Reference Data

Complete ^{13}C NMR Assignment of the Dental Adhesive Monomer 4-Methacryloyloxyethyl Trimellitate Anhydride and its Hydrate

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The ^{13}C-NMR spectra of 4-methacryloyloxyethyl trimellitate anhydride (4-META; **1**) and its hydrate (4-MET; **2**) have been completely assigned using a combination of 2D NMR experiments (^{13}C–^{1}H HETCOR and HMBC) and a heteronuclear NOE experiment.

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INTRODUCTION

The 4-methacryloyloxyethyl trimellitate anhydride (**1**)–methyl methacrylate–tributylborane system is widely used in density as a restorative material,[1,2] and the commercial source contains appreciable amounts of 4-methacryloyloxyethyltrimellitic acid (**2**), a hydrate of **1**.[3] In connection with investigations of the bonding mechanism between monomers and mineralized tooth surfaces,[4] we have found the characteristic downfield shift of the aromatic three-proton signals at the trimellitic acid moiety of **2** by the addition of calcium phosphate to an aqueous solution of **2** using high-resolution ^{1}H NMR spectroscopy, suggesting that a certain intermolecular interaction occurs between the trimellitic moiety and calcium ions. The carboxylic functions of **1** and **2** are expected to have some potential interactions with calcium ions, and we therefore focused on the carbon component in order to clarify the interactive profile of the carboxylic groups of **1** and **2**, and report here the complete assignment of the ^{13}C NMR spectra of **1** and **2**.

EXPERIMENTAL

Materials

DMSO-d_6 (Isotec, 99.9 atom% D) and $CDCl_3$ (CEA, 99.8% D) were treated with thoroughly dried molecular sieves (3 Å). Trimellitates **1** and **2** were prepared as described previously[1,5] and were used as *ca.* 100 mM DMSO-d_6 or $CDCl_3$ solutions.

NMR spectra

All 1D and 2D NMR spectra were obtained on a JEOL Alpha-500 spectrometer equipped with a 5 mm tunable probe and operating at 37 °C. One-dimensional ^{1}H (500 MHz) and ^{13}C (125 MHz) spectra were acquired using standard conditions with 16K data ponts to give 0.61 and 2 Hz digital resolutions per point, respectively. Data were processed with an exponential window function and the chemical shifts are given in ppm from internal TMS. Two-dimensional heteronuclear coherence spectra were processed in the absolute value mode. Carbon detected HETCOR spectra[6] were collected in a 1024 × 256 matrix with a spectral width of 16 700 Hz in the carbon domain and 4900 Hz in the proton domain and zero filled to a 1024 × 512 matrix before processing. Fourier transformation and a shifted sine-bell squared window function was applied in both dimensions. Inverse proton detected HMBC spectra[7] were collected in a 1024 × 512 matrix with a spectral width of 4800 Hz in the proton domain and 20 400 Hz in the carbon domain and zero filled to 1024 × 1024 data points. The experiment was carried out applying various delays optimized for long-range coupling constants of 8 Hz (62.5 ms), 5.6 Hz (125 ms) and 2.5 Hz (200 ms). Data were processed using parameters similar to those used in the HETCOR experiment. The heteronuclear NOE experiment on **1** (400 mM solution in $CDCl_3$) was performed using the ^{13}C–$\{^{1}H\}$ NOE pulse sequence.[8] The selected proton was irradiated at an attenuation level 360 and more than 4000 scans were acquired, applying a 0.48 s acquisition time and a 7 s relaxation delay.

RESULTS AND DISCUSSION

The ^{13}C NMR, DEPT and ^{13}C–^{1}H HETCOR data for **1** in DMSO-d_6 and in $CDCl_3$ are summarized in Table 1. In the ^{13}C–^{1}H HETCOR spectrum of **1**, which provides good ^{13}C resolution, the signals are well resolved to allow determination of the chemical shifts of four protonated sp^2 carbons at the methacryloyl and trimellitic sites. The assignment of the non-protonated carbon signals and two carbon signals of the ethylenedioxy portion was accomplished using a combination of HMBC experiments and heteronuclear selected NOE experiments for **1**. In both solvent systems, HMBC experiments for **1** showed connectivities between H-15 and C-13, between H-15 and C-12, between H-11 and C-12 and between H-10 and C-9, as shown in Fig. 1 to facilitate the assignment of the methacryloyloxyethyl moiety.

