Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AS1207). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Fait, C. (1994). *XSCANS Users Manual*. Version 2.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.

Ramadas, K., Srinivasan, N. & Janarthanan, N. (1993). *Tetrahedron Lett.* **34**, 6447–6450.

Ramnathan, A., Sivakumar, K., Subramanian, K., Janarthanan, N., Ramadas, K. & Fun, H.-K. (1995*a*). *Acta Cryst.* **C51**, 1627–1629.

Ramnathan, A., Sivakumar, K., Subramanian, K., Janarthanan, N., Ramadas, K. & Fun, H.-K. (1995*b*). *Acta Cryst.* **C51**, 2446–2450.

Sarkis, G. Y. & Faisal, E. D. (1985). *J. Heterocycl. Chem.* **22**, 137–140.

Sheldrick, G. M. (1990*a*). *Acta Cryst.* **A46**, 467–473.

Sheldrick, G. M. (1990*b*). *SHELXTL/PC Users Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Acta Cryst. (1996). C**52**, 658–660

A Rigid Bis-Bidentate Bridging Ligand: 1,4-Bis(2,2′-bipyrid-4-yl)benzene

WEI WANG, AARON BABA, RUSSELL H. SCHMEHL AND JOEL T. MAGUE*

Department of Chemistry, Tulane University, New Orleans, LA 70118, USA. E-mail: joelt@mailhost.tcs.tulane.edu

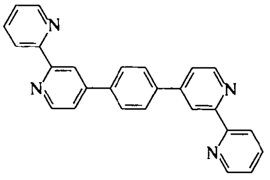
(*Received 18 April 1995; accepted 5 September 1995*)

Abstract

The title compound, $C_{26}H_{18}N_4$, possesses crystallographically imposed centrosymmetry. The bipyridyl moieties adopt an *anti* conformation and have a torsion angle of 24.3 (1)° with respect to the attached benzene ring.

Comment

Polymetallic Ru^{II}–diimine complexes are efficient sensitizers for large-band-gap semiconductors and photoelectrochemical cells constructed from these sensitized electrodes exhibit very high incident photon-to-current efficiencies (Bard & Fox, 1995; Pechy *et al.*, 1995; Nazeeruddin *et al.*, 1993; O'Regan & Grätzel, 1991; Bignozzi, Argazzi, Indelli & Scandola, 1994; Meyer *et al.*, 1994; Amadelli, Argazzi, Bignozzi & Scandola, 1990). As a result, this class of sensitized electrodes offers a promising approach to the development of active solar-energy conversion devices. A key feature in these systems is the ease of migration of energy from the absorbing metal center to that attached to the semiconductor surface. We have found recently that in $[(bpy)_2Ru(\mu\text{-bphb})Ru(tpy)(CN)](PF_6)_3$ [bpy is 2,2′-bipyridyl, bphb is 1,4-bis(2,2′-bipyrid-4-yl)benzene, (1), and tpy is 2,2′,6′,2″-terpyridyl] energy transfer from the $\{(bpy)_2Ru(bphb)\}$ chromophore to the tpy-containing chromophore is 100% efficient even in frozen matrices at 20 K, implying that a nearly activationless intramolecular electronic energy migration occurs (Liang, Baba & Schmehl, 1995). In order to evaluate electronic coupling more thoroughly in bimetallic complexes bridged by the bphb ligand in light of recent theoretical work on the extent of electronic coupling through adjacent aromatic ring systems (Cave, Marcus & Sidars, 1986), the structure of bphb was determined.



(1)

Compound (1) possesses crystallographically imposed centrosymmetry and therefore the bipyridyl moieties adopt an *anti* conformation about the central benzene ring. Additionally, the two rings of the bipyridyl unit have an *anti* conformation. These two rings show a dihedral angle of 6.5 (4)° between their planes, while that between the benzene ring and the attached pyridyl ring is 24.3 (1)°. This latter angle is within the range considered to favor efficient energy migration between linked aromatic rings (Cave, Marcus & Sidars, 1986) and while a comparable angle would not necessarily be adopted by a bphb-bridged bimetallic complex, it is clear that there are no structural features of the bphb ligand itself that would prevent this.

