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Lignin-like Molecules: Structure and Photophysics of Crystalline α-Guaiacoxyacetoveratrone

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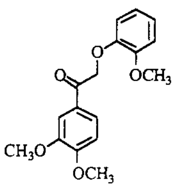
α-Guaiacoxyacetoveratrone (I) has been widely used as a lignin model in photochemical studies, and its solution photochemistry is known to resemble closely the processes which are responsible for the light-induced yellowing of lignin-rich paper products. In the solid state, I proved to be essentially photostable under lamp irradiation. Laser flash photolysis studies with diffuse reflectance detection reveal no detectable intermediate triplet states and/or free radicals. A combination of solid-state NMR, X-ray crystallography, and fluorescence studies led to the conclusion that this unexpected stability of I in the solid state is due to the stacking of molecules in an excimer-like arrangement. This leads to significant excited singlet-state stabilization, which is also reflected in a large red-shift of the fluorescence. The crystal structure of I reveals an asymmetric unit containing four molecules in different conformations; solid-state ^{13}C NMR data on I is consistent with the conformational differences revealed by the crystallographic data. It is suggested that the photostabilization that I achieves spontaneously may lead to possible ways of improving on the stability of lignin-rich products.

Introduction

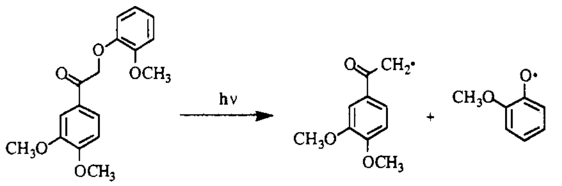
α-Guaiacoxyacetoveratrone, I, has been frequently employed as a model for the photochemistry of lignin. The



details of the solution photochemistry are now relatively well understood,[1] although a few features related to solvent effects on its excited states and decay mechanisms of its ketyl radical are worth pursuing in more detail.[2-4]

The photodecomposition of lignin which is responsible for the light-induced yellowing of lignin-rich papers takes place not in solution but in the solid state where chromophore mobility may be quite restricted. It is of interest to examine the photochemistry of models in environments where the diffusional or conformational mobility of I and other lignin models would be greatly restricted. In our laboratory we have examined briefly the phenomena involved in the laser flash photolysis of I in micelles and zeolites.[5]

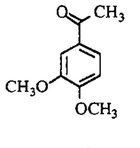
The main features of the photolysis of I in solution reveal that a considerable part of its photofragmentation occurs from the singlet state according to reaction 1.[2,3] Inter-



I II III (1)

system crossing to the triplet manifold occurs with only modest efficiency (e.g., $\Phi \sim 0.4$ in ethanol). The lowest triplet state of I has π,π^* character and typical lifetimes are $\leq 1\ \mu s$. Triplet decay involves a competition of β-aryl quenching, a well-known triplet deactivation mechanism,[6-10] and the fragmentation illustrated in reaction 1. The relevance of the latter process from the triplet manifold is strongly solvent dependent.

The triplet state of I is a very poor hydrogen abstractor, as expected from both the π,π^* character of the triplet and the low triplet energy. Acetoveratrone, IV, is basically unreactive toward hydrogen abstractions from C-H bonds.



IV

We reasoned that a good entry to the understanding of the photochemistry of I in organized and microheterogeneous systems would be to study I in the crystalline state, where the conformations and packing could be

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[1] A recent symposium held during the 203rd ACS National Meeting (San Francisco, April 1992) emphasized recent advances in this area. The papers will be published as part of the ACS Symposium Series: *Photochemistry of Lignocellulosic Materials*; ACS Symp. Ser.; Heitner, C., Scaiano, J. C., Eds.; American Chemical Society: Washington, DC, in press.

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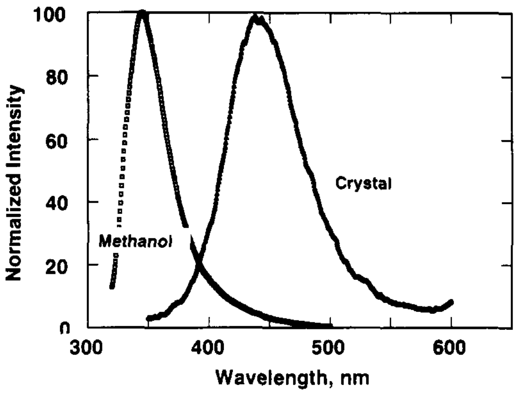


Figure 1. Normalized fluorescence spectra for I in methanol and in the solid state. Excitation wavelength 310 nm.

readily determined by X-ray crystallography and solid-state NMR. Although I proved to be essentially photostable under these conditions, structural studies have allowed a detailed understanding of the reasons for this unexpected bahavior.

