

***p*-Methoxybenzaldehyde 9-fluorenylidenehydrazone**

Hoong-Kun Fun,<sup>a\*</sup> Suchada Chantrapromma,<sup>a†</sup> Ibrahim Abdul Razak,<sup>a</sup> Anwar Usman,<sup>a</sup> Wen Ma,<sup>b</sup> Yu Peng Tian,<sup>c‡</sup> Sheng Yi Zhang,<sup>b</sup> Jie Ying Wu<sup>b</sup> and Fu Xin Xie<sup>b</sup>

<sup>a</sup>X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia, <sup>b</sup>Department of Chemistry, Anhui University, Hefei, Anhui 230039, People's Republic of China, and <sup>c</sup>State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, People's Republic of China

† Permanent address: Department of Chemistry, Faculty of Science, Prince of Songkla University, Hat-Yai, Songkhla 90112, Thailand.

‡ Permanent address: Department of Chemistry, Anhui University, Hefei, Anhui 230039, People's Republic of China.

Correspondence e-mail: hkfun@usm.my

**Key indicators**

Single-crystal X-ray study

*T* = 293 K

Mean  $\sigma(\text{C}-\text{C}) = 0.005 \text{ \AA}$

*R* factor = 0.052

*wR* factor = 0.124

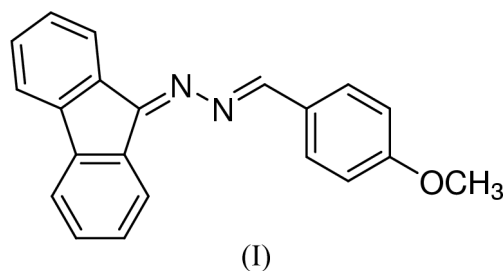
Data-to-parameter ratio = 10.0

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

In the title compound,  $\text{C}_{21}\text{H}_{16}\text{N}_2\text{O}$ , the molecule is nearly planar, with a dihedral angle of  $11.2(1)^\circ$  between the benzaldehyde and fluorene moieties. The attached methoxy group makes an angle of  $3.6(4)^\circ$  with the benzaldehyde moiety.

**Comment**

The design and development of new materials with the potential to operate at the molecular level has recently become a burgeoning topic within the physical sciences and chemistry in particular. Non-linear optics is drawing steady attention because of its possible wide application in the photonics-based technologies, including optical signal processing, optical switching, and optical sensing. A wide variety of materials including inorganic and organic crystals, thin films, and organic polymers and polymeric composites possess non-linear optical (NLO) properties (Moerner & Silence, 1994; Bredas *et al.*, 1994; Cumpston *et al.*, 1999). Many organic molecules with extensive conjugation in a planar skeleton have large NLO responses (Prasad & Williams, 1991; Marder *et al.*, 1997). We have synthesized the title compound, (I), in order to find potential new organic species for NLO crystals. As part of this attempt, an X-ray crystal structure analysis of (I) was undertaken to confirm and examine its non-centrosymmetric crystal packing.

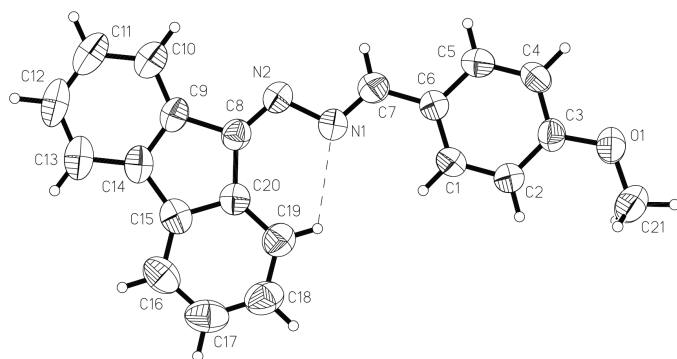


The bond lengths and angles in the title compound (Table 1) have normal values (Allen *et al.*, 1987). The double-bond character is localized at both the C–N bonds. The alternating single- and double-bond bridge between the benzaldehyde and fluorene moieties results in the planarity of the molecule of (I) (except for the methyl H atoms) to within  $\pm 0.222(4) \text{ \AA}$  and a dihedral angle of  $11.2(1)^\circ$  between the benzaldehyde and fluorene moieties. In the fluorene moiety, the five-membered ring makes dihedral angles of  $2.0(2)^\circ$  and  $3.0(2)^\circ$  with the benzene rings, while the two benzene rings themselves make an angle of  $4.6(2)^\circ$ . The attached methoxy group also lies in the plane through the benzaldehyde with a torsion angle of  $3.6(4)^\circ$ . The planarity of the title compound and the

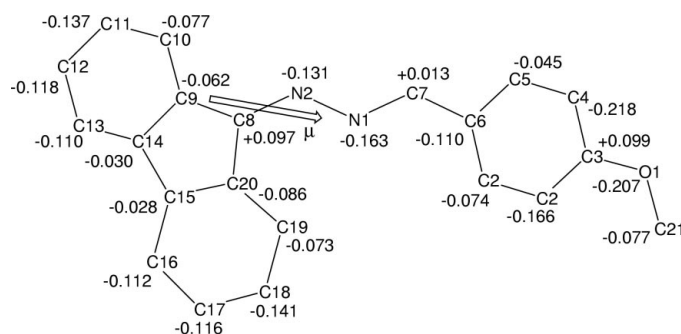
Received 19 September 2001

Accepted 4 October 2001

Online 13 October 2001



**Figure 1**  
The structure of (I) showing 50% probability displacement ellipsoids and the atom-numbering scheme.



**Figure 2**  
The MOPAC AM1 calculated charge distribution of the title compound (I). The direction of the dipole moment (1.7 D) is indicated by the arrow.

