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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–S19.
Chinnakali, K., Fun, H.-K., Sriraghavan, K. & Ramakrishnan, V. T. (1998). *Acta Cryst.* **C54**, 370–371.
Crouse, D. J., Hurlbut, S. L. & Wheeler, D. M. S. (1981). *J. Org. Chem.* **46**, 374–378.
Hauck, F. P., Cimarusti, C. M. & Sundeen, J. E. (1977). *Chem. Abstr.* **86**, 43447u.
Marshall, J. L., Faehl, L. G., McDaniel, C. R. Jr & Ledford, N. D. (1977). *J. Am. Chem. Soc.* **99**, 321–325.
Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.
Sheldrick, G. M. (1990). *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.
Siemens (1994). *XSCANS Users Manual.* Version 2.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

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2-(1-Methyl-1,2-dihydro-2-pyridylidene-aminomethylene)propanedinitrile

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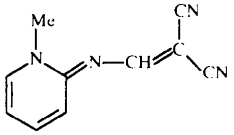
Abstract

The title compound, $C_{10}H_8N_4$, belongs to a series of conjugated molecules that offer potential utilization as organic dyes. As indicated by the planarity of the molecule and the pattern of bond lengths and angles, a considerable amount of π-electron density is transferred from the dihydropyridineimine portion of the molecule to the cyano groups. The principal packing interaction seems to be π–π stacking of the heterocyclic rings.

Comment

This work is part of our continuing study on the relationship between molecular and electronic structures, and absorption properties of polarized molecules having electron-releasing and electron-accepting groups bonded to an ethylene skeleton. These molecules absorb in the near-ultraviolet and visible regions due to delocalization of π electrons, and exhibit pronounced colour changes depending on the nature of the substituents attached to the ethylene-type C atoms. Consequently, it is of interest to examine the extent of conjugation in these molecules by combined use of theoretical and experimental methods. We report herein the crystal structure of the title compound, (I), a derivative having a dihydropyridine-imine chromophore and two cyano groups bonded to an ethylene skeleton.



(I)

Bond lengths and angles within the 1,2-dihydropyridine-2-imine moiety are affected by conjugation. The bonds N1—C2 and N1—C6 have partial double-bond character (Burke-Laing & Laing, 1976) and hence are much shorter than the essentially single bond N1—C14. The N1 atom is sp^2 hybridized, as evidenced by the sum of the valence angles around this atom [360.1 (2)°], with the lone-pair electrons available for π bonding. The intra-ring C—C bond distances, perhaps with the exception of the C5—C6 bond which approximates to a double bond, are equivalent. These facts indicate π-electron delocalization within the heterocyclic ring. A similar pattern of bond distances and angles has been observed in two other compounds containing the 1-methyl-1,2-dihydropyridine-2-imine substructure (Rodier *et al.*, 1986; Hammen *et al.*, 1989), as revealed by a search of the Cambridge Structural Database (Allen *et al.*, 1983).

Considering the exocyclic bonds, the formally double bond C2═N7 is even longer than the formally single bond N7—C8, the ethylene double bond C8═C9 is considerably longer than the reported value of 1.314 (6) Å in unpolarized ethylene (van Nes & Vos, 1977), and the C9—C10 and C9—C12 bond lengths [1.411 (3) and 1.412 (3) Å, respectively] are shorter than the value expected for a pure C_{sp^2}—C_{sp} single bond (Hummel & Procher, 1986). There is, therefore, an indication that π density concentrated in the dihydropyridineimine chromophore is transferred, at least in part, to the acceptor (cyano) groups.

Due to conjugation, the dihydropyridine ring is planar within experimental error [r.m.s. deviation 0.007 (2) Å] and atoms N7 and C14 are displaced from this plane on opposite sides, with respective out-of-plane displacements of −0.040 (3) and 0.038 (3) Å. As can be seen from the exocyclic torsion angles, the molecule as a whole is also approximately planar.

The molecules stack in the **b** direction, the heterocyclic rings being required to be parallel by symmetry, but they do not lie directly over one another. The perpendicular distance between them is 3.380 Å; however, the distance between their centroids is b = 3.956 Å, *i.e.* the rings are 'slipped' by 2.058 Å from their fully overlapped position. Such a stacking geometry is in line with the model of π–π interactions presented by Hunter & Saunders (1990).