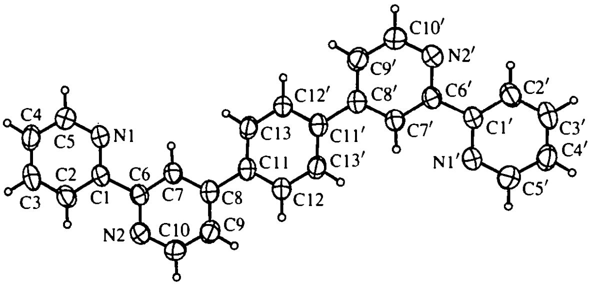


Fig. 1. *ORTEP*II drawing (Johnson, 1976) of compound (1). Displacement ellipsoids for non-H atoms are drawn at the 30% probability level. H atoms are represented by spheres of arbitrary radii.

Experimental

Compound (1) was prepared as described by Baba, Wang, Kim, Strong & Schmehl (1994) and was crystallized by slow diffusion of diethyl ether into a chloroform solution.

Crystal data

$C_{26}H_{18}N_4$
$M_r = 386.46$
Monoclinic
$P2_1/n$
$a = 10.025\,(1)$ Å
$b = 8.689\,(1)$ Å
$c = 12.063\,(1)$ Å
$\beta = 114.01\,(1)°$
$V = 959.9\,(4)$ Å^3
$Z = 2$
$D_x = 1.34$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 11–19°$
$\mu = 0.075$ mm^{-1}
$T = 293$ K
Block
0.53 × 0.46 × 0.33 mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
1922 measured reflections
1685 independent reflections
1091 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int} = 0.038$
$\theta_{\rm max} = 24.97°$
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 10$
$l = -14 \rightarrow 13$
2 standard reflections
frequency: 120 min
intensity decay: <1.0%

Refinement

Refinement on F
$R = 0.038$
$wR = 0.047$
$S = 1.494$
1091 reflections
136 parameters
H-atom parameters not refined

$w = 4F_o^2/[\sigma^2(F_o^2) + 0.0016F_o^4]$
$(\Delta/\sigma)_{\rm max} = 0.007$
$\Delta\rho_{\rm max} = 0.18$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.14$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
N1	0.5122 (2)	0.2379 (2)	0.9877 (1)	0.0603 (5)
N2	0.8044 (1)	−0.0197 (2)	1.0165 (1)	0.0508 (4)
C1	0.6380 (2)	0.1625 (2)	1.0420 (1)	0.0419 (5)
C2	0.7197 (2)	0.1731 (2)	1.1656 (2)	0.0536 (6)
C3	0.6710 (2)	0.2621 (2)	1.2352 (1)	0.0598 (6)
C4	0.5410 (2)	0.3368 (3)	1.1810 (2)	0.0600 (6)
C5	0.4669 (2)	0.3219 (3)	1.0582 (2)	0.0710 (7)
C6	0.6850 (2)	0.0679 (2)	0.9618 (1)	0.0418 (5)
C7	0.6076 (2)	0.0716 (2)	0.8369 (1)	0.0425 (5)
C8	0.6526 (2)	−0.0160 (2)	0.7620 (1)	0.0438 (5)
C9	0.7753 (2)	−0.1081 (2)	0.8197 (1)	0.0517 (5)
C10	0.8454 (2)	−0.1051 (2)	0.9440 (2)	0.0555 (6)
C11	0.5735 (2)	−0.0102 (2)	0.6276 (1)	0.0427 (5)
C12	0.6433 (2)	−0.0453 (2)	0.5518 (1)	0.0472 (5)
C13	0.4281 (2)	0.0351 (2)	0.5725 (1)	0.0485 (5)

Table 2. *Selected geometric parameters (Å, °)*

N1—C1	1.333 (2)	C4—C5	1.367 (3)
N1—C5	1.333 (3)	C6—C7	1.387 (2)
N2—C6	1.344 (2)	C7—C8	1.389 (3)
N2—C10	1.333 (3)	C8—C9	1.394 (3)
C1—C2	1.382 (2)	C8—C11	1.487 (2)
C1—C6	1.484 (3)	C9—C10	1.373 (3)
C2—C3	1.369 (3)	C11—C12	1.392 (3)
C3—C4	1.361 (3)	C11—C13	1.390 (3)
C1—N1—C5	117.1 (2)	C1—C6—C7	120.7 (2)
C6—N2—C10	116.4 (2)	C6—C7—C8	120.5 (2)
N1—C1—C2	121.6 (2)	C7—C8—C9	116.4 (2)
N1—C1—C6	116.1 (2)	C7—C8—C11	121.3 (2)
C2—C1—C6	122.3 (2)	C9—C8—C11	122.3 (2)
C1—C2—C3	119.8 (2)	C8—C9—C10	119.3 (2)
C2—C3—C4	119.0 (2)	N2—C10—C9	124.7 (2)
C3—C4—C5	117.9 (2)	C8—C11—C12	121.4 (2)
N1—C5—C4	124.6 (2)	C8—C11—C13	121.4 (2)
N2—C6—C1	116.7 (2)	C12—C11—C13	117.2 (2)
N2—C6—C7	122.6 (2)		

