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Dimethyl (1*R*,8*R*)-1,11,11-trimethyl-2,3-diazatricyclo[6.2.1.$0^{2,6}$]undeca-3,5-diene-4,5-dicarboxylate, a chiral molecule with an approximate centrosymmetric crystal structure

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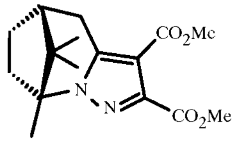
The crystal structure of the title compound, $C_{16}H_{22}N_2O_4$, has two independent chiral molecules related by a pseudo-inversion centre. 14 of the 22 non-H atoms have a centrosymmetric counterpart within a tolerance of 0.17 Å. A search of the Cambridge Structural Database [Spring 2000; Allen & Kennard (1993). *Chem. Des. Autom. News*, **8**, 1, 31–37] shows at least 10% of the crystal structures reported in the literature with space group $P2_1$ and Z = 4 to be chiral compounds with a pseudo-$P2_1/c$ packing.

Comment

The structure of the title compound, (I), contains two crystallographically independent molecules (Fig. 1). Equivalent bond distances and angles between the two molecules agree within experimental uncertainty, except for the C13—O2 bond length of 1.191 (3) Å which appears slightly too short due to the large thermal motion of atom O2. The conformation angles within the bicyclooctane groups of both molecules are rather similar; torsion angles about related bonds agree within 3°. The torsion angles about related bonds in the pyrazoledicarboxylate groups of the two molecules, however, have opposite signs. The pyrazole groups are planar. π-Bonding in the pyrazole rings is considerably delocalized. The carboxylate groups attached to C2 and C18 are almost coplanar with the pyrazole planes. The carboxylate groups attached to C1 and C17 are almost perpendicular to the pyrazole planes. Consequently, the C2—C15 and C18—C31 bonds are about 0.03 Å shorter than the corresponding C1—C13 and C17—C29 bonds due to resonance.

The molecules show no short intramolecular contacts. The crystal packing shows four intermolecular C—H$\cdots$O interactions with H$\cdots$O distances between 2.42 and 2.57 Å and C—H—O angles between 157 and 170° (Table 1). There are also two intermolecular C—H$\cdots\pi$ interactions between methyl groups and the π-system of the pyrazole groups with H$\cdots$*Cg* distances of 2.70 and 2.64 Å and C—H$\cdots$*Cg* angles of 155 and 151° (*Cg*1 represents the midpoint of the pyrazole ring of molecule 1 and *Cg*2 the midpoint of the pyrazole ring of molecule 2). A close inspection of the crystal structure shows a pseudo-centrosymmetric packing of the molecules. The achiral parts of the two molecules are symmetrically arranged about a pseudo-inversion centre at 0.5, 0.5, 0.25. 14 atom pairs among those groups satisfy the centre of symmetry within a tolerance of 0.17 Å. The two shortest intermolecular C—H$\cdots$O contacts connect the molecules of this pseudo-centrosymmetric dimer (Figs. 1 and 2). The H$\cdots$O distances of about 2.45 Å are short for C—H$\cdots$O interactions involving methyl groups (Desiraju & Steiner, 1999). The chiral parts of the molecules result in deviations from a centrosymmetric structure. The structure has a pseudo-$P2_1/c$ packing. The average intensity of the *h*0*l* reflections with *l* odd is only about 25% of the average intensity of general reflections. Approximate $P2_1/c$ symmetry in space group $P2_1$ with $Z = 4$ was also observed by one of us in the crystal structure of a 23 atom containing molecule with two chiral C atoms (Volk *et al.*, 1998, CSD refcode: JOGYAF). The achiral atoms of the two independent molecules in that structure are very closely related by a pseudo-inversion centre. 19 non-H atoms have centrosymmetric counterparts within a tolerance of 0.23 Å. In order to get an idea of the number of crystal structures of chiral compounds which crystallize in $P2_1$ with two independent molecules related by a pseudo-inversion centre, a search for such structures was performed in the spring 2000 release of the Cambridge Structural Database (Allen & Kennard, 1993). The search was limited to a subset



(I)

