

cobalticinium metal-organic complexes in the crystalline nonasil framework. The direct crystallization of aligned chromophore-zeolite composites is a promising new synthesis route for such nanocomposites, since it yields a homogeneous distribution of aligned molecules, all of which experience the same micro-environment and stabilization by the host framework. With regard to the relatively large crystals obtained in the case of $[\text{Cocp}_2^{\oplus}\text{F}^{\ominus}]$ -NON, applications in linear optical devices, e.g., as a polarizer, seem possible.

The direct incorporation of acentric or donor-acceptor substituted metal complexes^[19] during zeolite synthesis could be a way to obtain chromophore-zeolite composites with nonlinear optical properties. In parallel to this work, we report the use of other metal-organic complexes for the synthesis of zeotype compounds,^[20] and Balkus, Gabrielov and Shepelev have recently shown that the cobalticinium cation can also be used as a structure-directing agent for the formation of AlPO_4 molecular sieves, yielding AlPO_4 -5 (AFI) and AlPO_4 -16 (AST).^[21] The direct inclusion of metal-organic complexes during zeotype synthesis may thus possess a broader applicability than might have been anticipated.

Experimental

Single crystals of $[\text{Cocp}_2^{\oplus}\text{F}^{\ominus}]$ -NON of uniform size ($80 \times 140 \times 170 \mu\text{m}$) were grown according to the procedure described in [13]. For the spectroscopic measurements crystals of excellent optical homogeneity and transparency exhibiting strong and sharp extinction behavior were selected.

Light microscopic examinations in transmitted linearly polarized light and photographic documentation were performed using a Wild M400 photomicroscope from Leica (Heerbrugg, Switzerland). For the photographs a halogen illuminator and a Kodak Ektachrome EPY 64T/19° film suitable for artificial light sources was applied.

UV/vis absorption spectra on single crystals were recorded with a microscope photometer UMSP80 from Zeiss (Oberkochen, Germany) in the range from 250 to 800 nm using an XBO lamp. The optical slit width of the grating monochromator was $5 \mu\text{m}$. For the polarization experiments the transmitted light was analyzed using a Glan polarizer. The crystals were placed on a quartz plate. Its spectral transmission was used as a reference. According to the crystal size a field size of $20 \mu\text{m}$ was chosen.

Infrared absorption spectra on single crystals were registered with a FTIR microscope which was constructed as follows: A Spectra Tec Research Plan microscope was connected to a Nicolet 5SXB-E FTIR spectrometer. Polarization of the infrared radiation was achieved using a ZnSe wire grid polarizer. The crystals were placed on NaCl slides for the measurements under standard conditions. For the temperature-dependent experiments a high-vacuum cell with CaF_2 windows was used. The temperature was controlled by an Eurotherm 818 P PID controller. For further experimental details see [18].

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¹³C-CPMAS NMR Characterization and Molecular Dynamics of Oligothiophenes in the Solid State**

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The great current interest in oligothiophenes as new materials for electronic and electrooptical devices^[1] has led to an increasing demand for a better characterization of these compounds in the solid state. In fact, despite the growing number of papers dealing with oligothiophenes published in the recent literature, information about the factors determining the molecular organization, the conformational properties and the packing preferences of these compounds in the solid is still scarce.

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One of the most powerful ways to obtain such information is through X-ray diffraction studies on single crystals. Oligothiophenes, however, are difficult to crystallize, and only in recent years have X-ray structure determinations on bi-,^[2] ter-,^[3] quater-^[4] and sexithiophenes^[5] been reported. Very recently, Garnier et al. have succeeded in obtaining single crystals of unsubstituted sexithiophene, which show a very regular geometry of the thiophene units and an all-*anti* nearly planar conformation.^[6] X-ray powder diffraction studies on several oligothiophenes have also been published, furnishing data on unit cell parameters and interlayer spacing.^[7]

Information on solid-state properties can, in principle, also be obtained by ¹³C-CPMAS (cross polarization magic angle spinning) NMR. This well known high-resolution solid-state nuclear magnetic resonance technique—combining sample rotation at the magic angle, dipolar ¹H decoupling from the observed ¹³C nucleus and transfer of magnetization from proton to carbon—provides knowledge about solid-state structure and conformation, molecular dynamics and crystal modifications.^[8] CPMAS NMR has the advantage that it can be applied to solid systems lacking the long-range order required for X-ray structure determinations and that useful information can even be obtained from amorphous materials. Despite the great potential of the technique, however, only little ¹³C-CPMAS NMR data on oligothiophenes has been published so far.^[9]

