# $^{13}$C NMR Spectroscopic Characterization of Trimethylol Propane Ester Lubricants

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**The ability to identify the different acyl groups present in lubricants composed of mixed acid esters of trimethylol propane by $^{13}$C nuclear magnetic resonance spectroscopy is demonstrated. The technique discriminates between esters with acyl groups containing between 5 and 10 carbon atoms and can be used similarly to identify acyl groups in pentaerythritol or neopentyl glycol ester lubricants.**

KEY WORDS: $^{13}$C NMR, NPG esters, PE esters, synthetic lubricants, TMP esters.

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Esters of trimethylol propane (TMP), together with pentaerythritol (PE) esters, are commonly known as neopentyl polyol or "hindered" esters, and are frequently used in modern synthetic lubricating oils (1). Optimum lubricant properties are often obtained from selected mixtures of these esters and, hence, a detailed knowledge of their composition is required. To obtain such information a number of analytical procedures may be required, such as saponification followed by chromatographic identification of the free acids (2) or their methyl ester derivatives. Polyol esters are typically produced by esterification of single short-chain monobasic fatty acids, or mixtures of acids, typically containing from 5 to 10 carbons with the requisite polyhydric alcohol, in this case trimethylol propane.

This paper describes how $^{13}$C nuclear magnetic resonance (NMR) spectroscopy can be used to provide a rapid identification of the acyl composition of mixtures of TMP esters encountered in synthetic lubricants, without resorting to saponification and chromatographic identification. Six triester standards of trimethylol propane were examined, individually initially, and then in combination. In each standard, the three acyl groups were identical and contained linear arrangements of 5, 6, 7, 8, 9 and a mixture of 8 and 10 carbon atoms, respectively.

## EXPERIMENTAL PROCEDURES

Five standard TMP esters (Fig. 1) were prepared by esterification of trimethylol propane with pentanoic, hexanoic, heptanoic, octanoic and nonanoic acid, respectively, by using catalytic amounts of concentrated sulfuric acid (3). The resulting esters are denoted as TMP C5, TMP C6, etc., where the C number refers to the number of carbon atoms in the acid chain. The sixth TMP standard was a commercial sample of a mixture of C8 and C10 TMP esters from Unichema (Bebington, Wirral, U.K.).

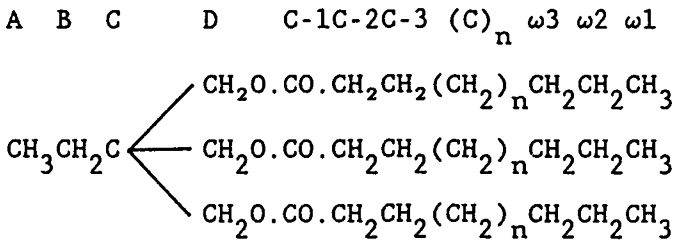

**FIG. 1. Trimethylol propane triester carbon assignments.**

The $^{13}$C NMR spectra were recorded at ambient temperature at 62.9 MHz on a Bruker AC 250 NMR spectrometer (Coventry, U.K.) with a 5-mm dual $^1$H/$^{13}$C probe. Waltz-16 proton decoupling was employed. Typically, 400 transients were acquired for each sample. Other acquisition parameters were such as to give generally a digital spectral resolution of 0.45 Hz/point. The samples were dissolved in deuterochloroform to give approximately 30% v/v solutions. Chemical shift values are in ppm with respect to tetramethylsilane.

Gas chromatographic confirmation of the bulk acyl group distribution of unknown mixed acid polyol esters was performed by preparing and analyzing the methyl esters of these acids. Initially, the polyol esters were saponified to yield their respective acids (4). These were then converted to methyl esters by refluxing 2 g of the acids with 20 cm$^3$ of 5% HCl in methanol. Water was then added and the mixture was extracted with diethyl ether. The acid distribution of the methyl esters was determined in a Hewlett Packard 5880A gas chromatograph (Bracknell, Berkshire, U.K.) equipped with a flame ionization detector (temperature 300°C) and a BP1 (12 m × 0.22 mm i.d., 0.25 μm film thickness) capillary column (Scientific Glass Engineering, Milton Keynes, U.K.). Helium was the carrier gas (3 cm$^3$/min). Injection was *via* a split injector (50:1 held at 270°C). The initial column temperature of 45°C was held for 5 min, then increased by 6°C/min to 240°C, and held for 10 min at 240°C. The unknown methyl esters were identified by comparing their retention times and peak areas with those for standards.

## RESULTS AND DISCUSSION

Table 1 lists the assignments and relative chemical shift values of the TMP triester standards. The peak assignments are in agreement with the recently published paper by Black and Gunstone (5) on the synthesis and spectral characterization of C8, C9, C10 and C12 TMP triesters.

