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5,5′-Dimethyl-*N*,*N*′-(iminodiethylene)-bis(1*H*-pyrazole-3-carboxamide)

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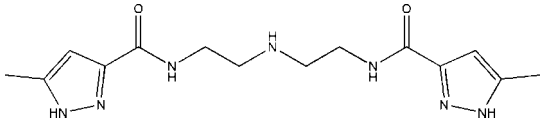
Key indicators: single-crystal X-ray study; T = 294 K; mean σ(C–C) = 0.002 Å; R factor = 0.041; wR factor = 0.117; data-to-parameter ratio = 15.7.

The title compound, $C_{14}H_{21}N_7O_2$, was synthesized from methyl 5-methylpyrazole-3-carboxylate and diethylenetriamine without solvent. Each molecule in the crystal structure interacts with five neighbouring molecules through intermolecular N—H···N and N—H···O hydrogen bonds, to form a two-dimensional layer network.

Related literature

For related literature, see: Mohamed *et al.* (2007); Won *et al.* (2007).



Experimental

Crystal data

$C_{14}H_{21}N_7O_2$
M_r = 319.38
Monoclinic, $C2/c$
a = 37.091 (6) Å
b = 7.5543 (12) Å
c = 11.6123 (18) Å
β = 99.874 (2)°
V = 3205.5 (9) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 294 (2) K
0.26 × 0.24 × 0.14 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.976, T_{max} = 0.987
8706 measured reflections
3303 independent reflections
2386 reflections with $I > 2\sigma(I)$
R_{int} = 0.029

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.117
S = 1.02
3303 reflections
210 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···N4^{i}	0.86	2.06	2.9005 (19)	166
N3—H3···N2^{i}	0.86	2.22	3.0247 (19)	156
N4—H4*A*···O1^{ii}	0.91	2.63	3.367 (2)	139
N5—H5···O1^{iii}	0.86	2.22	2.8481 (18)	130
N7—H7···O2^{iv}	0.86	2.00	2.8535 (19)	170

Symmetry codes: (i) $-x, y, -z+\frac{3}{2}$; (ii) $x, -y, z+\frac{1}{2}$; (iii) $x, -y+1, z+\frac{1}{2}$; (iv) $x, -y+2, z+\frac{1}{2}$.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: AT2491).

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supplementary materials

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5,5'-Dimethyl-*N*,*N*'-(iminodiethylene)bis(1*H*-pyrazole-3-carboxamide)

J. Hu, G. Chen, G. Ma and H. Song

Comment

In recent years, the pyrazole derivatives have appealed much attention by their structures and coordination (Mohamed *et al.*, 2007 and Won *et al.*,2007) properties. We report here the crystal structure of N1, N5-bis-(5-methyl-1*H*-pyrazole-3-carbonyl)diethylenetriamine in order to elucidate its molecular conformation.

In the molecule of the title compound, (I), (Fig. 1), the structure consists of two pyrazole rings with a dihedral angle of 66.6 (2) °. As can be seen from the packing diagram (Fig 2), there exists N—H···N and N—H···O intermolecular hydrogen bonds, which link the molecules into a two-dimensional layer networks parallel to the crystallographic *ac* plane.

Experimental

5-Methyl pyrazole-3-carboxylic acid methyl ester (1 g, 7.1 mmol) was dissolved in diethylenetriamine (360.5 mg, 3.5 mmol) and heated at 373 K under nitrogen for 4 h. After cooling to room temperature the crude product was washed with methanol and dried *in vacuo* to yield N1,N5-bis-(5-methyl-1*H*- pyrazole-3-carbonyl)diethylenetriamine as a white powder·The compound was crystallized by slow evaporation of the methanol solution in 7 d. (yield; 904 mg, 81%, m.p. 484 (5) K).

Refinement

All H atoms were positioned geometrically and refined as riding [C—H = 0.96–0.98Å and N—H = 0.86 Å], with a displacement parameter U_{iso} set equal to 1.2 (CH, NH and CH_2) or 1.5 (CH_3) times U_{iso} of the parent atom.

