O'Donnell, M. & Polt, R. L. (1982). *J. Org. Chem.* **47**, 2663-2666.
Rao, Y. S. & Filler, R. (1975). *Synthesis*, pp. 749-764.
Wong, R. Y. (1978). *Acta Cryst.* B**34**, 3482-3484.

Acta Cryst. (1993). C**49**, 1818-1821

Structures of 1,1-Diphenyl-2-aza-1,3-butadienes. II. 3-Cyano-4-(*n*-fluorophenyl)-1,1-diphenyl-2-aza-1,3-butadienes (*n* = 2, 4)

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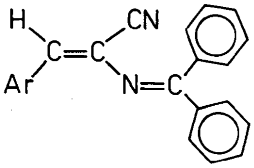
Abstract

The title compounds, 2FPD and 4FPD [3-(2-fluorophenyl)-2-(diphenylmethyleneamino)propenonitrile and 3-(4-fluorophenyl)-2-(diphenylmethyleneamino)propenonitrile], each crystallize in a *Z* configuration. The azabutadiene fragment in both 2FPD and 4FPD is twisted around the single N—C bond at 132.1 (3) and 129.2 (4)°, respectively. The non-substituted phenyl rings in 2FPD are tilted in respect to the $N1{=}C(C_{Ph})—C_{Ph}$ plane at 29.6 (1) and 51.3 (1)°; in 4FPD these angles are 21.7 (2) and 57.4 (2)°. The dihedral angle between these rings is 71.5 (1) (2FPD) and 71.7 (1)° (4FPD). The fluorophenyl ring in 2FPD is more rotated with respect to the planar $N—C(C_{CN}){=}CH—C_{Ph}$ group [15.2 (1)°] than that in 4FPD [5.2 (3)°]. No plane-to-plane coupling among the phenyl rings occurs. The molecular packing in both structures is dominated by van der Waals forces and the weak C—H···N bond to the cyano group [H3*c*···N 2.549 (3), 2.545 (3) Å, C3*c*—H3*c*···N 168.4 (3), 152.7 (3)°, in 2FPD and 4FPD, respectively].

Comment

2-Aza-1,3-dienes (I) are useful intermediates for the preparation of heterocyclic compounds (Boger & Weinreb, 1987; Barluenda, Joglar, Gonzales & Fustero, 1990; Barluenda, Aznar, Fustero & Tomas, 1990; Barluenda, Carlon, Pelaez, Joglar & Lopez Ortiz, 1992). Structural investigations on substituted 1,1-diphenyl-2-aza-1,3-butadienes were begun recently for three 3-cyano-4-(*n*-methoxyphenyl)-1,1-diphenyl-2-aza-1,3-butadienes, MOPDs (*n* = 2, 3, 4) (Angelova, Macíček & Dryanska, 1993).



(I)

The title compounds are *Z* isomers like the MOPD analogues. Most interatomic distances and angles in both FPDs are equal within the e.s.d.'s to those in the three MOPDs. Notable differences were found only in 4FPD, where N1—C2 is longer by 0.019 Å than the average bond length of 1.405 (3) Å in 2FPD and the three MOPDs, while C3—C1*c* is shorter by 0.013 Å than the average bond length of 1.457 (5) Å.

Bond angles in the azabutadiene fragment substantially differ from the ideal for sp^2-hybridized C and N atoms, probably because of electron crowding and spatial hindrance between the cyano group and adjacent substituents. It is interesting that the largest angle C2—C3—C1*c* [128.7 (3) (2FPD) and 130.2 (3)° (4FPD)] is formed by the least obstructed substituent, *i.e.* the *c* phenyl ring. The C1—N1—C2—C3 torsion angles [132.1 (3) (2FPD) and 129.2 (4)° (4FPD)] are slightly smaller than the corresponding angles in the MOPDs [135.4 (2)-139.5 (3)° (Angelova *et al.*, 1993)].

