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**Concepción Foces-Foces,^{a*}
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Cierva, 3, E-28006 Madrid, SpainCorrespondence e-mail: cfoces@iqfr.csic.es**Key indicators**

Single-crystal X-ray study

T = 170 K

Mean $\sigma(\text{C}-\text{C}) = 0.008 \text{ \AA}$

Disorder in main residue

R factor = 0.086

wR factor = 0.198

Data-to-parameter ratio = 13.7

For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.**Supramolecular assembly of diethyl 1*H*-pyrazole-
3,5-dicarboxylate 0.33-hydrate**

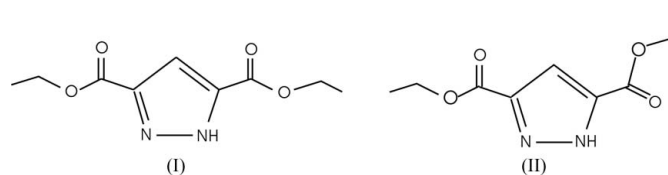
In the title structure, $\text{C}_9\text{H}_{12}\text{N}_2\text{O}_4 \cdot 0.33\text{H}_2\text{O}$, the molecules are present as two conformers, one of which is disordered. Another type of disorder involves $\text{N}-\text{N}-\text{H}/\text{H}-\text{N}-\text{N}$ tautomerism. Two crystallographically independent water molecules reside on a threefold axis and some water H atoms are also disordered. Six diethyl 1*H*-pyrazole-3,5-dicarboxylate molecules (three pairs of conformers) and two water molecules are assembled into a supramolecular aggregate *via* $\text{N}-\text{H} \cdots \text{N}$, $\text{Ow}-\text{H} \cdots \text{N}$, $\text{Ow}-\text{H} \cdots \text{Ow}$ and $\text{N}-\text{H} \cdots \text{Ow}$ hydrogen bonds.

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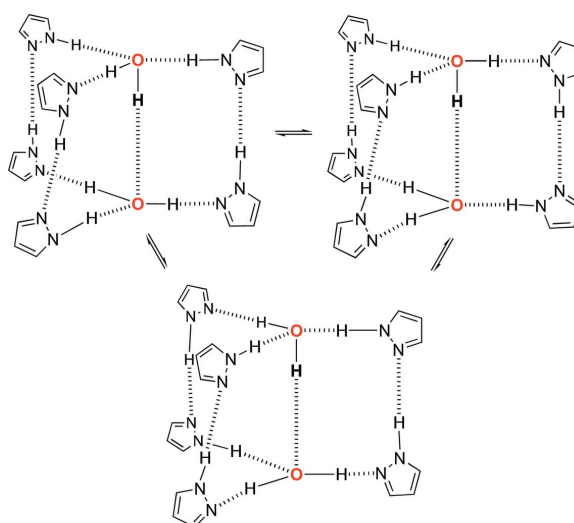
Accepted 5 July 2006

Comment

The title compound was investigated as part of structural studies on hydrogen-bonding motifs in pyrazole derivatives (Foces-Foces *et al.*, 2000; Alkorta *et al.*, 2006).



The asymmetric unit consists of two independent diethyl 1*H*-pyrazole-3,5-dicarboxylate molecules and one-third each of two water molecules. The pyrazole molecules are present in two conformations, (I), which is disordered and (II) (Fig.1). The two conformers are also present in the anhydrous structure (Yin *et al.*, 2004) in which no disorder was observed.



