On the Analysis of the A_2B_2 Spectrum of the 1,3-Dioxolane Ring in 3-Bromo-2-thiophene Aldehyde Ethylene Acetal

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In connection with work on the structures of the thiophene analogues of phthalaldehydic acids [1,2] the conformation of the dioxolane ring in 2-(3-bromo-2-thienyl)-1,3-dioxolane has been studied using NMR-spectroscopy. The spectrum of the dioxolane ring is that of a strongly coupled A_2B_2 system.

An ordinary A_2B_2 spectrum consists of 24 lines, but in this case it was possible to resolve only 12 lines in the 60 Mcps- and 10 lines in the 40 Mcps-spectrum (Fig. 1). From the symmetry assumed for the dioxolane ring one obtains with the notation used by Pople et al.[3] $J_A = J_B$. This assumption reduces the number of lines to 20. The bands nearest to the center are so broad that these must consist of several overlapping lines (*cf.* Fig. 1).

Information from the spectral moments [3] gives the value of $\nu_0\delta$ to be 1.25 ppm and of the root-mean-square coupling between the nuclei in *different* chemical groups $[\frac{1}{2}(J^2 + J'^2)]^{1/2}$ to be 8.5 cps. For the spectral moments, and especially the fourth central moment, the weak outer signals are of great importance but due to poor signal-to-noise ratio it is difficult to determine their intensites. Therefore the figures deduced from the spectral moments must be considered as uncertain. Together with some published data of coupling constants in a dioxolane ring [4] they could, however, be used as starting points for the full analysis. The analysis was carried out using the expressions given by Pople et al.[3] The 4 × 4 matrix for the spin zero state was diagonalized numerically on the IBM 1620 computer at this University. The relative shift and the coupling constants were determined by adjusting the calculated spectra to agree with the observed ones. Full agreement within 0.05 cps was attained. The lines in the figure are numbered according to the notation cf

Pople et al.[3]. For the 60 Mcps spectrum lines 5 and 8 are missing. They are theoretically situated at 25.11 and 16.95 cps but are of such low intensity that they cannot be observed. For the 40 Mcps spectrum even lines 9 and 10 are missing for the same reason. The analysis of the spectra recorded at both 40 and 60 Mcps in a 13 % solution in cyclohexane gave the following constants:

$\nu_0\delta = 1.33 \pm 0.02$ ppm, $J = -7.75 \pm 0.10$ cps, $J' = 6.15 \pm 0.10$ cps, $J_A = J_B = 7.00 \pm 0.30$ cps.

