# Molecular Structure of Gaseous Succinic Anhydride Studied by Gas Electron Diffraction

K. BRENDHAUGEN, M. KOLDERUP FIKKE and H. M. SEIP

*Department of Chemistry, University of Oslo, Oslo 3, Norway*

Succinic anhydride has been shown by Ehrenberg[1] to have an essentially planar heavy atom skeleton in the crystal. We have now shown by electron diffraction that the same is probably true in the gas phase.

Diffraction diagrams of succinic anhydride were recorded with Balzers Eldigraph KDG2.[2,3] Four plates recorded with a nozzle-to-plate distance of 49.88 cm and five plates with a distance of 24.89 cm were used. The electron wavelength was in both cases 0.04941 Å and the nozzle temperature about 140°C. The data were treated in the usual way.[4] Intensity values covering the $s$-range 1.50 – 36.0 Å$^{-1}$ were obtained, but the quality of the outer data was not satisfactory, and the final refinements were carried out with a composite intensity curve in the $s$-range 1.5 – 28.0 Å$^{-1}$.

*Results and discussion.* The parameters ($r_a$ distances[5]) obtained by least-squares refinement using a diagonal weight matrix are given in Table 1. The Bastiansen-Morino shrinkage effect[5,6] was neglected and all the asymmetry constants assumed to be zero.[4,7] Because of many nearly equally long distances, it was difficult to refine all the bond distances in the ring, and C3 – C4 (*cf.* Fig. 1) was assumed to be

*Table 1.* Distances, angles and mean amplitudes of vibration obtained for succinic anhydride. Standard deviations applied to the last decimal place are given in parentheses. Mean amplitudes calculated from spectroscopic data and the results found by X-ray diffraction are also given.

| | $r_a$ (Å) | $u$ (Å) | $u_{calc}$ (Å) | X-ray results (Å) |
|---|---|---|---|---|
| C=O | 1.190 (2) | 0.035 (3) | 0.039 | 1.19, 1.19 (1) |
| C–O | 1.389 (3) | 0.040 | 0.051 | 1.38, 1.37 (1) |
| C2–C3 | 1.510 (4) | 0.043 (5)[d] | 0.050 | 1.47, 1.48 (1) |
| C3–C4 | 1.535 [c] | 0.043 | 0.050 | 1.51 (1) |
| C–H | 1.118 (9) | 0.077 [c] | 0.078 | |
| C2···C5 | 2.274 (7) | 0.065 | 0.054 | |
| O1···C3 | 2.383 (6) | 0.067 | 0.056 | |
| O1···O6 | 2.259 (5) | 0.066 (4)[d] | 0.057 | |
| C2···C4 | 2.396 (3) | 0.068 | 0.057 | |
| C3···O7 | 2.425 (7) | 0.071 | 0.060 | |
| C3···O6 | 3.556 (5) | 0.072 (6)[d] | 0.062 | |
| C2···O6 | 3.401 (5) | 0.068 | 0.058 | |
| O6···O7 | 4.467 (4) | 0.086 (8) | 0.063 | |
| | Angles (degrees) | | | Angles (degrees) |
| ∠C5O1C2 | 109.9 (5) | | | 110.1 |
| ∠O1C2C3 | 110.5 (4) | | | 110.2, 110.4 |
| ∠C2C3C4 | 103.8 (5) | | | 105.2, 104.1 |
| ∠O1C2O7 | 122.1 (4) | | | 119.6, 119.2 |
| ∠C3C2O7 | 127.8 (4) | | | 130.3, 130.4 |
| ∠HCH | 110.0 [c] | | | |
| $\alpha$ [a] | 52.3 [e] | | | |
| $\phi$ [b] | 4.1 (20) | | | |

[a] Angle between the intersection of the planes through C2C3C4 and HCH and the C2 – C3 bond. [b] Torsional angle C5O1C2C3. [c] Assumed value. [d] The differences between the $u$ values were assumed. [e] The parameter was not refined with the other parameters.

