

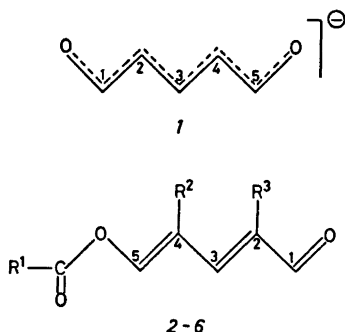
Short Communications

Derivatives and Reactions of Glutacondialdehyde. VIII. ^{13}C NMR Studies

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The glutacondialdehyde anion (*1*) first prepared by Baumgarten¹ has been assumed to have the all-*trans* configuration. This is mainly based



Scheme 1. 2, $\text{R}^1 = \text{CH}_3$, $\text{R}^2 = \text{R}^3 = \text{H}$; 3, $\text{R}^1 = \text{C}_6\text{H}_5$, $\text{R}^2 = \text{R}^3 = \text{H}$; 4, $\text{R}^1 = \text{C}_6\text{H}_5$, $\text{R}^2 = \text{CH}_3$, $\text{R}^3 = \text{H}$; 5, $\text{R}^1 = \text{C}_6\text{H}_5$, $\text{R}^2 = \text{CH}_3\text{O}$, $\text{R}^3 = \text{H}$; 6, $\text{R}^1 = \text{C}_6\text{H}_5\text{O}$, $\text{R}^2 = \text{R}^3 = \text{H}$.

on the X-ray structure of the derivative 5-hydroxy-2,4-pentadienal acetate (*2*)² and the existence of only three sets of lines in the ^1H NMR spectrum of *1*.^{3,4} However, several other configurations are able to explain the equivalence in the proton spectrum of *1*. The H,H coupling constants⁴ of *1* do not provide any conclusive evidence for the all-*trans* configuration, but do in fact indicate the possibility of having *cis* configuration of at least one of the double bonds. The number of known cyclization reactions of *1* may also be taken as an obstacle for the conception of *1* having the all-*trans* configuration. The assignment of *1* to a *cis* configuration or the depicting of *1* with an uncertain structure can be seen in numerous text-books and reviews.⁵

In order to clarify the problem related to the structure of *1* we have recorded the ^{13}C NMR

spectra of this compound and of some simple derivatives. Furthermore, we have measured the ^{13}C spin lattice relaxation times, $T_1(^{13}\text{C})$, of *1* and shown that these dynamical parameters in this case can be used in structure elucidation.

The ^{13}C chemical shifts of *1* and some simple derivatives in DMSO- d_6 are given in Table 1. The assignments are based upon gated decoupled spectra. In the case of *5* the penta-deuteriophenyl analogue has been used as an aid in the assignment. The spectrum of *1* consists in accordance with the proton spectrum of three lines only. The value of C-1 is shifted upfield to the area of normal α,β -unsaturated aldehydes⁶ due to the delocalization of the excess charge. Wolkowski *et al.*⁷ have established a correlation [$\delta_{\text{C}} = -220P(\text{C}) + 1020$] between ^{13}C chemical shift, δ_{C} , and the charge density, $P(\text{C})$, on the carbon atoms for α,β -unsaturated aldehydes. By use of this correlation the following charge densities in *1* can be evaluated from the ^{13}C chemical shifts: $P(\text{C}-1) = 3.81$, $P(\text{C}-2) = 4.16$ and $P(\text{C}-3) = 3.92$. These values show the same trend as the ones calculated by Becher *et al.*² without known geometry of the molecule. A positive charge is associated with C-1 and C-3, a negative charge is associated with C-2. The excess charge in *1* does therefore not merely induce an increasing negative charge on all the carbon atoms, but do in fact reduce the electron density on C-3, thus, explaining the various reactions of *1*.⁸

The ^{13}C chemical shifts of *2* to *6* show the usual pattern of α,β -unsaturated aldehydes as well as the one of enol esters.⁹ A downfield shift of 25 ppm of C-2 is observed when *1* is acylated. Under the assumption of unchanged value of the excitation energy⁹ this shift indicates that the pronounced negative charge of C-2 in *1* is greatly diminished by acylation. The upfield shift of C-3 on acylation can likewise be taken as a reduction of the positive charge on this carbon atom.