Table 1 shows that each of the different acyl groups, from C5 to C10, contains at least one carbon atom that gives a resonance unambiguously assignable to that acyl group. The various acyl groups, C5, C6, C7, C8, C9 and C10, thus can be readily identified in a $^{13}$C spectrum of a sample containing a mixture of TMP C5, TMP C6, TMP C7, TMP C8, TMP C9 and TMP C10 triesters. Such mixtures of TMP esters are frequently encountered in commercial synthetic lubricant samples. If the spectrum is recorded under quantitative conditions, an assessment of the relative amounts of the different esters may be made.

For the C5 acyl chain, any of the $^{13}$C resonances from carbons denoted as C-2, C-3, ω2 or ω1 (in Fig. 1) can be used as identifiers. For the C6 to C10 groups, the chemical shift of the carbon ω3 signal is the best resolved identifier

**TABLE 1**

**$^{13}$C Chemical Shifts in ppm Relative to Tetramethylsilane for TMP Triester Standards**

| Triester | Acyl chainlength | Carbon assignments in Figure 1 | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | A | B | C | D | C-1 | C-2 | C-3 | $(C)_n$ | ω3 | ω2 | ω1 |
| TMP C5 | 5 | 7.37 | 23.08 | 40.65 | 63.72 | 172.89 | 34.02 | 27.05 | [a] | [a] | 22.29 | 13.71 |
| TMP C6 | 6 | 7.39 | 23.09 | 40.70 | 63.68 | 173.32 | 34.19 | 24.68 | [a] | 31.35 | 22.37 | 13.92 |
| TMP C7 | 7 | 7.40 | 23.12 | 40.76 | 63.65 | 173.19 | 34.22 | 24.99 | 28.91 | 31.57 | 22.60 | 14.06 |
| TMP C8 | 8 | 7.42 | 23.17 | 40.81 | 63.63 | 173.00 | 34.19 | 25.06 | 29.24<br>29.10 | 31.84 | 22.74 | 14.11 |
| TMP C9 | 9 | 7.39 | 23.11 | 40.71 | 63.65 | 173.20 | 34.21 | 25.01 | 29.32<br>29.23 | 31.91 | 22.72 | 14.12 |
| TMP C10[b] | 10 | 7.39 | 23.11 | 40.72 | 63.66 | 172.23 | 34.22 | 25.02 | 29.54<br>29.37<br>29.23 | 31.96 | 22.75 | 14.14 |

[a] These carbons are not present in C5 and C6 acyl chains.

[b] These assignments and chemical shift values were taken from the $^{13}$C spectrum of the mixed TMP C8 and TMP C10 sample.

