

MAGIC-ANGLE C-13 NMR CONFORMATIONAL
ANALYSIS OF 1,3,5-TRIMETHOXYBENZENE

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Magic-angle ^{13}C nmr has been used in the analysis of conformational isomerism of solid polymers in the glassy state.¹ Frozen conformations create unique chemical environments for nominally equivalent carbons of poly(phenylene oxide), polysulfone, and a variety of polycarbonates, and the isotropic chemical shift differences generated by these environments can be readily detected. The same situation can occur for small organic molecules.^{2,3}

For example, crystalline 1,4-dimethoxybenzene occurs as a single symmetric form rather than as a mixture of the two possible isomers. The preferred anti conformation produces two types of chemical environments for the protonated ring carbons, and this difference can be detected by nmr experiments on the solid.^{2,3} In the absence of intramolecular interactions between methoxy groups in 1,3,5-trimethoxybenzene, a 1:3 mixture of symmetric and asymmetric isomers is possible. If in forming the crystal only a single isomer were allowed, we might expect the symmetric form, by analogy with the situation for 1,4-dimethoxybenzene.

We were, therefore, surprised by the ^{13}C magic-angle spectrum shown in Figure 1. This cross-polarization spectrum was obtained at 15.1 MHz from a polycrystalline sample contained in a Beams-Andrew design Kel-F hollow rotor (0.7 cc internal volume) spinning at 1300 Hz. By comparison with the Fourier transform high-resolution spectrum of 1,3,5-trimethoxybenzene in solution, it is clear that all three protonated aromatic carbons are chemically non-equivalent in the solid state, and give rise to three lines of nearly equal intensity. This result is only consistent with the existence of a single asymmetric conformational isomer in the solid. (The non-equivalence of the other carbons is not resolved.)

This conclusion has been confirmed by single-crystal x-ray analysis. Single crystals of 1,3,5-trimethoxybenzene, grown by slow solvent evaporation from a saturated methanol solution, are in the non-centrosymmetric, monoclinic space group Cc with lattice para-

meters: $a=12.028(3)\text{\AA}$, $b = 9.541(2)\text{\AA}$, $c = 7.735(1)\text{\AA}$, $\beta=96.02(1)^\circ$, $V=882.7(3)\text{\AA}^3$ and $Z=4$. The benzene ring and the three oxygen atoms are planar with the three methoxy carbons being displaced by -0.071\AA , 0.003\AA , and 0.192\AA , respectively. This structure is illustrated in Figure 1. (Complete structural details will be published in Cryst. Struct. Comm.).

The ability of magic-angle ^{13}C nmr experiments to provide conformational information has particular importance in systems where x-ray analysis is impossible because of the inability to grow large single crystals. The conformations of such molecules should be amenable to the sort of nmr analysis illustrated here.

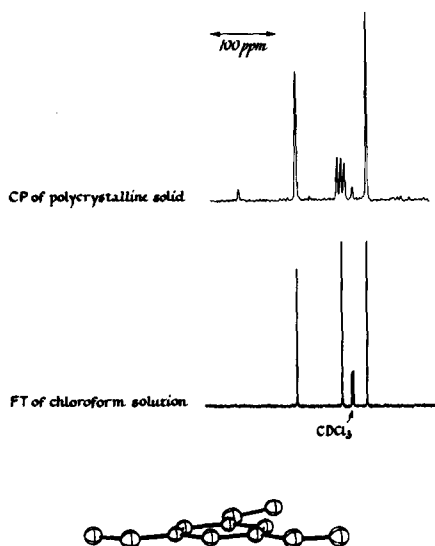


Figure 1.

Cross-polarization ^{13}C nmr spectrum of polycrystalline 1,3,5-trimethoxybenzene spinning at the magic angle (top) and Fourier transform ^{13}C nmr spectrum of a chloroform solution (middle). The conformation of the asymmetric isomer is also shown (bottom). The chemical non-equivalence of the protonated aromatic carbons is evident by the mid-field triplet of lines. Two minor spinning side bands of the low-field non-protonated aromatic-carbon resonance are also apparent. Details of the nmr and spinning techniques are in references 1 and 2.

REFERENCES

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