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(1*E*)-2-(Diacetylamino)-1-methylprop-1-enyl acetate

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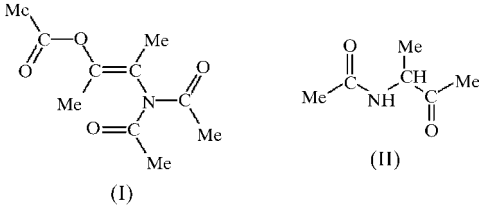
The analysis of the title compound, $C_{10}H_{15}NO_4$, firmly establishes the configuration of the double bond as *E*, a stereochemistry that had been assigned tentatively by other methods. The diacetylamine and acetate substituents are approximately coplanar to one another, but approximately perpendicular to the planar ethene core. H atoms of the ethene methyl substituents are found within the ethene plane, indicating that hyperconjugation does not play an important role in stabilizing the double bond.

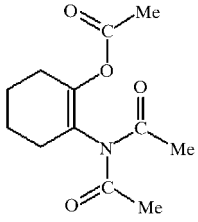
Comment

The reaction of the α-amino acid alanine with acetic anhydride and pyridine gives (1*E*)-2-(diacetylamino)-1-methylprop-1-enyl acetate, (I). The Dakin–West reaction (Dakin & West, 1928) would normally be expected to give *N*-(1-methyl-2-oxopropyl)acetamide, (II), but further reaction with acetic anhydride and pyridine gives (I), which was assigned the *E* configuration (Zav'yalov & Ezhova, 1977) on the basis of the observation that 2-(diacetylamino)cyclohexyl-1-enyl acetate, (III), yields 2-methyl-4,5,6,7-tetrahydrobenzoxazole, (IV), when partially hydrolyzed (Bhatt *et al.*, 1976). Lack of oxazole formation when (I) is partially hydrolyzed was taken as evidence for the *E* configuration of (I). Xue & Liang (1986) tentatively assigned the *E* configuration to (I) using the results of a difference nuclear Overhauser experiment.

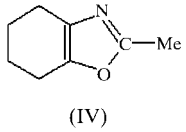


(I)

(II)



(III)



(IV)

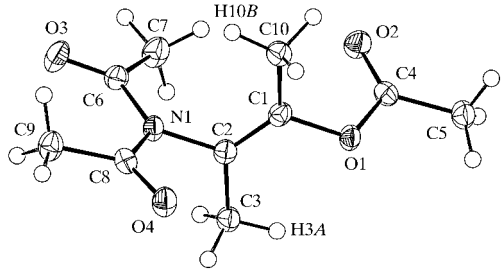


Figure 1
A view of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

dimensions are given in Table 1. The C1═C2 ethene bond length corresponds to the value expected for a C═C double bond, and bond lengths to substituent atoms of the ethene group correspond to expected values for single bonds involving these elements. Thus, no resonance is found between the amide and acetate substituents and the central ethene group. This is not surprising, since the planar acetate and amide substituents are oriented approximately perpendicular to the ethene plane (and approximately coplanar to one another), with angles of 90 (3) and 105 (3)° between the ethene core and the amide and acetate mean planes, respectively. The diacetylamine and acetate substitutents exhibit essentially planar geometries, as expected.

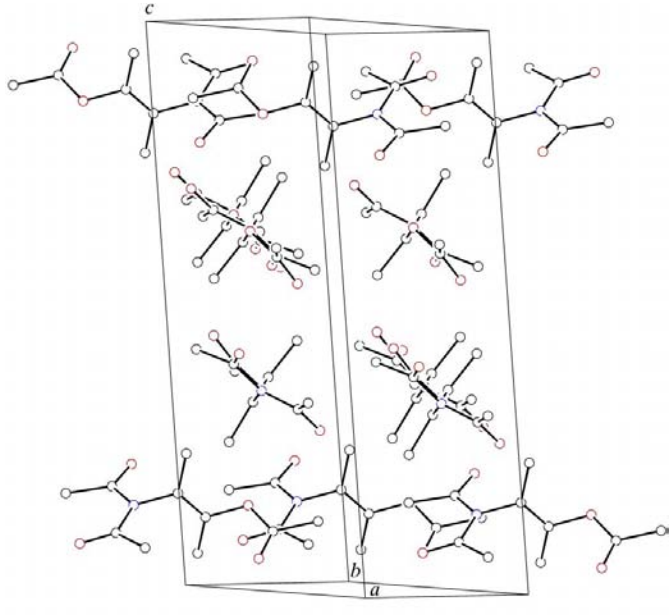


Figure 2
A unit-cell packing diagram for (I). H atoms have been omitted for clarity.

