Molecular and crystal structure of 5*Z*-carboxymethylene-2-chloro-4,4-dimethoxy-3-*N*,*N*-dimethylaminocyclopent-2-en-1-one

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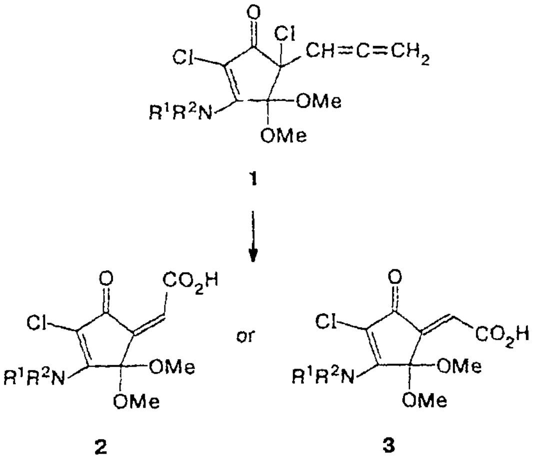
In the crystal, the 5*Z*-carboxymethylene-2-chloro-4,4-dimethoxy-3-*N*,*N*-dimethylaminocyclopent-2-en-1-one molecule has an intramolecular hydrogen bond (stabilized in the chelate form) between the proton of the carboxy group and the oxygen atom of the keto group. The methoxy groups are in an antiperiplanar conformation and are synclinal with respect to the dimethylamino group and the double bond of the carboxylmethylene fragment.

Key words: intramolecular hydrogen bond, *Z*-carboxymethylidenecyclopentenones, X-ray structural analysis.

Oxidative cleavage of the allene double bond of compounds 1 by the $NaIO_4$—$RuCl_3$ system (catalyst)[1] afforded acids (which are, according to the data of ^1H and ^{13}C NMR spectroscopy, individual compounds) in good yields.[2] With the aim of choosing unambiguously one of the possible geometric isomers (2 or 3) for the acid obtained from *N*,*N*-dimethyl substituted compound 1 ($R^1 = R^2 = CH_3$), we carried out an X-ray structural analysis.



The results of X-ray structural analysis demonstrated that oxidative cleavage of compound 1 gave exclusively 5*Z*-carboxymethylenecyclopentenones 2. The structure of molecule 2 is shown in Fig. 1.

The short distance between the proton of the carboxyl group and the O(1) atom and the short O(1)...O(3) distance (2.527(4) Å) are indicative of the occurrence of a strong asymmetrical linear intramolecular hydrogen bond. The hydrogen bond occurs in the almost planar seven-membered ring (deviations within 0.04 Å). The O(1)...H(3) distance is 1.69(4) Å, and the angle at the H atom is 168°(4). The ring system of the cyclopentenone molecule is virtually planar. The C(1)—C(2)—C(3)—C(5) fragment is planar to within 0.004 Å. The C(4) atom deviates from this plane by 0.098 Å. The N, Cl, and O(1) atoms are located in the plane of the cyclopentenone fragment. Each OMe group is synclinal with respect to the NMe_2 groups (Fig. 2, *a*) and the double bond of the carboxymethylidene fragment (Fig. 2, *b*). Unlike the related formaldehyde dimethyl acetal, which occurs in a *gauche,gauche* conformation,[3] the two methoxy groups of molecule 2 are in an almost antiperiplanar configuration

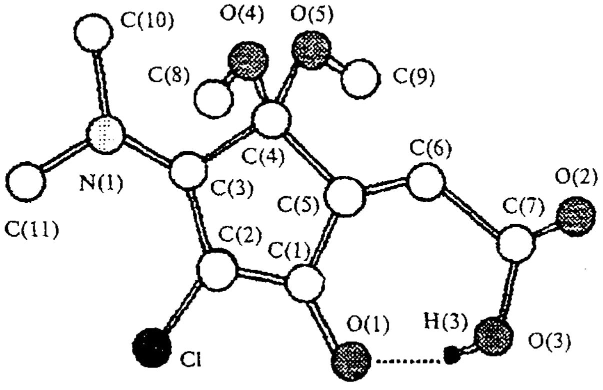


Fig. 1. Three-dimensional structure of molecule 2.

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Table 1. Atomic coordinates ($\times 10^4$; $\times 10^3$ for H atoms) and equivalent isotropic temperature factors (Å^2)

