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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1090). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Methyl 5-Cyano-1-[2-(methoxycarbonyl)phenyl]-4,5-dihydro-3-pyrazolecarboxylate

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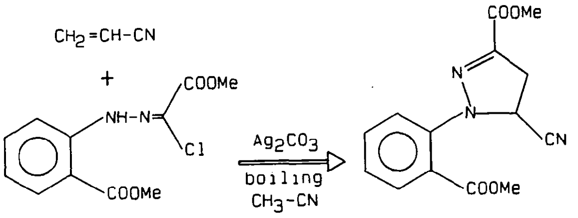
Abstract

The title compound, $C_{14}H_{13}N_3O_4$, has two molecules in the asymmetric unit which have quite different geometries, in spite of the absence of strong intramolecular contacts. This is a result of the flexibility of the 4,5-dihydropyrazole ring. Similar compounds which show the same ring variability can be found in the literature.

Comment

Continuing a series of 1,3-dipolar cycloaddition reactions, Garanti (1993) added the chlorohydrazone (1) and Ag_2CO_3 (to generate the corresponding nitrilimmine) to acrylonitrile in boiling acetonitrile, obtaining the title compound (2).



(1) (2)

The present work confirms the expected conformation of the reaction product. There are two crystallographically independent molecules in the asymmetric unit of (2) and there is no particular relation between them. Fig. 1 shows molecule *A*, with the numbering scheme of the heavy atoms. The same numbering is applied to molecule *B*. The intermolecular packing interactions are not particularly relevant. In fact only three weak hydrogen bonds are present: $\mathrm{C18}A\cdots\mathrm{O13}B^{\mathrm{i}}$ = 3.232 (3), $\mathrm{H181}A\cdots\mathrm{O13}B^{\mathrm{i}}$ = 2.52 (3) Å and $\mathrm{C18}A$—$\mathrm{H181}A\cdots\mathrm{O13}B^{\mathrm{i}}$ = 129 (3)°; $\mathrm{C4}A\cdots\mathrm{O17}B^{\mathrm{ii}}$ = 3.328 (3), $\mathrm{H42}A\cdots\mathrm{O17}B^{\mathrm{ii}}$ = 2.62 (3) Å and $\mathrm{C4}A$—$\mathrm{H42}A\cdots\mathrm{O17}B^{\mathrm{ii}}$ = 128 (2)°; $\mathrm{C4}B\cdots\mathrm{O17}A^{\mathrm{iii}}$ = 3.485 (3), $\mathrm{H41}B\cdots\mathrm{O17}A^{\mathrm{iii}}$ = 2.67 (3) Å and $\mathrm{C4}B$—$\mathrm{H41}B\cdots\mathrm{O17}A^{\mathrm{iii}}$ = 142 (2)° [symmetry codes: (i) $1-x, -y, 1-z$; (ii) $-x, 1-y, 1-z$; (iii) $-x, -y, 1-z$]. Nevertheless, the two molecules are quite different, as can be seen from Fig. 2.

The main difference between the molecules is in the conformation of the heterocycle (N1, N2, C3, C4, C5), which is practically planar in molecule *A* [total puckering amplitude Q_t = 0.029 (2) Å (Cremer &

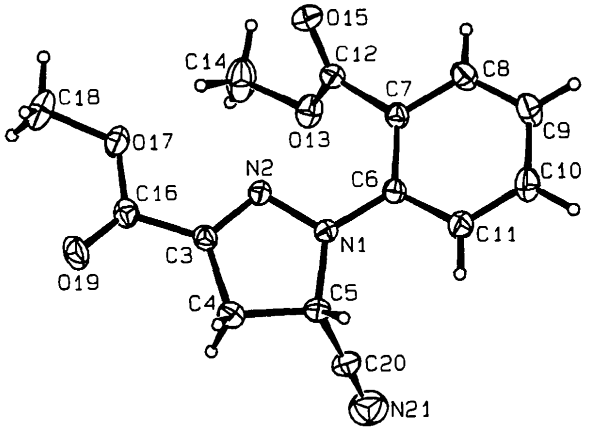


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of molecule *A* with the numbering scheme of the heavy atoms, the same numbering was applied to molecule *B*. Displacement ellipsoids are drawn at the 20% probability level; H atoms are not to scale.

