A Polarized, Twisted, Ethylene: Structure of Methyl 2-(1,3-Dimethyl-2-imidazolidinylidene)-3-oxobutyrate Dihydrate, C₁₀H₁₆N₂O₃.2H₂O

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Abstract. $M_r = 248$, monoclinic, $P2_1/n$, $a = 12\cdot028$ (2), $b = 7\cdot168$ (2), $c = 15\cdot187$ (5) Å, $\beta = 91\cdot88$ (2)°, $Z = 4$, $V = 1308\cdot6$ Å³, $D_m = 1\cdot26$, $D_x = 1\cdot263$ Mg m⁻³, λ (Cu $K\alpha$) = $1\cdot5418$ Å, $\mu = 0\cdot86$ mm⁻¹, $F(000) = 536$, $T = 293$ K. Final $R = 5\cdot6\%$ for 2120 observed reflexions. Owing to the push–pull effect, the C=C bond distance is as long as $1\cdot464$ (2) Å with the twist angle about the bond $62\cdot6°$.

Introduction. We report our findings on the molecular geometry of the title compound (I), a push–pull ethylene. We have reported earlier the results obtained for a few such push–pull ethylenes (Adhikesavalu & Venkatesan, 1981, 1982, 1983). A sample of the compound was kindly provided by Professor Jan Sandström, University of Lund, Sweden.

(I)
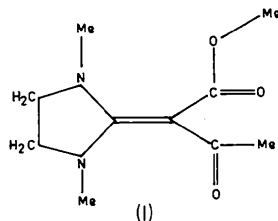
Experimental. D_m measured by flotation using KI solution. Single crystals obtained from toluene by slow evaporation, approximate dimensions $0\cdot8 \times 0\cdot4 \times 0\cdot4$ mm. Preliminary Weissenberg photographs indicated that the crystals are monoclinic with space group $P2_1/n$. Lattice parameters refined using 25 reflexions. Nonius CAD-4 diffractometer, graphite-monochromated Cu $K\alpha$ radiation, $\omega/2\theta$ mode, scan speed $1°$ min⁻¹, $\theta < 70°$. Two standard reflexions (400 and $3\overline{1}0$) monitored every 50 reflexions showed only statistical fluctuations. 2520 total reflexions of which 2120 judged significant, $|F_o| \geq 3\sigma|F_o|$. Data not corrected for absorption.

Structure solved by direct methods using *SHELX*76 (Sheldrick, 1976) in space group $P2_1/n$. Full-matrix refinement of a scale factor, positional and anisotropic thermal parameters (isotropic thermal parameters for H atoms, located from a difference map) converged to $R = 5\cdot6\%$, $R_w = 6\cdot0\%$, $S = 0\cdot15$; function minimized $\sum w(|F_o| - |F_c|)^2$ where $w = 1\cdot0/(a + b|F_o| + c|F_c|^2)$ (Cruickshank, Pilling, Bujosa, Lovell & Truter, 1961), with $a = 2\cdot50$, $b = 1\cdot0$, $c = 0\cdot30$. In final cycles of refinement Δ/σ for non-H atoms about $0\cdot03$. Final difference map featureless. Atomic scattering factors for non-H atoms from Cromer & Waber (1965), for H from Stewart, Davidson & Simpson (1965). Least-squares program originally by Gantzel, Sparks & Trueblood (1966) modified by T. N. Bhat to suit an IBM 360/44 computer.

