# Unexpected Results from the Comparison of Solid-State Conformations and $^{13}$C NMR Spectra of Poly (trimethylene terephthalate) and Its Model Compounds

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## INTRODUCTION

Analyses of the high-resolution solid-state $^{13}$C NMR spectra of bulk polymers have revealed a sensitivity of the resonance frequencies observed to the local conformations of the chain fragment containing a particular carbon nucleus.[1] The connection between the resonance frequencies and local conformational environments is provided by the $\gamma$-gauche effect illustrated in Figure 1. For the all-carbon chain fragment examined there, it is noted that, when carbon nuclei o and $\gamma$ are gauche to each other, they experience an ~5 ppm shielding from the applied magnetic field, which is absent when they are further removed in their trans conformational arrangement.

Whether polymers are constrained in their crystals to adopt a single rigid conformation or are molten, mobile, and free to interconvert rapidly on the megahertz time scale between conformations, it has been repeatedly demonstrated[1−10] that the resonance frequencies observed for their carbon nuclei in high resolution solid-state $^{13}$C NMR spectra depend principally upon and can be analyzed by means of the conformationally sensitive $\gamma$-gauche effect.

The conformations and resonance frequencies (in ppm vs TMS) of the central methylene carbons in the butylene glycol fragments of poly(butylene terephthalate) (PBT) and several of its model compounds, as observed in their crystals, are presented in Figure 2. It has been shown that the central methylene carbons in the butylene glycol fragment that are gauche to their $\gamma$-substituent ester oxygens are shielded (Figure 2) and resonate (3−4 ppm) upfield from those that are in a trans arrangement, consistent with the $\gamma$-gauche effect. PBT is a particularly relevant example, because here we compare the high-resolution solid-state $^{13}$C NMR spectra and conformations of the closely related aromatic polyester poly(trimethylene terephthalate) (PTT) whose structure is shown in Figure 3.

## EXPERIMENTAL SECTION

High-resolution solid-state $^{13}$C NMR experiments were carried out on two different spectrometers: at 50 MHz on a Chemagnetics CMX-200S (PTT) and at 75 MHz using a Bruker DSX-300 [trimethylene glycol dibenzoate and the solid cyclic dimer of PTT (TMGDB and TT-2, respectively)], both with cross-polarization and with magic angle spinning (CP/MAS), and with high-power proton dipolar decoupling (DD) at spinning speeds ranging from 3 to 8 kHz. $^{13}$C chemical shifts were referenced relative to TMS. CMX-200S spectra were obtained with
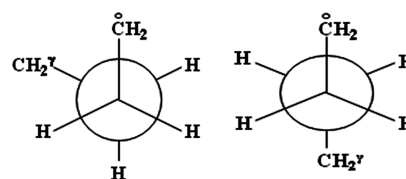


**Figure 1.** Carbon-13 nuclei separated by three bonds in the shielding (~5 ppm) gauche (left) and nonshielding (0 ppm) trans (right) conformations.

1000 transients, 1.0 ms contact time, and 3.0 s pulse delay. The spectral width was 15 kHz in 2K data points, which were zero-filled to 8K before Fourier transformation. DSX-300 magic-angle spinning (MAS) NMR measurements for the solid and melt states of TMGDB, and for the solid cyclic PTT dimer TT-2, were collected with a 4 mm double-resonance MAS probe. For the melt-state measurements, the probe temperature was calibrated using PbNO$_3$ to within ±1 K. Comparisons of single-pulse $^{13}$C spectra, acquired with high-power $^1$H decoupling, to cross-polarization (CP) spectra acquired with a 1 ms contact time and $^1$H decoupling, revealed no differences in isotropic chemical shift positions for either TMGB or TT-2.

## MOLECULAR MODELING

Molecular modeling was used to evaluate the distances between the "central" methylene carbons (CH$_2$°) and the centers of the phenyl rings in plane ($\rho$) and perpendicular to the plane ($z$) of the phenyl rings in their crystalline unit cells. For both molecules, the calculation was the same, using atomic coordinates that are available in the literature for PTT[12] and TMGDB.[13] With Accelrys' Materials Studio software [accelrys] version 5.5, a periodic box consisting of several unit cells was created for both PTT and TMGDB, and a free energy minimization was performed using the PCFF force field for 5000 steps using the Discover module.

