

N,N-Diethyl-*N'*-[(*E*)-4-pyridylmethylene]benzene-1,4-diamine: a combined X-ray and density functional theory study

Rüdiger W. Seidel,^{a*} William S. Sheldrick,^a Tsonko M. Kolev^b and Bojidarka B. Koleva^c

^aAnalytische Chemie, Ruhr-Universität Bochum, Universitätsstrasse 150, 44780 Bochum, Germany, ^bInstitute of Organic Chemistry, Bulgarian Academy of Science, Academician G. Bonchev Street, Building 9, 1113 Sofia, Bulgaria, and ^cDepartment of Analytical Chemistry, University of Sofia St. Kliment Ohridski, J. Bourchier Boulevard 1, 1164 Sofia, Bulgaria
Correspondence e-mail: ruediger.seidel@rub.de

Received 31 May 2009

Accepted 1 July 2009

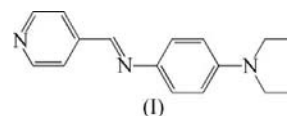
Online 11 July 2009

The crystal structure of the title compound, C₁₆H₁₉N₃, comprises neutral molecules of a dipolar Schiff base chromophore. A density functional theory (DFT) optimized structure at the B3LYP/6-31G(*d*) level is compared with the molecular structure in the solid state. The compound crystallizes in the noncentrosymmetric space group *Pna*2₁ with a herring-bone packing motif and is therefore a potential candidate for nonlinear optical effects in the bulk.

Comment

During the past decade, the design of new materials with nonlinear optical (NLO) properties has attracted considerable interest (Papadopoulos *et al.*, 2006). For the observation of second-order NLO effects, such as frequency doubling (second-harmonic generation, SHG) in the bulk, noncentrosymmetric molecular and crystallographic symmetry is required. Besides the criterion of overall noncentrosymmetric character, large hyperpolarizabilities (β values) are also required. Typical synthetic targets are dipolar donor– π -acceptor (push–pull) molecules having the desired high β values. In particular, stilbazolium derivatives such as *trans*-4'-dimethylamino-*N*-methyl-4-stilbazolium 4-toluenesulfonate (DAST) have been intensively studied (Marder *et al.*, 1989, 1994; Ruiz *et al.*, 2008). Related Schiff base chromophores have also been studied (Corradin *et al.*, 1996; Coe *et al.*, 2002; Sliwa *et al.*, 2005). In this context, Coe and co-workers reported the crystal structures of two salts containing the Schiff base cations *trans*-4-[4-(dimethylamino)phenyliminomethyl]-*N*-phenylpyridinium (Coe *et al.*, 2000) and *trans*-4-[4-(dimethylamino)phenyliminomethyl]-*N*-methylpyridinium (Coe *et al.*, 2001). The use of organic salts enables modifica-

tion of the crystal packing by variation of the counter-ions. It is noteworthy that the noncentrosymmetric crystal structure of unsubstituted *trans*-*N*-(4-pyridylmethylene)aniline has been known for more than two decades (Wiebcke & Mootz, 1982). A related derivative containing an amide group in the *para* position of the benzene ring, which crystallizes centrosymmetrically, has also been structurally characterized (Aakeroy *et al.*, 2006). However, to the best of our knowledge, and based on a search of the Cambridge Structural Database (CSD; Version 5.3, with February 2009 updates; Allen, 2002), the present study of the title compound, (I), is the first crystallographic study of a neutral *N,N*-dialkyl-*N'*-[(*E*)-4-pyridylmethylene]benzene-1,4-diamine derivative.



Compound (I) was prepared by a Schiff base condensation of pyridine-4-carbaldehyde and *N,N*-diethyl-*p*-phenylenediamine in the presence of 4-toluenesulfonic acid. The well defined band in the IR spectrum at 1649 cm^{−1} was assigned to the $\nu_{C=N}$ stretching vibration. Crystals of (I) suitable for X-ray analysis were grown from an ethanolic solution. A displacement ellipsoid plot is depicted in Fig. 1. The molecular geometry parameters are within expected ranges. As observed in *trans*-4-[4-(dimethylamino)phenyliminomethyl]-*N*-phenylpyridinium hexafluorophosphate (Coe *et al.*, 2000) and *trans*-4-[4-(dimethylamino)phenyliminomethyl]-*N*-methylpyridinium 4-toluenesulfonate (Coe *et al.*, 2001), the benzene ring in (I) shows partial quinone character, which reveals some ground-state charge separation. The average C2...C3 and C5...C6 bond length is 1.373 (2) Å, while the average of the other four benzene C...C distances is 1.404 (5) Å. These observations are supported by the density functional theory (DFT) structure optimization. The corresponding calculated values are 1.387 and 1.412 Å, respectively. The other calculated bond lengths of (I) are also in agreement with the crystallographically determined values. For example, the observed and calculated C=N bond lengths are 1.281 (2) and 1.283 Å, respectively. The dihedral angle between the mean planes of the C1–C6 and

