Structure of 3-Methoxycarbonyl-1-methyl-4-nitropyrazole-5-carboxylic Acid Monohydrate

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Abstract. $C_7H_7N_3O_6.H_2O$, $M_r = 247.16$, ortho-rhombic, $Fdd2$, $a = 31.535$ (8), $b = 14.313$ (5), $c = 9.446$ (3) Å, $Z = 16$, $V = 4263.6$ Å^3, $D_x = 1.54$ g cm^{-3}, $\lambda(Mo\ K\alpha) = 0.71069$ Å, $\mu = 1.31$ cm^{-1}, $F(000) = 2048$, room temperature, final $R = 0.0368$ for 1223 observed reflections. The pyrazole ring is planar. The methoxycarbonyl, nitro and acid groups make angles of 8.1, 74.5 and 16.7°, respectively, with the pyrazole ring. The water of crystallization forms strong hydrogen bonds with the acid proton of one molecule and the unsubstituted pyrazole N atom of a symmetry-related molecule.

Experimental. Colourless crystals of the title compound were recrystallized from methanol and a suitable crystal of dimensions $0.25 \times 0.21 \times 0.15$ mm was mounted on an Enraf–Nonius CAD-4 diffractometer. Density was not measured. Cell dimensions were determined from a least-squares refinement of 25 widely dispersed reflections. Intensity data were collected using Mo $K\alpha$ radiation to a maximum $\theta = 25°$ with variable-speed $\omega/2\theta$ scans. Intensity data of 4602 reflections were collected with indices h -12 to 12, k -12 to 0, l -21 to 21, in a triclinic cell, cell constants $a = 8.574$ (1), $b = 8.579$ (2), $c = 16.471$ (5) Å, $\alpha = 99.10$ (2), $\beta = 99.08$ (2), $\gamma = 113.16$ (2)°. The cell and data were later transformed to the orthorhombic cell of the final refinement. There were no non-statistical variations in the intensities of three standard reflections monitored throughout the data collection. The data were corrected for Lorentz and polarization effects but absorption was ignored. The measured intensities were merged to give 1572 unique reflections ($R_{int} = 0.04$) of which 1223 were considered observed [$I > 2.5\sigma(I)$]. The non-H atoms were located by direct methods using *SHELXS*86 (Sheldrick, 1986) and subsequent refinement was carried out using *SHELX*76 (Sheldrick, 1976) based on F. To fix the origin, the z coordinate of the O1 atom was fixed. Anisotropic thermal parameters were used for all non-H atoms and isotropic for H atoms, found from successive difference Fourier maps. Final R and wR values were 0.0368 and 0.0406, respectively, with w

Table 1. *Final fractional coordinates of non-*H *atoms with e.s.d.'s in parentheses and equivalent isotropic temperature factors* (Å^2)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
C1	0.23989 (10)	0.11162 (19)	0.5548 (5)	0.0419
C2	0.28033 (9)	0.1343 (2)	0.5166 (5)	0.0410
C3	0.28123 (9)	0.1401 (2)	0.3709 (5)	0.0434
C4	0.22095 (10)	0.0947 (2)	0.6971 (5)	0.0478
C5	0.31860 (11)	0.1570 (2)	0.2794 (6)	0.0507
C6	0.3430 (2)	0.1766 (5)	0.0490 (8)	0.0908
C7	0.17357 (11)	0.0858 (4)	0.4093 (6)	0.0579
O1	0.18779 (8)	0.0548 (2)	0.71270	0.0624
O2	0.24475 (9)	0.1272 (2)	0.7962 (5)	0.0684
O3	0.32807 (8)	0.22670 (19)	0.6343 (4)	0.0662
O4	0.33099 (8)	0.0793 (2)	0.6661 (5)	0.0858
O5	0.35369 (8)	0.1615 (2)	0.3277 (5)	0.0701
O6	0.30802 (8)	0.1645 (2)	0.1461 (4)	0.0659
OH	0.20763 (14)	0.1077 (3)	0.0345 (5)	0.0850
N1	0.24273 (8)	0.1218 (2)	0.3197 (5)	0.0459
N2	0.21842 (8)	0.10506 (17)	0.4319 (4)	0.0426
N3	0.31567 (8)	0.1476 (2)	0.6138 (5)	0.0493

