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DERIVATIVES AND REACTIONS OF GLUTACONDIALDEHYDE V

THE CRYSTAL AND MOLECULAR STRUCTURE OF 5-HYDROXY-TRANS-2, TRANS-4-PENTADIENAL ACETATE. THE CHARGE DISTRIBUTION IN THE GLUTACONDIALDEHYDE ANION

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Abstract—The structure of 5-hydroxy-*trans*-2, *trans*-4-pentadienal acetate has been determined, using three-dimensional diffractometercollected X-ray data. The compound has the all-*trans* configuration with the atoms C-1 to C-5 in a plane. The charge distribution in the acetate and in the glutacondialdehyde anion have been calculated using the CNDO/2 approximation. In both compounds higher negative charges were found on carbon atoms C-2 and C-4 than on C-1, C-3 and C-5.

By ^{1}H NMR spectroscopy simple *O*-acylated derivatives of the glutacondialdehyde anion **1** have been assigned[1,2] the all-*trans* structure.

To obtain more detailed information on the structure and electron distribution in such compounds, the present X-ray study of 5-hydroxy-*trans*-2, *trans*-4-pentadienal acetate **2** and calculation of charge distributions in **1** and **2** were carried out.

EXPERIMENTAL

The crystals of **2** used in the X-ray investigation were obtained by sublimation (50°C/1 mmHg). The three dimensional X-ray data were obtained using a three-circle Enraf–Nonius diffractometer and Zr filtered MoKα radiation. A reflection was designated not observed if $I \leq 1.50\ \delta(I)$. With this criterion 671 out of 1268 (independent measured) reflections were regarded as observed. Lorentz and polarization corrections were applied, but no extinction or absorption corrections were made. The crystal size was $(0.4 \times 0.5 \times 0.7)$ mm^3, ω-scan was used. The maximum value of $\sin\theta/\lambda$ was 0.594.

All calculations were performed on a IBM 370/165 computer using the X-ray system.[3]

The structure was solved by direct methods and the structural parameters were refined by full-matrix least squares. Positions for the hydrogen atoms H1–H5 were calculated. The positional hydrogen parameters (H1–H5) were refined in the last refinement cycles. Unobserved reflections were not included in the calculations. The quantity minimized was $\Sigma w(|F_o| - |F_c|)^2$ with $w = (5.08 + F_o + 0.16 \cdot F_o^2)^{-1}$. The final R index was 0.078. Atomic scattering factors were taken from International Tables.[4]

RESULTS

Structure determination

Crystal data. **2** has a formular weight of 140.14. The crystals are colourless prisms. M.p.: 76–77°C. Space group $P\ 2_1/c$ (No. 14). $a = 11.309$ (2) Å, $b = 4.0797$ (5) Å, $c = 17.016$ (2) Å, $\beta = 103.64$ (1)°, $Z = 4$, $D_m = 1.22$ (1) g cm^3, $D_x = 1.22$ g cm^{-3}.

Charge distribution. In order to get some insight in the charge distribution of the molecules CNDO/2 calculations were performed with the original parameterisation given by Pople and Segal.[5] The dimensions of **2** from the present study were used, and for **1** the distances and angles were assumed to have the values: all C–C (1.41 Å), all C–O (1.26 Å) and all angles (120°). The results are shown in Fig. 2; and the frontier orbital coefficients for **1** were: $O_1^2 = 0.187$, $C_1^2 = 4.6 \times 10^{-3}$, $C_2^2 = 0.308$ and $C_3^2 = 0.00$ while the relative charge density[6] P for **1** is $O_1/C_1 = 1.72$, $O_1/C_2 = 1.51$ and $O_1/C_3 = 1.66$.

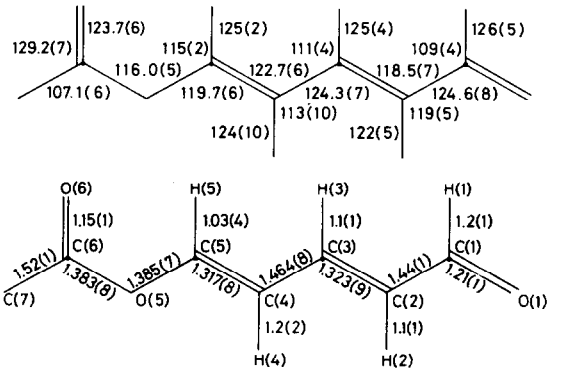


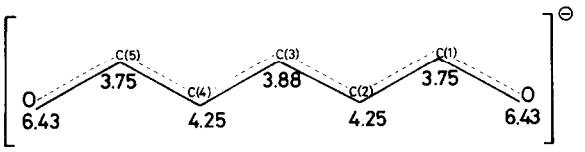
Fig. 1. Molecular dimensions from the X-ray investigation. Interatomic distances in Å, and bond angles in degrees. Estimated standard deviations in parentheses.