A larger tilting of the *c* phenyl ring in 2FPD than in 4FPD is seen with the two molecules superimposed onto the central C2—C4 bond (Fig. 4). Similarly, in 2MOPD this angle [19.6 (1)°] is larger than in 3MOPD and 4MOPD [5.8 (5) and 5.2 (5)°, respectively (Angelova *et al.*, 1993)].

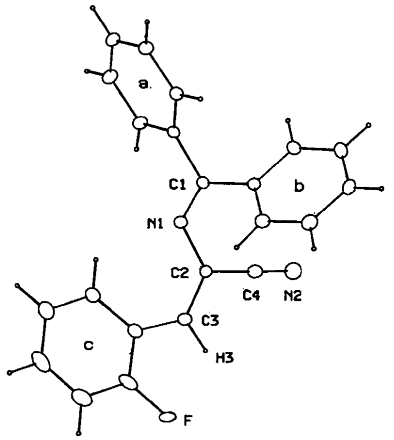


Fig. 1. *ORTEP* (Johnson, 1976) drawing of the 2FPD molecule with the atom-numbering scheme and 10% probabily thermal ellipsoids. H-atom spheres are arbitrarily reduced.

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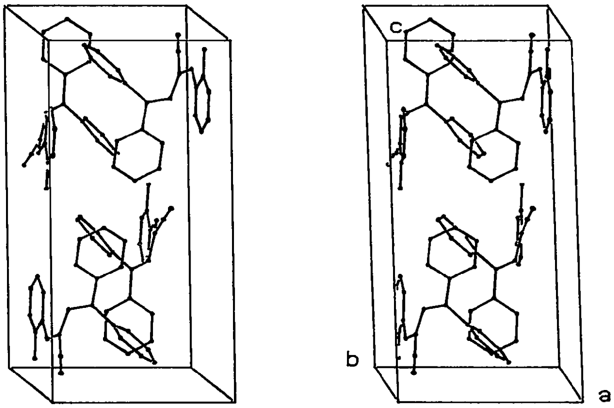

Fig. 2. Stereoscopic view of the molecular packing in 2FPD.

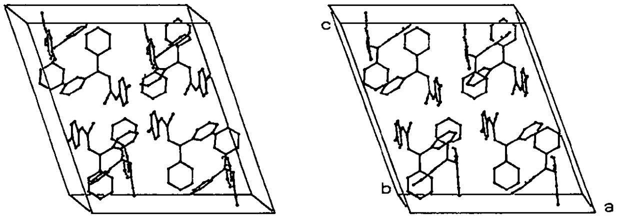

Fig. 3. Stereoscopic view of the molecular packing in 4FPD.

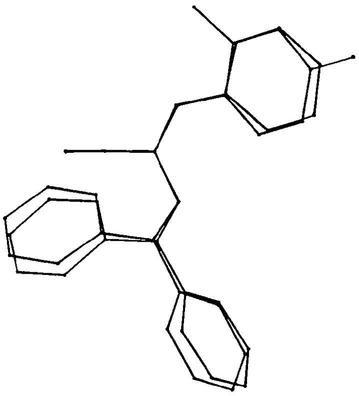

Fig. 4. View of the two molecules superimposed on the C2—C4 bond.

Intermolecular contacts between non-H atoms shorter than 3.3 Å are: F···F $(1-x,-y,1-z)$ 3.079 (3) Å in 2FPD and F···C1 $(x,1+y,z)$ 3.288 (3) Å, N2···C3 $(\frac{3}{2}-x,\frac{1}{2}-y,\frac{1}{2}-z)$ 3.288 (3) Å in 4FPD.