Figures

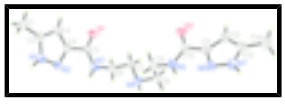

Fig. 1. The molecular structure of the title molecule, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

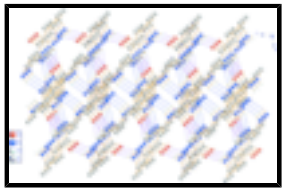

Fig. 2. The packing of (I), showing the two-dimensional hydrogen-bonded layer. Dashed lines indicate hydrogen bonds.

5,5'-Dimethyl-*N*,*N*'-(iminodiethylene)di-1*H*-pyrazole-3-carboxamide

Crystal data

$C_{14}H_{21}N_7O_2$ F_{000} = 1360

M_r = 319.38	D_x = 1.324 Mg m^{-3}
Monoclinic, *C*2/*c*	Melting point: 484(5) K
Hall symbol: -C 2yc	Mo *K*α radiation λ = 0.71073 Å
a = 37.091 (6) Å	Cell parameters from 3176 reflections
b = 7.5543 (12) Å	θ = 2.8–26.4º
c = 11.6123 (18) Å	μ = 0.09 mm^{-1}
β = 99.874 (2)º	*T* = 294 (2) K
V = 3205.5 (9) Å^3	Prism, colourless
Z = 8	0.26 × 0.24 × 0.14 mm

Data collection

Bruker SMART CCD area-detector diffractometer	3303 independent reflections
Radiation source: fine-focus sealed tube	2386 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.029
T = 294(2) K	θ_{max} = 26.4º
φ and ω scans	θ_{min} = 1.1º
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	*h* = −44→46
T_{min} = 0.976, T_{max} = 0.987	*k* = −9→6
8706 measured reflections	*l* = −14→14

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.041	H-atom parameters constrained
$wR(F^2)$ = 0.117	$w = 1/[\sigma^2(F_o^2) + (0.0593P)^2 + 1.278P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.02	$(\Delta/\sigma)_{max}$ = 0.003
3303 reflections	$\Delta\rho_{max}$ = 0.28 e Å^{-3}
210 parameters	$\Delta\rho_{min}$ = −0.23 e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

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 $F^2 > 2\text{sigma}(F^2)$ is used only for calculat-

ing *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 ($Å^2$)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.08168 (3)	0.13264 (19)	0.55742 (10)	0.0495 (4)
O2	0.18691 (3)	0.71700 (17)	0.87177 (10)	0.0463 (3)
N1	−0.03681 (4)	0.26049 (19)	0.52806 (12)	0.0380 (3)
H1	−0.0590	0.2715	0.5398	0.046*
N2	−0.00997 (4)	0.1880 (2)	0.60646 (11)	0.0367 (3)
N3	0.05988 (3)	0.08529 (18)	0.72415 (11)	0.0350 (3)
H3	0.0415	0.0909	0.7602	0.042*
N4	0.11299 (4)	0.23640 (18)	0.94525 (12)	0.0355 (3)
H4A	0.1168	0.1454	0.9966	0.043*
N5	0.14426 (4)	0.70679 (19)	0.98940 (12)	0.0397 (4)
H5	0.1364	0.7552	1.0475	0.048*
N6	0.17739 (4)	0.98883 (19)	1.11651 (12)	0.0389 (3)
N7	0.20363 (4)	1.09440 (19)	1.17462 (12)	0.0407 (4)
H7	0.2004	1.1607	1.2322	0.049*
C1	−0.05128 (5)	0.3985 (3)	0.33162 (15)	0.0480 (5)
H1A	−0.0628	0.3085	0.2795	0.072*
H1B	−0.0380	0.4776	0.2897	0.072*
H1C	−0.0696	0.4635	0.3629	0.072*
C2	−0.02556 (5)	0.3141 (2)	0.42924 (14)	0.0361 (4)
C3	0.01084 (5)	0.2744 (2)	0.44409 (14)	0.0391 (4)
H3A	0.0267	0.2944	0.3914	0.047*
C4	0.01941 (4)	0.1978 (2)	0.55471 (13)	0.0328 (4)
C5	0.05602 (4)	0.1350 (2)	0.61240 (14)	0.0333 (4)
C6	0.09507 (4)	0.0216 (2)	0.78541 (15)	0.0379 (4)
H6A	0.1064	−0.0495	0.7319	0.045*
H6B	0.0909	−0.0546	0.8491	0.045*
C7	0.12142 (4)	0.1679 (2)	0.83466 (15)	0.0376 (4)
H7A	0.1462	0.1223	0.8474	0.045*
H7B	0.1200	0.2637	0.7784	0.045*
C8	0.13643 (4)	0.3846 (2)	0.99312 (15)	0.0386 (4)
H8A	0.1615	0.3602	0.9840	0.046*
H8B	0.1359	0.3958	1.0760	0.046*
C9	0.12403 (4)	0.5582 (2)	0.93204 (15)	0.0406 (4)
H9A	0.1276	0.5526	0.8513	0.049*
H9B	0.0981	0.5751	0.9323	0.049*
C10	0.17441 (4)	0.7729 (2)	0.95714 (14)	0.0330 (4)
C11	0.19332 (4)	0.9133 (2)	1.03436 (14)	0.0335 (4)
C12	0.22949 (5)	0.9704 (2)	1.04128 (15)	0.0417 (4)
H12	0.2460	0.9368	0.9933	0.050*
C13	0.23555 (5)	1.0858 (2)	1.13336 (16)	0.0425 (4)
C14	0.26925 (6)	1.1819 (3)	1.1904 (2)	0.0675 (6)
H14A	0.2665	1.2164	1.2680	0.101*