For both systems, the atomic coordinates for a molecule within the center of the box and its nearest neighboring phenyl rings were extracted. Distances were calculated from phenyl rings on the same chain to all neighboring "central" methylene groups. The distances were calculated by using the normal to the phenyl ring and the
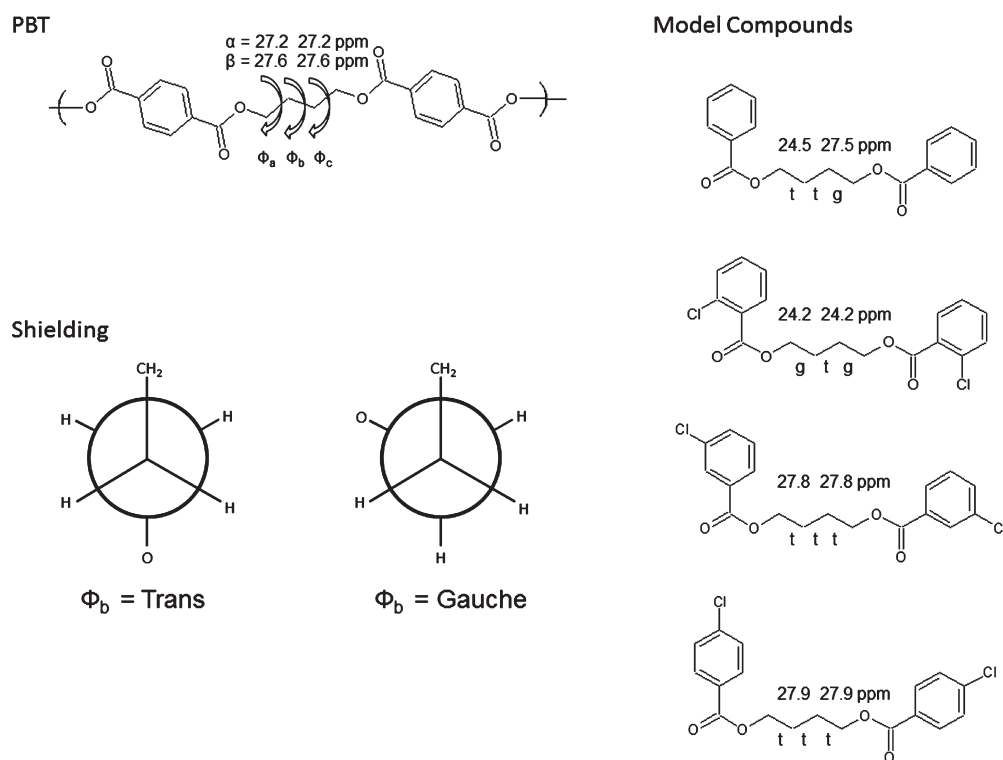
**Figure 2.** Conformations and $^{13}C$ NMR resonances observed for the central methylene carbons in crystals of PBT and its model compounds.[5,11]
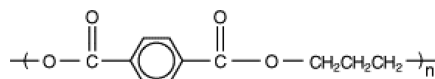


**Figure 3.** PTT repeat unit.

distance vector from the methylene carbon. The center of each phenyl ring was determined by averaging the atomic positions of the carbon atoms within the ring. The normal to the phenyl ring was then determined by defining vectors between carbons within the ring, calculating the cross product, and then normalizing it. The distance between the ring centers and "central" methylene carbons were then found. The distance perpendicular to the plane ($z$) was the dot product of the phenyl ring normal vector and the distance vector, and because $z$ and $\rho$ form a right triangle, the magnitude of $\rho$ was calculated from the Pythagorean theorem.

Distances between carbonyl groups and $CH_2°$s were similarly calculated by setting the plane center 0.6 Å away from carbonyl carbon along the bisector of the two oxygen atoms bonded to the carbonyl carbon.

To mimic the conformational flexibility of TMGDB in the melt or solution, the distance calculations were repeated for a dynamic TMGDB molecule in vacuum to obtain a conformationally weighted average of the distances. MD simulations were performed with the LAMMPS software package {Plimpton, S. Fast Parallel Algorithms for Short-Range Molecular Dynamics. *J. Comput. Phys.* **1995**, *117*, 1;http://lammps.sandia.gov/index. html}. The PCFF force field with a time step of 1 fs (for 10 000 time steps) was employed at 298 K and 1 atm in the *NVT* ensemble (constant number of atoms, constant volume, and constant temperature), with periodic boundary conditions. At each time step, the distances were measured and the potential energy of that configuration was calculated. A weighted average was

obtained across the trajectory by weighing the distance from each conformation by its Boltzmann factor ($\exp(-E/RT)$), where the term $E$ is the potential energy for that conformation.