There exist several observations demonstrating the chemical nonequivalence of protons 1 and 3 or 2 and 4 in compounds in which the dioxolane ring is not entirely free to invert its configuration.[5,6] Evidence against the possibility that the molecule has more than two sets of non-equivalent protons was found by the fact that the spectra, run at 40 and 60 Mcps display the same symmetry.[6] The same conclusion can be made of the compound studied here. The spectrum of the protons shows that there are two pairs of two equivalent nuclei. The fact that not all protons are equivalent demonstrates that the compound does not execute a thermal vibration, which rapidly inverts its conformation. Sheppard et al.[7] found in the case of 1,3-dioxolane the value of 1.3 cps for the difference between the experimentally determined coupling constants J_A and J' and the value of 13.3 cps for their sum. This result has been confirmed by Lemieux et al.[8], who also gave a thorough discussion on the conformation of the 1,3-dioxolane ring, applying Karplus' relation of the vicinal coupling constants to the dihedral angle defined by the hydrogens.[9] They found that the general shape of the Karplus' curve is substantially correct but it must be displaced upwards by 2.2 cps to account for the neighbouring hydrogens in both 1,3-dioxolane and its 2,2-dimethyl derivatives. By calculating the values of $J_A - J'$ from the Karplus' curve for varying amounts of puckering of the ring and comparison with experimental data they found that the dihedral angle between the *cis* neighbouring hydrogens is about 35°. Thus there are two energetically equivalent conformations for 1,3-dioxolane in which one of the C-methylene groups is puckered out of the plane of the other four atoms in the ring. In the compound studied here it is found that $J_A - J' = 0.85$ cps giving a puckered conformation with a dihedral angle be-
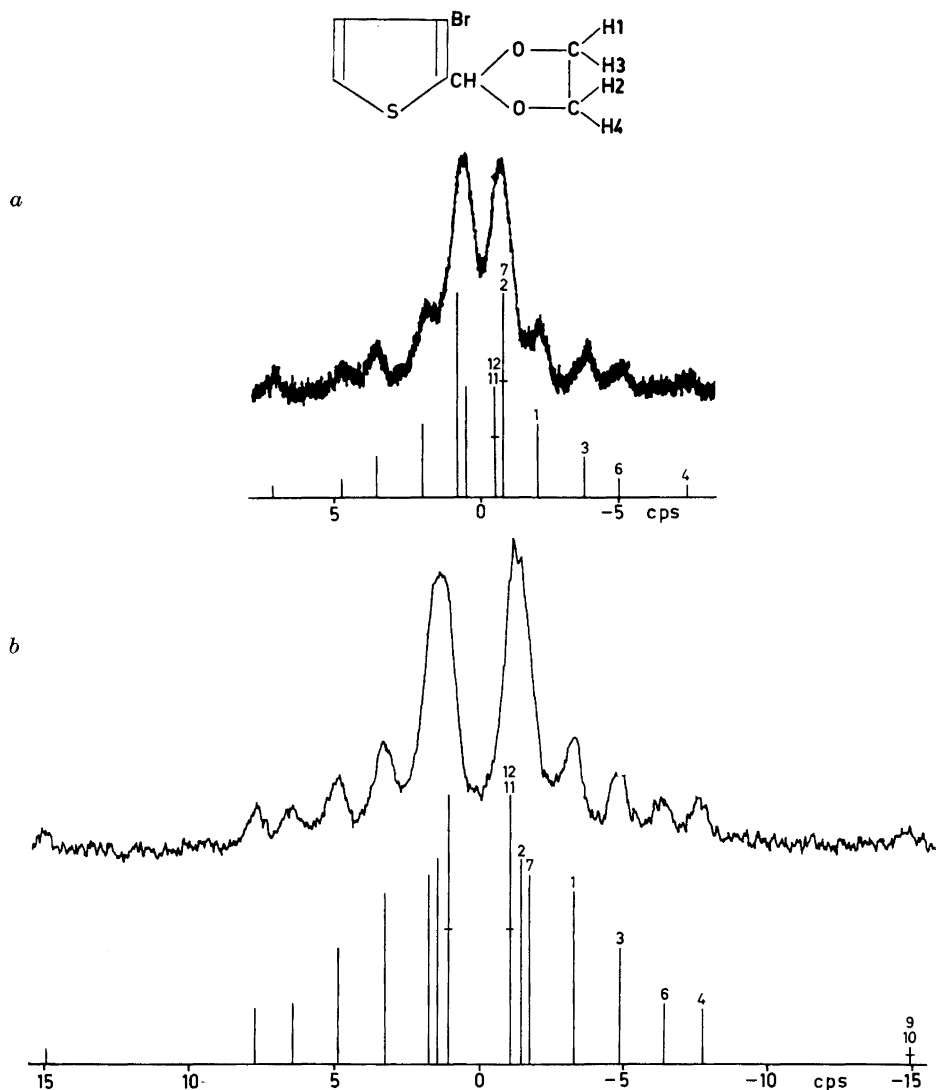
Fig. 1. NMR-spectra of the 1.3-dioxolane ring in 3-bromo-2-thiophene aldehyde ethylene acetal at a) 40 Mcps; b) 60 Mcps.

tween the *cis* neighbouring hydrogens of about 37°, which means a somewhat greater puckering of the ring.

It may be noted that the sign of the geminal coupling is opposite to the vicinal one. This was first observed by Frazer *et al.*[4] and was contradictory to Karplus' theories. Since then similar observations have been made for several compounds [10],[11] and it is now generally accepted that the geminal and vicinal coupling are of opposite sign in sp^3 hybridized carbon compounds.

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Mechanism of Peptization of Aluminium Soap Gels in Hydrocarbons

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Two theories of the mechanism of peptization of aluminium soap gels have been given earlier. Gray and Alexander [1] suggested that the peptizing molecule was coordinated preferentially to the metal ion and the polymeric chains were consequently broken. Bauer et al.[2,3] gave some years later a new theory by which the peptizer was connected to the carboxyl group of the soap by a hydrogen bond. This reaction induced a disturbancy of the symmetry in the carboxyl ion and changed the absorption in infrared from 6.3 μm (symmetric carboxyl ion) to 5.8 μm (carbonyl absorption of an associated carboxylic acid). The association complex chains were supposed not to be broken, only weakened. Yamamuto [4] has recently published a great many spectra of aluminium soap gels peptized by different compounds and has concluded that the main mechanism must be hydrogen bonding of the peptizer. In the present work gels of very pure aluminiumhydroxide-distearate in dry cyclohexane have been peptized by octadecanoic acid, 1-octadecanol and octadecylamine. The chain length has been the same both of the soap and of the peptizers in order to eliminate the influence of this variable, which can be pronounced.[5] The acid and the alcohol caused only a slight change in the rheological properties of the gels, and the change in infrared spectra can well be explained by the hydrogen bond mechanism. The amine on the other hand made the gel liquid and changed the absorption in infrared in a quite different way. The absorption at 6.3 μm, representing *intermolecular* coordination of the carboxyl ion, did not change to 5.8 μm but to 6.2 μm, which band represents *intramolecular* coordination.

These results give evidence of a new peptization mechanism, where the peptizing molecule changes the coordination of the carboxyl ion. Details of results and of research devices will appear later in a more complete report.

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