We report here a ¹³C-CPMAS NMR study on the homologous series of unsubstituted oligothiophenes from bi- to sexithiophene (1–5). For comparison, some data relative to an end-capped quaterthiophene are also given (6). The aims of this work were to establish whether ¹³C-CPMAS NMR is capable of detecting changes in symmetry properties of unsubstituted oligothiophenes and of gathering information on the conformational mobility of these

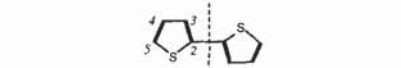
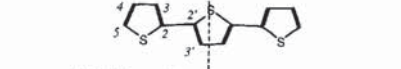

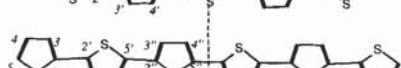
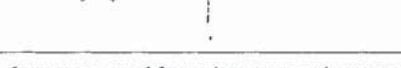

compounds as a function of the length of the aromatic skeleton.

Table 1 gives the chemical structure, the numbering scheme and the isotropic shifts (measured with respect to adamantane and scaled to TMS) of bi-, ter-, quater-, quinque- and sexithiophene. The assignment of the chemical shifts was made on the basis of NQS (non-quaternary suppression) experiments^[8d] and by analogy with available solution data.^[10] NQS experiments allow for the unambiguous identification of non-protonated (quaternary) carbons. Among each of the two classes of quaternary and protonated carbon atoms, a few assignments given in Table 1 are tentative and could be reversed. However, these ambiguities are insignificant with respect to the aims of the present work. Table 1 also gives, for comparison, the isotropic ¹³C-CPMAS shifts of 5,5''-dimethyl-2,2':5',2'':5'',2'''-quaterthiophene **6**, a compound whose single-crystal X-ray structure has already been reported and discussed in detail.^[4a,b]

It can be seen that on increasing the number of thiophene units there are variations in the isotropic shifts of comparable carbon atoms which do not exceed 2.0 ppm. Since ¹³C-CPMAS isotropic shifts are very sensitive to conformational changes,^[8a] this indicates that compounds 1–5 have similar conformations in the solid state, in agreement with X-ray data.^[2–7]

The ¹³C spectra of bi-, ter- and quaterthiophene in solution (quinque- and sexithiophene are insoluble) show a number of signals which is half the number of carbon atoms, owing to molecular symmetry that makes the two halves of the molecule equivalent. Thus, for example, the ¹³C spectrum of bithiophene in chloroform consists of four resonances, two of which are separated by only 0.5 ppm. In a solid, such a resolution cannot be achieved and in the ¹³C-CPMAS spectrum of bithiophene only three signals, approximately in 1:1:2 signal intensity ratios, were detected.

Table 1. Structure, numbering scheme and ¹³C-CPMAS isotropic shifts^[a] of compounds 1–6.

	C ₂	C ₃	C ₄	C ₅	C _{2'}	C _{3'}	C _{4'}	C _{5'}	C _{2''}	C _{3''}	C _{4''}	C _{5''}	
	138.7	124.8	128.8	124.8	(1)								
	139.4	125.3	128.9	122.9	136.4	125.3	(2)						
	137.7	126.6	128.0	124.4	135.9	126.6	124.4	137.7	(3)				
	139.4	126.5	128.3	124.4	135.7	126.5	124.4	136.6	135.7	124.4	(4)		
	137.3	124.6	127.1	125.1	135.9	127.1	124.6	137.3	135.9	127.1	124.6	137.3	(5)
	139.5	125.1	127.6	136.7	136.5	125.1	122.3	136.7	(b)	(6)			

[a] In ppm, measured from adamantane and converted to TMS. (b) $\delta_{Me} = 13.0$ ppm.

Not only for **1**, but also for **3**, **5** and **6**, we found that the number of lines detected in the solid was less than half the number of carbon atoms, with some lines being twice or even three times more intense than the others. Thus, within the limits of linewidth resolution, in the solid state spectrum of bi-, quater- and sexithiophene as well as in dimethylquaterthiophene, the asymmetric unit is half a molecule. This is in agreement with X-ray data which indicate a nearly planar centrosymmetric conformation for these compounds and a unit crystal cell containing two or four molecules (in *one* set of crystallographically independent molecules).^[2-7] The effects of symmetry and of chemical shift equivalence are well illustrated by the spectrum of 5,5^{'''}-dimethylquaterthiophene **6**, which is shown in Figure 1.