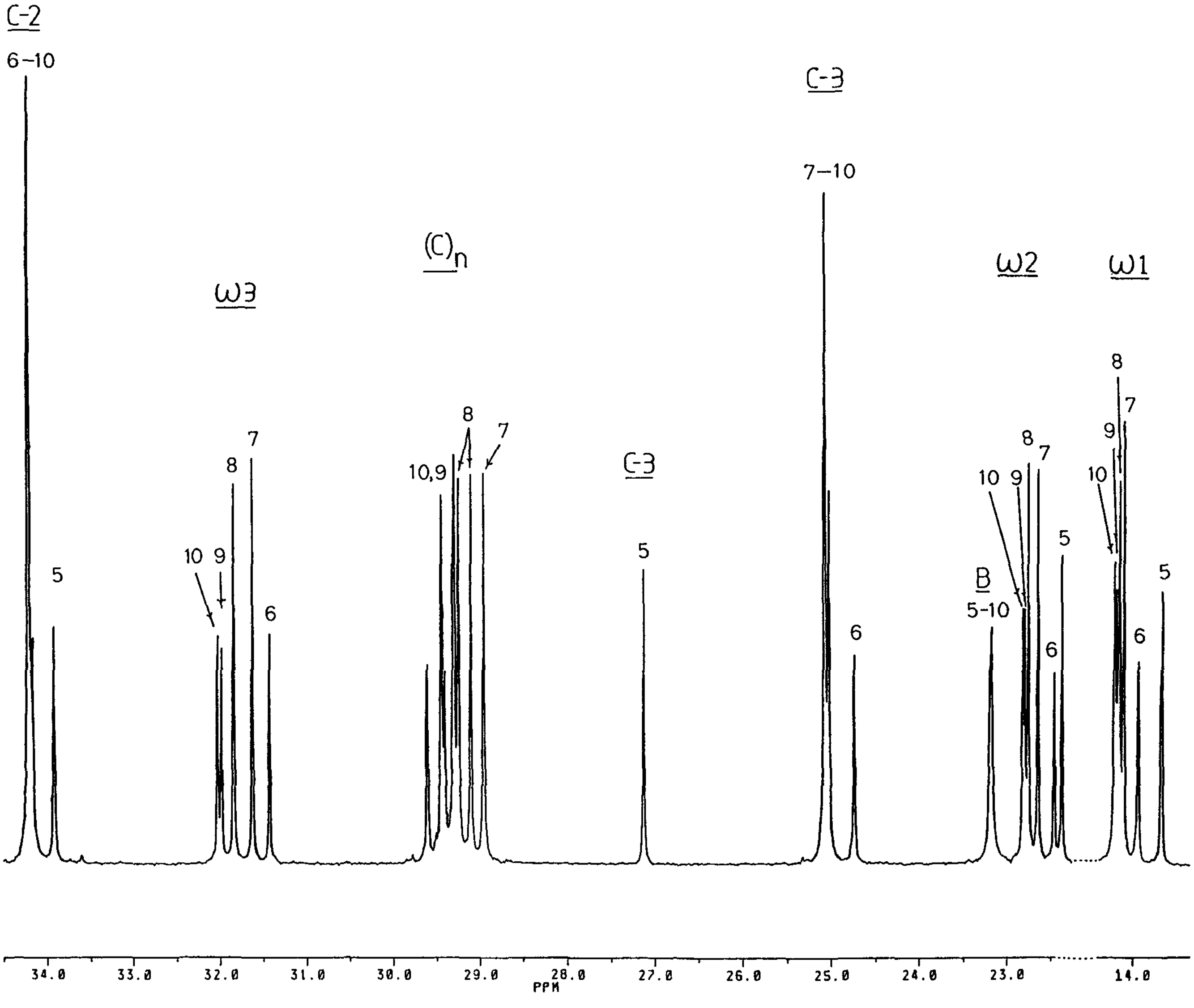

FIG. 2. $^{13}$C spectrum of a mixture of C5, C6, C7, C8, C9 and C10 TMP triesters.

TABLE 2

$^{13}$C Chemical Shifts in ppm Relative to Tetramethylsilane for a Mixed Sample Containing TMP C5, C6, C7, C8, C9 and C10 Triesters

| Triester | Acyl chainlength | Carbon assignments in Figure 1 | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | A | B | C | D | C-1 | C-2 | C-3 | $(C)_n$ | ω3 | ω2 | ω1 |
| TMP C5 | 5 | 7.42 | 23.17 | 40.82 | 63.64 | 173.02 | 33.91 | 27.12 | [a] | [a] | 22.36 | 13.74 |
| TMP C6 | 6 | 7.42 | 23.17 | 40.82 | 63.64 | 173.02 | 34.20 | 24.73 | [a] | 31.42 | 22.45 | 13.95 |
| TMP C7 | 7 | 7.42 | 23.17 | 40.82 | 63.64 | 173.02 | 34.20 | 25.06 | 28.94 | 31.62 | 22.63 | 14.07 |
| TMP C8 | 8 | 7.42 | 23.17 | 40.82 | 63.64 | 173.02 | 34.20 | 25.06 | 29.24<br>29.09 | 31.84 | 22.75 | 14.11 |
| TMP C9 | 9 | 7.42 | 23.17 | 40.82 | 63.64 | 173.02 | 34.20 | 25.06 | [b] | 31.98 | 22.78 | 14.14 |
| TMP C10 | 10 | 7.42 | 23.17 | 40.82 | 63.64 | 173.02 | 34.20 | 25.06 | [b] | 32.02 | 22.80 | 14.16 |

[a] These carbons are not present in C5 and C6 acyl chains.

[b] The assignment of these peaks to either C9 or C10 chains is uncertain, the peaks occur at 29.29, 29.30, 29.40, 29.43 and 29.60 ppm.

of the particular acyl group. Although chemical shift differences are also found for carbons ω2 and ω1 in the C6 to C10 chains, their separation is reduced compared to the difference for the ω3 carbon resonances. This makes their assignment more difficult.

Figure 2 shows the most informative portions of the $^{13}$C spectrum obtained from a mixture containing two drops each (from a Pasteur pipette) of the six triester standards. The carbon assignments are as in Figure 1, and the numbers refer to the length of the acyl chain responsible for that resonance. The resonances from the $(C)_n$ carbons in the C9 and C10 TMP acyl groups overlap, and some of the signals are from more than one carbon. Hence, these signals are not specifically assigned on the spectrum.

Table 2 lists the assignments and relative chemical shifts of this mixed ester sample. The assignment of signals to the various acyl chainlengths was made by examining 1:1 (by volume) mixtures of the different triester standards. Synthetic lubricant samples containing mixed acid esters of TMP, of pentaerythritol (PE) or of neopentylglycol (NPG), can be examined similarly by $^{13}$C NMR spectroscopy, and their acyl group chainlengths can be identified if they contain eleven or fewer carbon atoms. Confirmatory evidence of the bulk acyl group distribution, predicted *via* $^{13}$C NMR for such mixed acid esters, was obtained *via* gas chromatographic examination of the methyl esters of the saponified polyol esters.

Depending on the specific lubricant examined, there may be slight variations in the chemical shift values to those reported here. However, the relative ordering of the resonances appears to be generally preserved, with the chemical shift values in the order C10 > C9 > C8 > C7 > C6 > C5 for the resonances of carbons ω3, ω2 and ω1 in each of the acyl chains in TMP, PE and NPG esters.

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