Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

One-dimensional hydrogen-bonded molecular tapes in 1,4-bis[(4-pyridinio)ethynyl]benzene chloranilate

Md. Akhtaruzzaman,[a] Masaaki Tomura[b]* and Yoshiro Yamashita[c]

[a]Department of Structural Molecular Science, The Graduate University for Advanced Studies, Myodaiji, Okazaki 444-8585, Japan, [b]Institute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan, and [c]Department of Electronic Chemistry, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 226-8502, Japan

Correspondence e-mail: tomura@ims.ac.jp

Key indicators

Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.005 Å
R factor = 0.053
wR factor = 0.161
Data-to-parameter ratio = 12.0

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

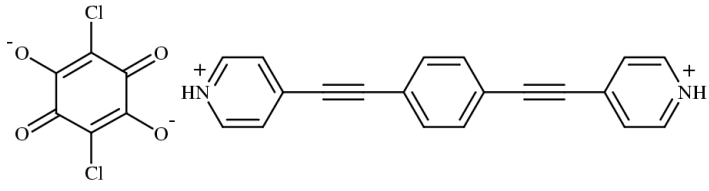
© 2001 International Union of Crystallography
Printed in Great Britain – all rights reserved

Received 8 March 2001
Accepted 15 March 2001
Online 23 March 2001

The structure of the title compound, $C_{20}H_{14}N_2^{2+}\cdot C_6Cl_2O_4^{2-}$, contains one-dimensional hydrogen-bonded molecular tapes along the [113] direction. The molecular tapes are connected *via* two N—H···O hydrogen bonds in $R_1^2(5)$ patterns.

Comment

We have recently shown that the simple combination of chloranilic acid and dipyridyl-type ligands can create a variety of supramolecular architectures involving infinite one-dimensional molecular tape structures (Zaman *et al.*, 1999, 2000). In the course of our crystal engineering studies on chloranilic acid, we have obtained the title compound, (I), a 1:1 co-crystal of chloranilic acid and 1,4-bis[(4-pyridyl)-ethynyl]benzene. A long rigid and conjugated bridging ligand has received much current interest for the construction of self-assembling macrocyclic architectures (Lehn, 1995; Fujita, 1999) and the development of molecular wires (Tour, 1996). However, we have found only two examples (Lin *et al.*, 1995, 1998) of structures containing a 1,4-bis[(4-pyridyl)ethynyl]-benzene unit in the Cambridge Structural Database (Allen & Kennard, 1993). We report here the structure of (I) with hydrogen-bonded molecular tapes.



(I)

The molecular structure of (I) is shown in Fig. 1, and both molecules are located on inversion centers. A one-dimensional molecular tape is observed in the structure of (I), as shown in Fig. 2. The molecular tape is nearly flat. The angles between the molecular planes of the chloranilate and the pyridinium ring, and of the pyridinium ring and the benzene ring are 7.3 (2) and 11.8 (4)°, respectively. The molecular tapes are connected *via* $R_1^2(5)$ couplings with two intermolecular N—H···O hydrogen bonds (Table 1), where both H atoms of chloranilic acid have transfered to the pyridine rings. In previous work (Zaman *et al.* 2000), we have shown that the flat molecular tapes form segregated stacks of each molecule. However, overlaps between the chloranilate–pyridinium ring–benzene ring–pyridinium ring–chloranilate are observed in the stacks of the molecular tapes of (I). A short C—Cl···π interaction [Cl1···(C7≡C8) 3.440 (7), Cl1···C7 3.503 (4), Cl1···C8 3.480 (4) Å; Cl1···C7≡C8 79.1 (3) and

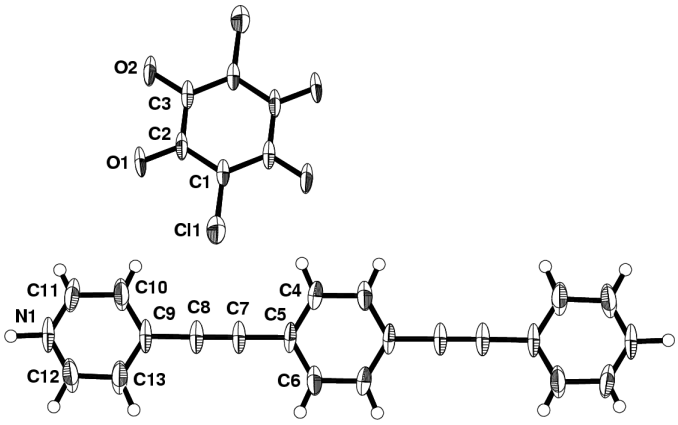


Figure 1
The molecular structure of (I) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