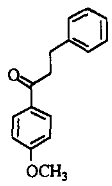
Results

This section is divided according to the technique employed. We start with photochemical methods and lead into structure determination.

Fluorescence. The fluorescence spectrum from solid crystalline I is shown in Figure 1, along with that recorded in methanol solution. While quantitative measurements of emission yields are difficult with the solid, the signals are intense and readily detectable and suggest an efficient process. Single-photon-counting studies of the decay of the fluorescence from I reveal a predominantly (>98%) monoexponential decay with a lifetime of ca. 5.0 ns. This is much longer than the emission in solution which proved to be within the time resolution of our instrument. The rise time for the emission was within the time resolution (≤0.5 ns) of our instrument.

Laser Flash Photolysis. These experiments were performed using the time-resolved diffuse reflectance technique,[11] since the samples are opaque. No evidence for the triplet state could be obtained, indicating that either the triplet is not populated or its lifetime is less than 200 ns. We note that the time resolution of the technique (usually better than 50 ns) is limited in this case by the fluorescence mentioned in the previous section.

We were concerned as to whether our failure to detect the triplet state could be due to instrumental problems and/or unusual scattering properties of the solid samples of I. To test this, we prepared a 1:3 intimate mechanical mixture of I and V. The triplet state of V has been detected



V

in the solid state in other work from our laboratory[12] and the solution spectra of triplets I and V are very similar.

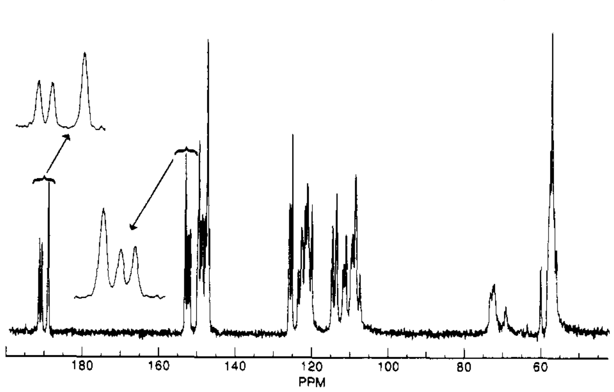


Figure 2. CP MAS NMR ^{13}C spectrum of crystalline I.

Under these conditions triplet V was readily detectable. This experiment makes us confident that the failure to detect triplet I is not due to experimental difficulties.

Solid-State NMR of I. ^{13}C CPMAS NMR studies on crystalline I reveal the presence of three different carbonyl resonances present in approximately a 2:1:1 ratio. Figure 2 shows the relevant part of the ^{13}C spectrum. The chemical shifts for the carbonyl signals are 189.62 (2), 191.35 (1), and 192.08 (1) ppm. This unexpected observation suggests the presence of two identical or very similar carbonyl groups, plus two other distinct carbonyl groups. Other positions in the molecule (e.g., C_1 in the phenoxy moiety) reveal a similar distribution. In comparison, the ^{13}C NMR spectrum of 1 in solution ($CDCl_3$, 50 MHz) shows only a single carbonyl resonance at δ 193.0.

We show below that these NMR results are fully consistent with the crystallographic data for I.

Crystallographic Data. Details on data collection, reduction, and refinement are given in the Experimental Section. Full details on the structure of I are provided as part of the supplementary material (see paragraph at end of paper). Compound I crystallizes in the triclinic system: the space group is $P\bar{1}$. The unit cell (17.314 Å × 25.127 Å × 7.2515 Å) contains four molecules per asymmetric unit, with a $Z = 2$. A stereoview of the unit cell is illustrated in Figure 3. Figure 4 shows an ORTEP plot of a set of four molecules illustrating the four basic conformations within the crystal.

