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Monoclinic polymorph of 2,5-bis[4-(dimethylamino)styryl]-3,6-dimethylpyrazine

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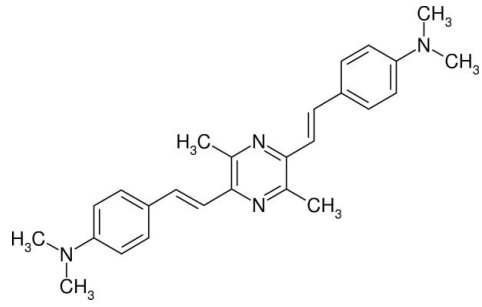
Key indicators: single-crystal X-ray study; T = 193 K; mean σ(C–C) = 0.003 Å; R factor = 0.056; wR factor = 0.170; data-to-parameter ratio = 19.0.

The title compound, $C_{26}H_{30}N_4$, was prepared by condensation of tetramethylpyrazine and dimethylaminobenzaldehyde and crystallizes from chloroform/methanol in two different forms. Block-shaped crystals belong to the monoclinic crystal system and plates to the triclinic system. The two crystal forms differ in the arrangement of the centrosymmetric molecules, which have nearly identical geometries. In the monoclinic crystals reported here, planar molecules [maximum deviation = 0.062 (2) Å], with a *transoid* arrangement of the (*E*)-styryl units and completely planarized dimethylamino groups [sum of the C—N bond angles = 359.9 (2)°], form layers connected *via* H–π-stacking. The dihedral angle between the central and pendant rings is 1.30 (8)°. The triclinic polymorph contains two half molecules, both completed by crystallographic inversion symmetry.

Related literature

The title compound was synthesized as a fundamental chromophore in a larger project focusing on solvatochromic and acidochromic dyes for sensing applications *via* one and two-photon excited fluorescence, see: Nemkovich *et al.* (2010); Schmitt *et al.* (2008); Detert & Schmitt (2006); Strehmel *et al.* (2003). Starting with 2,5-dimethylpyrazine, linear distyrylpyrazines had been prepared by acid-catalyzed condensations with benzaldehyde (Takahashi & Satake, 1952) as well as *via* Siegrist reaction with the anils of alkoxybenzaldehydes (Zerban, 1991). Crystal data for the triclinic form have been deposited (CCDC 807782).



Experimental

Crystal data

$C_{26}H_{30}N_4$
M_r = 398.54
Monoclinic, $P2_1/c$
a = 6.0635 (5) Å
b = 15.5187 (13) Å
c = 12.8009 (12) Å
β = 113.449 (6)°
V = 1105.06 (17) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.07 mm^{-1}
T = 193 K
0.49 × 0.45 × 0.27 mm

Data collection

Bruker SMART CCD diffractometer
13517 measured reflections
2637 independent reflections
1711 reflections with $I > 2\sigma(I)$
R_{int} = 0.057

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.056
$wR(F^2)$ = 0.170
S = 1.02
2637 reflections
139 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.27 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}

Data collection: *SMART* (Bruker, 2006); cell refinement: *SAINT* (Bruker, 2006); data reduction: *SAINT*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *PLATON*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SI2330).

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supporting information

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Monoclinic polymorph of 2,5-bis[4-(dimethylamino)styryl]-3,6-dimethylpyrazine

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S1. Comment

The title compound (Fig1.) is formed *via* base-catalyzed condensation of *p*-dimethylaminobenzaldehyde and tetramethylpyrazine. Monoclinic and triclinic crystals are obtained by crystallization from chloroform/methanol.

The monoclinic crystal is built from parallel layers (Fig. 2) with a distance of the mean planes of 3.5 Å indicating a π-π-interaction of neighbouring molecules. Perpendicular to the pyrazine-N are the nitrogen atoms of the dimethylamino groups of molecules in the lower and upper layer. Each molecule is connected to six neighbouring molecules *via* H-π-interactions with distances H–centroid of the π-system in the range of 2.27 - 2.88 Å. These CH-π-bonds connect pyrazinmethyl groups C4—H with anilines, and dimethylamino groups C14—H with pyrazines and C15—H with aniline rings. The molecules are planar, C14 shows the largest deviation (0.062 (2) A) from the plane defined by all 15 non H-atoms. The bond length C10—N13 of only 1.368 (2) Å is close to the bond lengths in the central heterocycle (N1—C2: 1.333 (2) Å; N1—C3: 1.353 (2) Å) indicating a strong electronic interaction of terminal donors and the central pyrazine acceptor.