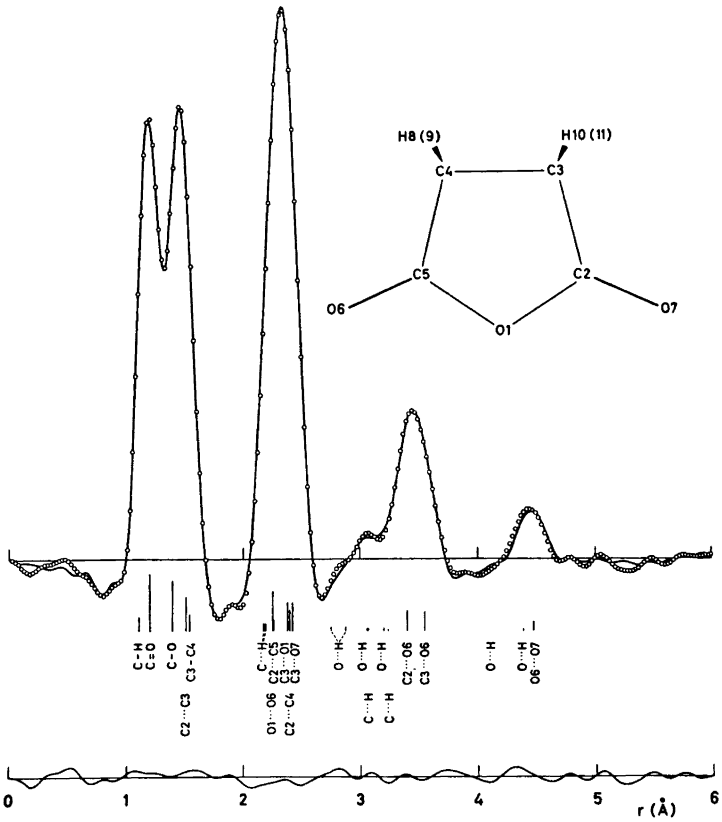


*Fig. 1.* Experimental (circles) and theoretical (full line) radial distribution curves calculated with an artificial damping constant $k = 0.002$ Å$^2$.[2] The differences between experimental and theoretical values are also shown. The positions and approximate areas of the peaks corresponding to all interatomic distances, except H···H, are indicated.

1.535 Å. The value found in the X-ray investigation, 1.51 Å, seems unreasonably small. The uncertainty (standard deviation of 0.01 Å) in this assumed value,[7] as well as the effect of correlation between the data,[8] has been estimated and included in the standard deviations in Table 1. Further assumptions made in the refinement are given in Table 1. The experimental and theoretical radial distribution curves [4] are compared in Fig. 1.

The deviation from planarity in the skeleton is given by the torsional angle, $\phi$, about the O1 – C2 bond. This parameter refines to about 4°, but the standard deviation is so large (2.0°) that the value can only be regarded as a slight indication of a small distortion, or, more probable, of fairly large out-of-plane vibrations. It should be remembered that the shrinkage effect has been neglected since the force constants for out-of-plane motions are not known. This may lead to a small apparent deviation from planarity.

Table 1 shows that the bond distances found in the present investigation are somewhat longer than those obtained in the X-ray investigation except for the C = O bond, where the agreement is exact. The agreement in the bond angles is fairly good.

The mean amplitudes of vibration [6] ($u$), calculated by the method described by Stølevik *et al.*[9] using the force constants in Ref. 10, are included in Table 1. Because

of the rather limited $s$-range used in this investigation and the large number of nearly equal distances, the $u$-values are not very well determined by this electron-diffraction study. The conclusion drawn about the skeleton structure does not depend critically on the $u$-values as shown by carrying out a refinement keeping the mean amplitudes for all distances C2···C5 to C2···O6 in Table 1 equal to the values calculated from spectroscopic data ($u_{calc}$). The torsional angle refined then to $\phi = 4.8°$.


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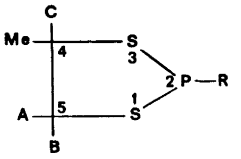
# PMR Analysis of the *cis* and *trans* Isomers of 2-Chloro-4-methyl- and 2-Phenyl-4-methyl-1,3,2-dithiaphospholanes

KNUT BERGESEN and MALVIN BJORØY

*Chemical Institute, University of Bergen, N-5000 Bergen, Norway*

In the last two years the ring conformation of 1,3,2-dithiaphospholanes and 1,3,2-oxathiophospholanes have received some attention. The PMR spectra of 2-phenyl-[1,2] and 2-fluoro-1,3,2-dithiaphospholanes [3] have been completely analysed. The spin-system confirms the existence of pseudorotation with a pseudo-axial phenyl or fluor group. The PMR analysis of 2-chloro-, 2-phenyl-, and 2-phenoxy-1,3,2-oxathiaphospholanes [4] have shown that the five-membered oxathiaphospholane ring exists mainly in an equilibrium between two envelope conformations, with the carbon atom 5 out of the ring plane. This paper reports the PMR analysis of the *cis* and *trans* isomers of 2-chloro- and 2-phenyl-4-methyl-1,3,2-dithiaphospholanes, I and II.




I: R = Cl.
II: R = Ph.

The PMR spectra of I and II show that there are two kinds of methyl groups in magnetically different environments in the ratio approx. 1:3. The reasonable interpretation of the spectra is that the two kinds of methyl groups are *cis* and *trans* to the substituent attached to the phosphorus atom.

The 100 MHz spectrum of I (Fig. 1) consists of three main regions ($\delta = 4.7$ to 4.3, 4.2 to 3.9, and 3.8 to 2.8). The low field band is due to the methine proton at carbon 4 of the *cis* and *trans* isomers and the band in the region 4.2 to 3.9 is assigned to one of the protons at carbon 5 of the *cis* isomer. The complex high field region