Of particular interest in connection with possible triplet deactivation is the conformation of the O=C—C—O—Ar linkage between the two aromatic rings. While all molecules of I are in a cisoid conformation which appears suitable for β-aryl quenching, the distances between the carbonyl oxygen and C1 in the β-aryl rings range from 3.16 to 3.25 Å. In our experience this may be enough to induce β-aryl quenching, but very unlikely to reduce the triplet lifetime beyond our detection limit. Further, the unusually red-shifted and relatively long-lived fluorescence suggests that an alternate explanation involving processes in the excited singlet surface should be considered. Another noticeable characteristic of the crystal packing is the presence of pairs of molecules (see center of unit cell in Figure 3) with the 3,4-dimethoxybenzoyl group almost perfectly stacked in a head-to-tail arrangement. The distance between the two rings for the example in Figure 3 is approximately 3.43 Å. We note however, that a similar arrangement is achieved by the molecules of I at the edges of the unit cell, by interaction with molecules at the edge of the neighboring unit cells located at comparable distances, although in some cases the stacking of these molecules leads to a zigzag arrangement. Such arrange-

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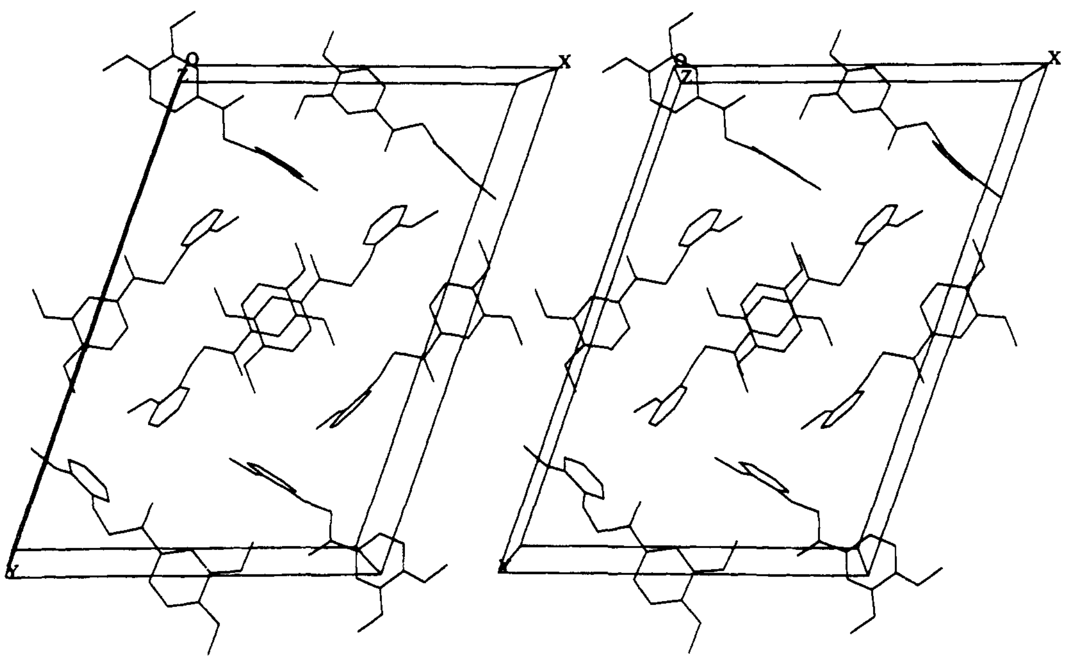

Figure 3. Stereoview of the unit cell in I.

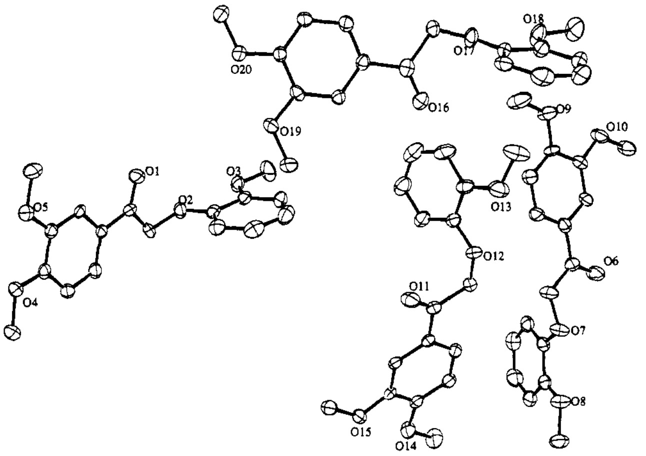

Figure 4. ORTEP diagram showing the four different molecules of I in the unit cell.

ment may not be as favorable as that for the pair of molecules in the center of the unit cell; these pairs are in turn aligned with those in neighboring unit cells leading to long range stacking of the molecules.

