

1,2,4,5-Tetrakis(2-vinylpyridyl)-benzene–dichloromethane (1/2)

Brian T. Holmes, Clifford W. Padgett and William T. Pennington*

Clemson University, Chemistry Department, HL Hunter Research Laboratories, Clemson, SC 29634-0973, USA
Correspondence e-mail: billp@clemson.edu

Received 17 October 2002

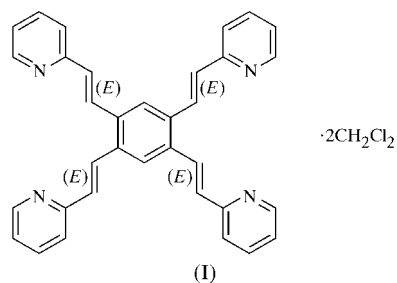
Accepted 15 January 2003

Online 11 February 2003

The title compound, $C_{34}H_{26}N_4 \cdot 2CH_2Cl_2$, lies about an inversion center. The solvent molecules interact with the benzene molecule both through $C-H \cdots N$ hydrogen bonding to span pyridine N atoms of adjacent vinyl groups, possibly stabilizing the rotational conformation observed, and through a π interaction between a dichloromethane Cl atom and a pyridyl ring $C-C$ bond of a c -glide-related molecule. The benzene molecules form stacks along the a axis such that two of the four olefin groups are properly oriented for photo-reactivity (2+2 cycloaddimerization).

Comment

Polyvinyl aromatic polymers have been researched extensively as potentially active materials in optoelectronic devices (Bao *et al.*, 1998). Monomeric precursors incorporate vinyl groups that photopolymerize through [2+2]-cycloaddition, ultimately breaking the conjugation between aromatized systems (Hasegawa *et al.*, 1969). We are investigating pyridyl diolefins



as halogen-bonding donors and as bridging ligands for metal complexation. Specifically, we are interested in the role that the acceptor molecules or metal centers in these complexes play in the orientation of the olefins to control photoactivity. The title compound, (I), offers the possibility of crosslinking in two dimensions to give a layered polymer with sustainable cavities. However, when (I) crystallizes as the methylene chloride solvate reported here, only one pair of *para*-olefin groups is properly oriented for photoactivity.

The 1,2,4,5-tetrakis(2-vinylpyridyl)benzene molecule is situated about an inversion center at the mid-point of the cell (see Fig. 1 and Table 1). The molecule is approximately planar (r.m.s. deviation = 0.127 Å), with a slightly bowed shape. The pyridyl rings in the 2 and 4 positions, which are associated with atoms N1 and N2A, are displaced to the same side of the central benzene plane by 0.367 (3) and 0.203 (3) Å, respectively, and make dihedral angles with the central ring of 9.3 (2) and 4.5 (2)°, respectively.

The methylene chloride solvent molecules span the two adjacent pyridyl rings on either side of the benzene ring through $C-H \cdots N$ interactions (Table 2); compound (I) has the potential for a wide variety of rotational conformers, and this solvent interaction may act to stabilize the conformation observed. One of the Cl atoms (Cl1) of each of the two solvent molecules extends, almost normally, from the molecular plane into a hydrophobic cavity of the molecules above and below Cl1 in the stack. Weak $C-H \cdots Cl$ interactions are present between two of the CH groups in the cavity and this Cl atom. The resulting one-dimensional stacks pack in a herring-bone fashion, with adjacent stacks related by glide-plane symmetry (Fig. 2). There are also close contacts between atom Cl2 of the solvent molecule and the C9–C10 bonding pair of the glide-related stack (at $x, \frac{3}{2} - y, -\frac{1}{2} + z$), with $Cl \cdots C$ distances of 3.295 (4) and 3.399 (4) Å, respectively, and a $Cl \cdots$ centroid(C9–C10) distance of 3.278 (4) Å. This π interaction between a dichloromethane Cl atom and a pyridyl ring $C-C$ bond is very similar to many others that have been observed (Irving, 1997; Irving & Irving, 1994). There is one weak intramolecular contact between the H atom on C11 and N2 [H \cdots N = 2.51 (3) Å].

As a result of the crystal packing, molecules stacked along the a axis have inversion-related olefins (associated with C4 and C5) in close contact [the centroid-to-centroid distance is

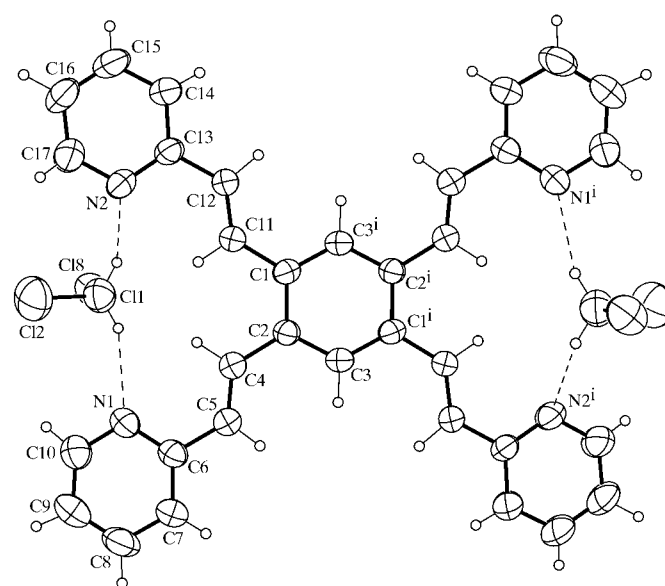


Figure 1
The molecular structure of (I). Displacement ellipsoids are shown with 50% probability and H atoms are of arbitrary radii. [Symmetry code: (i) $1 - x, 1 - y, 1 - z$.]