Discussion. Final positional coordinates are provided in Table 1 and bond lengths, bond angles and torsion angles in Table 2.* Fig. 1 is a view of the molecule. There is extensive electron delocalization involving the donor imidazolidine ring and the acceptor acetyl and methoxycarbonyl groups as reflected in the molecular dimensions. The C=C bond distance is $1\cdot464$ (2) Å which is very much greater than that of the C=C bond in ethylene [$1\cdot336$ (2) Å; Bartell, Roth, Hollowell, Kuchitsu & Young, 1965]. There is a corresponding reduction in the lengths of donor–ethylenic C and acceptor–ethylenic C bonds: N(1)–C(6) and N(2)–C(6) are $1\cdot327$ (2) and $1\cdot323$ (2) Å respectively which are shorter than $1\cdot452$ (2) Å reported for an N–C$_{sp^2}$ bond (Ammon, Mazzocchi, Regan & Colicelli, 1979). On the acceptor side, the C(3)–C(2) and C(3)–C(4) bonds are $1\cdot424$ (3) and $1\cdot426$ (3) Å respectively which are significantly shorter than $1\cdot487$ (5) Å reported for a C$_{sp^2}$–C$_{sp^2}$ single bond (Shmueli, Shanan-Atidi, Horwitz & Shvo, 1973). Because of the delocalization, the acceptor part of the molecule assumes a carbanion-like structure. The acetyl and methoxycarbonyl groups assume an *EZ* conformation (Sandström, 1983).

The steric interaction involving the methyl groups at the N atoms and the acetyl and methoxycarbonyl groups has resulted in a large rotation about the C=C

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* Lists of structure factors, anisotropic thermal parameters, H-atom positions and hydrogen-bond parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38664 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

bond. The twist angle measured as the angle between the plane defined by the atoms N(1), N(2) and C(6) and the plane defined by the atoms C(2), C(3) and C(4) is 62·6 (3)°. It is of interest to note that in the corresponding acyclic compound methyl 2-bis-(dimethylamino)methylene-3-oxobutyrate (II) (Kamath & Venkatesan, 1982), the C=C bond length is 1·461 (2) Å, the twist about the C=C bond being 56·8 (3)°. In 3-(1,3-dimethyl-2-imidazolidinylidene)-2,4-pentanedione (III) (Adhikesavalu & Venkatesan, 1983), which has two acetyl groups as acceptors, the C=C bond length is 1·468 (3) Å and the twist angle is 72·9°. It is noteworthy that the C=C bond lengths do not differ significantly in the three molecules discussed above, although the twist angles about the C=C bond differ considerably which seems to indicate that the C=C length is invariant beyond a certain value for the angle of rotation.

(II)   (III)
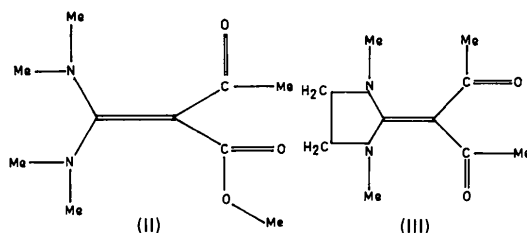
The packing of the molecules in the unit cell is shown in Fig. 2. There are two water molecules in the asymmetric unit and both are hydrogen-bonded to one carbonyl O and two other water molecules. The water molecules form a helical arrangement with the crystallographic 2_1 screw axes located at $(\frac{1}{4}, y, \frac{3}{4})$ and $(\frac{3}{4}, y, \frac{1}{4})$ as

the helix axes. Such a hydrogen-bonded helical arrangement is common in several hydrated carbohydrate structures (Chu & Jeffrey, 1967). The geometry about the water molecule $W(1)$ is almost planar with $W(1)$ deviating from the plane of the three H atoms by 0·197 (1) Å. However, $W(2)$ deviates more [0·515 (2) Å] from the plane through its three hydrogen-bonded neighbours.