The one bond C,H spin spin coupling constants in *1* are given by: $^1J_{\text{C}-\text{H}-1} = 155.3 \pm 0.5$ Hz, $^1J_{\text{C}-\text{H}-2} = 152.1 \pm 1.0$ Hz and $^1J_{\text{C}-\text{H}-3} = 155.8 \pm 1.0$ Hz. These values indicate an almost identical percentage *s*-character in all the C–H bonds.¹⁰ The $^1J_{\text{C}-\text{H}-1}$ coupling constant in *1* can be compared to the corresponding value in *2* of 171.5 ± 0.5 Hz. The increasing *p*-character in the C–H bonds between *2* and *1* is clearly demonstrated. Two long range C,H coupling constants have been found greater than 1.0 Hz in *1* and assigned to $^2J_{\text{C}-\text{H}-4} = 6.8 \pm 0.5$ Hz and

Table 1. ^{13}C Chemical shift, δ_i (ppm),^a of glutacondialdehyde anion (1) and some simple derivatives (2–6).

Compound	C-1	C-2	C-3	C-4	C-5	$-\text{C}\begin{smallmatrix} \text{O} \\ \diagup \diagdown \\ \text{O}- \end{smallmatrix}$	C(ω) ^b	C(α)	C(m)	C(p)
1	184.79	106.75	160.29	106.75	184.74					
2 ^c	193.17	131.18	145.80	113.12	149.11	166.98				
3	193.29	131.70	146.06	114.29	148.92	163.37	127.67	129.88	129.04	134.50
4	193.36	128.32	142.49	120.20	152.82	162.11	127.80	129.82	129.04	134.43
5	192.71	129.94	127.22	141.19	146.77	161.59	—	129.55	128.97	134.30
6 ^d	193.43	131.57	147.49	113.12	148.85	151.39				

^a Uncertainty: ± 0.07 ppm. ^b Quaternary ring carbon. ^c δ 20.14 ppm (CH_3). ^d δ 13.84 ppm (CH_3), 65.30 ppm (CH_2).

$^2J_{\text{C-H-1}} = 21.3 \pm 0.5$ Hz. The corresponding values in 2 cannot be determined because of influence of second order effects in the proton spectrum. The value of $^2J_{\text{C-H-1}}$ in 1 is close to the values reported for various aldehydes.¹¹

The spin lattice relaxation rate, $1/T_1$, due to intra-molecular dipole dipole mechanism is given by:¹²

$$1/T_1 = \hbar^2 \gamma_C^2 \gamma_H^2 (1/r_{\text{CH}}^6) \tau_c$$

in which γ_C and γ_H are the magnetogyric ratios of carbon and hydrogen, and r_{CH} the distance between the two nuclei. τ_c is the rotational correlation time for the C–H axis. If association tendency, where aggregation is long-lived compared to the rotational correlation time, is neglected, the relaxation behaviour of 1 can be discussed in terms of free molecules. Since 1 is a highly non-spherical molecule τ_c will differ amongst the various C–H axes, unless these axes are parallel.¹³ This would give rise to different values of T_1 , if the carbon atoms possess non-parallel C–H axes. Such a behaviour has been observed in several cases for instance in substituted benzenes.⁶

The $T_1(^{13}\text{C})$ relaxation times have been measured in a saturated solution of 1 in DMSO- d_6 with the following results: $T_1(\text{C-1}) = 2.7 \pm 0.15$ s $T_1(\text{C-2}) = 2.5 \pm 0.3$ s and $T_1(\text{C-3}) = 2.6 \pm 0.3$ s. Nuclear Overhauser effect measurements of the carbon atoms in 1 revealed that the relaxation is completely dominated by the intra-molecular dipole dipole mechanism. T_1 measurements in non-saturated solutions were less accurate but did confirm that the relaxation times for all the carbon atoms in 1 are identical. This implies that all C–H axes in 1 are parallel since only a small deviation caused by different C–H bonds and different C–C–H angles would be possible in this case. As it can be established that the C–H axes in 1 are parallel the all-*trans* configuration has been proved.

The possibility that 1 may exist as a rapid equilibrium between the all-*trans* and one or

more of the other configurations may, *a priori*, not be neglected. However, it seems unlikely that such a situation should give rise to identical relaxation times for all the carbon atoms.