Atom	*x*	*y*	*z*	B_{iso}^{eq}
Cl	2196(8)	2194(3)	10134(9)	4.07(1)
O(1)	5339(2)	2609(7)	11932(3)	4.30(4)
O(2)	8322(2)	4194(1)	14030(3)	5.93(5)
O(3)	7630(2)	3204(9)	13565(3)	5.52(4)
O(4)	3959(2)	4370(7)	8600(2)	3.43(3)
O(5)	2796(2)	4559(6)	11237(2)	3.12(3)
N	0821(2)	3646(9)	8986(3)	3.28(4)
C(1)	4457(2)	3035(1)	11270(3)	2.88(4)
C(2)	2935(3)	2957(3)	10374(3)	2.81(4)
C(3)	2237(2)	3519(9)	9777(3)	2.59(4)
C(4)	3465(2)	4059(9)	10221(3)	2.60(4)
C(5)	4820(2)	3720(9)	11303(3)	2.65(4)
C(6)	6033(3)	4041(1)	12116(3)	3.16(4)
C(7)	7414(3)	3813(1)	13309(3)	4.00(5)
C(8)	5066(3)	4050(1)	07443(4)	4.20(5)
C(9)	2112(3)	4385(1)	12978(4)	4.06(5)
C(10)	337(3)	4273(1)	8309(4)	4.59(6)
C(11)	−485(3)	3172(1)	8791(4)	5.11(6)
H(3)	695(3)	296(1)	1304(3)	5.2(6)
H(6)	607(2)	446(9)	1191(3)	3.0(4)
H(8.1)	475(3)	365(1)	729(4)	7.9(8)
H(8.2)	619(3)	407(1)	796(4)	7.3(7)
H(8.3)	520(3)	429(1)	626(4)	7.3(7)
H(9.1)	178(3)	476(1)	1360(4)	6.8(7)
H(9.2)	288(3)	414(1)	1373(4)	8.0(8)
H(9.3)	98(3)	417(1)	1278(4)	8.2(8)
H(10.1)	121(2)	455(1)	820(3)	4.4(5)
H(10.2)	−59(3)	442(1)	919(4)	7.1(7)
H(10.3)	−20(3)	425(1)	712(4)	6.1(6)
H(11.1)	−73(3)	315(1)	758(5)	9.2(9)
H(11.2)	−131(3)	331(1)	941(4)	8.2(8)
H(11.3)	−17(3)	276(1)	886(4)	10.8(1)

Table 2. Bond lengths (*d*) and bond angles (ω) in molecule **2a**

Bond	*d*/Å	Bond	*d*/Å
Cl—C(2)	1.724(3)	N—C(10)	1.456(4)
O(1)—C(1)	1.240(3)	N—C(11)	1.473(5)
O(2)—C(7)	1.203(4)	C(1)—C(2)	1.406(4)
O(3)—C(7)	1.305(4)	C(1)—C(5)	1.472(4)
O(3)—H(3)	0.85(4)	C(2)—C(3)	1.377(4)
O(4)—C(4)	1.397(3)	C(3)—C(4)	1.550(4)
O(4)—C(8)	1.419(4)	C(4)—C(5)	1.520(4)
O(5)—C(4)	1.399(3)	C(5)—C(6)	1.328(4)
O(5)—C(9)	1.424(4)	C(6)—C(7)	1.484(4)
N—C(3)	1.313(4)		
Angle	ω/deg	Angle	ω/deg
C(7)—C(3)—H(3)	117.0(3)	C(2)—C(3)—C(4)	107.3(2)
C(4)—O(4)—C(8)	117.7(3)	O(4)—C(4)—O(5)	101.8(2)
C(4)—O(5)—C(9)	115.4(2)	O(4)—C(4)—C(3)	114.1(2)
C(3)—N—C(10)	124.0(3)	O(5)—C(4)—C(3)	112.8(2)
C(3)—N—C(11)	123.2(3)	O(5)—C(4)—C(5)	112.8(2)
C(10)—N—C(11)	112.7(3)	C(3)—C(4)—C(5)	103.3(2)
O(1)—C(1)—C(2)	126.8(3)	C(1)—C(5)—C(4)	107.6(2)
O(1)—C(1)—C(5)	125.7(3)	C(1)—C(5)—C(6)	131.0(3)
C(2)—C(1)—C(5)	107.5(2)	C(4)—C(5)—C(6)	121.4(3)
Cl—C(2)—C(1)	117.6(2)	C(5)—C(6)—C(7)	130.2(3)
Cl—C(2)—C(3)	128.6(2)	O(2)—C(7)—O(3)	120.9(3)
C(1)—C(2)—C(3)	113.8(2)	O(2)—C(7)—C(6)	119.3(3)
N—C(3)—C(2)	131.9(3)	O(3)—C(7)—C(6)	119.8(3)
N—C(3)—C(4)	120.8(2)		

(Fig. 2, *c*, *d*). The bond angles at the C(4) atom vary from 101.8(2) to 114.1(2). The lengths of the endocyclic geminal bonds at the C(4) atom (1.550(4) and 1.520(4) Å for C(4)—C(3) and C(4)—C(5), respectively) differ from the standard C(sp^3)—C(sp^3) bond length (1.512 Å) in cyclopentanes.[4] The C(2)—C(3) and C(1)—C(2) bond lengths (1.377(4) Å and 1.406(6) Å, respectively) have values intermediate between the C(sp^2)=C(sp^2) (1.323 Å) and C(sp^2)—C(sp^2) (1.478 Å) bond lengths of the C=C—C=C conjugated system.[4] The N—C(3) bond length (1.313(4) Å) is substantially smaller, and the C(1)—O(1) bond length (1.240(3) Å) is larger than the corresponding standard value of the N—C(sp^2) (1.425 Å) and C=O (1.208 Å) bond lengths in cyclopentenones. The bond lengths and the planarity of the N—C(3)—C(2)—C(1)—O(1) fragment are indicative of an extensive delocalization of π-electrons. Another characteristic feature of structure **2** is the fact that the C(1)—C(5) and C(5)—C(6) bond lengths (1.472 Å and 1.328 Å, respectively) agree closely with the standard single and double bond lengths (1.478 Å and 1.323 Å, respectively). The presence of the *trans-cis*-divinyl ketone fragment in molecule **2** favors the formation of the all-inclusive linear conjugated system involving the C(5)—C(6) bond.