Table 2. *Molecular geometry*

(a) Bond lengths (Å) with e.s.d.'s in parentheses

O(1)—C(1)	1·439 (3)	N(1)—C(6)	1·327 (2)
O(2)—C(2)	1·224 (2)	N(2)—C(6)	1·323 (2)
O(3)—C(4)	1·248 (2)	N(1)—C(7)	1·438 (2)
O(1)—C(2)	1·364 (2)	N(1)—C(8)	1·465 (2)
C(2)—C(3)	1·424 (3)	C(8)—C(9)	1·508 (3)
C(3)—C(4)	1·426 (3)	N(2)—C(9)	1·469 (2)
C(4)—C(5)	1·508 (3)	N(2)—C(10)	1·449 (2)
C(3)—C(6)	1·464 (2)		

(b) Bond angles (°) (e.s.d.'s 0·1°)

C(1)—O(1)—C(2)	116·3	C(3)—C(6)—N(2)	124·1
O(1)—C(2)—O(2)	120·5	N(1)—C(6)—N(2)	110·6
O(1)—C(2)—C(3)	112·1	C(6)—N(1)—C(8)	111·3
O(2)—C(2)—C(3)	127·4	C(6)—N(2)—C(9)	111·4
C(2)—C(3)—C(4)	125·0	N(1)—C(8)—C(9)	103·2
C(2)—C(3)—C(6)	119·2	C(8)—C(9)—N(2)	103·0
C(4)—C(3)—C(6)	115·8	C(6)—N(1)—C(7)	126·8
C(3)—C(4)—C(5)	121·1	C(7)—N(1)—C(8)	121·7
C(3)—C(4)—O(3)	121·5	C(6)—N(2)—C(10)	127·1
C(5)—C(4)—O(3)	117·4	C(6)—N(2)—C(9)	111·4
C(3)—C(6)—N(1)	125·3	C(10)—N(2)—C(9)	121·5

(c) Torsion angles (°) with e.s.d.'s in parentheses

O(1)—C(2)—C(3)—C(4)	−175·3 (1)	C(5)—C(4)—C(3)—C(6)	−173·1 (1)
O(1)—C(2)—C(3)—C(6)	4·7 (2)	C(4)—C(3)—C(6)—N(1)	−116·7 (2)
C(1)—O(1)—C(2)—O(2)	0·8 (2)	C(4)—C(3)—C(6)—N(2)	61·9 (2)
C(1)—O(1)—C(2)—C(3)	−179·6 (1)	C(3)—C(6)—N(1)—C(7)	4·2 (2)
O(2)—C(2)—C(3)—C(4)	4·2 (3)	C(3)—C(6)—N(2)—C(10)	2·8 (3)
O(2)—C(2)—C(3)—C(6)	−175·8 (2)	N(1)—C(6)—N(2)—C(9)	3·9 (2)
O(3)—C(4)—C(3)—C(2)	−174·4 (2)	C(6)—N(2)—C(9)—C(8)	0·7 (2)
O(3)—C(4)—C(3)—C(6)	5·6 (2)	N(2)—C(9)—C(8)—N(1)	6·4 (2)
C(2)—C(3)—C(4)—C(5)	7·0 (2)	C(9)—C(8)—N(1)—C(6)	−4·7 (2)
C(2)—C(3)—C(6)—N(1)	63·3 (2)	C(8)—N(1)—C(6)—N(2)	0·7 (2)
C(2)—C(3)—C(6)—N(2)	−118·1 (2)		

Table 1. *Final fractional coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($\times 10^2$) for non-H atoms with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{4}{3} \sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	B_{eq} (Å²)
O(1)	4229 (1)	2911 (2)	1678 (1)	374 (3)
O(2)	4383 (1)	−1 (2)	2217 (1)	419 (3)
O(3)	1912 (1)	−1441 (2)	291 (1)	438 (4)
W(1)	6517 (1)	−1405 (2)	2575 (1)	515 (4)
W(2)	2077 (2)	−425 (2)	−1471 (1)	605 (5)
N(1)	3365 (1)	2931 (2)	−170 (1)	322 (3)
N(2)	1702 (1)	2748 (2)	352 (1)	327 (3)
C(1)	5077 (2)	3477 (3)	2313 (1)	481 (5)
C(2)	3940 (1)	1071 (2)	1685 (1)	294 (4)
C(3)	3103 (1)	645 (2)	1032 (1)	269 (3)
C(4)	2578 (1)	−1127 (2)	921 (1)	310 (4)
C(5)	2789 (2)	−2681 (3)	1574 (1)	438 (5)
C(6)	2732 (1)	2102 (2)	414 (1)	258 (3)
C(7)	4502 (2)	2492 (3)	−349 (1)	419 (5)
C(8)	2732 (2)	4311 (2)	−691 (1)	399 (5)
C(9)	1563 (2)	4077 (3)	−380 (1)	391 (4)
C(10)	778 (2)	2224 (3)	887 (1)	436 (5)