## ■ RESULTS AND DISCUSSION

PTT is believed to crystallize with its propylene glycol fragments in alternating tg± g± t (... tg+ g+ t tg− g− t ...) conformations, where all −O—$CH_2$− and −$CH_2$—O− bonds are trans (t) and −$CH_2$ −$CH_2$− bonds are gauche (g±).[12] All central methylene carbons in the propylene glycol fragments would be trans ($\varphi_{1,4}$ = t) to both of their $\gamma$-substituent carbonyl carbons in the proposed crystalline conformation of PTT and, so, would be unshielded by them, because they are not in the requisite gauche shielding arrangement. On the other hand, in solution, in the melt, and in the amorphous solid regions, the −O—$CH_2$− and −$CH_2$—O− bonds in PTT would adopt both trans and gauche conformations ($\varphi_{1,4}$ = t and g±). As a consequence, the central methylene carbons ($CH_2°$) would be expected to experience significant shielding from their immediately adjacent (C=O)'s [∼ 5 ppm for each $\gamma$-(C=O) in a gauche arrangement] and to resonate upfield from their crystalline counterparts.
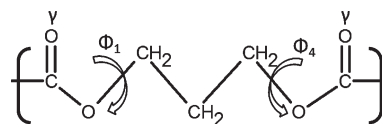


As seen in Figure 4, the high resolution solid-state $^{13}C$ NMR spectra of amorphous and semicrystalline PTTs exhibit $CH_2°$ resonances at $\delta(^{13}C)$ = 28.8(amorphous) and 26.1 ppm (crystalline) vs TMS, respectively. In other words the $CH_2°$ methylene carbons in the crystalline regions of PTT are shielded
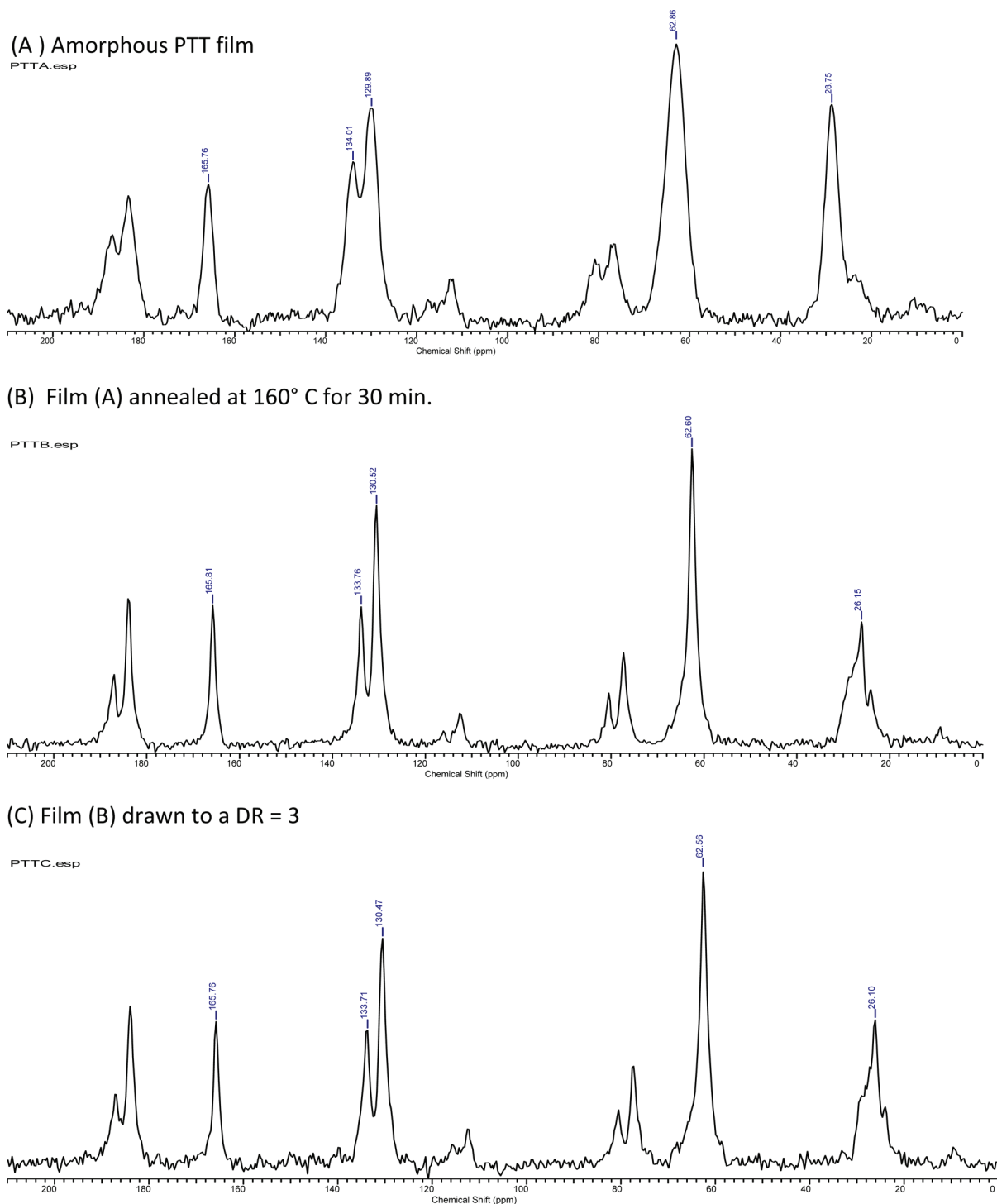
(A) Amorphous PTT film