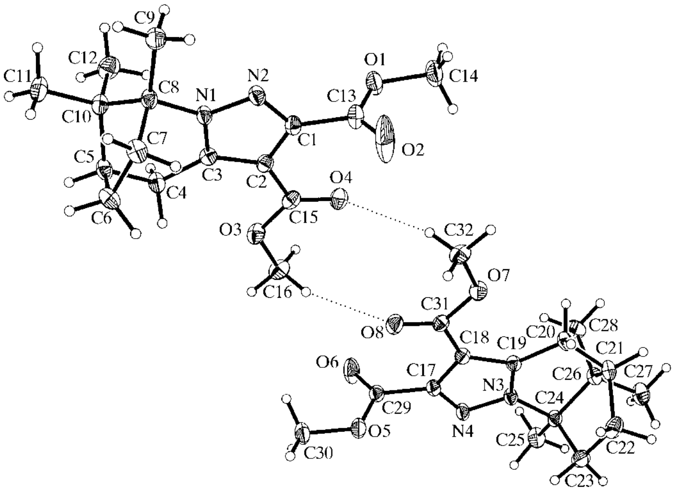


Figure 1
The pseudo-centrosymmetric dimer of (I) with two independent molecules connected by C—H$\cdots$O interactions. The displacement ellipsoids are drawn at the 50% probability level. H atoms are drawn as small circles of arbitrary radii.

containing the first 34 378 entries in the database (*i.e.* the refcodes starting with the characters A, B and C). The number of crystal structures with space group $P2_1$ and $Z = 4$ in this subset with coordinates reported is 318. All 318 structures were searched for pseudo-inversion centres using the *ADDSYM* option in program *PLATON* (Spek, 1998). For a number of structures, pseudo-inversion centres were detected at 0.25, *y*, 0, 0, *y*, 0.25 or 0.25, *y*, 0.25. Thus, these structures approximately have $P2_1/a$, $P2_1/c$ or $P2_1/n$ symmetry. In a final test, the coordinates of the independent molecules were directly compared. A total of 31 chiral structures were found with pseudo-$P2_1/c$ (or the equivalent pseudo-$P2_1/a$ and pseudo-$P2_1/n$) symmetry. The CSD refcodes are: ADRBFT10, AIPTHL10, APFMHA, ATRVND10, BABJIX, BADMUO, BAGMEB10, BAGMOL10, BAPZUN, BECSOR10, BIWFIW, BOJWAY, BOSWEL, BOXCPT10, BOXYOC, BPICAM, BRUDAG, BUYGUX, CAKHAX, CAMMEI, CAMPHX10, CELNAI, CITSUT10, CMETPT10, COBDAY, COGBIJ, COHRUM, COKWOO, COKWUU, CONHUI and CUCCIM. Some of these structures were reported as pseudo-centrosymmetric in the original publications (Goodwin *et al.*, 1984; Kurihara *et al.*, 1983, 1984; Ohashi *et al.*, 1982; Perales *et al.*, 1984; Trowitzsch *et al.*, 1981; Uchida *et al.*, 1984; Ziolo *et al.*, 1982). Thus, about 10% of the crystal structures reported in the literature with space group $P2_1$ and $Z = 4$ are chiral compounds with a pseudo-$P2_1/c$ packing. This number is probably a low estimate of the real number of pseudo-symmetric structures, as *ADDSYM* with default parameters only selects structures with at least 80% of the atoms fulfilling the (pseudo) symmetry criterium within a tolerance of 0.45 Å. Larger misfit tolerances result in additional hits. The space group $P2_1/c$ is not allowed for chiral compounds. The present investigation shows, however, that in some cases an approximate $P2_1/c$-type packing is preferred for chiral compounds.

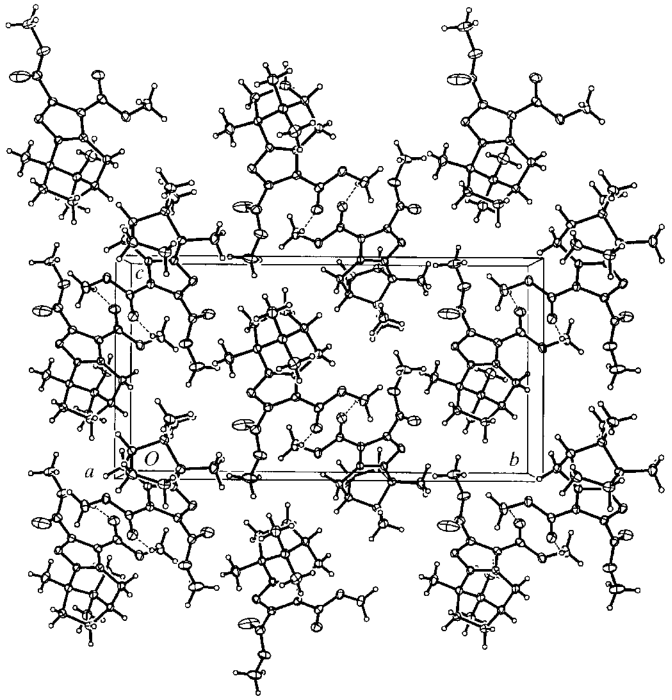


Figure 2
The crystal packing of (I) viewed down **a**.