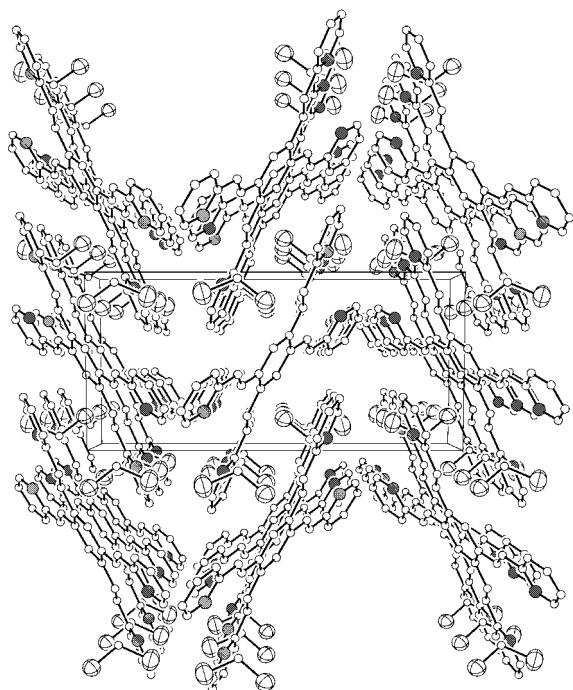


Figure 2

The packing diagram for (I), viewed along the *c* axis. Cl atoms are shown as 50% probability ellipsoids, N atoms are shown as shaded circles and C atoms are shown as open circles.

3.993 (6) Å] and exactly parallel. This distance is somewhat longer than that observed in related compounds, *viz.* 3.910 Å in 1,4-bis[2-(2-pyridyl)vinyl]benzene (Nakanishi *et al.*, 1972), 3.939 Å in 2,5-distyrylpyrazine (Sasada *et al.*, 1971) and 3.846 (7)–3.941 (6) Å in a mixed crystal of these two compounds (Nakanishi *et al.*, 1979), but like these compounds (Hasegawa *et al.*, 1973), (I) should be suitable for photoactivity by solid-state polymerization.

We have also prepared a chloroform solvate of 1,2,4,5-tetrakis(2-vinylpyridyl)benzene, but attempts to structurally characterize this solvate have been unsuccessful because of its rapid solvent loss. Our continuing investigation of 1,2,4,5-tetrakis(2-vinylpyridyl)benzene will focus on its potential for photoactivity, its solvent-inclusion behavior and the role that the solvent might play in isolating other rotational conformations.

Experimental

In a heavy-walled flask, 1,2,4,5-tetraiodobenzene (0.30 g, 0.52 mmol), 2-vinylpyridine (0.67 ml, 6.2 mmol), palladium(II) acetate (0.0046 g, 4 mol%), tri-*o*-tolylphosphine (0.0063 g, 4 mol%), sodium acetate (0.21 g, 2.6 mmol) and dimethylformamide (15 ml) were sealed under nitrogen and heated to 403 K with stirring for 4 d. The reaction mixture was quenched with water, extracted with dichloromethane, dried with magnesium sulfate and filtered. Following column chromatography (silica gel, hexane/dichloromethane), the resultant mixture was dissolved in dichloromethane and the solvent was

allowed to evaporate slowly in a refrigerator. Several diffraction-quality crystals were removed from the solution.

Crystal data

$C_{34}H_{26}N_4 \cdot 2CH_2Cl_2$
 $M_r = 660.44$
 Monoclinic, $P2_1/c$
 $a = 8.928$ (2) Å
 $b = 18.596$ (4) Å
 $c = 10.015$ (2) Å
 $\beta = 99.822$ (6)°
 $V = 1638.4$ (6) Å³
 $Z = 2$

$D_x = 1.339$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 8789 reflections
 $\theta = 2.8$ – 26.4 °
 $\mu = 0.39$ mm⁻¹
 $T = 298$ (2) K
 Rod, yellow
 $0.41 \times 0.14 \times 0.12$ mm

Data collection

Mercury AFC-8S diffractometer
 ω scans
 Absorption correction: multi-scan (REQABA; Jacobson, 1998)
 $T_{min} = 0.676$, $T_{max} = 1.000$
 15 828 measured reflections
 3339 independent reflections