Experimental. The ^{13}C proton noise decoupled NMR spectra were recorded on a JEOL FX60 FT NMR spectrometer with internal deuterium lock. 8 K data points and a spectral width of 4000 Hz were used. The pulse length was 6 μs corresponding to a flip angle of 60°. The T_1 measurements were performed by the usual 180°– τ –90° pulse sequence. The nuclear Overhauser effect was measured by comparing the gated decoupled spectrum with no spin spin splitting and the normal noise decoupled spectrum.¹⁴ The compounds used have been prepared according to the methods described earlier.¹⁵

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Synthesis of [2₄](2,5)Thiophenophanetetraene or [24]Annulene Tetrasulfide

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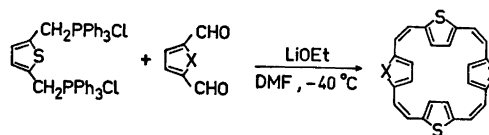
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We have recently developed a convenient method for the preparation of various [2₄]-cyclophanes and related compounds from aromatic dialdehydes and bistrisphenylphosphonium salts of bis(halomethyl)arenes by Wittig reactions at low temperatures.^{1,2} Such cyclophanes are interesting starting materials for the synthesis of circulenes,³ helicenes,⁴ and annulenes. [2₄]Paracyclophanetetraene and the thiophene and furan derivatives contain a conjugated perimeter with 24 electrons and could formally be regarded as derivatives of [24]annulene. Although reasonably planar,⁵ [2₄]paracyclophanetetraene does not show a paramagnetic ring current, i.e. it is not paratropic.⁶ Among the bridged [18]annulenes, [18]annulene trioxide or [2₃]furanophanetriene has

been characterized as aromatic.⁸ In the corresponding sulfur compound, the three sulfur atoms are too large to be accommodated in a planar conformation. Thus the compound cannot sustain a diamagnetic ring current over the perimeter,⁷ nor can [2₃]paracyclophanetriene.⁹

The heterobridged [24]annulenes have been studied less. Two isomers of [2₄]furanophanetetraene or [24]annulene tetroxide have been reported, both being similar to [24]annulene.¹⁰ Some uncertainty in the structural assignment (*cis/trans* isomerism) has made conclusions less firm.

We now report the synthesis of [2₄](2,5)-thiophenophanetetraene, **1**, from 2,5-thiophenedicarbaldehyde and the bistrisphenylphosphonium salt of 2,5-bis(chloromethyl)thiophene. An unstable [2](2,5)furan[2](2,5)thiopheno[2](2,5)furan[2](2,5)thiophenophanetetraene, **2**, was also prepared analogously from 2,5-furandicarbaldehyde (Scheme 1). The symmetrical structure of the compounds follows from their simple ¹H NMR spectra. Both cyclophanes were isolated as the all-*cis* isomers. [2₄](2,5)-Thiophenophanetetraene, **1**, shows a simple mass spectrum with the singly and doubly charged molecular ions as the major peaks. The absorption maximum (354 nm) is shifted 51 nm towards longer wavelengths as compared with [2₄]paracyclophanetetraene.¹ An attempted photocyclization of [2₄](2,5)thiophenophanetetraene in the presence of air and traces of iodine to give tetrathia[8]circulene was not successful, nor was the photocyclization of [2₄]paracyclophanetetraene,³ [2](2,5)-thiopheno[2]paracyclo[2](2,5)thiopheno[2]paracyclophanetetraene or [2](2,5)furan[2]paracyclo[2](2,5)furan[2]paracyclophanetetraene.²



Scheme 1. 1 X=S, 2 X=O.

Molecular models show that [2₄](2,5)thiophenophanetetraene should be a rather flexible molecule. A conformation in which the sulfur atoms point outwards from the ring (A in Scheme 2) could be planar enough to allow for some overlap between the *p*-orbitals in the thiophene rings and the olefinic bridges. The thiophene protons are located inside the ring and the olefinic protons outside the ring in this conformation. A delocalized 24 π -electron system should result in a downfield shift of the inner protons and a smaller upfield shift of the outer protons, as is observed in the NMR spectrum of [2₄](2,5)thiophenophanetetraene. The effect, which is enhanced on cooling, is much smaller than in [24]annulene, however.