PTTA.esp



(B) Film (A) annealed at 160° C for 30 min.

PTTB.esp



(C) Film (B) drawn to a DR = 3

PTTC.esp



**Figure 4.** $^{13}$C CP-MAS NMR spectra of PTT films: (A) amorphous PTT Film, (B) film (A) annealed at 160 °C for 30 min, and (C) film (B) drawn to a DR = 3.

in comparison to those in the amorphous regions and so resonate upfield. This is in direct opposition to expectation based on the crystalline conformation proposed for PTT, with $\varphi_{1,4} =$ t (trans) $-O-CH_2-$ and $-CH_2-O-$ bonds and therefore no $\gamma$-(C=O)'s in a gauche shielding arrangement.

Single crystal X-ray diffraction of the PTT model compound trimethylene glycol dibenzoate (TMGDB, shown in Figure 5) has revealed a crystalline conformation essentially identical to that proposed for crystalline PTT.[13] Though the spectra are not



**Figure 5.** Trimethylene glycol dibenzoate.

presented here, we have observed the following resonance frequencies for the central methylene carbons (CH$_2$°) in TMGDB:
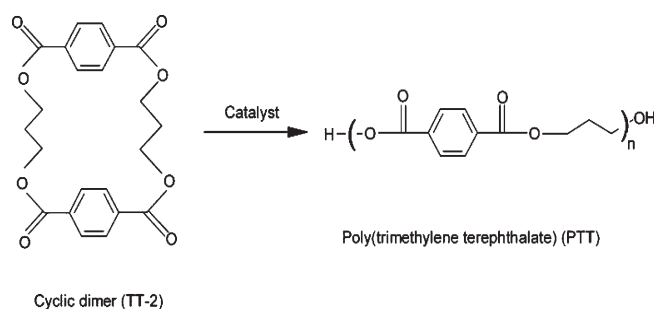
**Figure 6.** TT-2 the cyclic dimer of PTT used in its ring-opening polymerization.
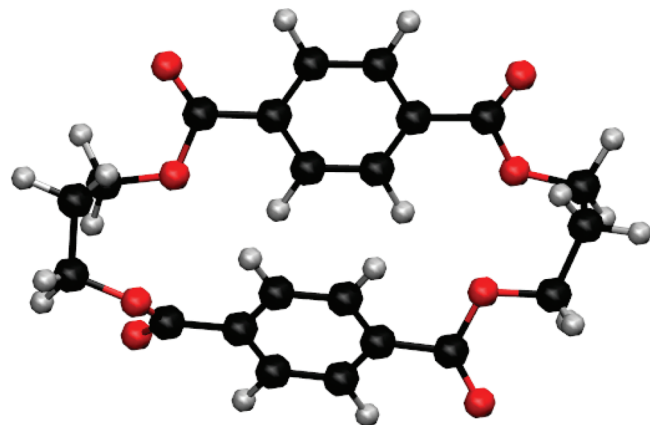


**Figure 7.** TT-2 crystalline conformation (Kamau et al.[14]).

30.0 ppm (melt, 60 °C), 28.7 ppm (solution), 27.4 ppm (crystal). Again, unexpectedly, but in agreement with PTT, the central methylene carbons in crystalline TMGDB resonate substantially upfield from those in its melt or solution. Like the chemical shifts observed for the central methylene carbons in crystalline and amorphous regions of PTT, the $CH_2°$s in the TMGDB crystal resonate nearly 3 ppm upfield from its resonance in the melt.