Experimental

2FPD

Crystal data

$C_{22}H_{15}FN_2$
M_r = 326.37
Monoclinic
$P2_1/c$
a = 9.436 (2) Å
b = 9.983 (2) Å
c = 18.341 (2) Å
β = 92.98 (1)°
V = 1725.2 (9) Å^3
Z = 4
D_x = 1.256 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 24 reflections
θ = 17.94–19.47°
μ = 0.07 mm^{-1}
T = 292 K
Prismatic
0.59 × 0.17 × 0.12 mm
Yellow

Data collection

Enraf-Nonius CAD-4 diffractometer
Continuous-scan profiles
Absorption correction: none
3816 measured reflections
3592 independent reflections
2016 observed reflections [$I > 2.0\sigma(I)$]

$R_{\rm int}$ = 0.015
$\theta_{\rm max}$ = 26°
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 12$
$l = -22 \rightarrow 22$
1 standard reflection
frequency: 120 min
intensity variation: 0.3%

Refinement

Refinement on F
Final R = 0.060
wR = 0.072
S = 1.405
2016 reflections
226 parameters
H-atom parameters not refined

$w = 1/[\sigma^2(F) + (0.030F)^2]$
$(\Delta/\sigma)_{\rm max}$ = 0.216
$\Delta\rho_{\rm max}$ = 0.312 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.273 e Å^{-3}
Atomic scattering factors from *SDP/PDP* (Enraf-Nonius, 1985)

4FPD

Crystal data

$C_{22}H_{15}FN_2$
M_r = 326.37
Monoclinic
$C2/c$
a = 18.505 (5) Å
b = 10.077 (3) Å
c = 20.153 (8) Å
β = 111.3674°
V = 3500 (3) Å^3
Z = 8
D_x = 1.238 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 22 reflections
θ = 17.98–19.01°
μ = 0.07 mm^{-1}
T = 292 K
Tabular
0.33 × 0.26 × 0.16 mm
Yellow

Data collection

Enraf-Nonius CAD-4 diffractometer
Continuous-scan profiles
Absorption correction: none
3752 measured reflections
3424 independent reflections
1432 observed reflections [$I > 2.0\sigma(I)$]

$R_{\rm int}$ = 0.011
$\theta_{\rm max}$ = 26°
$h = 0 \rightarrow 22$
$k = 0 \rightarrow 12$
$l = -24 \rightarrow 23$
3 standard reflections
frequency: 120 min
intensity variation: −0.6%

Refinement

Refinement on F
Final $R = 0.060$
$wR = 0.029$
$S = 1.387$
1432 reflections
226 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F) + (0.015F)^2]$
$(\Delta/\sigma)_{\max} = 0.004$
$\Delta\rho_{\max} = 0.207$ e Å^{-3}
$\Delta\rho_{\min} = -0.186$ e Å^{-3}
Atomic scattering factors from *SDP*/*PDP* (Enraf-Nonius, 1985)

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

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

	x	y	z	$U_{\rm eq}$
F	0.3803 (2)	0.0886 (2)	0.4661 (1)	0.0559 (6)
N1	0.2823 (3)	0.4768 (2)	0.2935 (1)	0.0438 (7)
N2	0.3681 (4)	0.6459 (3)	0.4535 (2)	0.086 (1)
C1	0.1696 (3)	0.5445 (3)	0.2763 (2)	0.0377 (8)
C2	0.3256 (3)	0.4453 (3)	0.3659 (2)	0.0425 (8)
C3	0.3660 (3)	0.3235 (3)	0.3903 (2)	0.0453 (9)
C4	0.3479 (4)	0.5564 (3)	0.4155 (2)	0.057 (1)
C1*a*	0.1494 (3)	0.5841 (3)	0.1985 (2)	0.0362 (7)
C2*a*	0.2678 (3)	0.6030 (3)	0.1577 (2)	0.0461 (9)
C3*a*	0.2539 (3)	0.6330 (4)	0.0843 (2)	0.053 (1)
C4*a*	0.1199 (4)	0.6435 (3)	0.0507 (2)	0.053 (1)
C5*a*	0.0015 (3)	0.6254 (3)	0.0903 (2)	0.0502 (9)
C6*a*	0.0157 (3)	0.5969 (3)	0.1639 (2)	0.0430 (8)
C1*b*	0.0591 (3)	0.5817 (3)	0.3275 (2)	0.0386 (8)
C2*b*	0.0111 (3)	0.7137 (3)	0.3323 (2)	0.0476 (9)
C3*b*	−0.0904 (4)	0.7458 (4)	0.3806 (2)	0.055 (1)
C4*b*	−0.1473 (4)	0.6498 (4)	0.4240 (2)	0.060 (1)
C5*b*	−0.1025 (4)	0.5187 (4)	0.4189 (2)	0.060 (1)
C6*b*	0.0008 (3)	0.4852 (3)	0.3714 (2)	0.0509 (9)
C1*c*	0.3603 (3)	0.1960 (3)	0.3516 (2)	0.0450 (8)
C2*c*	0.3709 (3)	0.0794 (3)	0.3932 (2)	0.060 (1)
C3*c*	0.3714 (4)	−0.0461 (4)	0.3619 (2)	0.077 (1)
C4*c*	0.3623 (4)	−0.0566 (4)	0.2868 (2)	0.082 (1)
C5*c*	0.3517 (4)	0.0571 (4)	0.2434 (2)	0.069 (1)
C6*c*	0.3500 (3)	0.1823 (3)	0.2753 (2)	0.0524 (9)

