Dynamic Nuclear Magnetic Resonance Investigation of Formic Anhydride. Conformation and Torsional Barrier

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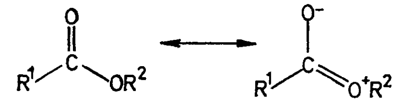
Summary Formic anhydride adopts the *EZ*-configuration in solution with a low barrier (18 ± 1 kJ mol^{-1}) for topomerization.

The magnitude of barriers to rotation about carbon–oxygen formal single bonds in esters and related compounds has been a topic of discussion and speculation for some time.[1] Although dynamic n.m.r. spectroscopy is a potentially useful tool for the study of torsional barriers, this method has been only recently used for the investigation of compounds of this type. Such barriers are an experimentally observable reflection of the importance of π-bonding between carbon and oxygen, as represented by the charged canonical structure (**1b**).

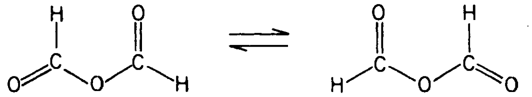


(1a) (1b)

An estimate of the barrier to rotation about an ester C–O single bond was obtained from the barrier to topomerization in $\gamma\gamma$-difluoro-ϵ-caprolactone.[2] The experimental barrier, together with an analysis of the possible pathways for topomerization, allowed an estimate of 42 kJ mol^{-1} (10 kcal mol^{-1}) as an approximate lower limit for the free energy of activation for conversion of an acyclic ester from the *E* into the *Z* configuration. More recently, the *E* to *Z* barrier in t-butyl formate was found to be 37 kJ mol^{-1} (8·8 kcal mol^{-1}).[3] Destabilization of the ground states in t-butyl formate probably lowers the barriers in this ester, relative to the values to be expected for other alkyl formates.

We report the first measurement of a barrier to rotation about C–O bonds in an anhydride. In addition, our work allows an unequivocal assignment of the conformational preference in formic anhydride (**2**), the parent compound in this series.

If the C–O bonds have partial double-bond character, resulting in planar or nearly planar structures, three diastereoisomeric conformations are possible, corresponding to *EE*-, *EZ*-, and *ZZ*-configurations at the C–O bonds. While both *EE*-(**2**) and *ZZ*-(**2**) must give rise to single



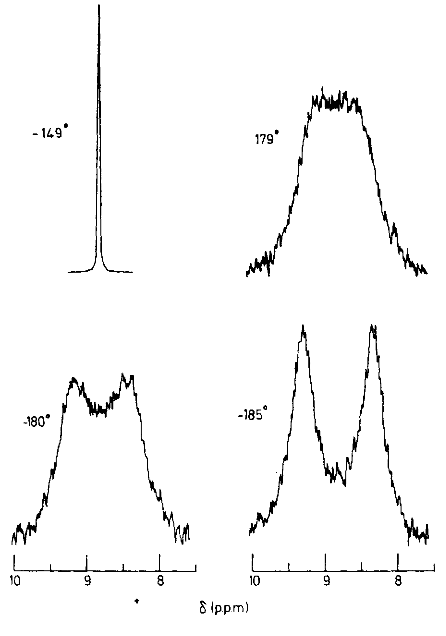
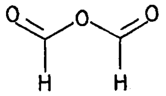
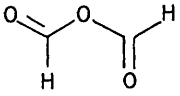


FIGURE. ^{1}H N.m.r. spectra of formic anhydride in $CDClF_2$–$CDCl_2F$ (4:1) (at 60 MHz).

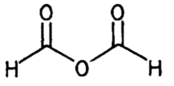
resonances for the formyl protons, regardless of the rate of rotation about the carbon–oxygen bonds, *EZ*-(**2**) should exhibit two resonances for diastereotopic formyl protons when rotation is slow on the n.m.r. time scale.



EE-(2)



EZ-(2)



ZZ-(2)

The observation of two equally intense formyl singlets at δ 8·28 and 9·23 at −185° in $CDClF_2$–$CDCl_2F$ (4 : 1) provides unequivocal evidence for the predominance of the *EZ*-configuration (see Figure). The signals coalesce at higher temperatures and a sharp singlet is observed at −149°. A first-order rate constant of 107 s^{-1} was obtained by complete line shape analysis of the spectrum recorded at −179°, corresponding to a free energy of activation for topomerization of 18 ± 1 kJ mol^{-1} (4·4 ± 0·2 kcal mol^{-1}).

Our configurational assignment is in accord with the twisted *EZ*-conformation assigned to formic anhydride in the gas phase by electron diffraction.[4] In contrast, formimide, the nitrogen analogue of (**2**) prefers the *EE*-configuration in solution[5] and the *EZ*-configuration in the gas phase.[6]

The low barrier for topomerization found for (**2**) emphasizes the diminished importance of resonance in anhydrides in comparison to esters[2,3] and imides.[5]

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