DISCUSSION

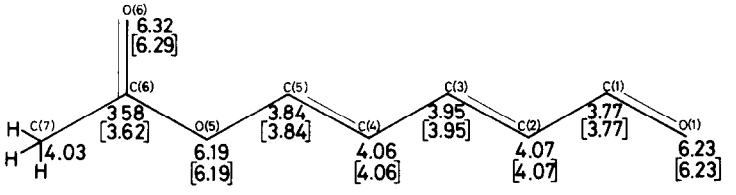
The molecular structure of **2**. The estimated standard deviations of the structural parameters are relatively high due to the small number of reflections used in the calculations. However, the dimensions are accurate enough for a discussion of the chemistry of **2** in relation to the structure.

2 has an all-*trans* configuration as inferred from the spectroscopic data.[1,2] The interpretation of the gas phase microwave spectra presumed a *cis* conformation for O(6), C(6), O(5), C(5). The correctness of this assumption has been confirmed by the present X-ray investigation. The atoms C(1)–C(5) lie in a plane. The remaining atoms O(1), O(5), O(6), C(6) and C(7) only show small displacements (0.02–0.20 Å) from this plane (Fig. 3). The carbon oxygen distances C(5)–O(5), C(6)–O(5) and C(6)–O(6) agree with distances of equivalent bonds in phenolic esters[7] rather than with those in aliphatic ones.[8,9]

This is in agreement with the observations that **2** is very easily hydrolysed and gives strong IR-absorptions



1



2

Fig. 2. The numbers shown are the atomic valence-electron population calculated from the diagonal elements of the density matrix. The numbers in parentheses come from a calculation where the methyl group had been replaced by a hydrogen atom.

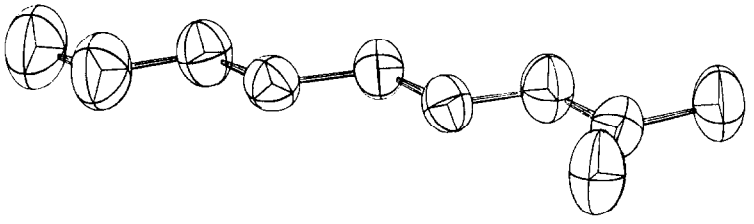


Fig. 3. Perspective drawing of 2. Atoms are represented by ellipsoids enclosing 50% of the thermal displacements.

at 1210 cm^{-1} (C=O) and 1755 cm^{-1} (–C–O–) (KBr) in accordance with the stretching vibrations for phenolic and α,β-unsaturated acetates.[10] It is also of interest to note that the conformation found in the gas phase[2] and in the crystal are identical.

The charge distribution. We have shown previously that the reactions of the ambident glutacondialdehyde anion **1** can be understood on the basis of the principle of hard and soft acids and bases.[11] It was found that reactions with soft acids take place at C(2) whereas reactions with hard acids take place at the oxygen anion RO^-. Therefore, the valence electron population at C(2) must be relatively high:

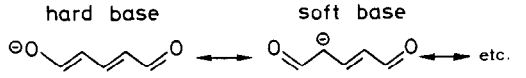


Table 1. Final atomic coordinates with estimated standard deviations in parentheses

Atom	x	y	z
O(1)	0.5572(6)	0.9983(17)	0.1627(4)
O(5)	0.1525(3)	0.9271(12)	0.4224(2)
O(6)	0.1805(4)	0.6003(15)	0.5304(3)
C(1)	0.6322(8)	0.9089(25)	0.2216(6)
C(2)	0.7577(7)	0.0078(19)	0.2410(4)
C(3)	0.8305(6)	0.8911(16)	0.3077(4)
C(4)	0.9597(5)	0.9731(16)	0.3352(4)
C(5)	0.0304(5)	0.8439(16)	0.4006(4)
C(6)	0.2199(6)	0.7827(19)	0.4922(5)
C(7)	0.3499(6)	0.9059(21)	0.5042(5)
H(1)	0.618(8)	0.708(29)	0.267(7)
H(2)	0.793(8)	0.157(27)	0.195(7)
H(3)	0.803(8)	0.718(24)	0.350(6)
H(4)	0.989(20)	0.189(62)	0.299(12)
H(5)	0.002(3)	0.679(10)	0.438(2)

Recently, Gompper and Wagner[6] have suggested the use of the relative charge-density ($P = P_x/P_\gamma$), where x and γ are the reactive centers of an ambident anion, as a method to predict if the alkylation of such anions gives *C*- or *O*-alkylated products.

The charge distribution, the frontier orbital coefficients as well as P calculated for the glutacondialdehyde anion **1** in the present paper, show that there is a very good agreement between the experimental facts[12] and the calculations.

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[12] Further reactions of **1** for example with chlorine also supports this (J. Becher, to be published).