek, A. L. (1998). *PLATON*98 for Windows. University of Utrecht, The Netherlands.

Yeap, G. Y., Teoh, S. G., Teo, S. B., Valle, G. & Calogero, S. (1998). *Z. Krist. New Cryst. Struct.* **213**, 489–490.

Yuzawa, T., Takahashi, H. & Hamaguchi, H. (1993). *Chem. Phys. Lett.* **202**, 221–226.