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## A Functionalized Dimethyl 1,3-Butadiene-2,3-dicarboxylate

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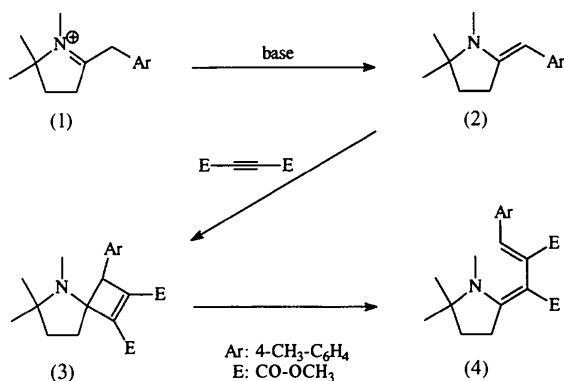
### Abstract

The crystal structure of dimethyl *syn*-(*Z*)-2-(4-methylphenylmethylene)-3-(1,5,5-trimethylpyrrolidin-2-ylidene)butanedioate,  $C_{21}H_{27}NO_4$ , has been determined in order to establish its constitution and configuration, and to characterize the preferred conformation in the solid state. There are notable differences in the conformations of the functional groups; the essential structural features are discussed and compared.

### Comment

The experimental investigations have been carried out as part of reactivity studies with specifically substituted 1-methyl-3,4-dihydro-2*H*-pyrrolium salts and dimethyl acetylenedicarboxylate under basic conditions. The formation of dimethyl *syn*-(*Z*)-2-(4-methylphenylmethylene)-3-(1,5,5-trimethyl-1,3,4,5-tetrahydro-2*H*-pyrrolidene)butanedioate, (4), can be explained as a result of consecutive transformations. Deprotonation of 5-(4-methylphenylmethyl)-1,2,2-trimethyl-3,4-dihydro-2*H*-pyrrolium trifluoromethane sulfonate, (1), by ethyldiisopropylamine generates 2-(4-methylphenylmethylene)-1,5,5-trimethylpyrrolidine, (2). The reactive enamine, (2), undergoes a [2+2] cycloaddition with dimethyl

acetylenedicarboxylate to afford the spiro-annulated intermediate, (3), followed by a cycloreversion to yield the title compound, (4). These consecutive reactions are of particular interest with respect to the reactivity of the semicyclic 1-azaallyl system and the spiro-annulated cyclobutenyl ring system (*cf.* reviews concerning enamines: Chinchilla & Bäckvall, 1994; Hickmott, 1994; Hubschwerlen, Fleury & Fritz, 1976; Jung 1991).



The constitution of the reaction product, (4), can be deduced by 1D and 2D  $^1H$  and  $^{13}C$  NMR experiments (COSY and COLOC). A signal degeneration and spreading for the cyclic methylene groups is observed in  $^1H$  NMR spectra ( $CDCl_3$ , 400 MHz) measured at 296 K; this phenomenon disappears when the temperature is increased to 330 K. In  $^{13}C$  NMR spectra ( $CDCl_3$ , 100.6 MHz) analogous behaviour is observed for the methyl groups at position 5 of the heterocyclic ring. Obviously, the ring inversion is sterically hindered by the methyl groups; in accordance with this assumption the spectroscopic phenomenon does not occur if the 5-position is unsubstituted (Zellmer, Preut & Kreher, 1997). X-ray diffraction was carried out in order to confirm the NMR results and to determine the configuration and characterize the conformation in the solid state.

The C=C double bond connected to the phenyl ring has the *Z* configuration and the C=C double bond linked to the heterocyclic ring has the *E* configuration. The butadienyl C11=C3—C4=C21 segment, with a non-planar sequence of alternating single and double bonds, prefers a *syn*-(*Z*) conformation in the solid state. Structural evidence that  $\pi$ -delocalization appears to be restricted comes from the typical values of single and double bonds (*cf.* Table 1).

The angles around the N atom [C21—N1—C27 123.9 (2) and C27—N1—C24 120.0 (2)°, and the somewhat compressed C24—N1—C21 angle of 114.3 (2)° inside the five-membered heterocycle] are indications of the planarity of the nitrogen environment. The short N1—C21 distance of 1.355 (3) Å, in contrast to the bond lengths N1—C24 of 1.480 (3) and N1—C27 of 1.454 (3) Å, demonstrates the double-bond character of N1—C21 and the conjugation of the lone pair at the

heteroatom with the semicyclic C<sub>21</sub>=C<sub>4</sub> double bond. The O<sub>3</sub>=C<sub>5</sub>—O<sub>4</sub>—C<sub>6</sub> methoxycarbonyl group is out of the plane (N1, C<sub>21</sub>, C<sub>4</sub>) and cannot participate in full conjugation.