In principle, the symmetry elements of unsubstituted oligothiophenes will depend on whether they are planar or twisted or exist as *syn* or *anti* conformers. Assuming, in agreement with literature data, that, in the solid state, oligothiophenes **1-5** are all-*anti* and quasi planar,^[2-7] it follows that only even-numbered oligothiophenes (**1**, **3**, **5** and **6**) can possess an inversion center, located in the middle of the inner carbon-carbon bond, whereas odd-numbered oligothiophenes (**2** and **4**) can only possess either a plane or an axis of symmetry, which bisect the central ring.

Examination of Table 1 shows that, in terms of isotropic shifts, the ¹³C-CPMAS technique is capable of distinguishing between even- and odd-numbered oligothiophenes. In fact, in ter- and quinquethiophene the signal of the terminal quaternary carbon, C-2, splits into two peaks, contrary to even-numbered oligothiophenes for which only a single peak for every carbon, including C-2, was always observed. Figure 2 shows the 132-142 ppm region of the CPMAS spectrum of ter- and quinquethiophene, showing the splitting of carbon C-2 in both compounds.

As far as we are aware, there are two possible explanations for the splitting of the C-2 resonance observed for odd-numbered oligothiophenes. The first, is that in ter- and

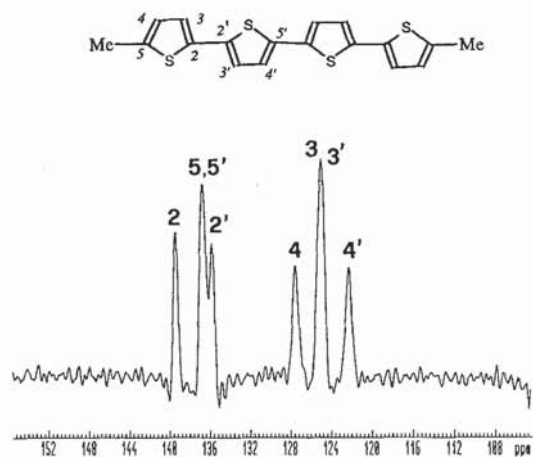


Fig. 1. ¹³C-CPMAS spectrum of 5,5^{'''}-dimethyl-2,2':5',2'':5'',2'''-quaterthiophene obtained at $T = 27^\circ\text{C}$ with a contact time of 1.3 ms.

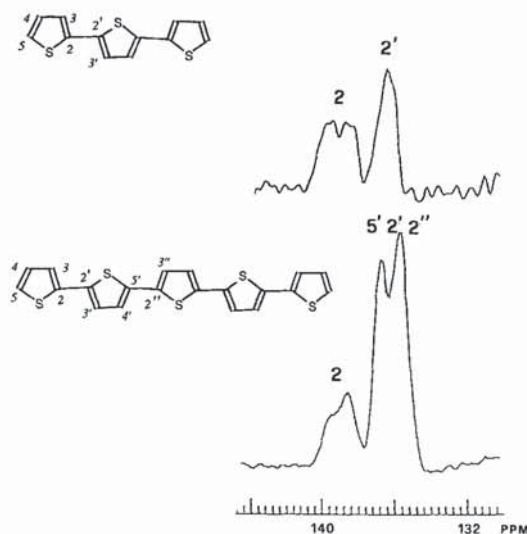


Fig. 2. 132-142 ppm region of the ¹³C-CPMAS spectrum of terthiophene **2** (top) and quinquethiophene **4** (bottom) showing the splitting of the terminal carbon C-2.

quinquethiophene the torsion angle formed by one of the terminal rings with the adjacent thiophene unit is different from that formed by the other terminal ring. The second, is that the unit cell of the microcrystalline sample used for the ¹³C-CPMAS experiment contains *two* sets of crystallographically independent molecules, which experience a different chemical environment. It is known, in fact, that splitting of the resonances is found in CPMAS spectra when molecules are located at crystallographically non-equivalent positions in the unit cell.^[8] In the first, as well as in the second case, one would expect each carbon in the molecule to be split. The fact that in **2** and **4** only the splitting of carbon C-2 is experimentally observed depends on the greater sensitivity of this nucleus to the effect and also on the linewidths.

According to the data reported in the literature on the single crystal X-ray structure of terthiophene,^[3a] the conformation of this compound in the crystal is such that the outer rings are rotated around the C-C bonds connecting them to the inner ring by nearly the same amount, namely 6-9°. Moreover, the crystal unit cell does contain 8 molecules in *two* sets of crystallographically independent molecules.^[3a] A difference of 1-3° in the interring twist angles can hardly justify in itself the marked splitting of the C-2 resonance of terthiophene reported in Figure 2. Thus, the observed splitting is either entirely due to the different chemical environments of the two types of crystallographically independent molecules contained in the unit cell of terthiophene (see Fig. 2 of [3a]) or it is the result of the joint effects of both factors acting in the same direction.

