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# $^1$H NMR Spectra of *cis* and *trans* 2,5-Diacetoxy-2,5-dihydrofuran

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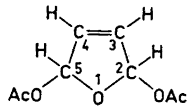
Recently 2,5-diacetoxy-2,5-dihydrofuran (I) has become commercially available, and its increased synthetic importance has prompted us to report the isolation of the *cis* and *trans* isomers as well as their complete $^1$H NMR spectroscopic data.

In 1952 Clauson-Kaas [1] reported the separation of I into two isomers. $^1$H NMR spectra later revealed that one of the proposed isomers was a 1 : 1 mixture of *cis* and *trans* isomers while the other was a pure isomer here denoted Ia. Barbier *et al.*[2] later copied the work mentioned above, with identical result. They also succeeded in separating the mixture into the pure isomers by column chromatography, reporting the $^1$H NMR data for both isomers as indicated in Table 1. We here report a separation of the isomers using a simpler chromatographic column, as well as more accurate and complete $^1$H NMR data.

The $^1$H NMR spectrum of Ia consists of three groups of lines (see Table 1). The ring protons form an AA'BB' system in which the intense lines are located within regions of 0.7 Hz. The weak lines necessary for interpretation of the spectrum in terms of coupling constants can most conveniently be observed by applying a large amplitude analytical field, which saturates the strong lines but yields strong signals with good signal to noise ratio for the weak lines. Further information is obtained from the time averaged $^{13}$C satellites. Iteration on all observed lines resulted in the data reported in Table 1. The RMS error was 0.039 Hz. A similar analysis of the spectrum of Ib leads to an RMS error of 0.040 Hz and the data listed in Table 1.

*Table 1.*




Chemical shift and coupling constants in *cis* and *trans* 2,5-diacetoxy-2,5-dihydrofuran.

| | Chemical shift ($\delta$ ppm) | | Coupling constants (Hz)[c] | | | | | | Dipole moments (debye) |
|---|---|---|---|---|---|---|---|---|---|
| | H-2 | H-3 | $J_{23}$ | $J_{24}$ | $J_{25}$ | $J_{34}$ | $^1J_{CH-2}$ | $^1J_{CH-3}$ | |
| Ia[a] | 6.81 | 6.11 | $\pm$1.14 | $\mp$1.14 | 3.60 | 5.88 | 179.2 | 178.4 | 2.5 |
| Ia[b] | | | 1.0 | 1.0 | 3.5 | 5.5 | | | |
| Ib[a] | 6.64 | 6.19 | $\pm$1.16 | $\mp$0.91 | 0.21 | 5.77 | 181.8 | 179.2 | 3.3 |
| Ib[b] | | | 1.0 | 1.0 | 0.4 | 5.6 | | | |

[a] This work.
[b] Reference 2.
[c] Probable errors on coupling constants are $\pm$ 0.05 Hz for $J_{HH}$ and $\pm$ 0.1 Hz for $J_{CH}$. Probable errors in reference 2 are $\pm$ 0.1 Hz.

The experimental values found for Ib are very similar to the data reported earlier.[2] Taking $J_{34}$ to be positive [3] we find $J_{25}$ to be positive, in agreement with recent data for 2,5-dihydrofurans by Barfield *et al.*[4] From the experimental data it was not possible to determine the sign of $J_{23}$ and $J_{24}$ relative to the larger coupling constants, but we could conclude that they are of opposite sign. The $^1J$ coupling constant at C(2) is large, as could be expected from a qualitative estimate based on Malinowski's rule,[5] while the coupling involving C(3) is within the ordinary range for cases involving $sp^2$ hybridized carbon atoms. It follows from the arguments above, that closely similar $^1J_{CH}$ values would be expected for the compound Ia, and the data (Table 1) confirm this. For Ia we found different numerical values for $J_{23}$ and $J_{24}$, contradicting Barbier *et al.*,[2] who have somewhat arbitrarily fixed these coupling constants to 1.0 Hz in both isomers. As in the case Ib they are of opposite sign, but their sign relative to the larger coupling constants cannot be determined.

Under our assumption for $J_{34}$, $J_{25}$ is positive but its magnitude is considerably reduced in comparison to case Ib. A similar difference in $J_{25}$ values was found in methyl 2,5-dihydro-2-furoate by Barfield *et al.*[4] They did not discuss the steric significance of this difference. Barbier *et al.*[2] suggested that Ia should be assigned as the *cis* isomer due to the value of $J_{25}$. This assignment would be consistent with the idea that electrostatic forces tend to make the conformation having the C(2)–H(2) and C(5)–H(5) in the "ring plane" unfavourable in the *cis* compound, while it may contribute in the *trans* isomer. Under the assumption that the most effective long range coupling exists for a planar path this leads to the assignment given. To examine this point experimentally we have considered the dipole moments of the two isomers. A partial cancellation of bond dipole moments can be expected to occur in the *trans* isomer, but not to the same extent in the *cis* isomer. It can therefore be expected, that if the two dipole moments differ significantly the *cis* isomer should be assigned to the one having the larger moment. The experimental values of 3.3 and 2.5 debye are sufficiently different that we feel confident in assigning Ia to the *cis* and Ib to the *trans* isomer, in accordance with the earlier choice.

*Experimental* $^1$H NMR spectra were recorded on a Varian HA-100 spectrometer operating in frequency mode at 32°C. Samples were degassed 10 % solutions in $CCl_4$ where TMS was added as internal reference. Data accumulation was performed using a Varian Spectro System 100. Calculation of spectral parameters was carried out using the Laocn3 program.[6]

The mixture Ia+Ib was prepared according to the method of Clauson-Kaas;[1] the ratio between Ia+Ib was 2 : 1. Crystallization and recrystallization [1] from methanol yielded pure Ia m.p. 49.5–51.0°C; the corresponding literature data are 51–52°C [1] and 49°C.[2] From the 1 : 1 mixture, Ib was isolated by column chromatography. The column was prepared by mixing of 60 g silica and 60 g $CdCO_3$ to a slurry, in a liquid consisting of 25 % ether and 75 % hexane. The prepared column was 32 cm high with a diameter of 2 cm. Fractions of 5 ml were collected at the rate of six per hour. From the first fractions pure Ib was obtained with a m.p. 53.5°–55.5°C; Barbier *et al.*[2] reported 56°C.

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