These observations lead to the following conclusions:
1. PTT and TMGDB have closely similar crystalline conformations, as previously concluded by X-ray.[12,13]
2. The ^{13}C resonances of the central methylene ($CH_2°$) nuclei in both seem not to be influenced by the nuclear shielding usually produced by gauche conformational arrangements between carbon nuclei and their $\gamma$-carbon substituents.

The crystal structure of the cyclic dimer of PTT (TT-2) (Figures 6 and 7) has been reported,[14] and both "central" methylene carbons $CH_2°$ were found to be trans to one and gauche to the other immediately adjacent $\gamma$-(C=O)'s, which should not and should, respectively, shield them. Figure 8 presents the high resolution solid-state [13]C (CP-MAS) spectrum of TT-2.

There we observe the $CH_2°$ methylene carbons in crystalline TT-2 to exhibit a single resonance, as expected, however, at 29.4 ppm, or more than 3 ppm downfield from those in crystalline PTT (26.1 ppm). This comparison is once again contrary to the expectation based on the crystalline conformation of PTT, because there the central methylene carbons ($CH_2°$) should not be shielded by their $\gamma$-(C=O)'s, because the $-O-CH_2-$ and $-CH_2-O-$ bonds are trans ($\varphi_{1,4}$ = t).

The ^{13}C resonances of the "central" methylene ($CH_2°$) nuclei in PTT and its model compounds TMGDB and TT-2 are clearly
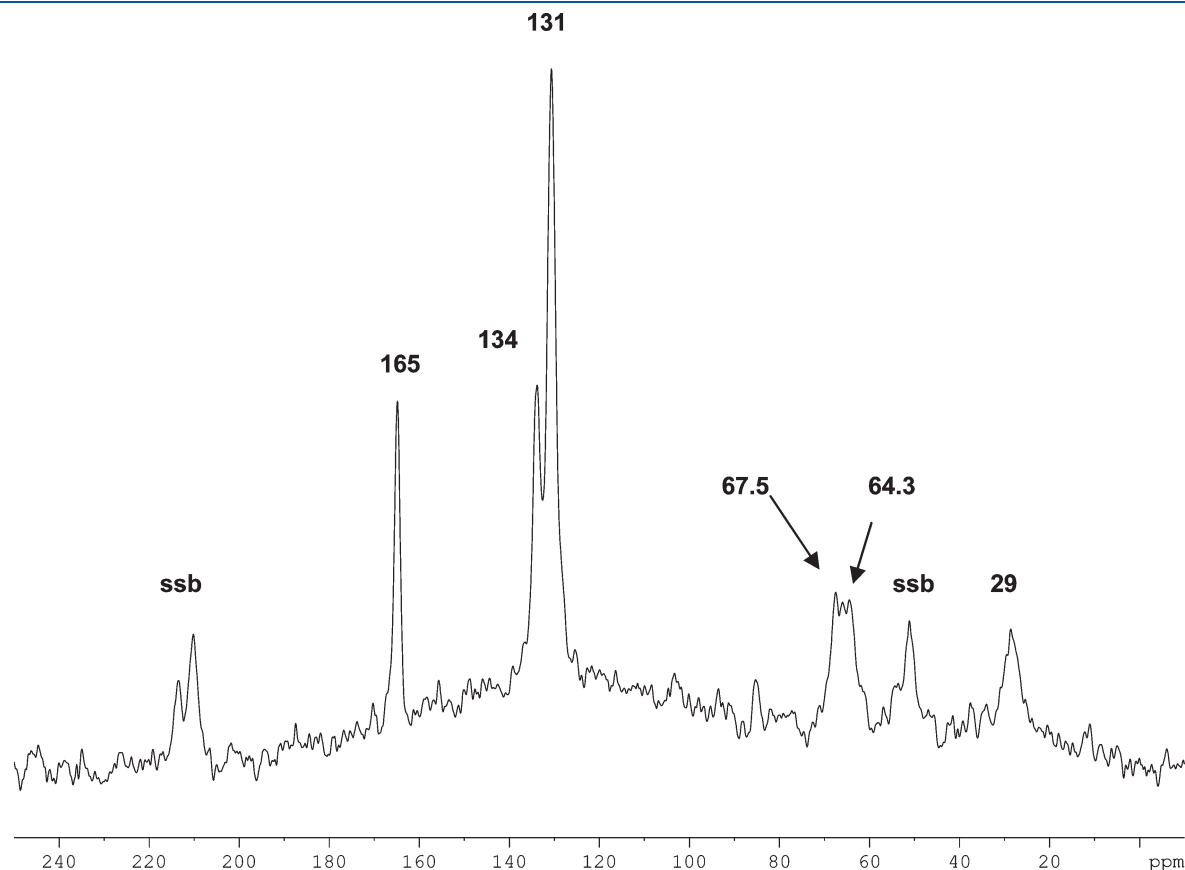