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Pople, 1975)], while in molecule *B* it has an envelope conformation [Q_t = 0.185 (2) Å, minimum displacement asymmetry parameter Δ_s(C5*B*) = 0.016 (1) (Nardelli, 1983*b*)]. The same difference is also observed for the torsion angles around the rings, which range between ±3.5° in molecule *A* and from −17.3 to 18.2° in molecule *B*.

Such a variability in the conformation of this ring in not unusual. In fact, inspecting the Cambridge Structural Database, we found torsion-angle values ranging between −1.4 and 1.6° in molecule *A* of SEGSUS (Umarov *et al.*, 1988), and between −16.5 and 16.4° in MPZPAZ (Yamazaki, Moroi & Sano, 1977). It is unusual to find so marked a difference in the same crystal structure and with a packing arrangement so 'soft'. This feature can be taken as a proof of the flexibility of a ring of this kind.

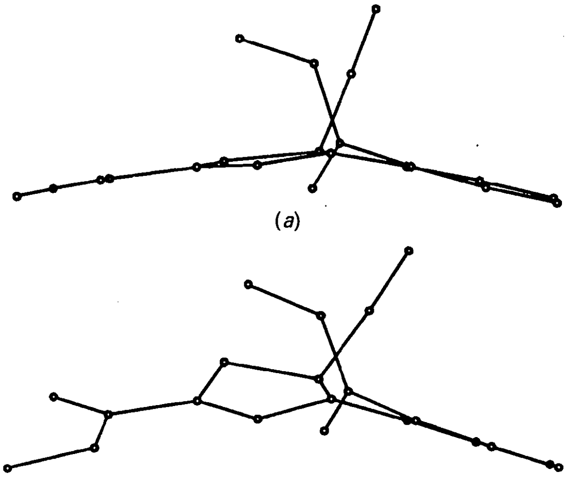
(*a*)
(*b*)

Fig. 2. Simplified drawing of molecules *A* and *B*. H atoms have been omitted. For both molecules, atoms N2, C6 and C7 lie in a plane perpendicular to the sheet.

Experimental

The compound was synthesized according to the procedure described by Garanti (1993).

Crystal data

$C_{14}H_{13}N_3O_4$
M_r = 287.27
Triclinic
$P\bar{1}$
a = 8.657 (1) Å
b = 9.234 (1) Å
c = 18.372 (2) Å
α = 93.59 (1)°
β = 97.44 (1)°
γ = 95.44 (1)°
V = 1445.5 (3) Å^3
Z = 4
D_x = 1.320 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 9.6–16.9°
μ = 0.0926 mm^{-1}
Room temperature
Hexagonal tablet
0.32 × 0.32 × 0.24 mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
5085 measured reflections
5070 independent reflections
3407 observed reflections [$F_o > 2.0\sigma(F_o)$]
$\theta_{\max}$ = 25.0°

$h = 0 \rightarrow 10$
$k = -10 \rightarrow 10$
$l = -21 \rightarrow 21$
1 standard reflection
frequency: 360 min
intensity variation: insignificant

Refinement

Refinement on F
R = 0.041
wR = 0.049
S = 2.080
3407 reflections
484 parameters
All H-atom parameters refined
Calculated weights $w = 4F_o^2/[\sigma^2(I) + (PF_o^2)^2]$ where P = 0.0300
$(\Delta/\sigma)_{\max}$ = 0.044

$\Delta\rho_{\max}$ = 0.278 e Å^{-3}
Extinction correction: Stout & Jensen (1968)
Extinction coefficient: 9.5 (5) × 10^{-7}
Atomic scattering factors from *International Tables for X-ray Crystallography* [1974, Vol. IV, Tables 2.2A, 2.3.1 (O, N, C) and 2.2C (H)]