General procedures for crystal orientation, unit-cell determination and data collection have been published elsewhere (Mague & Lloyd, 1988). The space group was uniquely determined by the systematic absences seen in the final data set. The initial E map provided locations for all the non-H atoms of the bipyridyl moiety, but this unit was clearly located too close to the crystallographic center of symmetry. This fragment was input into the *DIRP*1 routine of the *DIRDIF* package (Beurskens, 1984) which generated locations for the unique C atoms of the benzene ring, but the misplacement problem persisted. Using the locations for these latter atoms, the average position of the centroid of the benzene ring was determined and used to shift the complete asymmetric unit so that this point coincided with the crystallographic center. Subsequent refinement proceeded normally and all H atoms could be located in a difference map. Because of the relatively small number of observed data, the H atoms were placed in calculated positions (C—H 0.95 Å), with isotropic displacement parameters 20% larger than those of their attached C atoms, and updated periodically.

Data collection: *CAD-*4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-*4 *Software*. Data reduction: *MolEN PROCESS* (Fair, 1990). Program(s) used to solve structure: *SIR*88 (Burla *et al.*, 1989). Program(s) used to refine structure: *MolEN LSFM*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *MolEN CIF VAX* (Fair, 1990).

We thank the Chemistry Department of Tulane University for generous financial support of the X-ray diffraction facility.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CR1205). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Amadelli, R., Argazzi, R., Bignozzi, C. A. & Scandola, F. (1990). *J. Am. Chem. Soc.* **112**, 7099–7103.

Baba, A. I., Wang, W., Kim, W. Y., Strong, L. A. & Schmehl, R. H. (1994). *Synth. Commun.* **24**, 1029–1036.

Bard, A. J. & Fox, M. A. (1995). *Acc. Chem. Res.* **28**, 141–145.

Beurskens, P. T. (1984). *DIRDIF. Direct Methods for Difference Structures – an Automatic Procedure for Phase Extension and Refinement of Difference Structure Factors.* Technical Report 1984/1. Crystallography Laboratory, Toernooiveld, 6525 ED Nijmegen, The Netherlands.
Bignozzi, C. A., Argazzi, R., Indelli, M. T. & Scandola, F. (1994). *Sol. Energy Mater. Sol. Cells*, **32**, 229–244.
Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Polidori, G., Spagna, R. & Viterbo, D. (1989). *J. Appl. Cryst.* **22**, 389–393.
Cave, R., Marcus, R. & Sidars, P. (1986). *J. Phys. Chem.* **90**, 1436–1444.
Enraf–Nonius (1989). *CAD-4 Software*. Version 5. Enraf–Nonius, Delft, The Netherlands.
Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis.* Enraf–Nonius, Delft, The Netherlands.
Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Liang, Y., Baba, A. I. & Schmehl, R. H. (1995). In preparation.
Mague, J. T. & Lloyd, C. L. (1988). *Organometallics*, **7**, 983–993.
Meyer, T. J., Meyer, G. J., Pfennig, B. W., Schoonover, J. R., Timpson, C. J., Wall, J. F., Kobusch, C., Chen, X., Peek, B. M., Wall, C. G., Ou, W., Erickson, B. W. & Bignozzi, C. A. (1994). *Inorg. Chem.* **33**, 3952–3964.
Nazeeruddin, M. K., Kay, A., Rodicio, I., Humphrey-Baker, R., Liska, E., Vlachopoulos, N. & Grätzel, M. (1993). *J. Am. Chem. Soc.* **115**, 6382–6390.
O'Regan, B. & Grätzel, M. (1991). *Nature (London)*, **353**, 737–740.
Pechy, P., Rotzinger, F. P., Nazeeruddin, M. K., Kohle, O., Zakeeruddin, S. M., Humphrey-Baker, R. & Grätzel, M. (1995). *J. Chem. Soc. Chem. Commun.* pp. 65–66.