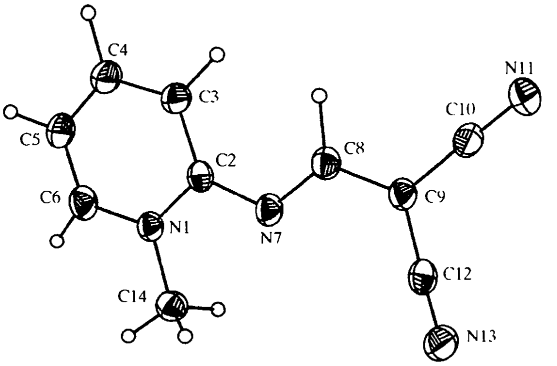


Fig. 1. View of the title molecule showing the labelling of the non-H atoms. Displacement ellipsoids are shown at 50% probability levels and H atoms have been drawn as small circles of arbitrary radii.

Experimental

To a solution of 2-imino-1-methyl-1,2-dihydropyridine hydroiodide (10 mmol), synthesized according to Bertho (1947), in dry ethanol (30 ml), was added dry triethylamine (10 mmol). After stirring for 10 min, a solution of freshly distilled ethoxymethylenepropanedinitrile (10 mmol) in ethanol (30 ml) was added dropwise and the mixture was refluxed for 4 h. When the reaction was terminated, the reaction mixture was cooled, evaporated to dryness, and finally subjected to chromatographic separation to obtain the product in 65% yield (m.p. 487–488 K).

Crystal data

$C_{10}H_8N_4$
M_r = 184.20
Monoclinic
$P2_1/n$
a = 11.686 (8) Å
b = 3.956 (2) Å
c = 20.404 (13) Å
β = 106.06 (7)°
V = 906.5 (10) Å^3
Z = 4
D_x = 1.350 Mg m^{-3}
D_m = 1.35 (1) Mg m^{-3}
D_m measured by flotation in bromoform–cyclohexane

Mo $K\alpha$ radiation
λ = 0.7107 Å
Cell parameters from 15 reflections
θ = 10–19°
μ = 0.088 mm^{-1}
T = 293 (2) K
Prism
0.30 × 0.25 × 0.15 mm
Yellow

Data collection

Syntex $P2_1$ diffractometer
$\theta/2\theta$ scans
Absorption correction: none
1611 measured reflections
1611 independent reflections
988 reflections with $I > 2\sigma(I)$

$\theta_{\max}$ = 25.07°
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 4$
$l = -24 \rightarrow 22$
2 standard reflections
frequency: 100 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.050
$wR(F^2)$ = 0.130
S = 1.004
1611 reflections
127 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o^2) + (0.0719P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 0.270 e Å^{-3}
$\Delta\rho_{\min}$ = −0.302 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

N1—C6	1.354 (3)	C5—C6	1.332 (3)
N1—C2	1.359 (3)	N7—C8	1.318 (3)
N1—C14	1.469 (3)	C8—C9	1.373 (3)
C2—N7	1.346 (3)	C9—C10	1.411 (3)
C2—C3	1.398 (3)	C9—C12	1.412 (3)
C3—C4	1.354 (3)	C10—N11	1.135 (3)
C4—C5	1.384 (4)	C12—N13	1.137 (3)
C6—N1—C2	121.7 (2)	N7—C2—C3	128.8 (2)
C6—N1—C14	119.0 (2)	N1—C2—C3	117.0 (2)
C2—N1—C14	119.4 (2)	C8—N7—C2	118.3 (2)
N7—C2—N1	114.2 (2)	N7—C8—C9	121.9 (2)
N1—C2—N7—C8	179.6 (2)	N7—C8—C9—C12	0.3 (4)
C2—N7—C8—C9	179.6 (2)		

H atoms were located from a difference Fourier map but were not refined; $U_{\rm iso}$ was set to $1.2U_{\rm eq}$ of the parent atom.

Data collection: Syntex $P2_1$ diffractometer system. Cell refinement: Syntex $P2_1$ diffractometer system. Data reduction: *XP*21 (Pavelčík, 1987). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976) . Software used to prepare material for publication: *SHELXL*93.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1002). Services for accessing these data are described at the back of the journal.

References

Allen, F. H., Kennard, O. & Taylor, R. (1983). *Acc. Chem. Res.* **16**, 146–153.
Bertho, A. (1947). *Chem. Ber.* **80**, 316–320.
Burke-Laing, M. & Laing, M. (1976). *Acta Cryst.* B**32**, 3216–3224.
Hammen, P. D., Berke, H., Bordner, J., Braisted, A. C., Lombardino, J. G. & Whipple, E. B. (1989). *J. Heterocycl. Chem.* **26**, 11–17.
Hummel, H.-U. & Procher, H. (1986). *Acta Cryst.* C**42**, 1602–1604.
Hunter, C. A. & Saunders, J. K. M. (1990). *J. Am. Chem. Soc.* **112**, 5525–5534.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Nes, G. J. K. van & Vos, A. (1977). *Acta Cryst.* B**33**, 1653–1654.
Pavelčík, F. (1987). *XP*21. *Program for Syntex P*2$_1$ *Data Reduction.* Comenius University, Slovakia.