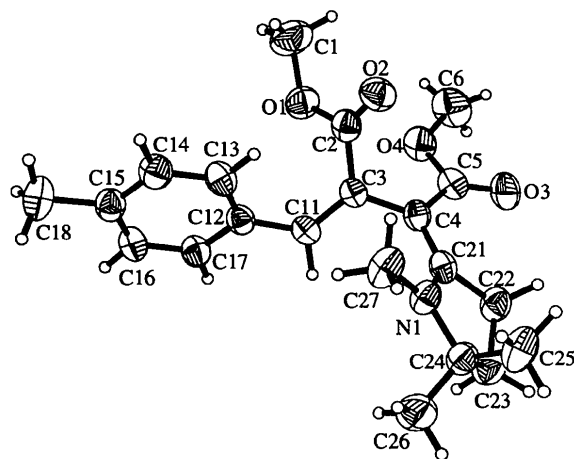


Fig. 1. View of the title compound showing the labelling of all non-H atoms. Displacement ellipsoids are shown at 50% probability levels. H atoms are drawn as circles of arbitrary radii.

The peripheral O-methyl (C<sub>1</sub> and C<sub>6</sub>) and C-methyl groups (C<sub>18</sub>, C<sub>25</sub> and C<sub>26</sub>) show higher displacement parameters than the other C atoms because of higher vibration. In this respect, the C<sub>27</sub> methyl group at the heteroatom is an exception. The vicinal methoxycarbonyl groups differ markedly in conformation with respect to the central single bond. The corresponding C=C and C=O double bonds adopt a *syn* conformation with respect to the C<sub>4</sub>—C<sub>5</sub> single bond. The conformation of the corresponding enone segment shows a significant difference and is not far from an *anti* orientation with respect to the connecting C<sub>2</sub>—C<sub>3</sub> single bond. The reaction sequence seems to be typical for heterocyclic enamines with similar structures (Zellmer, Preut & Kreher, 1997).

## Experimental

The title compound, (4), was prepared by the reaction of 5-(4-methylphenylmethyl)-1,2,2-trimethyl-3,4-dihydro-2H-pyrrolium trifluoromethane sulfonate, (1), with dimethyl acetylenedicarboxylate in the presence of ethyldiisopropylamine in dry dichloromethane at room temperature. The reaction product was isolated from the organic phase and purified by recrystallization from ethanol. In this simple manner also, single crystals suitable for X-ray diffraction measurements were obtained.

## Crystal data

C<sub>21</sub>H<sub>27</sub>NO<sub>4</sub>  
M<sub>r</sub> = 357.4

Mo K $\alpha$  radiation  
 $\lambda$  = 0.71073 Å

Triclinic

$P\bar{1}$

$a$  = 9.736 (3) Å

$b$  = 11.021 (4) Å

$c$  = 11.147 (6) Å

$\alpha$  = 88.07 (4)°

$\beta$  = 65.79 (3)°

$\gamma$  = 66.10 (4)°

$V$  = 984.7 (8) Å<sup>3</sup>

$Z$  = 2

$D_x$  = 1.206 Mg m<sup>-3</sup>

$D_m$  not measured

## Data collection

Enraf-Nonius CAD-4

diffractometer

$\omega$ -2 $\theta$  scans

Absorption correction: none

3673 measured reflections

3364 independent reflections

2294 reflections with

$I > 2\sigma(I)$

$R_{int}$  = 0.0120

Cell parameters from 25

reflections

$\theta$  = 14.6–17.1°

$\mu$  = 0.083 mm<sup>-1</sup>

$T$  = 293 (2) K

Prism

1.5 × 0.7 × 0.5 mm

Yellow

## Refinement

Refinement on  $F^2$

$R(F)$  = 0.0446

$wR(F^2)$  = 0.1355

$S$  = 1.051

3364 reflections

344 parameters

H atoms: see below

$w = 1/[\sigma^2(F_o^2) + (0.0761P)^2$

$+ 0.2477P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$  = 0.017

$\Delta\rho_{max}$  = 0.198 e Å<sup>-3</sup>

$\Delta\rho_{min}$  = -0.150 e Å<sup>-3</sup>

Extinction correction:

*SHELXL93* (Sheldrick, 1993)

Extinction coefficient:

0.016 (4)

Scattering factors from

*International Tables for Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °)