The observed connectivities between H-3 and C-1, C-5, C-8 and C-9, between H-5 and C-3, C-1, C-7 and C-9 and between H-6 and C-3, C-7, C-2 and/or C-4 served to elucidate three carbonyl carbon signals and the quaternary carbon signals in the trimellitic moiety except for C-2 and C-4. However, the observed three-bond connectivities starting from H-6 did not contribute to the discrimination of C-2 and C-4, and no two-bond connectivity could be observed between H-5 and C-4 under the three chosen conditions for the long-range coupling constant in either solvent system, resulting in an incomplete assignment with respect to C-2 and C-4. Therefore, we performed a heteronuclear ^{13}C–$\{^{1}H\}$ NOE experiment. The selective ^{13}C–$\{^{1}H\}$ NOE difference spectrum preirradiated at H-5 clearly showed NOEs at δ 137.32 ppm, which was identified as C-4, and at δ 163.72 ppm (C-9). Additionally, an identification of C-7 was also supported by selective preirradiation of H-6 showing a negative phase NOE at 137.17 ppm (C-5) and two positive phase NOEs at 134.52 ppm (C-1) and 161.81 ppm (C-7), respectively.

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Table 1. NMR data for 4-methacryloyloxyethyl trimellitates 1 and 2

	1			2	
Carbon	δC[a]	DEPT	HETCOR (δH)[a]	δC	HETCOR (δH)
1	135.00 (134.52)	C		137.76	
2	132.10 (131.69)	C		131.05	
3	125.10 (126.89)	CH	8.40 (8.65)	129.14	8.23
4	136.09 (137.32)	C		132.20	
5	136.35 (137.17)	CH	8.47 (8.58)	131.61	8.14
6	125.84 (125.92)	CH	8.22 (8.12)	128.71	7.79
7	162.40 (161.81)	C		168.13	
8	162.36 (161.72)	C		167.19	
9	163.77 (163.72)	C		164.27	
10	63.77 (64.13)	CH_2	4.63 (4.68)	63.11	4.59
11	62.14 (62.02)	CH_2	4.51 (4.54)	62.12	4.48
12	166.40 (167.08)	C		166.34	
13	135.58 (135.79)	C		135.56	
14	126.13 (126.41)	CH_2	H_a: 5.68 (5.62) H_b: 6.04 (6.15)	125.93	H_a: 5.68 H_b: 6.03
15	17.88 (18.26)	CH_3	1.88 (1.96)	17.77	1.87

[a] The chemical shifts are given in ppm from internal TMS observed in DMSO-d_6; the values in parentheses were measured in $CDCl_3$.

The same approach as exemplified above, except for the ^{13}C–$\{^1H\}$ NOE experiment, was utilized to assign all carbon chemical shifts of **2** in DMSO-d_6, and the results are summarized in Table 1. An HMBC experiment, optimized for a long-range coupling constant of 2.5 Hz, led to the complete assignment of C-4, showing a clear two-bond connectivity between H-5 (δ 8.14 ppm) and C-4 (δ 132.20 ppm) with good column resolution from C-2 (δ 131.05 ppm) and C-5 (δ 131.65 ppm), respectively.

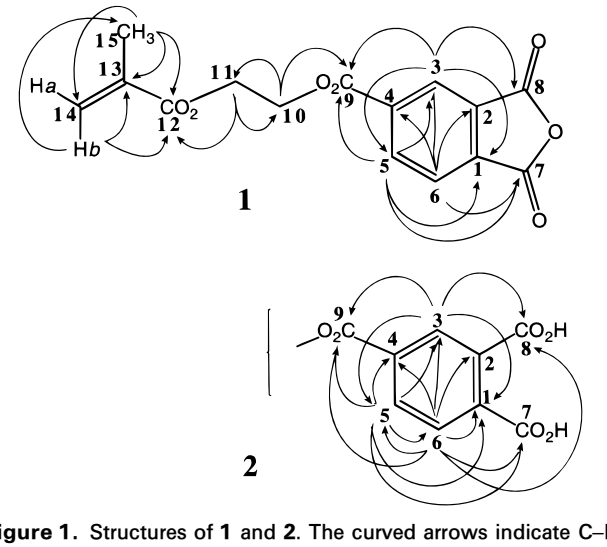

Figure 1. Structures of **1** and **2**. The curved arrows indicate C–H couplings observed in the HMBC experiments.

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