H14B	0.2727	1.2854	1.1455	0.101*
H14C	0.2901	1.1055	1.1942	0.101*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0330 (6)	0.0744 (10)	0.0444 (7)	−0.0001 (6)	0.0162 (5)	0.0015 (6)
O2	0.0492 (7)	0.0510 (8)	0.0423 (7)	−0.0020 (6)	0.0177 (6)	−0.0070 (6)
N1	0.0286 (7)	0.0476 (9)	0.0378 (7)	0.0020 (6)	0.0061 (6)	0.0018 (6)
N2	0.0302 (7)	0.0462 (8)	0.0340 (7)	0.0004 (6)	0.0067 (6)	0.0030 (6)
N3	0.0301 (7)	0.0426 (8)	0.0335 (7)	−0.0002 (6)	0.0085 (6)	−0.0012 (6)
N4	0.0335 (7)	0.0366 (8)	0.0364 (7)	−0.0026 (6)	0.0055 (6)	0.0011 (6)
N5	0.0354 (7)	0.0413 (8)	0.0445 (8)	−0.0044 (6)	0.0125 (6)	−0.0083 (7)
N6	0.0344 (7)	0.0412 (8)	0.0414 (8)	0.0000 (6)	0.0072 (6)	−0.0029 (7)
N7	0.0447 (8)	0.0378 (8)	0.0400 (8)	−0.0014 (7)	0.0081 (6)	−0.0063 (6)
C1	0.0536 (11)	0.0485 (11)	0.0392 (9)	0.0024 (9)	0.0002 (8)	0.0021 (9)
C2	0.0418 (9)	0.0344 (9)	0.0321 (8)	−0.0040 (7)	0.0065 (7)	−0.0033 (7)
C3	0.0386 (9)	0.0475 (10)	0.0333 (9)	−0.0041 (8)	0.0121 (7)	0.0012 (8)
C4	0.0332 (8)	0.0349 (9)	0.0313 (8)	−0.0052 (7)	0.0082 (7)	−0.0037 (7)
C5	0.0297 (8)	0.0361 (9)	0.0353 (9)	−0.0038 (7)	0.0091 (7)	−0.0049 (7)
C6	0.0370 (9)	0.0355 (9)	0.0403 (9)	0.0035 (7)	0.0042 (7)	−0.0024 (7)
C7	0.0304 (8)	0.0429 (10)	0.0397 (9)	0.0007 (7)	0.0072 (7)	−0.0007 (8)
C8	0.0308 (8)	0.0439 (10)	0.0391 (9)	−0.0019 (7)	0.0003 (7)	−0.0006 (8)
C9	0.0330 (8)	0.0409 (10)	0.0459 (10)	−0.0035 (8)	0.0004 (7)	−0.0025 (8)
C10	0.0313 (8)	0.0330 (9)	0.0340 (8)	0.0046 (7)	0.0037 (7)	0.0028 (7)
C11	0.0340 (8)	0.0321 (8)	0.0342 (8)	0.0021 (7)	0.0056 (7)	0.0043 (7)
C12	0.0369 (9)	0.0427 (10)	0.0483 (10)	−0.0046 (8)	0.0153 (8)	−0.0055 (8)
C13	0.0404 (9)	0.0389 (10)	0.0487 (10)	−0.0053 (8)	0.0093 (8)	−0.0022 (8)
C14	0.0577 (13)	0.0657 (14)	0.0792 (15)	−0.0218 (12)	0.0119 (11)	−0.0239 (12)