The triclinic form contains two independent half-molecules which both are completed by inversion symmetry [1 - *x*, 1 - *y*, 1 - *z* and -*x*, 1 - *y*, 1 - *z*], drawn with different colours in the packing diagram of Fig. 3.

These molecules are arranged in layers with a distance of 3.7 Å and a tilt angle of 4 °. The centroids of the pyrazine rings of layers A and B are collinear but the molecules are twisted about about 60 °. The layers are connected *via* hydrogen bonds from C14—H (A) to the aniline ring (B). Crystal data are deposited under CCDC 807782.

S2. Experimental

The title compound was prepared by adding potassium *tert*-butylate (1.50 g, 16.1 mmol) to a solution of tetramethylpyrazine (0.90 g, 6.70 mmol) and 4-dimethylaminobenzaldehyde (2.00 g, 13.41 mmol) in anhydrous DMF (25 ml). The mixture was stirred at 273 K under nitrogen until the aldehyde has been consumed (TLC). The mixture was diluted with water (75 ml) and the product extracted with chloroform, the solution dried with Na_2SO_4 and after evaporation of the solvent, the residue recrystallized from chloroform/methanol (1:1) to yield a mixture of block- and plate-shaped, dark red crystals. Yield: 1.42 g (54%), m.p.=522 K.

S3. Refinement

Hydrogen atoms attached to carbons were placed at calculated positions with C—H = 0.95 Å (aromatic) or 0.98–0.99 Å (sp^3 C-atom). All H atoms were refined in the riding-model approximation with isotropic displacement parameters (set at 1.2–1.5 times of the U_{eq} of the parent atom).

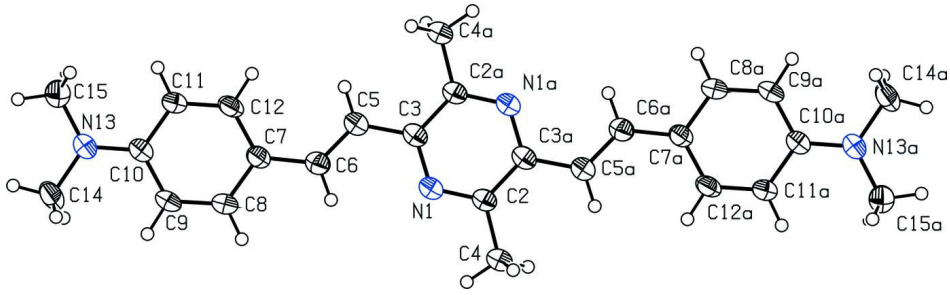

Figure 1

View of compound **I**. Displacement ellipsoids are drawn at the 50% probability level. Inversion-related atoms [1 - *x*, 1 - *y*, 1 - *z*] are shown with suffix a.

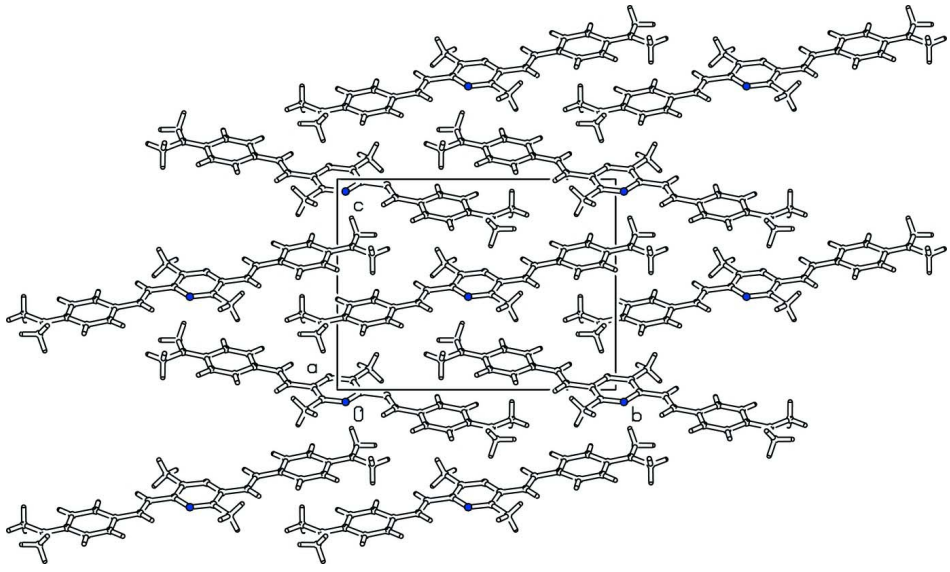

Figure 2

A packing section of the monoclinic crystal form viewed down the *a* axis.