We show later that this molecular stacking in the crystal is likely to be responsible for the photobehavior observed.

Discussion

Clearly the key to understanding the photochemical behavior of I must be contained in the details of its solid-state structure. The fact that no transients were detected in the laser flash photolysis of crystalline samples implies that triplet states and/or free radicals are either not formed in any significant yields or are remarkably short lived. We note that since solution results show that most of the radicals are formed from the singlet state, a short triplet lifetime would not necessarily explain the failure to detect free radicals.

We thought initially that as all the molecules in the unit cell show a cisoid conformation of the O=C—C—O— moiety, there could be an efficient excited-state deactivation pathway through β-aryl quenching,[10] such as occurs in β-phenylpropiophenone[13] or α-phenoxyacetophenone.[14] However, the distance between the carbonyl oxygen and the aromatic ring in the β-position appears to be too long (even at the closest carbon) to permit an effective interaction that would make the triplet state undetectable (see Table I). At the present time the most appealing explanation is simply that the triplet state is not detectable because it is formed very inefficiently or not at all. In other words, intersystem crossing must be very inefficient.

Table I. Selected Crystallographic Parameters

	dihedral angles[a] (deg)			distances[b] (Å)	
substrate	A	B	C	D	E
I (1)	4.4	15.6	76.6	2.712	3.192
I (2)	−1.5	2.0	−85.7	2.743	3.251
I (3)	2.9	− 0.3	−81.6	2.739	3.202
I (4)	4.9	12.7	−86.8	2.717	3.165

[a] Dihedral angles: A, C_{CO}—C_1—C_2—C_3; B, O=C—C—O ether; C, C_{CO}—C—O_{ether}—C_{aryl}. [b] Interatomic distances: D, *O*=C—CH_2—*O*; E, C_{CO}—C—O—C_{aryl}.

If the singlet state decays efficiently, at least there is no experimental evidence that such a decay yields free radicals. While it is conceivable that the free radicals from reaction 1 would back-react efficiently to regenerate the starting material, it is surprising that no radicals would survive and that no ortho-ring coupling (which requires very limited motion) would take place. In the latter case we anticipate that the primary product, VI, would be readily detectable before its conversion to VII.

In fact, MM2 calculations for VI suggest that its lowest energy conformation is rather similar to that for I. Comparison of the MM2 optimized ring-coupling product with the conformation of molecules of I based on the X-ray crystallographic data indicate that minimum motion would be required for this rearrangement. While explanations based on short-lived transients (triplets and/or free radicals) that decay exclusively and rapidly to yield the starting material would be consistent with our results, the

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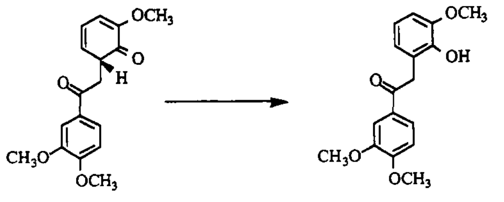

VI

VII

(2)

simplest explanation is clearly that such transients are not formed as a result of a competing efficient singlet deactivation.

The crystal packing for I actually provides a clear indication of a possible singlet deactivation mechanism. The stacking of pairs of molecules, such as that illustrated at the center of the unit cell in Figure 3, is ideally arranged for excimer-like interactions. These rings are perfectly parallel and located at a distance of 3.43 Å. Figure 5 shows a side view of this pair of molecules. We believe that the red-shifted fluorescence emission of Figure 1 is due to this arrangement of chromophores. From the shift in the fluorescence maximum, we estimate the excited-state stabilization energy at about 18 kcal/mol. Thus, the preformed dimers (or energy migration toward these sites) provide a mechanism for shifted fluorescence, as well as for efficient nonreactive decay from the singlet manifold. The two molecules involved are not perfectly overlapped but are rather somewhat shifted, as shown in Figure 5. Interestingly, pyrene crystals show very similar characteristics, with exclusively excimer emission from molecules in dimeric units separated by 3.53 Å.[15,16] The molecules are partially overlapped, just as in the case of I, and it is believed that they may tend to move toward improved overlap once excited, even if these motions are resisted by the environment. Interestingly, these distances are not very different from the characteristic interlayer spacing in graphite (3.35 Å).[17]