Acta Cryst. (1996). C**52**, 660–663

Ethyl and Butyl 4-[4-(4-*n*-Octyloxybenzoyloxy)benzylidene]aminobenzoates

Shoko Kurogoshi and Kayako Hori*

Department of Chemistry, Ochanomizu University, Otsuka, Bunkyo-ku, Tokyo 112, Japan. E-mail: khori@fs.cc.ocha.ac.jp

(*Received 3 August 1995; accepted 27 September 1995*)

Abstract

In order to clarify relationships between the mesophase behaviour and crystal structures, the X-ray structure determinations of the title compounds, ethyl 4-[4-(4-*n*-octyloxybenzoyloxy)benzylidene]aminobenzoate, $C_{31}H_{35}NO_5$, and butyl 4-[4-(4-*n*-octyloxybenzoyloxy)benzylidene]aminobenzoate, $C_{33}H_{39}NO_5$, have been performed. The compounds have different phase sequences, *i.e.* crystal–smectic A–nematic–isotropic and crystal–smectic C–smectic A–nematic–isotropic for the ethyl and butyl compounds, respectively.

Comment

The homologous series of *n*-alkyl 4-[4-(4-*n*-octyloxybenzoyloxy)benzylidene]aminobenzoates have the phase sequence crystal–smectic A–nematic–isotropic for $n \leq 3$ and crystal–smectic C–smectic A–nematic–isotropic for $n \geq 4$ (Lotke & Patil, 1989).

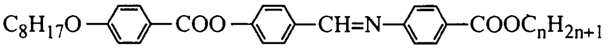


Fig. 1 shows the molecular structures and numbering schemes of both compounds. The butyl compound has two crystallographically independent molecules, *A* and *B*. In all three molecules, *i.e.* the single molecule of the ethyl compound and the *A* and *B* molecules of the butyl compound, the octyloxy chains have all-*trans* conformations. The core moieties, including the three phenylene rings, also have very similar conformations. The phenyl rings C1–C6 and C15–C20 are nearly coplanar, with dihedral angles of 1.7 (4), 2.1 (1) and 3.69 (7)° for $n = 2$, $n = 4$ (molecule *A*) and $n = 4$ (molecule *B*), respectively. The central ring, C8–C13, is twisted with respect to both of the terminal rings. The dihedral angles with rings C1–C6 and C15–C20 are 59.7 (2) and 60.5 (2)°, respectively, for $n = 2$, 54.0 (1) and 54.4 (1)° for $n = 4$ (molecule *A*), and 56.8 (1) and 54.3 (1)° for $n = 4$ (molecule *B*). The C21—O1—C22—C23 torsion angles are 172.9 (9), 179.3 (4) and 118.4 (6)° for $n = 2$, $n = 4$ (molecule *A*) and $n = 4$ (molecule *B*), respectively. The terminal atoms of the butyl chains are disordered in both molecules of the butyl compound.

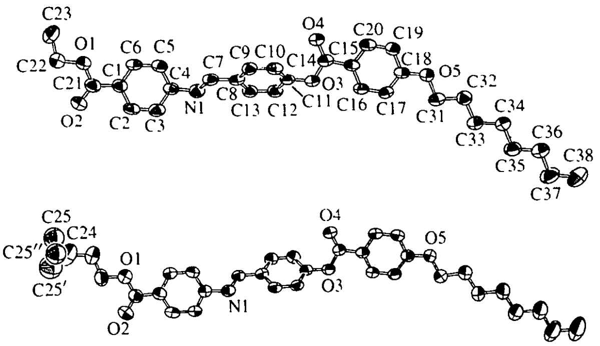


Fig. 1. The molecular structures of the ethyl (upper) and butyl (molecule *A*) compounds, with 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

Figs. 2 and 3 show the crystal structures of the ethyl and butyl compounds, respectively. Both crystals have smectic-like layer structures, with the layers parallel to the *bc* plane in the ethyl compound and parallel to the *ac* plane in the butyl compound. In the layers, adjacent molecules are arranged alternately so as to cancel their longitudinal dipole moments with one another. The core moieties overlap to a great extent in both crystals. The nearest neighboring phenyl rings of adjacent molecules

Acta Crystallographica Section C
ISSN 0108-2701 ©1996