Table 2. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2) *for* 4FPD

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

	x	y	z	$U_{\rm eq}$
F	0.9059 (1)	0.9049 (2)	0.2046 (1)	0.114 (1)
N1	0.8741 (1)	0.2538 (3)	0.1903 (1)	0.0534 (9)
N2	0.8163 (2)	0.0714 (3)	0.0343 (1)	0.078 (1)
C1	0.8276 (2)	0.1935 (3)	0.2147 (1)	0.046 (1)
C2	0.8526 (2)	0.2774 (4)	0.1159 (1)	0.053 (1)
C3	0.8574 (2)	0.3971 (4)	0.0882 (2)	0.057 (1)
C4	0.8314 (2)	0.1629 (4)	0.0693 (2)	0.059 (1)
C1*a*	0.8579 (2)	0.1631 (3)	0.2919 (1)	0.046 (1)
C2*a*	0.9371 (2)	0.1561 (4)	0.3292 (2)	0.070 (1)
C3*a*	0.9658 (2)	0.1325 (4)	0.4017 (2)	0.082 (2)
C4*a*	0.9157 (2)	0.1162 (4)	0.4377 (2)	0.069 (1)
C5*a*	0.8375 (2)	0.1227 (4)	0.4022 (2)	0.063 (1)
C6*a*	0.8083 (2)	0.1456 (3)	0.3293 (1)	0.053 (1)
C1*b*	0.7452 (2)	0.1604 (3)	0.1716 (1)	0.047 (1)
C2*b*	0.7175 (2)	0.0310 (4)	0.1672 (2)	0.060 (1)
C3*b*	0.6409 (2)	0.0034 (4)	0.1259 (2)	0.073 (1)
C4*b*	0.5917 (2)	0.1027 (4)	0.0903 (2)	0.076 (2)
C5*b*	0.6184 (2)	0.2317 (4)	0.0948 (2)	0.073 (1)
C6*b*	0.6947 (2)	0.2603 (4)	0.1353 (2)	0.058 (1)
C1*c*	0.8733 (2)	0.5260 (4)	0.1217 (2)	0.057 (1)
C2*c*	0.8643 (2)	0.6374 (4)	0.0782 (2)	0.079 (1)
C3*c*	0.8750 (2)	0.7641 (4)	0.1051 (2)	0.094 (2)
C4*c*	0.8955 (2)	0.7794 (4)	0.1770 (2)	0.077 (1)
C5*c*	0.9058 (2)	0.6745 (4)	0.2222 (2)	0.072 (1)
C6*c*	0.8945 (2)	0.5477 (4)	0.1951 (2)	0.063 (1)

Table 3. *Geometric parameters* (Å, °)