2172 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.086$
 $\theta_{max} = 26.4$ °
 $h = -10 \rightarrow 11$
 $k = -23 \rightarrow 23$
 $l = -12 \rightarrow 12$

Refinement

Refinement on F^2
 $R(F) = 0.065$
 $wR(F^2) = 0.137$
 $S = 0.99$
 3339 reflections
 259 parameters
 All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0125P)^2 + 1.973P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.18$ e Å⁻³
 $\Delta\rho_{min} = -0.28$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

N1–C6	1.338 (4)	C6–C7	1.378 (5)
N1–C10	1.342 (4)	C7–C8	1.376 (5)
C1–C3 ⁱ	1.388 (4)	C8–C9	1.356 (6)
C1–C2	1.417 (4)	C9–C10	1.361 (5)
C1–C11	1.467 (4)	C11–C18	1.752 (4)
C2–C3	1.397 (4)	C12–C18	1.741 (4)
C2–C4	1.469 (4)	C12···C9 ⁱⁱ	3.295 (4)
C4–C5	1.316 (4)	C12···C10 ⁱⁱ	3.399 (4)
C5–C6	1.472 (4)		
C6–N1–C10	116.8 (3)	N1–C6–C5	117.6 (3)
C13–N2–C17	117.3 (3)	C7–C6–C5	120.9 (3)
C3 ⁱ –C1–C2	118.4 (3)	N1–C10–C9	124.3 (4)
C3 ⁱ –C1–C11	120.3 (3)	C12–C11–C1	128.4 (3)
C2–C1–C11	121.3 (3)	C11–C12–C13	125.7 (3)
C3–C2–C1	117.6 (3)	N2–C13–C14	120.8 (3)
C3–C2–C4	120.9 (3)	N2–C13–C12	117.3 (3)
C1–C2–C4	121.5 (3)	N2–C17–C16	124.7 (4)
C1 ⁱ –C3–C2	124.0 (3)	C12–C18–C11	111.8 (2)
C5–C4–C2	127.0 (3)	C18–C12···C9 ⁱⁱ	174.1 (2)
C4–C5–C6	125.8 (3)	C18–C12···C10 ⁱⁱ	162.3 (2)
N1–C6–C7	121.5 (3)		

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

Table 2

Hydrogen-bonding geometry (Å, °).

<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>
C18–H14···N1	0.93 (5)	2.52 (5)	3.371 (6)	152 (4)
C18–H15···N2	0.94 (4)	2.64 (4)	3.445 (6)	144 (3)
C16–H12···N2 ⁱ	0.98 (4)	2.54 (4)	3.420 (5)	149 (3)
C5–H3···C11 ⁱⁱ	0.94 (3)	3.08 (4)	3.982 (4)	161 (3)
C12–H9···C11 ⁱⁱⁱ	0.99 (4)	2.95 (4)	3.926 (4)	167 (3)

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

The range of refined C—H distances is 0.83 (4)–1.00 (4) Å.

Data collection: *CrystalClear* (Rigaku Corporation, 2001); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 2000); program(s) used to refine structure: *SHELXTL-Plus*; molecular graphics: *SHELXTL-Plus*; software used to prepare material for publication: *SHELXTL-Plus*.

The financial support of the National Science Foundation for the purchase of the CCD-based X-ray system used in this study (CHE-9808165) and of SC-EPSCoR/BRIN for funding through the Collaborative Research Program is gratefully acknowledged.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GA1001). Services for accessing these data are described at the back of the journal.

References

- Bao, Z., Amundson, K. R. & Lovinger, A. J. (1998). *Macromolecules*, **31**, 8647–8649.
- Hasegawa, M., Suzuki, Y., Nakanishi, H. & Nakanishi, F. (1973). *Prog. Polym. Sci. Jpn*, **5**, 143–209.
- Hasegawa, M., Suzuki, Y., Suzuki, F. & Nakanishi, H. (1969). *J. Polym. Sci. Polym. Chem. Ed.* **7**, 743–752.
- Irving, A. (1997). *Supramol. Chem.* **8**, 267–268.
- Irving, A. & Irving, H. M. N. H. (1994). *J. Chem. Crystallogr.* **24**, 251–257.
- Jacobson, R. A. (1998). *REQABA*. Version 1.1. Molecular Structure Corporation, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Nakanishi, H., Jones, W. & Parkinson, G. M. (1979). *Acta Cryst.* **B35**, 3103–3106.
- Nakanishi, H., Ueno, K., Hasegawa, G. & Sasada, Y. (1972). *Chem. Lett.* pp. 301–302.
- Rigaku Corporation (2001). *CrystalClear*. Version 1.3. Rigaku/Molecular Structure Corporation, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Sasada, Y., Shimanouchi, H., Nakanishi, H. & Hasegawa, M. (1971). *Bull. Chem. Soc. Jpn*, **44**, 1262–1270.
- Sheldrick, G. M. (2000). *SHELXTL-Plus*. Version 6.10. Bruker AXS Inc., Madison, Wisconsin, USA.