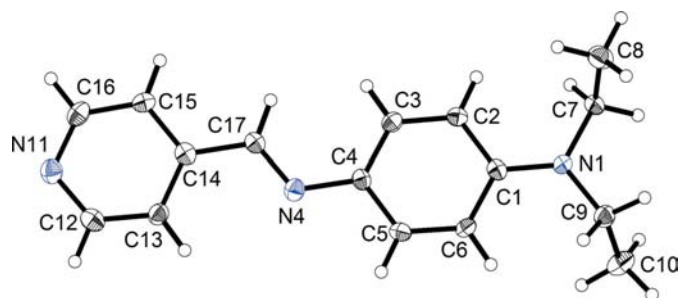


Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

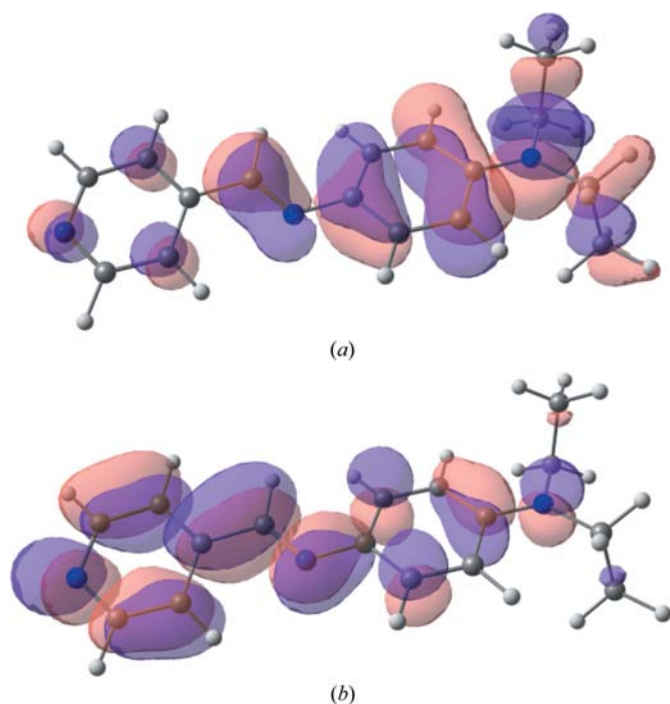


Figure 2
Representation of the DFT-optimized structure of (I), showing the isosurfaces of (a) the HOMO and (b) the LUMO with an isovalue of 0.02 a.u.

N11/C12–C16 rings is $5.8 (1)^\circ$. The corresponding value in the DFT-optimized structure is appreciably larger at 21.8° . The reason for the discrepancy between the observed value in the solid state and the calculated value is not entirely clear, but the effects of crystal packing should presumably be considered. These effects are not included in the DFT structure optimization. However, the calculated value of 21.8° lies within the expected range; an even larger value of $23.49 (6)^\circ$ has been crystallographically determined for the *trans*-4-[(4-dimethylaminophenyl)iminomethyl]-*N*-methylpyridinium cation (Coe *et al.*, 2001).

Compound (I) shows an intense absorption band in the visible region at $\lambda_{\text{max}} = 428 \text{ nm}$ ($\epsilon = 8881 \text{ l mol}^{-1} \text{ cm}^{-1}$) in acetonitrile. This band is attributed to an intramolecular charge transfer (ICT) from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). As expected, the DFT calculation reveals that the HOMO is primarily localized on the electron-rich diethylamine group, while the LUMO is primarily localized on the electron-deficient pyridine group (Fig. 2). For the hexafluorophosphate salt of the related *trans*-4-[4-(dimethylamino)phenyliminomethyl]-*N*-phenylpyridinium cation, an absorption band was reported at $\lambda_{\text{max}} = 534 \text{ nm}$ in acetonitrile (Coe *et al.*, 2000). The ICT band of (I) shows solvatochromism; in acetic anhydride the ICT band of (I) is bathochromically shifted to $\lambda_{\text{max}} = 541 \text{ nm}$ ($\epsilon = 9713 \text{ l mol}^{-1} \text{ cm}^{-1}$).