Experimental

Compound (I) was prepared by a procedure similar to that described by Jefferson & Warkentin (1992) for other compounds. (1*R*,4*R*)-Camphoracetylhydrazone (500 mg, 2.40 mmol; Somogyi, 1991) and lead tetraacetate (1.06 g, 2.40 mmol) in absolute methanol (6.5 ml) afforded 5-methoxy-1′,5,7′,7′-tetramethylspiro[Δ^3-1,3,4-oxadiazoline-(1′*R*,4′*R*)-2,2′-bicyclo[2.2.1]heptane] (250 mg, 43%) as a mixture of four diastereomers that were used without separation. A solution of the latter oxadiazoline (230 mg, 965 µmol) and dimethyl acetylenedicarboxylate (411 mg, 2.89 mmol) in diethyl ether (55 ml) was irradiated with a medium pressure mercury lamp at room temperature for 8 h. After the volatiles had been removed *in vacuo*, column chromatography (silica gel, hexane/ethyl acetate = 10:1) provided 210 mg (71%) of compound (I). Single crystals were obtained by slow evaporation of a solution in pentane/dichloromethane at 273 K.

Crystal data

$C_{16}H_{22}N_2O_4$
$M_r = 306.36$
Monoclinic, $P2_1$
$a = 7.3772$ (14) Å
$b = 20.063$ (3) Å
$c = 10.4576$ (12) Å
$\beta = 90.513$ (12)°
$V = 1547.7$ (4) Å^3
$Z = 4$

$D_x = 1.315$ Mg m$^{-3$}
Mo $K\alpha$ radiation
Cell parameters from 188 reflections
$\theta = 3$–23°
$\mu = 0.095$ mm^{-1}
$T = 143$ (2) K
Block, colourless
0.70 × 0.40 × 0.36 mm

Data collection

Siemens SMART diffractometer
ω scans
Absorption correction: numerical six indexed faces (*SHELXTL*; Sheldrick, 1996)
$T_{\min} = 0.943$, $T_{\max} = 0.969$
30 858 measured reflections
4858 independent reflections
4589 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.029$
$\theta_{\max} = 31°$
$h = -10 \rightarrow 10$
$k = -28 \rightarrow 29$
$l = -14 \rightarrow 15$
524 standard reflections
frequency: 600 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.096$
$S = 1.079$
4858 reflections
407 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.055P)^2 + 0.28P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.44$ e Å^{-3}
$\Delta\rho_{\min} = -0.30$ e Å^{-3}

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

*Cg*1 represents the midpoint of the pyrazole ring of molecule 1 and *Cg*2 the midpoint of the pyrazole ring of molecule 2.

D—H···A	D—H	H···A	D···A	D—H···A
C16—H16B···O8	0.98	2.42	3.349 (2)	157
C22—H22B···O4$^{\rm i}$	0.99	2.57	3.516 (2)	160
C25—H25A···O2$^{\rm ii}$	0.98	2.55	3.519 (3)	170
C32—H32A···O4	0.98	2.45	3.395 (2)	163
C16—H16C···$Cg2^{\rm iii}$	0.98	2.64	3.529 (3)	151
C32—H32C···$Cg1^{\rm i}$	0.98	2.70	3.617 (3)	155

Symmetry codes: (i) $x-1, y, z$; (ii) $-x, \frac{1}{2}+y, -z$; (iii) $1+x, y, z$.

A 0.8 mm collimator was used. Friedel opposites were averaged. The H atoms were taken from a difference Fourier synthesis and were refined with fixed individual displacement parameters [$U(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{C})$ and $U(\mathrm{H}) = 1.5U_{\mathrm{eq}}(\mathrm{C_{methyl}})$] using a riding model with fixed distances: H—C(methyl) = 0.98 Å, H—C(secondary) = 0.99 Å and H—C(primary) = 1.00 Å. Torsion angles about the C—C and C—O bonds of the methyl groups were refined.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 1996); software used to prepare material for publication: *CIF* in *SHELXL*97 (Sheldrick, 1997).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1429). Services for accessing these data are described at the back of the journal.

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