Crystal structure of diethyl 2-(1-methyl-5-nitro-1*H*-imidazol-4-ylmethylene)malonate, $C_{12}H_{15}N_3O_6$

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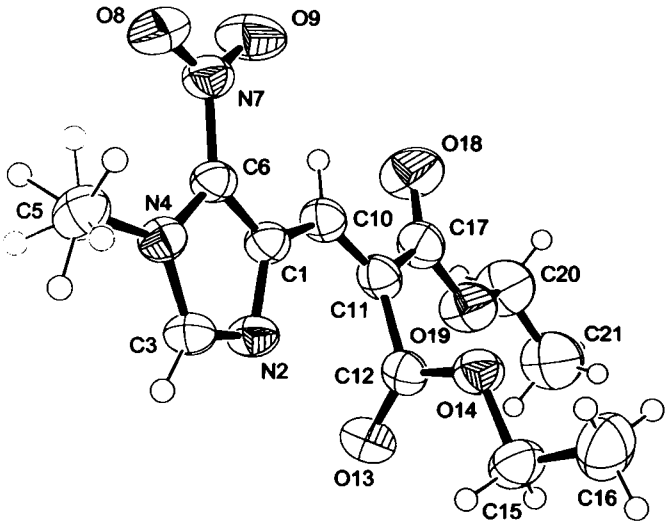

Abstract

$C_{12}H_{15}N_3O_6$, monoclinic, $P12_1/c1$ (no. 14), $a = 14.7940(7)$ Å, $b = 5.4610(1)$ Å, $c = 18.0420(9)$ Å, $\beta = 93.812(1)°$, $V = 1454.4$ Å^3, $Z = 4$, $R_{gt}(F) = 0.045$, $wR_{ref}(F^2) = 0.121$, $T = 293$ K.

Source of material

The synthesis of diethyl 2-(1-methyl-5-nitro-1*H*-imidazol-4-ylmethylene)malonate has been already reported [1].

Experimental details

Disordered H atoms at the C5 atom were found from Fourier difference maps and refined with occupation factors equal to 0.5. During the refinement they were allowed to rotate freely about the C—C bond with U_{iso}(H) restrained to $1.2\,U_{eq}$(C).

Discussion

1-Alkyl-5-nitroheterocycles that show the nitro group in β-position (*ortho*-like) against the diethyl methylenemalonate group are useful precursors for the synthesis of new pyridinones of pharmaceutical interest for the treatment of insomnia, anxiety, schizophrenia and Alzheimer's disease. To our knowledge, their crystal structures are the first examples of nitroheterocyclic compounds bearing the diethyl methylenemalonate to be structurally characterized by single crystal X-ray diffraction [2].

In the title structure, the nitro group is almost coplanar with the heterocyclic ring. The angle between NO_2 and the mean five-membered ring plane is 5(3)°. The methylene and one ester arm of the diethyl malonate are also almost coplanar. The maximum out-of-plane deviation from the mean plane C1-C10-C11-C17-O18-O19-C20-C21 (plane 2) is equal to 0.083(3) Å. The distances and angles involving the various heteroatoms are similar to those reported in the literature [3]. The dihedral angle between the nitro-heterocycle (plane 1) and plane 2 is equal to 14(4)° suggesting a strong conjugating effect all along the chains defining these two moieties. This electronic effect is one of the two stronger observed among the few examples of substituted methylenemalonate reported in the literature [4-10]. On another hand, the second ester arm of the diethyl malonate is quite perpendicular to the plane defined by the methylene and the first ester arm. The dihedral between plane 2 and the mean plane O13/C12/O14/C15 (plane 3) is equal 96(4)°. This conformation is comparable to those reported for other substituted methylenemalonate except in one case where the dihedral angle between the two ester arms is very small due to the constraint derived from an intramolecular hydrogen bond [8]. In the title structure, the H3 atom of the heterocycle and the H5D atom of the methyl make an H bond with the N2 atom of a symmetry-related molecule and the O8 atom of an ester arm of the same adjacent molecule, respectively (symmetry code $1-x,1-y,2-z$). Consequently, the two molecules form a dimer which is stabilized by a triple hydrogen bond, with each five-membered ring and one ester arm of each diethyl malonate lying on the same plane.

Table 1. Data collection and handling.

Crystal:	colorless prism, size 0.3 × 0.3 × 0.4 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	1.10 cm^{-1}
Diffractometer, scan mode:	Bruker-Nonius KappaCCD, φ
$2\theta_{max}$:	51.6°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	8345, 2692
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2311
$N(param)_{refined}$:	190
Programs:	SIR92 [11], SHELXL-97 [12]