	2FPD	4FPD
F—C2*c*	1.339 (5)	
F—C4*c*		1.366 (5)
N1—C1	1.285 (4)	1.288 (5)
N1—C2	1.406 (4)	1.424 (4)
N2—C4	1.143 (5)	1.132 (5)
C1—C1*a*	1.482 (4)	1.482 (4)
C1—C1*b*	1.487 (4)	1.492 (4)
C2—C3	1.343 (4)	1.345 (5)
C2—C4	1.443 (5)	1.448 (5)
C3—C1*c*	1.457 (4)	1.444 (5)
C1—N1—C2	123.1 (3)	120.7 (2)
N1—C1—C1*a*	116.1 (3)	116.6 (2)
N1—C1—C1*b*	125.1 (3)	124.6 (3)
C1*a*—C1—C1*b*	118.8 (2)	118.7 (3)
N1—C2—C3	125.5 (3)	123.4 (3)
N1—C2—C4	116.7 (3)	117.1 (3)
C3—C2—C4	117.2 (3)	119.3 (3)
C2—C3—C1*c*	128.7 (3)	130.2 (3)
N2—C4—C2	178.1 (4)	178.1 (3)
C2—N1—C1—C1*a*	172.3 (3)	174.7 (3)
C2—N1—C1—C1*b*	−9.4 (5)	−9.1 (5)
C1—N1—C2—C3	132.1 (3)	129.3 (4)
C1—N1—C2—C4	−57.4 (4)	−56.5 (4)
N1—C1—C1*a*—C2*a*	−28.5 (4)	−22.1 (5)
N1—C1—C1*b*—C2*b*	130.1 (3)	125.0 (4)
N1—C2—C3—C1*c*	−7.5 (5)	−9.4 (6)
C4—C2—C3—C1*c*	−177.9 (3)	176.5 (3)
C2—C3—C1*c*—C2*c*	−162.6 (3)	−171.3 (4)
C3—C1*c*—C2*c*—F	2.5 (4)	

The title compounds were obtained as single isomers according to a procedure described by Dryanska (1990) from *N*-diphenylmethyleneaminoacetonitrile and 2- and 4-fluorobenzaldehyde. 2FPD: m.p. 415–416 K (from ethanol); ^{1}H NMR (80 MHz, $CDCl_3$): δ 6.40–8.10 (*m*, 15H, alkene and aromatic H); elemental analysis, found (calc.): C 81.22 (80.96), H 4.48 (4.63), N 8.36 (8.58)%. 4FPD: m.p. 421–422 K (from ethanol); ^{1}H NMR (80 MHz, $CDCl_3$): δ 6.49 (*s*, 1H), 6.60–7.90 (*m*, 14H, aromatic H); elemental analysis, found (calc.): C 81.2 (80.96), H 4.90 (4.63), N 8.3 (8.58)%.

Data collection: CAD-4 software (Enraf-Nonius, 1988). Data reduction: *SDP*/*PDP* (Enraf-Nonius, 1985). Program(s) used to solve structure: *MULTAN*11/82 (Main *et al.*, 1982). Program(s) used to refine structure: *SDP*/*PDP*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *KAPPA* (Macíček, 1992).

This work has been stimulated by the participation of JM and OA in a Grant-in-Aid Project between the International Centre for Diffraction Data and the Institute of Applied Mineralogy.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71219 (24 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: KA1036]

References

Angelova, O., Macíček, J. & Dryanska, V. (1993). *Acta Cryst.* C**49**, 1813-1818.

Barluenda, J., Aznar, F., Fustero, S. & Tomas, M. (1990). *Pure Appl. Chem.* **62**, 1957-1966.

Barluenda, J., Carlon, R. P., Pelaez, E., Joglar, J. & Lopez Ortiz, F. (1992). *Tetrahedron*, pp. 9745-9752.

Barluenda, J., Joglar, J., Gonzalez, F. J. & Fustero, S. (1990). *Synlett*, pp. 129-138.

Boger, D. L. & Weinreb, S. (1987). *Hetero Diels-Alder Methodology in Organic Synthesis*. New York: Academic Press.