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The H atoms of each methyl-group substituent on the ethene double bond are oriented such that a C—H bond vector is almost coplanar with the ethene plane (N1—C2—C3—H3*A* = 179° and O1—C1—C10—H10*B* = 169°), which implies that hyperconjugation is not important in stabilizing the double bond in this molecule.

The *a* and *b* unit-cell parameters are almost equal and β is close to 90°, suggesting a quasi-tetragonal extended structure. This, indeed, appears to be the case, as shown in Fig. 2. The structure can be envisioned as a stacking of square-packed layers of molecules along the *c* axis. Within a given layer, the molecules are all translationally equivalent. The layers are then paired with an inversion-related neighboring layer, in which the central ethene planes are parallel to one another. These bilayer assemblies are then stacked together such that neighboring bilayers are related to one another by a twofold screw axis or an *n*-glide plane and the central ethene planes are at an angle of 68° with respect to one another.

Experimental

To a round-bottomed flask fitted with a reflux condenser were added alanine (1.0 g, 0.011 mol), acetic anhydride (6.24 ml, 0.066 mol) and pyridine (4.53 ml, 0.056 mol). After refluxing for 6 h, the solution was evaporated *in vacuo* to constant volume. The residue was dissolved in diethyl ether (50 ml) and extracted three times with sodium bicarbonate (10 ml, 10%). The sample was evaporated *in vacuo* after washing with distilled water (10 ml) and saturated sodium chloride (10 ml). The crude product was purified by column chromatography on Davisil 62 silica gel by eluting with diethyl ether and then crystallized from ligroine [m.p. 358.5–359.0 K; literature m.p. 357–358 K from ether (Bhatt *et al.*, 1976)]. The ^{1}H NMR spectrum gave three peaks (δ 1.7, 2.12 and 2.35), which integrated in the ratio 2:1:2. The ^{13}C NMR spectrum gave peaks at 15.292, 15.476, 20.565, 25.726, 125.348, 146.860, 168.748 and 172.245 p.p.m. The IR spectrum showed carbonyl peaks at 1715 (amide) and 1754 cm^{-1} (ester).

Crystal data

$C_{10}H_{15}NO_4$
M_r = 213.23
Monoclinic, $P2_1/n$
a = 7.6817 (4) Å
b = 7.8385 (3) Å
c = 18.0466 (9) Å
β = 97.708 (2)°
V = 1076.82 (9) Å^3
Z = 4
D_x = 1.315 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2533 reflections
θ = 2.9–27.5°
μ = 0.10 mm^{-1}
T = 100 K
Irregular, colorless
0.30 × 0.30 × 0.25 mm

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.4178 (16)	N1—C8	1.4117 (18)
O1—C4	1.3679 (17)	C1—C2	1.316 (2)
O2—C4	1.2029 (17)	C1—C10	1.489 (2)
O3—C6	1.2090 (17)	C2—C3	1.502 (2)
O4—C8	1.2178 (17)	C4—C5	1.487 (2)
N1—C2	1.4637 (18)	C6—C7	1.503 (2)
N1—C6	1.4138 (18)	C8—C9	1.494 (2)
C2—C1—O1	117.67 (12)	C1—C2—N1	117.14 (12)
C2—C1—C10	128.17 (13)	C1—C2—C3	127.11 (13)
O1—C1—C10	113.81 (12)	N1—C2—C3	115.65 (12)

Data collection

Nonius KappaCCD diffractometer
φ and ω scans
2629 measured reflections
2462 independent reflections
1859 reflections with $I > 2\sigma(I)$
R_{int} = 0.040
θ_{max} = 27.5°
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 10$
$l = -23 \rightarrow 23$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F)]$ = 0.042
$wR(F^2)$ = 0.099
S = 1.03
2462 reflections
152 parameters
Only H-atom *U*s refined
$w = 1/[\sigma^2(F_o^2) + (0.0324P)^2 + 0.488P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.37 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.015 (3)

Methyl H atoms were located from an electron-density difference map. Positional and displacement parameters for the H atoms were refined initially, but only displacement parameters were refined during the final cycles of refinement. The C—H distances are in the range 0.96–0.99 Å.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1724). Services for accessing these data are described at the back of the journal.

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