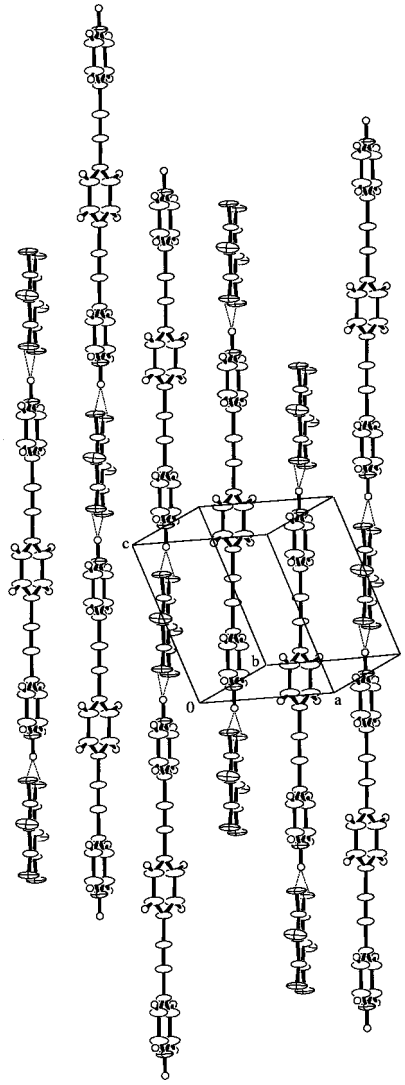


Figure 2
Packing diagram of (I). Dotted lines show the intermolecular N—H···O hydrogen bonds.

Cl1···C8≡C7 81.3 (3)°] exists between the stacks of the molecular tapes (Reddy *et al.*, 1996; Prasanna & Row, 2000). It is 1.7% shorter than the sum of the van der Waals radii of Cl and Csp^2 (Pauling, 1960).

Experimental

1,4-Bis[(4-pyridyl)ethynyl]benzene was prepared according to the literature (Lin *et al.*, 1995). Chloranilic acid was commercially available and purified by the usual method. A diffusion method for a solution of 1,4-bis[(4-pyridyl)ethynyl]benzene (0.02 mmol) and chloranilic acid (0.02 mmol) in acetonitrile (5 ml) using an H-tube gave crystals of (I) suitable for X-ray analysis.

Crystal data

$C_{20}H_{14}N_2^{2+}\cdot C_6Cl_2O_4^{2-}$
M_r = 489.29
Triclinic, $P\overline{1}$
a = 7.6279 (9) Å
b = 8.4019 (10) Å
c = 8.6291 (4) Å
α = 97.171 (6)°
β = 99.673 (6)°
γ = 95.728 (10)°
V = 536.76 (9) Å^3
Z = 1
D_x = 1.514 Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 23 reflections
θ = 5.9–43.0°
μ = 3.05 mm^{-1}
T = 296 (2) K
Needle, dark red
0.7 × 0.1 × 0.1 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.224, T_{max} = 0.750
2340 measured reflections
2187 independent reflections
1213 reflections with $I > 2\sigma(I)$
R_{int} = 0.041
θ_{max} = 74.3°
$h = -9 \rightarrow 9$
$k = -10 \rightarrow 10$
$l = 0 \rightarrow 10$
3 standard reflections
every 120 reflections
intensity decay: 2.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.053
$wR(F^2)$ = 0.161
S = 0.99
2187 reflections
182 parameters
All H-atom parameters refined
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.37 e Å^{-3}

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1^{i}	1.05 (7)	2.23 (6)	2.897 (4)	120 (5)
N1—H1···O2^{i}	1.05 (7)	1.62 (7)	2.609 (3)	154 (5)

Symmetry code: (i) $-x, 1-y, -z$.

All H atoms were located in the Fourier map and were refined isotropically.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1992); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *HELENA* (Spek, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*III (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL*97.

This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

References

Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 1, 31–37.
Burnett, M. N. & Johnson, C. K. (1996). *ORTEP*III. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.
Enraf–Nonius (1992). *CAD*-4 *EXPRESS*. Version 5.1. Enraf–Nonius, Delft, The Netherlands.
Fujita, M. (1999). *Acc. Chem. Res.* **32**, 53.
Lehn, J.-M. (1995). In *Supramolecular Chemistry*. Weinheim: VCH.
Lin, J. T., Sun, S.-S., Wu, J. J., Lee, L., Lin, K.-J. & Huang, Y. F. (1995). *Inorg. Chem.* **34**, 2323.
Lin, J. T., Yang, M.-F., Tsai, C. & Wen, Y. S. (1998). *J. Organomet. Chem.* **564**, 257.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Prasanna, M. D. & Row, T. N. G. (2000). *Cryst. Eng.* **3**, 135–154.
Pauling, L. (1960). In *The Nature of the Chemical Bond*. Ithaca: Cornell University Press.
Reddy, D. S., Craig, D. C. & Desiraju, G. R. (1996). *J. Am. Chem. Soc.* **118**, 4090–4093.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Spek, A. L. (1997). *HELENA*. University of Utrecht, The Netherlands.
Tour, J. M. (1996). *Chem. Rev.* **96**, 537–553.
Zaman, M. B., Tomura, M. & Yamashita, Y. (1999). *Chem. Commun.* pp. 999–1000.
Zaman, M. B., Tomura, M. & Yamashita, Y. (2000). *Org. Lett.* **2**, 273–275.