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

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

	x	y	z	$U_{\rm eq}$
O13*A*	0.3440 (2)	0.2756 (2)	0.59645 (7)	0.0639 (5)
O13*B*	0.37713	0.23951	0.14598	0.0574 (4)
O15*A*	0.2007 (2)	0.0641 (2)	0.6004 (1)	0.0899 (6)
O15*B*	0.3538 (2)	0.4675 (2)	0.1860 (1)	0.0948 (7)
O17*A*	0.4128 (2)	0.1764 (2)	0.80937 (8)	0.0663 (5)
O17*B*	−0.0895 (2)	0.3071 (2)	0.03942 (7)	0.0664 (5)
O19*A*	0.4078 (2)	0.3295 (2)	0.90848 (7)	0.0746 (5)
O19*B*	−0.2235 (2)	0.0919 (2)	0.0041 (1)	0.1135 (8)
N1*A*	0.1367 (2)	0.4333 (2)	0.69592 (8)	0.0525 (6)
N1*B*	0.1129 (2)	0.0985 (2)	0.21044 (9)	0.0555 (6)
N2*B*	0.0591 (2)	0.1852 (2)	0.15778 (8)	0.0508 (5)
N2*A*	0.2240 (2)	0.3340 (2)	0.72790 (8)	0.0457 (5)
N21*B*	0.1826 (3)	−0.2647 (3)	0.2267 (1)	0.1001 (9)
N21*A*	0.2203 (3)	0.8062 (3)	0.7018 (1)	0.1031 (9)
C3*A*	0.2742 (2)	0.3791 (2)	0.79511 (9)	0.0467 (6)
C3*B*	−0.0440 (2)	0.1090 (2)	0.1108 (1)	0.0516 (6)
C4*B*	−0.0685 (3)	−0.0474 (3)	0.1258 (1)	0.0775 (9)
C4*A*	0.2157 (3)	0.5186 (2)	0.8192 (1)	0.0654 (8)
C5*A*	0.1178 (2)	0.5571 (2)	0.7487 (1)	0.0522 (6)
C5*B*	0.0160 (2)	−0.0437 (2)	0.2046 (1)	0.0630 (7)
C6*B*	0.2160 (2)	0.1593 (2)	0.2722 (1)	0.0566 (6)
C6*A*	0.0429 (2)	0.3955 (2)	0.62825 (9)	0.0446 (6)
C7*A*	0.0710 (2)	0.2765 (2)	0.58212 (9)	0.0455 (6)
C7*B*	0.3252 (2)	0.2777 (2)	0.2670 (1)	0.0588 (7)
C8*B*	0.4200 (3)	0.3387 (3)	0.3310 (1)	0.0814 (9)
C8*A*	−0.0331 (3)	0.2350 (2)	0.5188 (1)	0.0589 (7)
C9*A*	−0.1569 (3)	0.3131 (3)	0.4979 (1)	0.0688 (8)
C9*B*	0.4106 (3)	0.2779 (3)	0.3973 (1)	0.1035 (10)
C10*A*	−0.1785 (2)	0.4339 (3)	0.5410 (1)	0.0659 (8)
C10*B*	0.3051 (3)	0.1576 (3)	0.4010 (1)	0.1021 (11)
C11*A*	−0.0812 (2)	0.4752 (2)	0.6059 (1)	0.0562 (7)
C11*B*	0.2081 (3)	0.0988 (3)	0.3399 (1)	0.0793 (9)
C12*B*	0.3503 (2)	0.3395 (2)	0.1961 (1)	0.0579 (8)
C12*A*	0.2092 (3)	0.1930 (2)	0.5959 (1)	0.0526 (6)
C14*A*	0.4850 (3)	0.2052 (3)	0.6167 (2)	0.0987 (11)
C14*B*	0.3837 (3)	0.2818 (3)	0.0719 (1)	0.0737 (9)
C16*A*	0.3724 (2)	0.2952 (2)	0.8437 (1)	0.0519 (6)
C16*B*	−0.1276 (3)	0.1666 (2)	0.0465 (1)	0.0607 (7)
C18*A*	0.5024 (3)	0.0812 (3)	0.8539 (2)	0.0880 (9)
C18*B*	−0.1788 (3)	0.3715 (3)	−0.0204 (1)	0.0856 (10)
C20*A*	0.1717 (3)	0.6941 (2)	0.7225 (1)	0.0558 (7)
C20*B*	0.1076 (3)	−0.1632 (2)	0.2182 (1)	0.0624 (7)