As mentioned above, noncentrosymmetric space-group symmetry is required for the observation of bulk NLO properties. The prediction of crystal packing, and hence the rational supramolecular synthesis of noncentrosymmetric

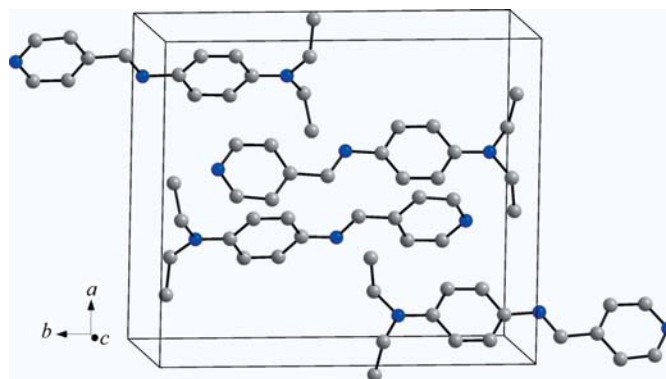


Figure 3
The arrangement of the molecules in the orthorhombic unit cell of (I). H atoms have been omitted for clarity.

crystals, are still a challenge in the field of crystal engineering. Interestingly, the crystal packing of (I) is quite different to that observed in *trans*-4-[4-(dimethylamino)phenyliminomethyl]-*N*-phenylpyridinium hexafluorophosphate (Coe *et al.*, 2000), which crystallizes in the polar space group *Cc*. In the latter, the dipolar cations are aligned head-to-tail forming polar cationic sheets, between which the hexafluorophosphate anions are located. It may be significant that the closely related compound *trans*-4-[4-(dimethylamino)phenyliminomethyl]-*N*-methylpyridinium 4-toluenesulfonate crystallizes in the centrosymmetric space group *P2₁/n* (Coe *et al.*, 2001). Compound (I) crystallizes in the polar orthorhombic space group *Pna2₁* with antiparallel alignment of the dipolar chromophores. The arrangement of the molecules in the orthorhombic unit cell is shown in Fig. 3. No face-to-face π – π stacking interactions occur in the crystal structure of (I), but edge-to-face stacking interactions are indicated by the C–H $\cdots\pi$ distances (Table 1). This arrangement leads to a herringbone packing motif, which is polar along the *c* axis. Compound (I) therefore possesses the potential to exhibit NLO effects in the bulk.

Experimental

All chemicals were purchased from Merck and used as received. *N,N*-Diethyl-*p*-phenylenediamine (32.850 g, 0.200 mol) was added to a solution of pyridine-4-carbaldehyde (21.422 g, 0.200 mol) in toluene (40 ml). 4-Toluenesulfonic acid (40 mg) was added and the mixture was refluxed for 2 h. The Schiff base that separated after cooling was filtered off and recrystallized from ethanol (yield 33.441 g, 66%). Elemental analysis calculated for $\text{C}_{16}\text{H}_{19}\text{N}_3$: C 75.85, H 7.56, N 16.59%; found: C 75.88, H 7.54, N 16.60%. Single crystals of (I) suitable for X-ray diffraction were obtained by slow evaporation from an ethanolic solution at room temperature.

Crystal data

$\text{C}_{16}\text{H}_{19}\text{N}_3$	$V = 1374.80 (10) \text{ \AA}^3$
$M_r = 253.34$	$Z = 4$
Orthorhombic, <i>Pna2₁</i>	Mo $K\alpha$ radiation
$a = 12.7984 (5) \text{ \AA}$	$\mu = 0.07 \text{ mm}^{-1}$
$b = 14.8116 (6) \text{ \AA}$	$T = 110 \text{ K}$
$c = 7.2524 (3) \text{ \AA}$	$0.36 \times 0.12 \times 0.09 \text{ mm}$

Table 1

Hydrogen-bond geometry (Å, °).

Cg1 is the centroid of the N11/C12–C16 ring and Cg2 is the centroid of the C1–C6 ring.

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C2—H2...Cg1 ⁱ	0.95	2.83	3.700 (2)	153
C6—H6...Cg1 ⁱⁱ	0.95	2.84	3.633 (2)	142
C12—H12...Cg2 ⁱⁱⁱ	0.95	2.92	3.754 (2)	147
C15—H15...Cg2 ⁱ	0.95	2.75	3.623 (2)	152

Symmetry codes: (i) $-x+1, -y+1, z+\frac{1}{2}$; (ii) $-x+\frac{1}{2}, y+\frac{1}{2}, z-\frac{1}{2}$; (iii) $-x+\frac{1}{2}, y-\frac{1}{2}, z-\frac{1}{2}$.**Data collection**