Of particular interest in the NMR spectrum is the carbonyl region where three resonances of 2:1:1 intensity are present. Further, one of the oxygen bearing aromatic carbon atoms also appears as a group of three resonances in a 2:1:1 intensity ratio. Although one must be careful when interpreting solid-state ^{13}C NMR data quantitatively, the data suggest that the crystal structure contains four molecules in its asymmetric unit. The number of molecules in the unit cell must therefore be a multiple of 4. Since in each group of resonances there are two of the same chemical shift, one may speculate that two of the molecules in the asymmetric unit have similar conformation; however, similar crystal packing forces may also lead to the same effect. There are no ^{13}C resonances in the enol region, indicating that this species is not present to any significant extent.

Implications for Lignin Photodegradation

The reasons underlying the detailed study of the photochemistry of I in this and other reports result from its similarity with some of the structural units present in lignin which are believed to be responsible for the light-induced yellowing of lignin-rich papers.[18-23] In general, attempts at stabilizing the color of these papers have been based on UV screens, excited state quenchers and/or free radical traps. The results obtained in this work show that I achieves excellent light stability spontaneously in the solid state by providing an energy sink for the excited singlet states via a preformed dimer that shows excimer emission and leads to little or no chemical change.

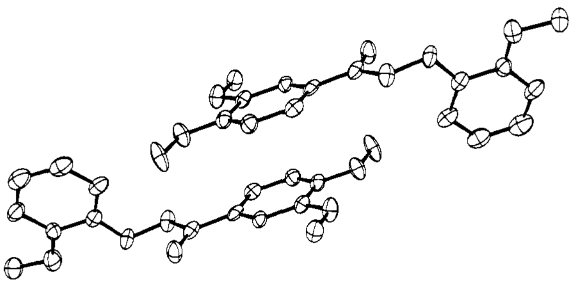

Figure 5. Side view of the central pair of molecule I in the unit cell. See Figure 3 for reference.

It is easy to see that an alternate way of stabilizing the color of lignin-rich products may involve addition of a molecule capable of forming an excimer or exciplex in a way similar to that illustrated in Figure 5. Clearly it would be preferable to utilize a molecule capable of ground-state association, so that stabilization does not rely on molecular mobility during the short singlet lifetime. It would be impractical to try to achieve this type of association for every aryl–carbonyl chromophore; to the extent that energy migration may take place, only a fraction of the chromophores would need to be stabilized. A further benefit of this approach may be that the blue fluorescence that can be expected through complexation (see Figure 1) may in fact improve the appearance of pulp and paper products.

Clearly putting these ideas to use will require considerable work in the area of energy migration and of ground- and excited-state complexation of methoxy-substituted benzoyl chromophores.

Experimental Section

Materials. α-Guaicoxyacetoveratrone was synthesized as previously described by Adler et al.[24] by the condensation of α-bromoacetoveratrone and guaiacol in dry acetone in the presence of base. The sample was >99.8% pure by gas chromatography. Acetoveratrone and guaiacol were purchased from Aldrich and used as received.

General Techniques. Fluorescence spectra were recorded, using front-face excitation, by a Perkin-Elmer LS-50 spectrofluorimeter equipped with an accessory for solid samples. Fluorescence lifetimes were measured with a PRA single-photon-counting instrument employing a hydrogen-filled lamp with a 1.5-ns pulse duration for excitation.

Steady-state photolyses were carred out in deaerated samples contained in Pyrex tubes in a photochemical reactor equipped with 300-nm lamps. Laser flash photolysis experiments using diffuse reflectance detection were carried out using for excitation a Lumonics EX-510 excimer laser operated with Xe/HCl/He mixtures (308 nm, ~6 ns, ≤35 mJ/pulse) and an experimental arrangement similar to that reported by Wilkinson et al.[11] The data were captured by a Tektronix 2440 digital scope interfaced

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via its GPIB port to a Macintosh-IIci computer operated with LabVIEW-2.2 software. This computer was also used to control the experiments and process the data.