C2—O2	1.202 (3)	C5—O3	1.209 (2)
C2—O1	1.338 (3)	C5—O4	1.352 (3)
C2—C3	1.490 (4)	C11—C12	1.475 (3)
C3—C11	1.331 (4)	C21—N1	1.355 (3)
C3—C4	1.485 (3)	C24—N1	1.480 (3)
C4—C21	1.372 (3)	C27—N1	1.454 (3)
C4—C5	1.455 (3)		
O2—C2—O1	123.6 (3)	C3—C11—C12	129.6 (3)
C11—C3—C4	121.0 (3)	N1—C21—C4	127.2 (2)
C11—C3—C2	122.5 (2)	N1—C21—C22	107.0 (2)
C4—C3—C2	116.5 (2)	C4—C21—C22	125.8 (2)
C21—C4—C5	117.9 (2)	C21—N1—C27	123.9 (2)
C21—C4—C3	123.9 (2)	C21—N1—C24	114.3 (2)
C5—C4—C3	118.2 (2)	C27—N1—C24	120.0 (2)
O3—C5—O4	121.0 (2)		
O1—C2—C3—C4	131.9 (2)	C3—C4—C21—N1	-21.1 (4)
C3—C4—C5—O3	170.8 (2)	C21—C4—C3—C11	-44.7 (3)

All H atoms were taken from difference Fourier syntheses and refined with independent isotropic displacement parameters.

Data collection: *SDP* (Frenz, 1978). Cell refinement: *SDP*. Data reduction: *SDP*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1991). Software used to prepare material for publication: *SHELXL93*.

Lists of structure factors, anisotropic displacement parameters, atomic coordinates and complete geometry have been deposited with the IUCr (Reference: NA1259). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## 1,13-Tridecanediol

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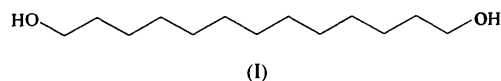
### Abstract

The crystal structure of tridecane-1,13-diol,  $C_{13}H_{28}O_2$ , a model for liquid crystals, has been determined by X-ray diffraction. The molecules form a layer structure along the *a* axis as in a smectic A liquid crystal. The skeleton of the molecule has an all-*trans* conformation. One of the terminal hydroxyl groups is in a *gauche* conformation, while the other is *trans*.

### Comment

Long-chain compounds such as *n*-higher primary alcohols and  $\alpha,\omega$ -disubstituted *n*-alkanes exhibit a high-temperature phase just below their melting points. It has

been proposed that the molecules rotate about their long axes in this phase (Asai, Yoda & Yamanaka, 1955), a fact which shows the molecules to have a considerable degree of motional freedom in the phase. The crystal structures of some long-chain compounds similar to the title compound, (I), have been determined previously (for example, Watanabe, 1961; Seto, 1962; Nakamura & Yamamoto, 1994). Almost all the structures reported are similar to that of a smectic liquid crystal, in which long molecules arrange themselves in parallel to form a layer. These long-chain compounds have been of great interest recently as liquid-crystal model materials.



The molecular structure of 1,13-tridecanediol is shown in Fig. 1. One of the hydroxyl groups of the molecule is in a *gauche* conformation, while the other is *trans*. The molecular skeleton of the hydrocarbon chain is all-*trans*. The *gauche* conformation has been observed in 1-heptadecanol (Seto, 1962), where the *gauche* and *trans* conformations of the hydroxyl groups appear alternately in laterally adjoining molecules in the layers, *i.e.* the hydroxyl group of a 1-heptadecanol molecule is in a *gauche* conformation if that of the longitudinally adjoining molecule in the adjoining layer is *trans*. As a result, interlayer hydrogen-bond formation is in a *trans/gauche*

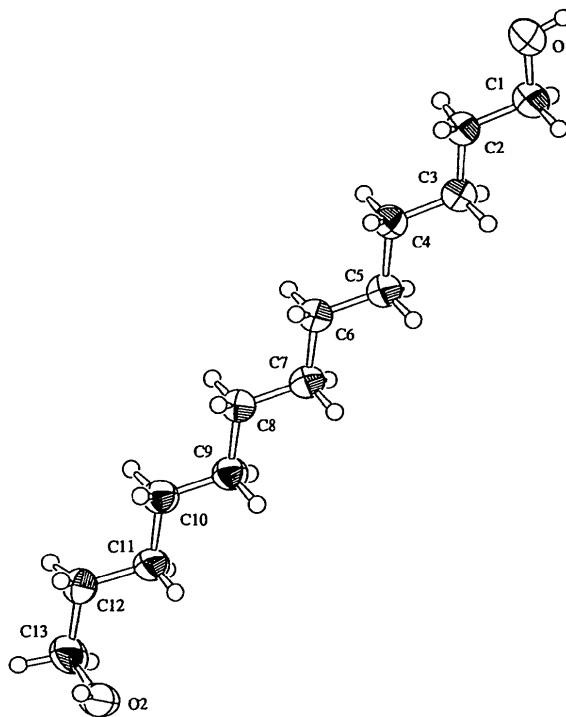


Fig. 1. An ORTEP (Johnson, 1976) view of the title molecule showing the crystallographic numbering scheme.