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Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	x	y	z	U_{iso}
H(3)	4e		0.5410	0.2538	0.9790	0.050
H(5A)	4e	0.5	0.5641	−0.2120	0.8427	0.062
H(5B)	4e	0.5	0.5824	−0.1972	0.9291	0.062
H(5C)	4e	0.5	0.6301	−0.0128	0.8778	0.062
H(5D)	4e	0.5	0.6171	−0.0528	0.9316	0.062
H(5E)	4e	0.5	0.6051	−0.0691	0.8320	0.062
H(5F)	4e	0.5	0.5526	−0.2979	0.8886	0.062
H(10)	4e		0.2745	0.3783	0.7837	0.054
H(15A)	4e		0.2921	0.5517	1.0868	0.071
H(15B)	4e		0.2036	0.7100	1.0781	0.071
H(16A)	4e		0.1803	0.3798	1.1584	0.097
H(16B)	4e		0.2048	0.2020	1.0946	0.097
H(16C)	4e		0.1163	0.3603	1.0859	0.097
H(20A)	4e		0.0766	1.0930	0.7891	0.094
H(20B)	4e		0.0088	0.8906	0.8122	0.094
H(21A)	4e		−0.0284	1.2659	0.8645	0.108
H(21B)	4e		0.0698	1.2767	0.9027	0.108
H(21C)	4e		0.0020	1.0743	0.9259	0.108

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(8)	4e	0.44994(9)	−0.2344(3)	0.76944(7)	0.0718(8)	0.0628(9)	0.0632(8)	0.0022(7)	0.0086(6)	−0.0261(7)
O(9)	4e	0.3356(1)	−0.0029(3)	0.73796(7)	0.0832(9)	0.078(1)	0.0520(8)	−0.0005(8)	−0.0241(7)	−0.0151(7)
O(13)	4e	0.30392(8)	0.8386(2)	0.96799(7)	0.0569(7)	0.0490(8)	0.0590(7)	−0.0032(6)	−0.0093(6)	−0.0035(6)
O(14)	4e	0.22277(8)	0.5023(2)	0.99027(6)	0.0554(7)	0.0541(8)	0.0412(6)	−0.0047(5)	0.0000(5)	−0.0010(5)
O(18)	4e	0.1440(1)	0.6481(3)	0.76165(8)	0.0679(8)	0.116(1)	0.0539(8)	0.0264(8)	−0.0237(7)	−0.0118(8)
O(19)	4e	0.12951(8)	0.8636(3)	0.86533(7)	0.0541(7)	0.078(1)	0.0589(8)	0.0217(6)	−0.0165(6)	−0.0028(7)
N(2)	4e	0.42245(9)	0.3833(3)	0.92898(7)	0.0477(7)	0.0450(8)	0.0371(7)	0.0048(6)	−0.0050(5)	−0.0049(5)
N(4)	4e	0.49909(8)	0.0655(2)	0.88783(7)	0.0438(7)	0.0379(7)	0.0360(6)	0.0011(5)	0.0034(5)	0.0002(5)
N(7)	4e	0.4021(1)	−0.0552(3)	0.77891(7)	0.0568(8)	0.0506(9)	0.0360(7)	−0.0102(7)	0.0048(6)	−0.0047(6)
C(1)	4e	0.3768(1)	0.2976(3)	0.86602(8)	0.0425(7)	0.0427(9)	0.0322(7)	−0.0029(6)	0.0004(6)	0.0009(6)
C(3)	4e	0.4944(1)	0.2424(3)	0.93948(8)	0.0463(8)	0.0414(9)	0.0362(7)	0.0021(6)	−0.0038(6)	−0.0028(6)
C(5)	4e	0.5756(1)	−0.1035(3)	0.8840(1)	0.056(1)	0.050(1)	0.0505(9)	0.0122(8)	0.0032(7)	−0.0019(7)
C(6)	4e	0.4240(1)	0.1002(3)	0.84041(8)	0.0449(8)	0.0410(9)	0.0298(7)	−0.0057(6)	0.0021(6)	0.0000(6)
C(10)	4e	0.2960(1)	0.4162(3)	0.83377(9)	0.0430(8)	0.054(1)	0.0364(8)	−0.0025(7)	−0.0040(6)	0.0022(7)
C(11)	4e	0.2469(1)	0.5819(3)	0.86736(9)	0.0375(7)	0.053(1)	0.0422(8)	−0.0015(7)	−0.0056(6)	0.0044(7)
C(12)	4e	0.2631(1)	0.6595(3)	0.94678(9)	0.0356(7)	0.045(1)	0.0458(8)	0.0057(6)	−0.0043(6)	0.0018(7)
C(15)	4e	0.2293(1)	0.5520(4)	1.0694(1)	0.065(1)	0.070(1)	0.0418(9)	0.0019(9)	0.0018(8)	−0.0031(8)
C(16)	4e	0.1782(2)	0.3570(5)	1.1056(1)	0.080(1)	0.101(2)	0.063(1)	−0.004(1)	0.014(1)	0.014(1)
C(17)	4e	0.1686(1)	0.6984(4)	0.8242(1)	0.0419(8)	0.069(1)	0.048(1)	0.0042(8)	−0.0072(7)	0.0026(8)
C(20)	4e	0.0551(1)	1.0032(5)	0.8301(1)	0.060(1)	0.097(2)	0.076(1)	0.032(1)	−0.018(1)	0.001(1)
C(21)	4e	0.0214(2)	1.1700(5)	0.8852(2)	0.069(1)	0.100(2)	0.099(2)	0.029(1)	−0.013(1)	−0.008(2)

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