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16α-Chloro-16β-cyano-3-methoxy-14,17αethenoestra-1,3,5(10)-trien-17β-yl Acetate

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Abstract

The X-ray structure analysis of the title compound, $C_{24}H_{26}CINO_3$, corrects the original incorrect assignment of configuration at C-16 [Bull *et al.* (1993). *J. Chem. Soc. Chem. Commun.* pp. 271–273].

Comment

As part of a study of the cycloaddition of ketene equivalents to 3-methoxyestra-1,3,5(10),14,16-pentaen-17 β -yl acetate, (I), the 2-chloroacrylonitrile adduct, (II), was synthesized (Bull *et al.*, 1993). The gross structure of the adduct was determined by standard spectroscopic techniques, and the configuration at C-16 was assigned as 16 β -chloro-16 α -cyano on the assumption that cyclo-addition proceeds with the preferred *endo*-orientation of the cyano group.



Subsequently, the structure of the related 2-acetoxyacrylonitrile cycloadduct, (III), was determined (Bull *et al.*, 1994) and the 16-cyano group was found to be in the *exo*-orientation, *i.e.* 16β . In the light of this finding, it was decided to determine the configuration at C-16 conclusively by a crystal structure determination of the 2-chloroacrylonitrile cycloadduct, (II), and to furnish additional structural information about this unusual class of bridged steroids. The result was also expected to clarify a more general question about the influence of competing steric and stereoelectronic factors upon transition-state geometry during cycloaddition. Numerous applications of 2-chloroacrylonitrile in synthesis (Ranganathan *et al.*, 1977) reveal uncertainty about the stereochemical outcome of such reactions, arising from

The asymmetric unit was found to consist of two crystallographically independent molecules. Both of these molecules have the same overall structure, with ring *B* as a 7α ,8 β -half-chair, ring *C* as an 8β ,12 α -chair and both five-membered rings adopting envelope conformations. This is readily apparent from an examination of the puckering parameters (Cremer & Pople, 1975) for the two molecules (Table 1). Both molecules also clearly showed that the relative orientations of the 16-position substituents are 16β -cyano and 16α -chloro, opposite to the original assignment.



Fig. 1. Perspective view of molecule *A*, showing the labelling scheme used. Displacement ellipsoids are shown at 50% probability levels and H atoms have been excluded for clarity.

Experimental

The cycloadduct was prepared as reported previously (Bull *et al.*, 1993) and crystallized from ethyl acetate.

Crystal data C24H26CINO3 Mo $K\alpha$ radiation $M_r = 411.91$ $\lambda = 0.71069 \text{ Å}$ Monoclinic Cell parameters from 24 reflections $P2_1$ $\theta = 16 - 17^{\circ}$ a = 15.638(3) Å $\mu = 0.206 \text{ mm}^{-1}$ b = 8.650(2) Å c = 15.778(2) Å T = 293 (2) K $\beta = 98.503 (14)^{\circ}$ Prism V = 2110.8 (6) Å³ $0.22\,\times\,0.22\,\times\,0.19$ mm Z = 4Colourless $D_x = 1.296 \text{ Mg m}^{-3}$ D_m not measured Data collection

Enraf-Nonius CAD-4 diffractometer $\omega/2\theta$ scans Absorption correction: none 4140 measured reflections 3987 independent reflections 2218 reflections with $l > 2\sigma(l)$ Refinement

Refinement on F^2	$(\Delta/\sigma)_{\rm max} = 0.014$
$R[F^2 > 2\sigma(F^2)] = 0.064$	$\Delta \rho_{\rm max} = 0.417 \ {\rm e} \ {\rm \AA}^{-3}$
$wR(F^2) = 0.161$	$\Delta \rho_{\rm min} = -0.285 \ {\rm e} \ {\rm \AA}^{-3}$
S = 0.972	Extinction correction: none
3987 reflections	Scattering factors from
525 parameters	International Tables for
H atoms not refined	Crystallography (Vol. C)
$w = 1/[\sigma^2 (F_o^2) + (0.1P)^2]$	Absolute structure: assigned
where $P = (F_o^2 + 2F_c^2)/3$	from the estrone precursor

Table 1. Puckering parameters (Å, °) (Cremer & Pople, 1975)

	Ring B			Ring C		
	Q	$\tilde{\varphi}$	θ	Q	$\bar{\varphi}$	θ
Molecule A	0.521	27.5	128.2	0.563	2.2	18.8
Molecule B	0.533	29.9	129.3	0.567	3.7	24.4
		Ring D			Ring E	
Molecule A	0.631	-	359.0	0.548	-	179.8
Molecule B	0.622	-	0.7	0.542	-	181.3

Data collection: CAD-4 Software (Enraf-Nonius, 1989). Cell refinement: CAD-4 Software. Data reduction: CAD-4 Software. Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: ZORTEP (Zsolnai & Pritzkow, 1994). Software used to prepare material for publication: SHELXL93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1056). Services for accessing these data are described at the back of the journal.

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3-Oxo-1-cyclohexene-1-carboxylic Acid: Catemeric Hydrogen Bonding and Flexional Ring Disorder in a γ-Keto Acid

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Abstract

The crystal structure of 3-oxo-1-cyclohexene-1-carboxylic acid, $C_7H_8O_3$, involves hydrogen-bonding catemers of an unusual type. Hydrogen bonds progress from the carboxyl H atom of one molecule to the ketone O atom of a glide-related molecule $[O \cdots O 2.703 (2) \text{ Å}]$, resulting in heterochiral chains. Parallel counterdirectional pairs of hydrogen-bonding chains proceed through the chosen cell. There are mutual close contacts of 2.65 Å between the ketone O and vinyl H atoms of centrosymmetrically related chains. Two of the tetrahedral C atoms of the molecule are flexionally disordered, and three of their associated H atoms show attractive intermolecular close contacts to O atoms.

Comment

Keto carboxylic acids offer options for varying the standard pattern of dimeric hydrogen bonding that dominates functionally unadorned acids. Usually the ketone fails to participate, resulting in typical carboxyl dimers, but less commonly intermolecular carboxyl-toketone hydrogen bonds occur, yielding a catemer. A third, rare arrangement has an internal hydrogen bond, two instances are known of acid-to-ketone dimerization and one of carboxyl catemerization (see below). Several cases also exist of hydrates with more complex hydrogen-bonding patterns. We have referenced and discussed numerous examples of these hydrogen-bonding modes (Thompson et al., 1992; Coté et al., 1996). Part of our continuing interest in this hydrogen-bonding behavior lies in the discovery of new hydrogen-bonding patterns. We have recently reported an instance of carboxyl catemerization not previously observed in keto acids (Lalancette et al., 1998), and we now report a hydrogenbonding pattern of a heretofore rarely observed type.

The title compound, (I), belongs to the category of γ -keto acids, one especially rich in hydrogen-bonding types, embracing dimers, internal hydrogen bonds, and carboxyl-to-ketone catemers. We further categorize such catemers as either homo- or heterochiral to denote the