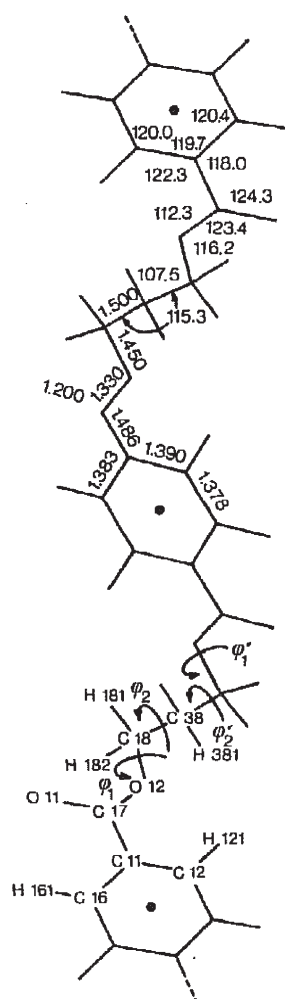**Figure 8.** CP-MAS ^{13}C -NMR spectrum of crystalline TT-2.

**Figure 9.** PTT crystalline conformation (Poulin-Dandurand et al.[12]).

**Table 1. Distances (Å) of "Central" Methylenes to Center of ($\rho$) and above or below ($z$) the Phenyl Rings in PTT and TMGDB[a]**

| | PTT | | | | |
|---|---|---|---|---|---|
| | | upper phenyl | | lower phenyl | |
| | distance from 1st chain | $\rho$ | $z$ | $\rho$ | $z$ |
| same chain | 0.00 | 5.85 | 0.01 | 5.84 | 0.00 |
| chain + a | 4.64 | 5.07 | −2.48 | 4.61 | −3.58 |
| chain + b | 6.27 | 9.58 | 2.60 | 8.65 | 3.10 |
| chain + a + b | 6.31 | 7.90 | −5.98 | 6.40 | −0.48 |

| | TMGDB | | | |
|---|---|---|---|---|
| | $\rho$ from ring 1 | $z$ from ring 1 | $\rho$ from ring 2 | $z$ from ring 2 |
| same chain | 5.90 | 0.21 | 5.90 | 0.21 |
| | 10.0 | −6.16 | 11.5 | 0.10 |
| same + 0.5a − 0.5c | 5.02 | −3.03 | 13.9 | 9.20 |
| | 5.00 | −3.14 | 12.6 | 2.83 |
| | 11.5 | 0.10 | 10.0 | −6.16 |
| | 7.61 | 3.24 | 12.7 | 2.94 |
| | 6.28 | 0.32 | 8.50 | 6.59 |
| | 5.93 | 3.35 | 13.0 | 9.31 |
| | 8.50 | 6.59 | 6.28 | 0.32 |
| | 12.7 | 2.94 | 7.61 | 3.24 |
| | 12.6 | 2.83 | 5.00 | −3.14 |
| same − 0.5a + 0.5c | 13.9 | 9.20 | 5.02 | −3.03 |
| | 13.0 | 9.31 | 5.93 | 3.35 |

[a] Note that shielding from ring-currents $\rightarrow 0$ for $\rho > 4$ Å or $z > 3$ Å (Bovey[17]).

not influenced by the nuclear shielding expected to be produced by gauche conformational arrangements with their $\gamma$-substituent C=O's. This despite the fact that $\gamma$-gauche shielding has been shown to successfully explain the ^{13}C resonances observed in the crystals of the closely related aromatic polyester PBT and its model compounds,[5,11] as well as those of many other crystalline polymers.[1−10]