Table 2. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

C2—C1	1.364 (6)	O2—C4	1.287 (6)
C4—C1	1.491 (7)	O5—C5	1.199 (6)
N2—C1	1.348 (6)	O6—C5	1.307 (6)
C3—C2	1.379 (7)	O6—C6	1.445 (7)
N3—C2	1.456 (6)	N2—C7	1.457 (6)
C5—C3	1.481 (6)	N3—O3	1.213 (5)
N1—C3	1.333 (6)	N3—O4	1.197 (5)
O1—C4	1.201 (5)	N2—N1	1.330 (5)
C4—C1—C2	130.7 (4)	O5—C5—C3	121.4 (5)
N2—C1—C2	105.0 (4)	O6—C5—C3	111.9 (4)
C4—C1—N2	124.4 (3)	O6—C5—O5	126.7 (4)
C3—C2—C1	107.3 (4)	C6—O6—C5	115.3 (5)
N3—C2—C1	125.4 (4)	N2—N1—C3	105.7 (4)
N3—C2—C3	127.2 (4)	C7—N2—C1	128.8 (4)
C5—C3—C2	127.5 (4)	N1—N2—C1	112.6 (3)
N1—C3—C2	109.3 (4)	N1—N2—C7	118.5 (4)
N1—C3—C5	123.0 (5)	O3—N3—C2	118.0 (3)
O1—C4—C1	122.5 (4)	O4—N3—C2	117.5 (4)
O2—C4—C1	111.3 (4)	O4—N3—O3	124.5 (4)
O2—C4—O1	126.2 (5)		

$= 1.6830/[\sigma^2(F) + 0.001776F^2]$. Refinement was terminated when the shift/e.s.d. was less than 0.06. The maximum and minimum residual electron densities in the final difference Fourier map were 0.185 and -0.218 e Å^{-3}, respectively. Scattering factors were

those incorporated in *SHELX76*. The final atomic parameters are given in Table 1.* Bond lengths and angles are given in Table 2. A view of the molecule with atomic numbering is shown in Fig. 1.

Related literature. Bonati & Bovio (1990) have recently compiled the known data on pyrazoles and derived a set of empirical rules for the bond angles about the ring and its substituents. Our results agree completely with their rules.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, bond lengths and angles, and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71059 (8 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HL1001]
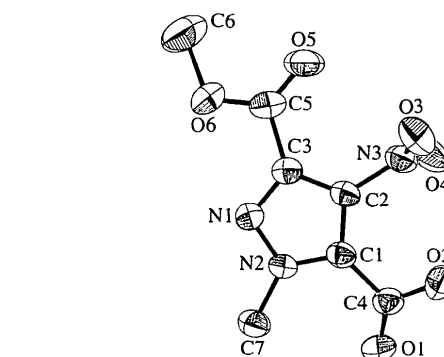

Fig. 1. *ORTEP* (Johnson, 1965) plot and atomic numbering scheme of the title compound.

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Structure of 5,5'-Dimethylsilanediyldi(phthalic anhydride):* a Model System for Aromatic Polyimides

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Abstract. 5,5'-Dimethylsilanediylbis(1,3-isobenzofurandione), $C_{18}H_{12}O_6Si$, $M_r = 352.4$, triclinic, $P\bar{1}$, $a = 9.0405$ (16), $b = 9.1893$ (15), $c = 10.6043$ (19) Å, $\alpha = 93.285$ (14), $\beta = 106.558$ (13), $\gamma = 101.730$ (13)°, $V = 820.5$ (2) Å^3, $Z = 2$, $D_m = 1.43$, $D_x = 1.43$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.710730 Å, $\mu = 0.167$ mm^{-1}, $F(000) = 364$, $T = 296$ (1) K, $R = 0.045$ for 2779 observed reflections with $|F_o| > 0$. This monomeric molecule is structurally similar to the repeat unit present in 'high peformance' polyimides. Of particular importance in terms of π-transfer complex formation is the overlap between the five- and six-membered rings. The separation between different molecules is 3.51 Å

for the ring system defined by C(11)—C(12)—C(13)—C(14)—O(4)—C(15)—C(16)—C(17)—C(18) (perpendicular distance between least-squares ring planes). The closest contact between atoms is 2.45 Å which is the interatomic separation between H(18) and O(2) at the equipoint $(x, 1 + y, z)$.

Experimental. Colorless triclinic crystals of the title compound were grown from saturated acetonitrile solution *via* vapor diffusion of diethyl ether. D_m was determined by neutral buoyancy in a benzene/CCl$_4$ solution. Melting point was obtained using a Fisher–Jones Melting Point Apparatus (stage technique); m.p. 450–451 K. A crystal of approximate dimensions $0.27 \times 0.50 \times 0.58$ mm was secured with epoxy to a glass fiber, mounted and aligned on a Syntex

* Alternative name: bis(3,4-dicarboxyphenyl)dimethylsilane dianhydride (SiDA).
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