Geometric parameters (Å, °)

O1—C5	1.2337 (18)	C2—C3	1.365 (2)
O2—C10	1.2386 (19)	C3—C4	1.395 (2)
N1—N2	1.3450 (19)	C3—H3A	0.9300
N1—C2	1.349 (2)	C4—C5	1.485 (2)
N1—H1	0.8600	C6—C7	1.521 (2)
N2—C4	1.3335 (19)	C6—H6A	0.9700
N3—C5	1.335 (2)	C6—H6B	0.9700
N3—C6	1.457 (2)	C7—H7A	0.9700
N3—H3	0.8600	C7—H7B	0.9700
N4—C8	1.467 (2)	C8—C9	1.524 (2)
N4—C7	1.467 (2)	C8—H8A	0.9700
N4—H4A	0.9053	C8—H8B	0.9700
N5—C10	1.336 (2)	C9—H9A	0.9700
N5—C9	1.447 (2)	C9—H9B	0.9700
N5—H5	0.8600	C10—C11	1.485 (2)
N6—C11	1.333 (2)	C11—C12	1.398 (2)
N6—N7	1.3466 (19)	C12—C13	1.368 (2)

N7—C13	1.353 (2)	C12—H12	0.9300
N7—H7	0.8600	C13—C14	1.498 (3)
C1—C2	1.493 (2)	C14—H14A	0.9600
C1—H1A	0.9600	C14—H14B	0.9600
C1—H1B	0.9600	C14—H14C	0.9600
C1—H1C	0.9600		
N2—N1—C2	113.38 (13)	C7—C6—H6B	108.7
N2—N1—H1	123.3	H6A—C6—H6B	107.6
C2—N1—H1	123.3	N4—C7—C6	111.46 (13)
C4—N2—N1	103.88 (13)	N4—C7—H7A	109.3
C5—N3—C6	120.37 (13)	C6—C7—H7A	109.3
C5—N3—H3	119.8	N4—C7—H7B	109.3
C6—N3—H3	119.8	C6—C7—H7B	109.3
C8—N4—C7	113.54 (13)	H7A—C7—H7B	108.0
C8—N4—H4A	108.3	N4—C8—C9	111.61 (13)
C7—N4—H4A	106.0	N4—C8—H8A	109.3
C10—N5—C9	123.63 (14)	C9—C8—H8A	109.3
C10—N5—H5	118.2	N4—C8—H8B	109.3
C9—N5—H5	118.2	C9—C8—H8B	109.3
C11—N6—N7	103.93 (13)	H8A—C8—H8B	108.0
N6—N7—C13	113.29 (14)	N5—C9—C8	111.22 (13)
N6—N7—H7	123.4	N5—C9—H9A	109.4
C13—N7—H7	123.4	C8—C9—H9A	109.4
C2—C1—H1A	109.5	N5—C9—H9B	109.4
C2—C1—H1B	109.5	C8—C9—H9B	109.4
H1A—C1—H1B	109.5	H9A—C9—H9B	108.0
C2—C1—H1C	109.5	O2—C10—N5	122.90 (15)
H1A—C1—H1C	109.5	O2—C10—C11	121.61 (15)
H1B—C1—H1C	109.5	N5—C10—C11	115.43 (14)
N1—C2—C3	105.67 (15)	N6—C11—C12	111.46 (15)
N1—C2—C1	121.56 (15)	N6—C11—C10	121.06 (14)
C3—C2—C1	132.77 (16)	C12—C11—C10	127.15 (15)
C2—C3—C4	105.77 (14)	C13—C12—C11	105.59 (15)
C2—C3—H3A	127.1	C13—C12—H12	127.2
C4—C3—H3A	127.1	C11—C12—H12	127.2
N2—C4—C3	111.28 (14)	N7—C13—C12	105.71 (15)
N2—C4—C5	122.26 (14)	N7—C13—C14	122.33 (16)
C3—C4—C5	126.45 (14)	C12—C13—C14	131.86 (17)
O1—C5—N3	122.36 (15)	C13—C14—H14A	109.5
O1—C5—C4	119.87 (14)	C13—C14—H14B	109.5
N3—C5—C4	117.76 (13)	H14A—C14—H14B	109.5
N3—C6—C7	114.05 (14)	C13—C14—H14C	109.5
N3—C6—H6A	108.7	H14A—C14—H14C	109.5
C7—C6—H6A	108.7	H14B—C14—H14C	109.5
N3—C6—H6B	108.7		
C2—N1—N2—C4	0.38 (18)	N3—C6—C7—N4	80.13 (17)
C11—N6—N7—C13	−1.02 (19)	C7—N4—C8—C9	79.30 (18)
N2—N1—C2—C3	−0.06 (19)	C10—N5—C9—C8	93.81 (19)