NMR Spectra. The ^{13}C CP/MAS NMR data were collected on Bruker CXP-180 NMR spectrometer equipped with a double-tuned Doty MAS probe using a 7-mm zirconia rotor. The duration of a ^{1}H 90° pulse was 3.4 s. A 3-ms contact time was used with a 4-s relaxation delay. The spinning rate was 5.6 kHz. For each of the 548 transients, 4 K data points were collected using a sweep width of 20 kHz. The free induction decay was zero filled to 16 K points prior to Fourier transformation. No line broadening or resolution enhancement was applied to the data. The chemical shifts in the spectrum are referenced externally to the methyl resonance of solid hexamethylbenzene at 16.9 ppm. Partial assignment of the spectrum was made by acquiring a similar spectrum using the dipolar dephasing technique with a dephasing time of 40 μs. In this spectrum all resonances due to proton-bearing carbons, except those of the methoxy groups, were absent. The ^{13}C NMR spectrum in solution was recorded on a Varian Gemini 200 MHz spectrometer.

Crystallographic Data. *Data collection*: A crystal of $O_5C_{17}H_{18}$ having approximate dimensions of 0.2 × 0.2 × 0.2 mm was mounted on a glass capillary. All the measurements were made on a Rigaku diffractometer with Mo Kα radiation. Crystal data are given in Table II. Detailed information is available as supplementary material.

Cell constants and an orientation matrix for data collection were obtained from least-squares refinements using the setting angles of 25 reflections in the range 40 < 2θ < 45; these corresponded to a triclinic cell with dimensions a = 17.314(5), b = 25.127(7), c = 7.251(a) Å, α = 90.73(3), β = 93.55(3), γ = 109.309(23)°. For Z = 8 and FW = 302.32, the calculated density is 1.352 g/cm^3. On the basis of the systematic absences, the space group was determined to be $P\bar{1}$. The data were collected at −130 °C using the ω–2θ scan technique to a maximum 2θ value of 45.

Data reduction: A total of 7776 reflections was collected. The unique set contains only 7454 reflections. The standards were measured after every 150 reflections. No crystal decay was notived. The data were collected for Lorentz and polarization effects.[25] No absorption correction was made.

Solution and refinement: The structure was solved by direct methods. All the atoms were refined anisotropically except the hydrogen. The hydrogen atoms were calculated, assuming a distance C–H of 1.04 Å. All the phenyl groups were refined as rigid groups to improve the ratio of reflections/parameters.

The final cycle of full matrix least-squares refinement was based on 5632 observed reflections ($I > 2.5\sigma(I)$) and 698 variable parameters. Weights based on counting statistics were used. The maximum and minimum peaks on the final differences Fourier map corresponded to 0.340 and −0.310 e/a^3, respectively.

Table II. Crystal Data

empirical formula	$O_5C_{17}H_{18}$
formula wt	302.32
cryst shape	cube
cryst dimens (mm)	0.2, 0.2, 0.2
cryst syst	triclinic
no. of reflns used for unit	25
cell dimension (2θ range)	40–45
lattice parameters	
a, Å	17.314 (5)
b, Å	25.127 (7)
c, Å	7.251 (2)
α, deg	90.73 (3)
β, deg	93.55 (3)
γ, deg	109.31 (23)
space group	$P\bar{1}$
Z	8
D_{calc} (g cm^{-3})	1.352
F(000)	1280.59
μ (mm^{-1})	0.05
no. of reflns measd	7776
no. of reflns unique	7454
no. of reflns obsd	5632
no. of atoms	160
no. of variables	698
R_f (sign refl)	0.067
R_w (sign refl)	0.043
R_f (all refl)	0.096
R_w (all refl)	0.044
goodness of fit	5.72
last difference fourier map	
max peak	0.340
min peak	−0.310

All the calculations were performed using the NRCVAX crystallographic software package.[26]

Acknowledgment. This work has been supported by Canada's program of Networks of Centres of Excellence through the Mechanical and Thermomechemical Wood Pulps Network. Thanks are due to Dr. G. Facey for recording the NMR spectra and assisting with its interpretation and to Dr. J. A. Ripsmeester for allowing the use of the solid-state NMR facilities at the National Research Council of Canada. J.C.S. is grateful to Drs. Françoise Winnik and Peter Kazmaier for valuable discussions.

Supplementary Material Available: Complete crystallographic data for I (17 pages); table of observed and calculated structure factors (41 pages). Ordering information is given on any current masthead page.

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