The crystalline conformation of PTT is illustrated in Figure 9, where it is apparent that, unlike the related terephthalate polyesters PBT and poly (ethylene terephthalate), the PTT chain is not fully extended. Rather, the trimethylene glycol segments gently serpentine back and forth about the line connecting the centers of their phenyl rings. This prompted us to investigate how ring currents generated by the $\pi$-electrons of the phenyl rings in PTT might affect the resonance frequencies of their "central" CH$_2^\circ$ carbons.[15−17]

The $x, y, z$ coordinates obtained from the crystal structures of PTT[12] and TMGDB[13] were used to evaluate the distances between the central methylene carbons (CH$_2^\circ$) and the centers ($\rho$) and planes ($z$) of all phenyl rings in their crystalline unit cells. The results are presented in Table 1. Potential ring-current effects in TT-2 could not be evaluated, because the $x, y, z$ coordinates of the TT-2 crystal structure were not presented.[14] It is clear from Table 1 that all of the central methylenes (CH$_2^\circ$) in both PTT and TMGDB are too far removed from their nearest phenyl rings to be significantly shielded by their ring-currents.

A similar calculation of the potential effects the magnetic susceptibility anisotropy of neighboring carbonyl groups might have on the nuclear shielding of the "central" methylene carbons CH$_2^\circ$ was also investigated. Here CH$_2^\circ$ distances in-plane and perpendicular to the plane of the >C=O group were calculated for rigid crystalline and flexible isolated TMGDB. Neighboring carbonyl group anisotropy effects for TMGDB were estimated according to the general procedure implemented previously by one of us,[18] in which the McConnell[19] and Pople[20] point-dipole approximation of the anisotropic neighboring group (i.e., the C=O group) was used. The value of the carbonyl group's magnetic susceptibility itself was approximated using the known value from the carbonyl group in formaldehyde.[21] Stated simply, the calculations should reveal whether or not the presence of nearby carbonyl groups, either within the same or within neighboring PTT chains can significantly shield the central methylene carbons (CH$_2^\circ$).

Calculations on both the rigid crystalline and conformationally averaged TMGDB model compound, in which minimum in-plane and out-of-plane distances exist between the nearest carbonyl groups and the "central" CH$_2^\circ$ carbons, resulted in estimates of the magnitude of expected shifts due to the neighboring anisotropic carbonyl groups. Minimum distances for TMGDB ranged from 2.0 to 4.7 Å, depending on whether the crystalline or amorphous coordinates were used, resulting in a maximum possible neighboring group shielding contribution to the observed shift of 2.2 ppm.

Recall the central methylene carbons ($CH_2{}^\circ$) in TMGDB resonate at 30.0 ppm (melt, 60 °C), 28.7 ppm (solution), and 27.4 ppm (crystal), or flexible TMGDB resonances come 1.3–2.4 ppm downfield from rigid crystalline TMGDB, while from $\gamma$-gauche conformational shielding we expected them to be more shielded than crystalline TMGDB by 3–4 ppm. Our estimate of the maximum shielding of "central" methylene carbons ($CH_2{}^\circ$) produced by the anisotropic magnetic susceptibility of neighboring carbonyl groups in TMGDB is $\delta$(rigid crystal) − $\delta$(flexible liquid) ~ 2.2 ppm, which is far short of that necessary to overcome the larger 5–7 ppm downfield shift expected from the lack of $\gamma$-gauche conformational shielding in the TMGDB crystal.

It must be remembered that PTT and TMGDB have closely similar crystalline conformations, with all "central" $CH_2{}^\circ$ methylenes and their $\gamma$-substituent carbonyl carbons in a trans conformational arrangement. Thus their crystalline $CH_2{}^\circ$ methylene resonances are expected to come several ppm downfield from the resonances observed in their melts and solutions. Instead, the crystalline $CH_2{}^\circ$ methylene resonances come several ppm upfield, so the discrepancies between resonance frequencies anticipated from consideration of conformationally sensitive $\gamma$-gauche effects and those observed are very large, in the range 5–7 ppm. Furthermore, they remain large even when account is taken of the potential effects of phenyl ring currents and anisotropic carbonyl group magnetic susceptibilities. As a consequence, we currently remain perplexed by this discrepancy.

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## ■ ACKNOWLEDGMENT

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