N2—N1—C2—C1	−179.83 (15)	N4—C8—C9—N5	172.62 (13)
N1—C2—C3—C4	−0.28 (19)	C9—N5—C10—O2	3.0 (3)
C1—C2—C3—C4	179.45 (18)	C9—N5—C10—C11	−173.98 (14)
N1—N2—C4—C3	−0.56 (18)	N7—N6—C11—C12	0.38 (18)
N1—N2—C4—C5	178.69 (14)	N7—N6—C11—C10	174.30 (14)
C2—C3—C4—N2	0.5 (2)	O2—C10—C11—N6	171.16 (15)
C2—C3—C4—C5	−178.67 (15)	N5—C10—C11—N6	−11.8 (2)
C6—N3—C5—O1	−1.4 (2)	O2—C10—C11—C12	−15.9 (3)
C6—N3—C5—C4	179.66 (14)	N5—C10—C11—C12	161.11 (17)
N2—C4—C5—O1	173.78 (15)	N6—C11—C12—C13	0.4 (2)
C3—C4—C5—O1	−7.1 (3)	C10—C11—C12—C13	−173.10 (16)
N2—C4—C5—N3	−7.2 (2)	N6—N7—C13—C12	1.3 (2)
C3—C4—C5—N3	171.91 (16)	N6—N7—C13—C14	−175.42 (18)
C5—N3—C6—C7	83.43 (18)	C11—C12—C13—N7	−0.93 (19)
C8—N4—C7—C6	−176.87 (13)	C11—C12—C13—C14	175.3 (2)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···N4^{i}	0.86	2.06	2.9005 (19)	166
N3—H3···N2^{i}	0.86	2.22	3.0247 (19)	156
N4—H4A···O1^{ii}	0.91	2.63	3.367 (2)	139
N5—H5···O1^{iii}	0.86	2.22	2.8481 (18)	130
N7—H7···O2^{iv}	0.86	2.00	2.8535 (19)	170

Symmetry codes: (i) −*x*, *y*, −*z*+3/2; (ii) *x*, −*y*, *z*+1/2; (iii) *x*, −*y*+1, *z*+1/2; (iv) *x*, −*y*+2, *z*+1/2.

Fig. 1

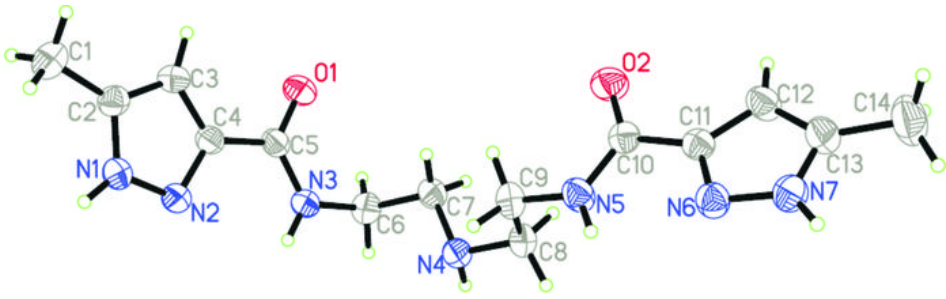
C1
C2
C3
C4
C5
O1
N1
N2
N3
C6
C7
N4
C8
C9
N5
O2
C10
C11
C12
C13
C14
N6
N7

Fig. 2