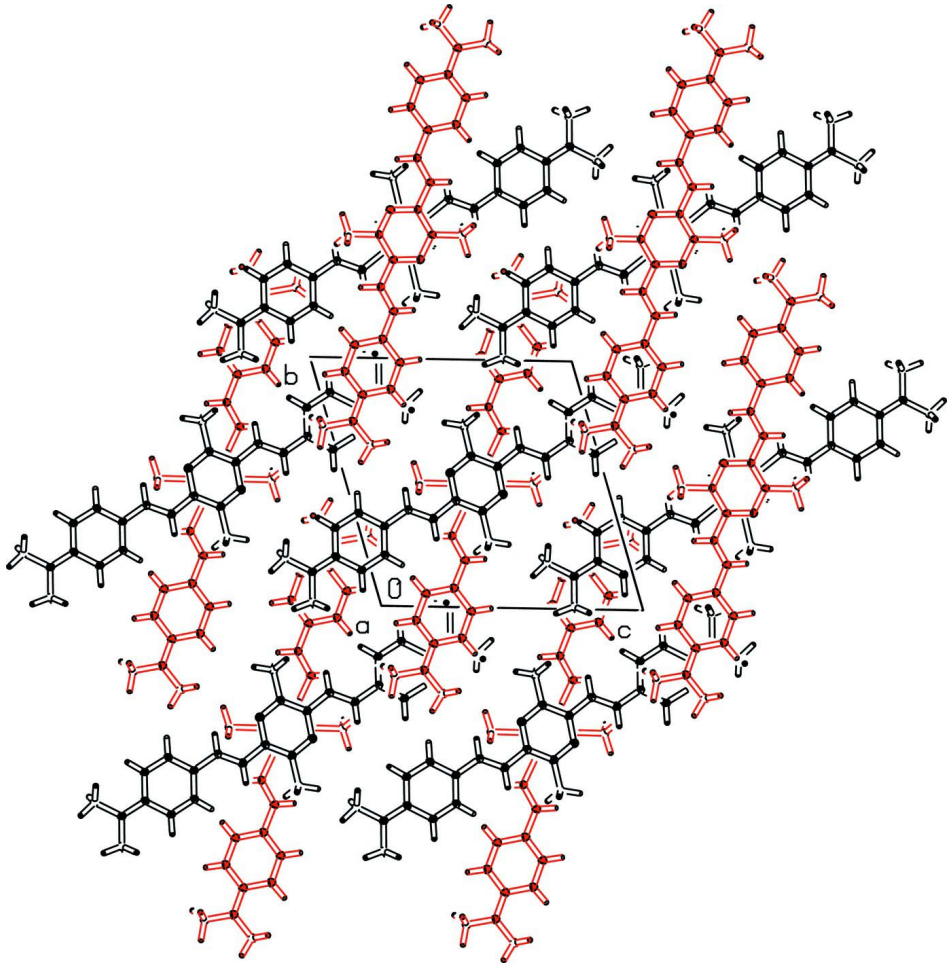

Figure 3

A packing section of the triclinic crystal form viewed down the *a* axis.

4-[2-(5-{2-[4-(dimethylamino)phenyl]ethenyl}-3,6-dimethylpyrazin-2-yl)ethenyl]- *N*,*N*-dimethylaniline

Crystal data

$C_{26}H_{30}N_4$
M_r = 398.54
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
a = 6.0635 (5) Å
b = 15.5187 (13) Å
c = 12.8009 (12) Å
β = 113.449 (6)°
V = 1105.06 (17) Å^3
Z = 2

$F(000)$ = 428
D_x = 1.198 Mg m^{-3}
Melting point: 522 K
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 3217 reflections
θ = 2.6–27°
μ = 0.07 mm^{-1}
T = 193 K
Block, orange
0.49 × 0.45 × 0.27 mm

Data collection

Bruker SMART CCD diffractometer
Radiation source: sealed Tube
Graphite monochromator

CCD scan
13517 measured reflections
2637 independent reflections
1711 reflections with $I > 2\sigma(I)$