Oxford Diffraction Xcalibur2 diffractometer	10508 measured reflections
Absorption correction: multi-scan (<i>ABSPACK</i> in <i>CrysAlis Pro</i> ; Oxford Diffraction, 2009)	1458 independent reflections
$T_{\min} = 0.971$, $T_{\max} = 0.992$	1069 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.041$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.030$	1 restraint
$wR(F^2) = 0.058$	H-atom parameters constrained
$S = 0.87$	$\Delta\rho_{\max} = 0.19 \text{ e } \text{\AA}^{-3}$
1458 reflections	$\Delta\rho_{\min} = -0.10 \text{ e } \text{\AA}^{-3}$
174 parameters	

In the absence of significant anomalous scattering effects, Friedel pairs were merged and the absolute structure was assigned arbitrarily. H atoms were placed at geometrically calculated positions and refined with a riding model and with $U_{\text{iso}}(\text{H})$ values of 1.2 (1.5 for methyl groups) times $U_{\text{eq}}(\text{C})$. The C—H bond lengths were constrained to 0.95 (aromatic and iminomethyl CH), 0.99 (methylene) and 0.98 Å (methyl).

The DFT quantum-chemical calculation was performed at the B3LYP/6–31G(*d*) level (Becke, 1993; Lee *et al.*, 1988) using *GAUSSIAN03* (Frisch *et al.*, 2004). Initial atomic coordinates for the DFT calculation were taken from the crystal structure. The harmonic vibrational analysis at the same level of theory confirmed that the stationary point represented a minimum. The DFT results were visualized with *CHEMCRAFT* (Zhurko & Zhurko, 2009).

Data collection: *CrysAlis Pro* (Oxford Diffraction, 2009); cell refinement: *CrysAlis Pro*; data reduction: *CrysAlis Pro*; program(s)

used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2008); software used to prepare material for publication: *enCIFer* (Allen *et al.*, 2004).

RWS thanks Malte Kokoschka and Dr Maik Finze for helpful discussions. BBK thanks the Alexander von Humboldt Foundation for a fellowship.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM3080). Services for accessing these data are described at the back of the journal.

References

- Aakeroy, C. B., Beatty, A. M. & Lorimer, K. (2006). *Mol. Cryst. Liq. Cryst.* **456**, 163–174.
- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
- Allen, F. H., Johnson, O., Shields, G. P., Smith, B. R. & Towler, M. (2004). *J. Appl. Cryst.* **37**, 335–338.
- Becke, A. D. (1993). *J. Chem. Phys.* **98**, 5648–5652.
- Brandenburg, K. (2008). *DIAMOND*. Version 3.1f. Crystal Impact GbR, Bonn, Germany.
- Coe, B. J., Harris, J. A., Asselberghs, I., Clays, K., Olbrechts, G., Persoons, A., Hupp, J. T., Johnson, R. C., Coles, S. J., Hursthouse, M. B. & Nakatani, K. (2002). *Adv. Funct. Mater.* **12**, 110–116.
- Coe, B. J., Harris, J. A., Coles, S. J. & Hursthouse, M. B. (2001). *Acta Cryst.* **C57**, 857–858.
- Coe, B. J., Harris, J. A., Gelbrich, T. & Hursthouse, M. B. (2000). *Acta Cryst.* **C56**, 1487–1489.
- Corradin, T., Clement, R., Lacroix, P. G. & Nakatani, K. (1996). *Chem. Mater.* **8**, 2153–2158.
- Frisch, M. J., *et al.* (2004). *GAUSSIAN03*. Gaussian Inc., Wallingford, Connecticut, USA.
- Lee, C., Yang, W. & Parr, R. G. (1988). *Phys. Rev. B*, **37**, 785–789.
- Marder, S. R., Perry, J. W. & Schaefer, W. P. (1989). *Science*, **245**, 626–628.
- Marder, S. R., Perry, J. W. & Yakymyshyn, C. P. (1994). *Chem. Mater.* **6**, 1137–1147.
- Oxford Diffraction (2009). *CrysAlis Pro*. Version 1.171.33.34d. Oxford Diffraction Ltd, Yarnton, Oxfordshire, England.
- Papadopoulos, M. G., Leszczynski, J. & Sadlej, A. J. (2006). *Nonlinear Optical Properties of Matter: From Molecules to Condensed Phases*. Dordrecht: Springer.
- Ruiz, B., Jazbinsek, M. & Günter, P. (2008). *Cryst. Growth Des.* **8**, 4173–4184.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Sliwa, M., Létard, S., Malfant, I., Nierlich, M., Lacroix, P. G., Asahi, T., Masuhara, H., Yu, P. & Nakatani, K. (2005). *Chem. Mater.* **17**, 4727–4735.
- Wiebecke, M. & Mootz, D. (1982). *Acta Cryst.* **B38**, 2008–2013.
- Zhurko, G. A. & Zhurko, D. A. (2009). *CHEMCRAFT*. Version 1.6. <http://www.chemcraftprog.com>.