alternating single- and double-bond bridge is favourable for the charge transfer from the electron-donor to the acceptor. Hence, the molecular dipole moment lies in the molecular plane. According to our MOPAC AM1 calculations (Stewart, 1990), the dipole moment of (I) is about 1.7 D, in the direction from atom C9 to atom N1. The calculated charge distribution on the molecule (I) is shown in Fig. 2.

In the title structure, the intramolecular C—H···N interaction forms a closed N1—N2—C8—C20—C19—H19A ring, with N···H = 2.4330 Å, C19···N1 = 2.946 (5) Å, and C19—H19A···N1 = 115°. The crystal packing is stabilized by van der Waals interactions.

## Experimental

The title compound was prepared by the reaction of 9-fluorenylidenehydrazone and anisaldehyde in a 1:1 molar ratio under reflux in ethanol solution for 5 h. Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of a methanol solution at room temperature.

### Crystal data

C<sub>21</sub>H<sub>16</sub>N<sub>2</sub>O  
*M<sub>r</sub>* = 312.36  
 Orthorhombic, *Pca*2<sub>1</sub>  
*a* = 22.9292 (6) Å  
*b* = 9.5033 (3) Å  
*c* = 7.5152 (2) Å  
*V* = 1637.59 (8) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 1.267 Mg m<sup>-3</sup>

Mo *K*α radiation  
 Cell parameters from 3444 reflections  
 $\theta$  = 1.8–28.3°  
 $\mu$  = 0.08 mm<sup>-1</sup>  
*T* = 293 (2) K  
 Slab, yellow  
 0.42 × 0.24 × 0.14 mm

### Data collection

Siemens SMART CCD area-detector diffractometer  
 $\omega$  scans  
 Absorption correction: empirical (SADABS; Sheldrick, 1996)  
*T<sub>min</sub>* = 0.968, *T<sub>max</sub>* = 0.989  
 10 420 measured reflections

2182 independent reflections  
 1156 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.097  
 $\theta_{\max}$  = 28.4°  
*h* = −24 → 30  
*k* = −11 → 12  
*l* = −9 → 9

### Refinement

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.052  
*wR*(*F*<sup>2</sup>) = 0.125  
*S* = 0.94  
 2182 reflections  
 219 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0544P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.21 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.16 \text{ e \AA}^{-3}$   
 Extinction correction: SHELXTL  
 Extinction coefficient: 0.050 (4)

**Table 1**

Selected geometric parameters (Å, °).

N1—C7	1.264 (4)	C6—C7	1.453 (4)
N1—N2	1.418 (3)	C8—C20	1.485 (4)
N2—C8	1.286 (4)	C8—C9	1.487 (4)
C7—N1—N2—C8	−172.4 (3)	C21—O1—C3—C2	−2.9 (5)
C21—O1—C3—C4	175.8 (4)	N2—N1—C7—C6	176.7 (3)

After checking their presence in a difference map, all H atoms were geometrically fixed and allowed to ride on the parent C atoms and refined isotropically.

Data collection: SMART (Siemens, 1996); cell refinement: SAINT (Siemens, 1996); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 1997); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL, PARST (Nardelli, 1995) and PLATON (Spek, 1990).

This work was supported by a grant for State Key Program of China, the National Natural Science Foundation of China (Nos. 9871001 and 20071001). The authors would like to thank the Malaysian Government and Universiti Sains Malaysia (R&D No. 305/PFIZIK/610961). YPT thanks the Ministry of Education of China, and AU thanks Universiti Sains Malaysia for a Visiting Postdoctoral Fellowship.

## 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.  
 Bredas, J. L., Adant, C. & Tackx, P. (1994). *Chem. Rev.* **94**, 243–278.  
 Cumpston, B. H., Ananthavel, S. P. & Barlow, S. (1999). *Nature*, **398**, 51–55.  
 Marder, S. R., Williams, E. T., Mirelle, B. D., Vincent, R., Stegeman, G. I., Gilmour, S. & Bredas, J. L. (1997). *Science*, **276**, 1233–1240.  
 Moerner, W. E. & Silence, S. M. (1994). *Chem. Rev.* **94**, 127–155.  
 Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.  
 Prasad, P. N. & Williams, D. J. (1991). *Introduction to Nonlinear Optical Effects in Molecules and Polymers*. New York: John Wiley and Sons Inc.  
 Sheldrick, G. M. (1996). SADABS. University of Göttingen, Germany.  
 Sheldrick, G. M. (1997). SHELXTL. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.  
 Siemens (1996). SMART and SAINT. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.  
 Spek, A. L. (1990). *Acta Cryst.* **A46**, C-34.  
 Stewart, J. J. P. (1990). MOPAC6.0. Frank J. Seiler Research Laboratory, US Air Force Academy, CO 80840, USA.