Rodier, N., Gillo, M.-P., Piessard, S. & Le Baut, G. (1986). *Acta Cryst.* C**42**, 1397–1402.
Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures.* University of Göttingen, Germany.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

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trans-2-(2-Thienyl)-3-(5-phenyl-2-furyl)-propenenitrile

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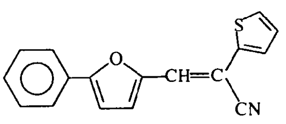
Abstract

The title compound, $C_{17}H_{11}NOS$, belongs to a series of extensively conjugated molecules which have potential as organic dyes. As indicated by the planarity of the molecule and bond-length patterns, the π-electron delocalization extends over the whole molecule. As expected, the arrangement of the phenylfuran and thiophene moieties at the double bond is *trans*.

Comment

As part of our study on the relationships between molecular and electronic structures and absorption properties of extensively delocalized molecules as potential organic dyes, we have prepared a series of 1-(2-furyl)-2-cyanoethylenes. These molecules absorb in the near ultraviolet and visible regions of the spectrum, and exhibit pronounced colour changes depending on the nature of the substituents attached to the ethylene C atom and the furan ring. Consequently, it is of interest to examine the extent of conjugation in these molecules by the combined use of theoretical and experimental methods. In this communication, we report on the crystal structure of the title phenyl–thienyl derivative, (1).



(1)

As shown in Fig. 1, the furyl and thienyl functions are *trans*-positioned at the C5═C7 double bond. This bond [1.346 (3) Å] is considerably longer than the bond length of 1.314 (6) Å in unsubstituted ethylene (van Nes & Vos, 1977), but falls into a range of values generally observed for polarized ethylenes (Banerjee *et al.*, 1985). Bond lengths and angles within the furan and thiophene rings also agree well with those found in other compounds containing these molecular fragments (Sanni *et al.*, 1987; Gilmore *et al.*, 1983; Bak *et al.*, 1961; Pavelčík *et al.*, 1989).

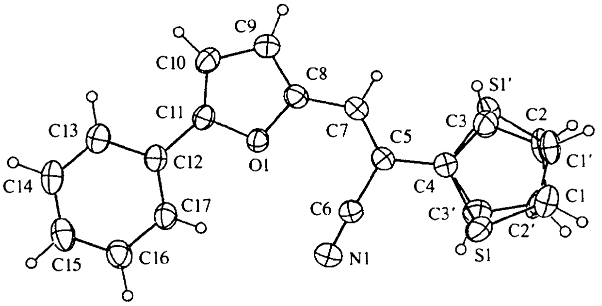


Fig. 1. *ORTEP*II (Johnson, 1976) view of the title molecule showing the labelling of the non-H atoms. Displacement ellipsoids are shown at the 50% probability level and H atoms are drawn as small circles of arbitrary radii. Both orientations of the disordered thiophene ring are shown.

The thiophene ring shows disorder; it adopts two different orientations related by a rotation of 172.3 (8)° about the C4—C5 bond. An unrestrained model of the disorder gave a reasonable fit to the experimental data but the resulting bond lengths and angles were unsatisfactory, particularly for the sites of lower occupancy. Therefore, restraints on both geometrical and displacement parameters as implemented in *SHELXL*93 (Sheldrick, 1993) were used. This resulted in a model with occupancies of 0.63 and 0.37 for the major and minor sites and a reasonable geometry for both rotamers.

The molecule as a whole is approximately planar. As expected, the furyl and phenyl rings are planar (r.m.s. deviations 0.000 and 0.003 Å, respectively), and the dihedral angle between these two planes is 2.8 (2)°. The twist about the ethylenic bond, as measured by the angle between the planes through C4, C5, C6 and H7, C7, C8 is 4.6 (9)°. While the furan ring lies in the plane of this double bond [dihedral angles 3.8 (4)°], the thiophene ring is substantially rotated out of the mean plane of the ethylenic bond [dihedral angle 13.2 (8) and 7.9 (9)° for the major and minor rotamers, respectively]. Thus, the planarity of the whole molecule is perturbed mainly by the thiophene moiety.

The extensive conjugation in the molecule is also observed in the C4—C5, C7—C8 and C11—C12 bond distances, which are all substantially shorter than the normal value of 1.487 Å reported for the C_{sp^2}—C_{sp^2} single bond (Shmueli *et al.*, 1973).