Fig. 1. A perspective view of the molecule showing atom numbering.
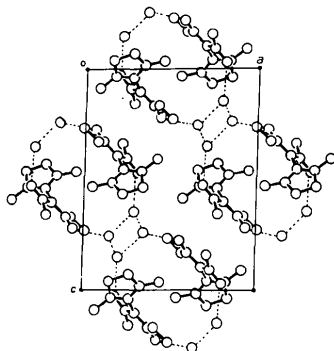
$C_{10}H_{16}N_2O_3.2H_2O$

Fig. 2. Packing of the molecules in the unit cell viewed down **b**.

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Structure of 6-(2,6-Dichlorophenyl)-2,3,6,7-tetrahydro-5H-pyrrolo[1,2-a]imidazole Hydrochloride Monohydrate (ICI-101187), $C_{12}H_{13}Cl_2N_2^+.Cl^-.H_2O$

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Abstract. $M_r = 309.6$, triclinic, $P\bar{1}$, $a = 8.320$ (1), $b = 8.326$ (1), $c = 11.166$ (2) Å, $\alpha = 102.96$ (1), $\beta = 104.26$ (1), $\gamma = 86.32$ (1)°, $V = 730.6$ (4) Å³, $Z = 2$, $D_x = 1.41$ Mg m⁻³, Cu $K\bar{\alpha}$, $\bar{\lambda} = 1.54178$ Å, $\mu = 11.17$ mm⁻¹, $F(000) = 320$, room temperature, final $R = 0.065$ for 1715 reflections. The title compound is an α_2-adrenoceptor agonist and antihypertensive agent. The two moieties of the molecule are almost perpendicular. N–H···Cl hydrogen bonds contribute to the crystalline cohesion.

Introduction. The class of 6-aryl-2,3,6,7-tetrahydro-5H-pyrrolo[1,2-a]imidazoles, including recently synthesized ICI-101187, were shown to be α-agonists. ICI-101187 is as potent as clonidine in lowering blood pressure while it is only one-tenth as active as a sedative (Clough, Hatton, Pettinger, Samuels Gillian & Shaw, 1978).

This work has been undertaken in order to compare the conformation of ICI-101187 with those of clonidine (Byre, Mostad & Rømming, 1976; Carpy, Hickel & Léger, 1979) and related analogues (Carpy, Léger, Leclerc, Decker, Rouot & Wermuth, 1982, and references therein).

Experimental. White elongated prism (from 2-propanol), $0.25 \times 0.20 \times 0.10$ mm, D_m not measured, Enraf–Nonius CAD-4 diffractometer, 25 reflections used for measuring lattice parameters ($6 < \theta < 30°$), $2760 \pm h \pm kl$ independent reflections with $\theta < 70°$, 1715 with $I \geq 3\sigma(I)$, Lp correction, absorption ignored; two check reflections ($2\bar{1}3, 0\bar{4}0$) measured every 5400s: no variation. Direct methods (MULTAN, Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), anisotropic diagonal-matrix refinement on F; weighting scheme: $w = 1$ if $|F_o| < P, P = (F_o^2 \text{ max.}/10)^{1/2}$, $w = (P/F_o)^2$ if $|F_o| > P$; H₂O and H from ΔF synthesis, H isotropic, final $R = 0.065$, $wR = 0.045$, $S = 0.980$; final maximum shift to error 0.295, max. and min. heights in final difference Fourier map ± 0.5 e Å⁻³; f_i of