Scheme 2

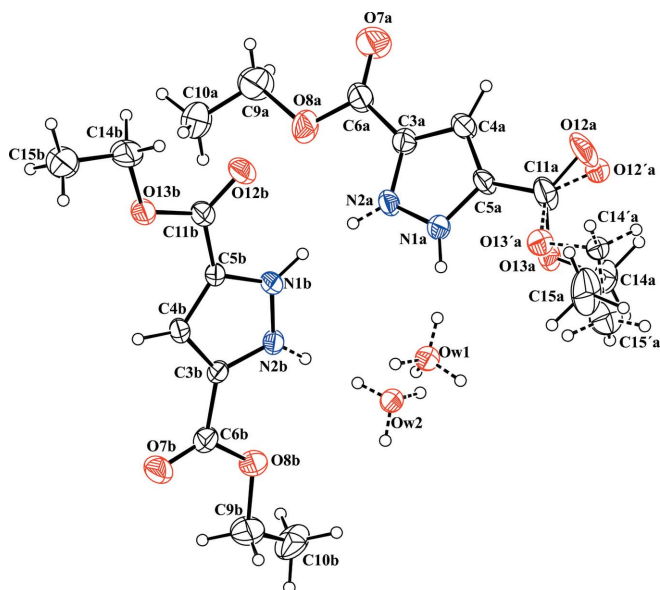


Figure 1

The asymmetric unit with anisotropic displacement parameters drawn at the 30% probability level. O12a–C15a and O12'a–C15'a refer to the disordered chains with occupancies of 0.77 (2) and 0.23 (2), respectively. The dashed bonds represent the minor components of the disordered groups. Suffixes *a* and *b* indicate conformers (I) and (II), respectively.

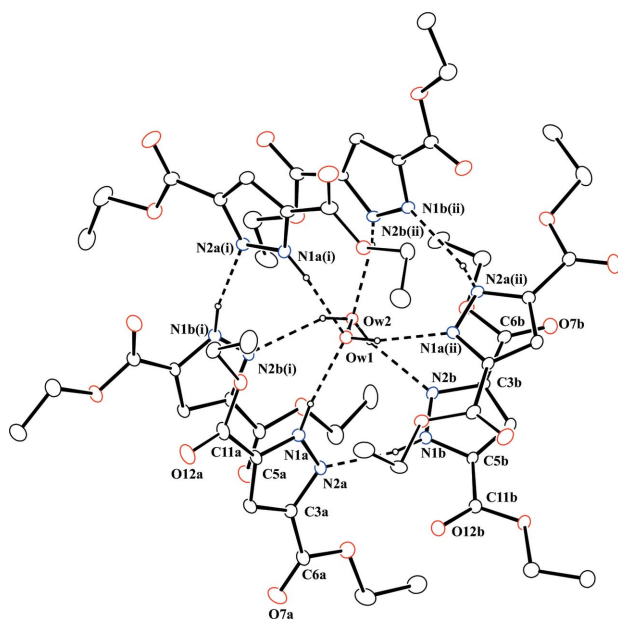


Figure 2

The supramolecular assembly. Atoms Ow1 and Ow2 are situated on the trigonal axis. For clarity, the minor component of the disordered ethoxycarbonyl chain has been omitted and only one of the three arrangements of the hydrogen-bonding network in Scheme 2 is shown. Suffixes *a* and *b* indicate conformers (I) and (II), respectively. [Symmetry codes: (i) $-x + y, 1 - x, z$; (ii) $1 - y, 1 + x - y, z$.]

An interesting feature of the structure is N–N–H/H–N–N tautomerism. There are three pieces of evidence for this phenomenon. First, it follows from consideration of the overall hydrogen-bond pattern (Table 1 and Scheme 2). The tautomerism is concomitant with the disorder of the water H atoms. Both kinds of disorder can be envisaged as a super-

position of the three arrangements in Scheme 2. Ow1 as well as Ow2 act simultaneously as donors and acceptors of hydrogen bonds and reside on the threefold axis. One H atom of Ow1 is located on this axis while the other H atoms are disordered over sets of three symmetry-related positions.

Second, the tautomerism is also evidenced by the bond angles at the protonated atoms N1a and N1b [109.2 (3) and 109.5 (3)°] and at the unprotonated atoms N2a and N2b [107.1 (3) and 107.7 (3)°] of both conformers. These angles significantly differ from those [113.6 (2) and 113.0 (2)°, and 103.9 (3) and 104.1 (2)°] in the ordered anhydrous compound (Yin *et al.*, 2004). Assuming a 2:1 tautomerism, the weighted average of the latter angles leads to values close to those in (I) and (II). This fact is also supported by the average values of 112.5 (11) and 104.6 (11)° (standard deviations of the sample are in parentheses) for 107 ordered pyrazole derivatives (Cambridge Structural Database, CSD, Version 5.27; Allen 2002).

Third, a build-up of the electron density (about $0.30 \text{ e } \text{Å}^{-3}$) corresponding to H2A and H2B atoms has been observed.