Dryanska, V. (1990). *Synth. Commun.* **20**, 1055-1061.

Enraf-Nonius (1985). *Structure Determination Package. SDP/PDP User's Guide*. Version 3.0. Enraf-Nonius, Delft, The Netherlands.

Enraf-Nonius (1988). *CAD-4 Manual*. Version 5.0. Enraf-Nonius, Delft, The Netherlands.

Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Macíček, J. (1992). *KAPPA*. Unpublished.

Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1982). *MULTAN11/82. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.

Acta Cryst. (1993). C**49**, 1821–1823

Structures of 1,1-Diphenyl-2-aza-1,3-butadienes. III. 3-Cyano-4-(4-cyanophenyl)-1,1-diphenyl-2-aza-1,3-butadiene

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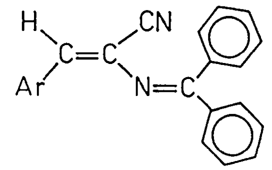
Abstract

The title structure, 4CNPD [3-(4-cyanophenyl)-2-(diphenylmethyleneamino)propenonitrile], consists of discrete *Z* diastereomeric molecules packed by van der Waals forces. The azabutadiene fragment, C1=N1—C2=C3, is twisted around the central single bond at 130.1 (7)°. The non-substituted phenyl rings are tilted with respect to the N1=C1(C1*a*)—C1*b* plane at 26.6 (2) and 55.8 (3)°. The dihedral angle between these rings is 73.7 (2)°. The cyano-substituted phenyl ring is almost coplanar with the N1—C2(C4)=C3—C1*c* plane. The phenyl rings are not plane-to-plane coupled. There are no intermolecular contacts between non-H atoms shorter than 3.3 Å.

Comment

2-Aza-1,3-dienes (I) have attracted considerable attention in recent years because of their application in the synthesis of heterocyclic compounds (Boger & Weinreb, 1987; Barluenda, Joglar, Gonzalez & Fustero, 1990; Barluenda, Aznar, Fustero & Tomas, 1990; Barluenda, Carlon, Pelaez, Joglar & Lopez Ortiz, 1992). Following our interest in the synthesis (Dryanska, 1990), chemistry (Dryanska, 1992) and structure (Angelova, Macíček & Dryanska, 1993; Macíček, Angelova & Dryanska, 1993) of functionalized 2-aza-1,3-butadienes, we present here the structural data for the title compound.



(I)

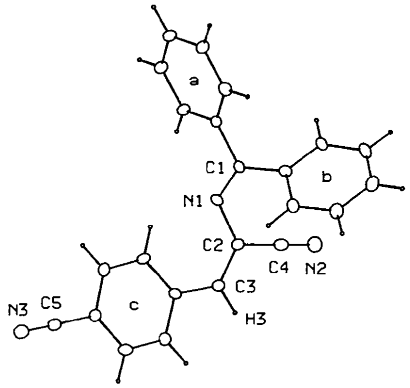


Fig. 1. *ORTEP* (Johnson, 1976) drawing of the 4CNPD molecule with the atom-numbering scheme and 30% probability thermal ellipsoids. H-atom spheres are arbitrarily reduced.

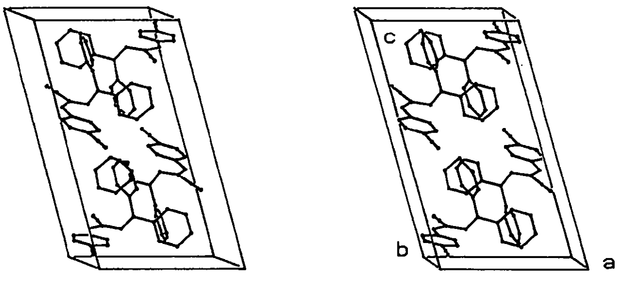


Fig. 2. Stereoscopic view of the molecular packing.

Experimental

Crystal data

$C_{23}H_{15}N_3$

M_r = 333.39

Mo $K\alpha$ radiation

λ = 0.71073 Å