R_{int} = 0.057
θ_{max} = 28.0°, θ_{min} = 2.2°
h = −7→7
k = −20→19
l = −16→16

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.056
$wR(F^2)$ = 0.170
S = 1.02
2637 reflections
139 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.093P)^2 + 0.1486P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.27 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	U_{iso}*/U_{eq}
N1	0.3645 (2)	0.52967 (9)	0.55807 (11)	0.0361 (4)
C2	0.3898 (3)	0.44536 (10)	0.54641 (13)	0.0340 (4)
C3	0.4723 (3)	0.58565 (10)	0.51230 (13)	0.0347 (4)
C4	0.2626 (3)	0.38669 (11)	0.59782 (16)	0.0437 (5)
H4A	0.3808	0.3592	0.6661	0.066*
H4B	0.1750	0.3423	0.5424	0.066*
H4C	0.1492	0.4203	0.6185	0.066*
C5	0.4434 (3)	0.67746 (11)	0.52817 (15)	0.0374 (4)
H5	0.5138	0.7174	0.4943	0.045*
C6	0.3227 (3)	0.70847 (11)	0.58799 (14)	0.0363 (4)
H6	0.2543	0.6666	0.6203	0.044*
C7	0.2832 (3)	0.79779 (11)	0.60981 (14)	0.0347 (4)
C8	0.1390 (3)	0.81714 (11)	0.66978 (16)	0.0424 (5)
H8	0.0713	0.7710	0.6959	0.051*
C9	0.0920 (3)	0.90040 (11)	0.69218 (15)	0.0424 (5)
H9	−0.0074	0.9101	0.7327	0.051*
C10	0.1880 (3)	0.97122 (11)	0.65634 (13)	0.0352 (4)
C11	0.3336 (3)	0.95248 (11)	0.59606 (14)	0.0374 (4)
H11	0.4019	0.9985	0.5700	0.045*
C12	0.3784 (3)	0.86880 (11)	0.57435 (14)	0.0383 (4)
H12	0.4776	0.8589	0.5338	0.046*
N13	0.1460 (3)	1.05436 (9)	0.67883 (13)	0.0443 (4)

C14	−0.0132 (4)	1.07191 (13)	0.73601 (18)	0.0524 (5)
H14A	−0.1665	1.0421	0.6962	0.079*
H14B	−0.0415	1.1341	0.7357	0.079*
H14C	0.0610	1.0513	0.8148	0.079*
C15	0.2474 (3)	1.12637 (12)	0.64153 (16)	0.0479 (5)
H15A	0.4228	1.1207	0.6724	0.072*
H15B	0.2044	1.1802	0.6688	0.072*
H15C	0.1838	1.1270	0.5581	0.072*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0347 (8)	0.0396 (8)	0.0399 (8)	0.0014 (6)	0.0210 (6)	−0.0010 (6)
C2	0.0300 (8)	0.0397 (9)	0.0351 (9)	0.0006 (6)	0.0161 (7)	−0.0006 (7)
C3	0.0304 (8)	0.0415 (10)	0.0342 (9)	0.0024 (6)	0.0151 (7)	−0.0013 (7)
C4	0.0462 (10)	0.0433 (10)	0.0542 (11)	0.0003 (8)	0.0334 (9)	−0.0002 (8)
C5	0.0374 (9)	0.0388 (9)	0.0416 (10)	0.0012 (7)	0.0215 (8)	−0.0008 (7)
C6	0.0342 (9)	0.0401 (9)	0.0378 (9)	−0.0004 (7)	0.0176 (8)	−0.0006 (7)
C7	0.0340 (9)	0.0390 (9)	0.0359 (9)	0.0022 (6)	0.0191 (7)	−0.0006 (7)
C8	0.0469 (10)	0.0433 (10)	0.0506 (11)	−0.0020 (7)	0.0338 (9)	0.0012 (8)
C9	0.0449 (10)	0.0476 (11)	0.0493 (11)	0.0020 (7)	0.0343 (9)	−0.0006 (8)
C10	0.0337 (9)	0.0408 (10)	0.0350 (9)	0.0029 (7)	0.0179 (7)	−0.0015 (7)
C11	0.0388 (9)	0.0398 (9)	0.0418 (10)	−0.0027 (7)	0.0249 (8)	−0.0008 (7)
C12	0.0363 (9)	0.0459 (10)	0.0424 (10)	0.0004 (7)	0.0258 (8)	−0.0024 (8)
N13	0.0517 (9)	0.0399 (9)	0.0532 (9)	0.0051 (6)	0.0336 (8)	−0.0023 (7)
C14	0.0531 (12)	0.0521 (11)	0.0653 (13)	0.0063 (9)	0.0376 (11)	−0.0115 (10)
C15	0.0501 (11)	0.0409 (11)	0.0577 (12)	−0.0017 (8)	0.0268 (10)	−0.0050 (8)

