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Dimethyl 4-bromo-1-methyl-3,5-pyrazoledicarboxylate

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Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.005 Å
R factor = 0.031
wR factor = 0.083
Data-to-parameter ratio = 10.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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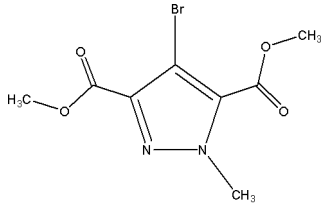
All the non-H atoms of the title compound, $C_8H_9BrN_2O_4$, lie on a mirror plane of the space group *Pnma*. The two methoxycarbonyl groups are *trans* with respect to the pyrazole ring. Intermolecular C—H···O and C—H···Br hydrogen bonds are responsible for the formation of chains. These interactions generate an $R_2^2(10)$ graph motif. Intramolecular C—H···O interactions are present, generating *S*(5) and *S*(6) ring patterns.

Comment

As a new multifunctional compound, the title compound, (I), is very useful in organic synthesis. It can be regarded as a key synthon of oligomeric carboxamides, which are known to bind to DNA by lodging in the groove (Lee *et al.*, 1989; Chambers & Denny, 1985). The fact that (I) can be selectively elaborated by acid or alkaline hydrolysis (Lee *et al.*, 1989) proves that the two methoxycarbonyl groups exist in different electronic environments. In addition, the existence of a bromine function at C2 affords the possibility of forming new C—C bonds through the Suzuki coupling reaction (Yin *et al.*, 2002) with a series of aromatic boron compounds, making it a useful intermediate for the synthesis of novel oligomeric carboxamides.



(I)

All bond distances are normal, but some exocyclic bond angles are unusually large, *viz.* N1—C1—C6, C2—C1—C6, N2—C3—C4 and C2—C3—C4 (Table 1). These discrepancies may be caused by steric factors, resulting from the Br atom at C2. Weak intermolecular C—H···O and C—H···Br hydrogen bonds (Berkovitch-Yellin & Leiserowitz, 1984; Desiraju, 1991, 1996; Steiner, 1997; Taylor & Kennard, 1982) link the molecules into chains extending along the *a* axis (Fig. 2). Specifically, a C5—H5···Br^{i} interaction (H···Br = 2.86 Å; symmetry code as in Table 2), with the Br atom of one molecule as acceptor and the methyl group from one ester group of a second molecule as donor, forms a *C*(7) chain motif (Bernstein *et al.*, 1995; Fig. 2). A C7—H7···O3^{ii} hydrogen bond (H···O = 2.53 Å; symmetry code as in Table 2), composed of an ester O atom from the second molecule as acceptor and the methyl group from an ester group of the first molecule as donor, is

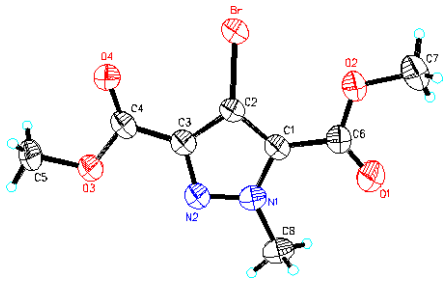


Figure 1
A view of the molecular structure of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

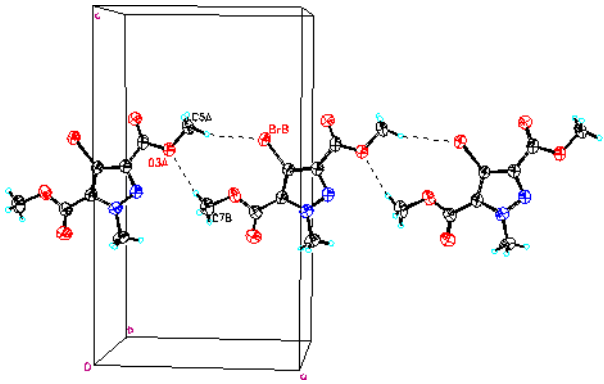


Figure 2
Packing of the title compound, showing the chain along the *a* axis linked *via* C—H···O and C—H···Br hydrogen bonds. The view is down the *b* axis.

also observed. The C—H···O chain has a graph-set motif of $C(9)$. Furthermore, these interactions form a ring of graph set $R_2^2(10)$. Remarkably, intramolecular C—H···O hydrogen bonds (Corey & Lee, 2001; Pálinkó, 1999) are observed in the molecular structure with $S(5)$ and $S(6)$ graph-set motifs, and their existence may also be partly responsible for the title compound being selectively hydrolyzed.

Experimental

The title compound was prepared by bromination of 3,5-bis-(methoxycarbonyl)-1-methylpyrazole in water. To 3,5-bis(methoxycarbonyl)-1-methylpyrazole in water containing CH_3COONa, Br_2 was added dropwise with vigorous stirring and the resulting solution was kept at boiling point for 3 h. The yield of the product was 88% (m.p. 397 K). The compound (100 mg) was dissolved in CCl_4 (3 ml). The solution was allowed to evaporate slowly over several days at room temperature. Colorless crystals suitable for single-crystal X-ray diffraction were formed.

Crystal data

$C_8H_9BrN_2O_4$
M_r = 277.08
Orthorhombic, *Pnma*
a = 9.4076 (12) Å
b = 6.8574 (9) Å
c = 16.242 (2) Å
V = 1047.8 (2) Å^3
Z = 4
D_x = 1.756 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5319 reflections
θ = 2.5–22.4°
μ = 3.92 mm^{-1}
T = 298 (2) K
Block, colorless
0.20 × 0.10 × 0.10 mm

Data collection

Bruker SMART 1K CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.508, T_{max} = 0.695
5013 measured reflections
1003 independent reflections
812 reflections with $I > 2\sigma(I)$
R_{int} = 0.032
θ_{max} = 25.0°
$h = -11 \rightarrow 11$
$k = -5 \rightarrow 8$
$l = -19 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.083
S = 1.05
1003 reflections
94 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0489P)^2 + 0.0035P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.32 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C2—C1	1.394 (5)	C3—N2	1.346 (4)
N1—C1	1.368 (4)	C3—C2	1.401 (5)
N1—N2	1.329 (4)		
O1—C6—O2	124.2 (4)	N2—C3—C4	121.0 (3)
O1—C6—C1	123.5 (4)	C1—N1—C8	129.5 (3)
O3—C4—C3	110.9 (3)	C1—C2—Br	128.0 (3)
O4—C4—O3	124.1 (4)	C2—C1—C6	132.6 (3)
O4—C4—C3	125.0 (3)	C2—C3—C4	128.8 (3)
N2—N1—C8	117.4 (3)	C3—C2—Br	126.1 (3)
N1—C1—C6	122.4 (3)	C4—O3—C5	115.4 (3)
N2—C3—C2	110.2 (3)	C6—O2—C7	117.6 (3)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C5—H5B···Br^{i}	0.96	2.86	3.782 (4)	162
C7—H7B···O3^{ii}	0.96	2.53	3.366 (6)	145
C8—H8B···O1	0.96	2.43	2.869 (5)	108
C7—H7C···O1	0.96	2.40	2.677 (6)	96
C5—H5C···O4	0.96	2.54	2.645 (5)	85

Symmetry codes: (i) $x-1, y, z$; (ii) $1+x, y, z$.

H atoms were placed in geometrically idealized positions, with Csp^3—H = 0.96 Å, and were constrained to ride on their parent atoms, with U_{iso}(H) = 1.5 U_{eq}(C).

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000) and *SHELXTL* (Bruker, 1999); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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