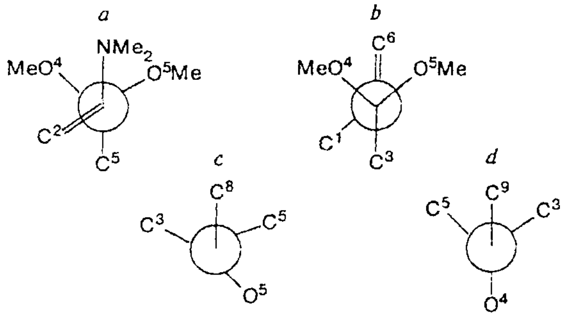

Fig. 2. Newman projections along the C(3)—C(4) (*a*), C(4)—C(5) (*b*), O(4)—C(4) (*c*), and O(5)—C(4) (*d*) bonds.

The spectral characteristics of compound **2** also confirm all the aforesaid. In the IR spectrum of compound **2**, absorption bands of the COOH group are absent in the 3000—3600 cm^{-1} region. In the ^{1}H NMR spectrum, the anomalously low-field signal, which is independent of the acid proton, is observed at δ 15.6. The signals of the *N*-methyl groups are diastereotopic. These data indicate that the resulting acid has the chelate 5*Z* structure stabilized by an H bond.

Experimental

The IR spectra were recorded on a UR-20 spectrophotometer. The ^1H and ^{13}C NMR spectra were measured on a Bruker AM-300 spectrophotometer (300 and 75.47 MHz, respectively). $CDCl_3$ was used as the solvent. $SiMe_4$ was used as the internal standard.

5*Z*-Carboxymethylene-2-chloro-4,4-dimethoxy-3-*N,N*-dimethylaminocyclopent-2-en-1-one (2). $RuCl_3 \cdot 3\ H_2O$ (~2 mg) was added to a stirred suspension of dichloroketone **1** (0.2 g, 0.6 mmol) and $NaIO_4$ (0.28 g, 1.3 mmol) in a CCl_4—MeCN—H_2O mixture (2 : 2 : 3 by volume, 14 mL). The reaction mixture was stirred at ~20 °C for 4—5 h. Then CH_2Cl_2 (10 mL) was added to the reaction mixture. The organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (4×30 mL). The combined organic extracts were dried with $MgSO_4$, filtered, and concentrated. The residue was crystallized from ether. Crystalline compound **2** was obtained in a yield of 0.17 g (90%), m.p. 144—145 °C. IR, ν/cm^{-1}: 725, 905, 920, 990, 1640, 1690, 1725, 2770, 3030, 3070. ^1H NMR ($CDCl_3$), δ: 3.30 (s, 6 H, OCH_3), 3.52 (s, 3 H) and 3.70 (s, 3 H, Me_2N), 6.10 (s, 1 H, CH=). ^{13}C NMR ($CDCl_3$), δ: 42.29 and 42.45 (Me_2N), 52.04 (OCH_3), 103.53 (C-4), 110.09 (C-2), 123.72 (CH=), 138.88 (C-5), 161.96 (C-3), 164.99 (CO_2H), 181.74 (C=O).

X-ray structural analysis of compound 2. Crystals of $C_{11}H_{14}NO_5Cl$ are monoclinic; at 20 °C, a = 8.280(3), b = 21.023(14), c = 7.111(5) Å, β = 91.63(4)°, V = 1236.80 Å^3, Z = 4, μ = 3.175 mm^{-1}, d_{calc} = 1.480 g cm^{-3}, space group $P2_1/n$. The unit cell parameters and intensities of 1375 reflections with $F > 3.0\sigma$ were measured on an automated Enraf-Nonius CAD-4 diffractometer (Mo-Kα radiation, graphite monochromator, $\omega/2\theta$ scanning technique, $2\theta \le 60°$).

The structure was solved by the direct method using the MULTAN 80 program and was refined anisotropically. All hydrogen atoms were located from the difference synthesis and refined isotropically. The final values of the R factors are as follows: R = 0.026 and wR = 0.025. All calculations were carried out on a PDP 11/23 computer using the SDP program. The overall view of the molecule is shown in Fig. 1. The atomic coordinates and equivalent isotropic temperature factors are given in Table 1. The bond angles and bond lengths are listed in Table 2.

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