Geometric parameters (Å, º)

N1—C2	1.333 (2)	C8—H8	0.9500
N1—C3	1.353 (2)	C9—C10	1.403 (2)
C2—C3^{i}	1.413 (2)	C9—H9	0.9500
C2—C4	1.504 (2)	C10—N13	1.368 (2)
C3—C2^{i}	1.413 (2)	C10—C11	1.415 (2)
C3—C5	1.459 (2)	C11—C12	1.377 (2)
C4—H4A	0.9800	C11—H11	0.9500
C4—H4B	0.9800	C12—H12	0.9500
C4—H4C	0.9800	N13—C15	1.445 (2)
C5—C6	1.341 (2)	N13—C14	1.451 (2)
C5—H5	0.9500	C14—H14A	0.9800
C6—C7	1.453 (2)	C14—H14B	0.9800
C6—H6	0.9500	C14—H14C	0.9800
C7—C12	1.401 (2)	C15—H15A	0.9800
C7—C8	1.406 (2)	C15—H15B	0.9800
C8—C9	1.378 (2)	C15—H15C	0.9800
C2—N1—C3	119.01 (14)	C8—C9—H9	119.4

N1—C2—C3^{i}	120.87 (15)	C10—C9—H9	119.4
N1—C2—C4	116.32 (14)	N13—C10—C9	122.27 (15)
C3^{i}—C2—C4	122.81 (15)	N13—C10—C11	121.15 (15)
N1—C3—C2^{i}	120.12 (15)	C9—C10—C11	116.58 (15)
N1—C3—C5	117.47 (14)	C12—C11—C10	121.31 (15)
C2^{i}—C3—C5	122.40 (15)	C12—C11—H11	119.3
C2—C4—H4A	109.5	C10—C11—H11	119.3
C2—C4—H4B	109.5	C11—C12—C7	122.44 (16)
H4A—C4—H4B	109.5	C11—C12—H12	118.8
C2—C4—H4C	109.5	C7—C12—H12	118.8
H4A—C4—H4C	109.5	C10—N13—C15	121.39 (14)
H4B—C4—H4C	109.5	C10—N13—C14	120.01 (15)
C6—C5—C3	123.56 (16)	C15—N13—C14	118.53 (14)
C6—C5—H5	118.2	N13—C14—H14A	109.5
C3—C5—H5	118.2	N13—C14—H14B	109.5
C5—C6—C7	128.43 (16)	H14A—C14—H14B	109.5
C5—C6—H6	115.8	N13—C14—H14C	109.5
C7—C6—H6	115.8	H14A—C14—H14C	109.5
C12—C7—C8	115.78 (15)	H14B—C14—H14C	109.5
C12—C7—C6	124.56 (15)	N13—C15—H15A	109.5
C8—C7—C6	119.66 (15)	N13—C15—H15B	109.5
C9—C8—C7	122.61 (15)	H15A—C15—H15B	109.5
C9—C8—H8	118.7	N13—C15—H15C	109.5
C7—C8—H8	118.7	H15A—C15—H15C	109.5
C8—C9—C10	121.28 (15)	H15B—C15—H15C	109.5

C3—N1—C2—C3^{i}	0.3 (3)	C8—C9—C10—N13	−179.19 (17)
C3—N1—C2—C4	−179.17 (14)	C8—C9—C10—C11	0.3 (3)
C2—N1—C3—C2^{i}	−0.3 (3)	N13—C10—C11—C12	179.28 (15)
C2—N1—C3—C5	−179.15 (14)	C9—C10—C11—C12	−0.2 (2)
N1—C3—C5—C6	2.0 (3)	C10—C11—C12—C7	0.2 (3)
C2^{i}—C3—C5—C6	−176.81 (17)	C8—C7—C12—C11	−0.3 (3)
C3—C5—C6—C7	179.74 (15)	C6—C7—C12—C11	179.28 (15)
C5—C6—C7—C12	−3.1 (3)	C9—C10—N13—C15	179.76 (16)
C5—C6—C7—C8	176.42 (18)	C11—C10—N13—C15	0.3 (3)
C12—C7—C8—C9	0.4 (3)	C9—C10—N13—C14	−3.5 (3)
C6—C7—C8—C9	−179.23 (16)	C11—C10—N13—C14	177.07 (16)
C7—C8—C9—C10	−0.4 (3)		

Symmetry code: (i) −*x*+1, −*y*+1, −*z*+1.