Table 2. *Selected geometric parameters* (Å, °)

	(*A*)	(*B*)
O13—C12	1.331 (2)	1.321 (2)
O13—C14	1.454 (3)	1.446 (2)
O15—C12	1.194 (2)	1.206 (2)
O17—C16	1.329 (2)	1.327 (2)
O17—C18	1.449 (3)	1.452 (2)
O19—C16	1.204 (2)	1.195 (2)
N1—N2	1.357 (2)	1.358 (2)
N1—C5	1.487 (2)	1.480 (2)
N1—C6	1.399 (2)	1.401 (2)
N2—C3	1.284 (2)	1.281 (2)
N21—C20	1.184 (3)	1.197 (3)
C3—C4	1.491 (2)	1.488 (3)
C3—C16	1.461 (2)	1.460 (2)
C4—C5	1.534 (2)	1.532 (2)
C5—C20	1.440 (2)	1.435 (2)
C7—C12	1.487 (3)	1.487 (2)
C12—O13—C14	115.8 (2)	117.9 (2)
C16—O17—C18	117.1 (2)	116.7 (2)
C5—N1—C6	125.3 (2)	126.0 (2)
N2—N1—C6	119.8 (2)	119.9 (2)
N2—N1—C5	112.3 (2)	111.5 (2)
N1—N2—C3	109.5 (2)	108.8 (2)
N2—C3—C16	122.1 (2)	124.0 (2)
N2—C3—C4	113.9 (2)	113.9 (2)
C4—C3—C16	123.9 (2)	122.0 (2)
C3—C4—C5	102.4 (2)	101.1 (2)
N1—C5—C4	101.7 (2)	101.0 (2)
C4—C5—C20	114.1 (2)	114.3 (2)
N1—C5—C20	110.8 (2)	112.7 (2)
N1—C6—C11	120.2 (2)	118.9 (2)
N1—C6—C7	120.9 (2)	121.0 (2)
C6—C7—C12	123.9 (2)	123.2 (2)
C8—C7—C12	117.2 (2)	118.1 (2)
O15—C12—C7	124.0 (2)	124.3 (2)
O13—C12—C7	112.5 (2)	112.5 (2)
O13—C12—O15	123.3 (3)	123.1 (2)
O19—C16—C3	122.6 (2)	121.9 (2)
O17—C16—C3	113.0 (2)	114.9 (2)
O17—C16—O19	124.4 (2)	123.1 (2)
N21—C20—C5	178.1 (3)	177.4 (2)
N1—N2—C3—C4	3.52 (3)	−2.22 (3)
N2—C3—C4—C5	−2.09 (2)	13.27 (3)
C3—C4—C5—N1	−0.07 (2)	−17.30 (2)
C4—C5—N1—N2	2.08 (2)	18.19 (2)
C5—N1—N2—C3	−3.55 (2)	−10.83 (2)
N2—N1—C6—C7	−19.52 (3)	−33.35 (3)
C6—C7—C12—O13	−61.22 (3)	−52.96 (3)
N2—C3—C16—O17	5.06 (3)	−0.12 (3)

Data collection and cell refinement: Enraf–Nonius CAD-4 software. Data reduction: *SDP* (Frenz, 1983). Program(s) used to solve structure: *SIR*88 (Burla *et al.*, 1989). Program(s) used to refine structure: *SDP*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *PARST* (Nardelli, 1983*a*).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1094). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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The Phenylhydrazone Form of 2-Phenylazo-1,3-indandione

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Abstract

In the solid state, 2-phenylazo-1,3-indandione, $C_{15}H_{10}N_2O_2$, exists as a keto–hydrazone tautomer 2-phenylhydrazono-1,3-indandione. The bond distance of one of the keto groups, is slightly elongated [1.230 (3) *cf.* 1.217 (2) Å] as a result of resonance. This resonance is also indicated by an averaging of the single and double bonds in the crystal structure. A strong intramolecular hydrogen bond is found between the elongated oxo group and the amine H atom.

Comment

The work reported here is part of a project aimed at providing a better understanding of the stereochemistry of azo compounds. The structure determination of the title compound was undertaken to establish whether the molecule has the hydrazone or