A pair of conformers (I) and (II) is connected through an N–H...N hydrogen bond. (I) is linked to Ow1 while (II) is bonded to Ow2. This molecular association is part of the Ow2...N2b–N1b...N2a–N1a...Ow1 synthon into which two water molecules are also included (Table 1 and Fig. 2). The combination of the three synthons generates, to the best of our knowledge (CSD), an unprecedented supramolecular framework (Fig. 2). The anhydrous structure (Yin *et al.*, 2004) forms a pseudo-dimer through N–H...N and N–H...O=C hydrogen bonds).

Experimental

The title compound was prepared from 3,5-pyrazoledicarboxylic acid monohydrate following the procedure of Schenck *et al.* (1985). Crystals suitable for X-ray analysis were obtained from CH₂Cl₂/hexane (1:1).

Crystal data

C₉H₁₂N₂O₄·0.33H₂O
M_r = 218.21
 Trigonal, *R*3̄c
a = 16.3410 (14) Å
c = 88.12 (6) Å
V = 20379 (13) Å³
Z = 72

D_x = 1.280 Mg m⁻³
 Mo Kα radiation
 μ = 0.10 mm⁻¹
T = 170 (2) K
 Quasi-spherical, colourless
 0.25 mm radius

Data collection

Nonius KappaCCD diffractometer
 φ and ω scans
 Absorption correction: none
 34593 measured reflections

4028 independent reflections
 2091 reflections with *I* > 2σ(*I*)
R_{int} = 0.106
 θ_{max} = 25.1°

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.086
wR(*F*²) = 0.198
S = 1.08
 4028 reflections
 294 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0621P)^2 + 45.7496P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 (Δ/σ)_{max} < 0.001
 Δρ_{max} = 0.35 e Å⁻³
 Δρ_{min} = -0.21 e Å⁻³

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
Ow2—H1W2···N2B	0.83	2.15	2.810 (3)	136
N1B—H1B···N2A	0.88	2.07	2.936 (5)	166
N1A—H1A···Ow1	0.88	1.94	2.793 (3)	164
Ow1—H1W1···Ow2	0.86	1.87	2.739 (7)	180
N2A—H2A···N1B	0.88	2.10	2.936 (5)	158
N2B—H2B···Ow2	0.88	2.00	2.810 (3)	153
Ow1—H2W1···N1A	0.86	1.96	2.793 (3)	161

Several data sets were collected from different samples, first on a four-circle diffractometer at room temperature, and then on a KappaCCD diffractometer at 170 K in order to reduce the large displacement parameters of the ethoxycarbonyl chains. The present data set was obtained from the data collection of the whole sphere of data. Refinement in $C2/c$, a sub-group of $R\bar{3}c$, gives a lower R value of 0.074, but with far more refined parameters, and the simpler rhombohedral description is preferred.

The disorder in the pyrazole conformer (I) has been modelled over two orientations. O—CH₂ and CH₂—CH₃ distances were restrained to 1.470 (5) Å. This value was retrieved from 150 structures measured between 160 and 180 K that are contained in the CSD. The occupancy factors are 0.77 (2) and 0.23 (2) for the major and minor components, respectively.

All H atoms were located in difference Fourier maps (water H atoms at the last stages of the structure determination). During the refinement, the H atoms were placed at idealized positions [for methyl, C—H = 0.98 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$, methylene C—H = 0.99 Å, aryl C—H = 0.95 Å, N—H = 0.88 Å, O—H = 0.86 Å, and

$U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C,N,O})$] and were treated as riding atoms except those of the water molecules which were kept fixed.

Data collection: *COLLECT* (Nonius, 2000); cell refinement: Please supply; data reduction: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*, *WinGX* (Farrugia, 1999) and *PLATON*.

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References

- Alkorta, I., Elguero, J., Foces-Foces, C. & Infantes, L. (2006). *ARKIVOC*, (ii), 15–30. (URL: <http://www.arkat-usa.org>.)
- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
- Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Foces-Foces, C., Alkorta, I. & Elguero, J. (2000). *Acta Cryst.* **B56**, 1018–1028.
- Nonius (2000). *KappaCCD Server Software*. Nonius BV, Delft, The Netherlands.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*. Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
- Schenck, T. G., Downes, J. M., Milne, C. R. C., Mackenzie, P. B., Boucher, H., Whelan, J. & Bosnich, B. (1985). *Inorg. Chem.* **24**, 2334–2337.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
- Yin, C., Huo, F., Gao, F. & Yang, P. (2004). *Acta Cryst.* **E60**, o320–o321.