No single-crystal X-ray diffraction data are available for quinquethiophene. By analogy with terthiophene, the fact that the ¹³C-CPMAS spectrum of quinquethiophene also displays the splitting of carbon C-2 would suggest that the

unit cell of the microcrystalline sample of quinquethiophene used for the CPMAS experiment has the same characteristics as those of terthiophene. However, this suggestion is not in agreement with the results of a powder X-ray diffraction study, indicating that the packing arrangement of quinquethiophene is similar to that of quater- and sexithiophene (four molecules in *one* set of crystallographically independent molecules in the unit cell) rather than to that of terthiophene.^[7b] According to the authors of this study, symmetry considerations between even- and odd-numbered oligothiophenes, which could be relevant *a priori*, are actually not very important. However, according to our results, if the splitting of C-2 in the ¹³C-CPMAS spectrum of quinquethiophene is due only to conformational reasons, then the conformation of this compound in solid must be much more distorted than predicted.^[7b]

Clearly, more work should be carried out to better understand the solid state properties of odd-numbered oligothiophenes. It is worth noting in this respect, that most X-ray studies carried out so far concern even-numbered and centrosymmetric oligothiophenes (which are easier to synthesize) and that single-crystal X-ray structure determinations have been reported only for two odd-numbered oligothiophenes, namely terthiophene and one of its trimethyl-substituted derivatives.^[3a,b]

Solid-state NMR may give valuable information on the motion of molecules in solids.^[8] Indeed, signal enhancement by cross-polarization implies that signal intensities are influenced by the kinetics of the transfer of magnetization from ¹H to ¹³C. Molecular mobility averages carbon-proton dipolar interactions and makes the cross-polarization process less efficient. In consequence, mobile molecules give poor quality spectra. To improve the signal-to-noise ratio a much longer contact time (time during which proton magnetization is transferred to carbon) than that employed for rigid molecules is required. The improvement of the signal-to-noise ratio is also obtained by lowering the temperature and thus limiting the degree of conformational mobility of the substrate.

According to ¹³C-CPMAS spectra obtained with variable contact times and temperatures, the conformational mobility of 1-5 in the solid state reaches a maximum in quaterthiophene and decreases markedly in quinque- and sexithiophene.

Figure 3 gives the ¹³C-CPMAS spectra of quaterthiophene at *T* = 27 °C, with contact times of 5 and 64 ms, and at *T* = -30 °C, with a contact time of 1 ms. At 27 °C and with a 5 ms contact time the spectrum is of poor quality, and the signals corresponding to the quaternary carbons are scarcely above the level of the noise even for 4000 scans. Long contact times (64 ms) are required to obtain the increase of the signal-to-noise ratio and the substantial growth of the signals of the quaternary carbons. By lowering the temperature to -30 °C, however, a good quality spectrum is obtained by using a contact time of only 1 ms and 400 scans, indicating that a much more efficient cross-

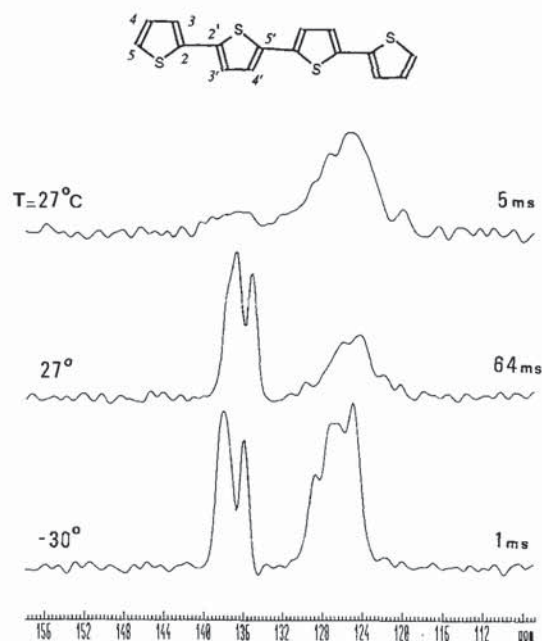


Fig. 3. ¹³C-CPMAS spectrum of quaterthiophene **3** at variable temperatures and contact times (*t_c*). From top to bottom: *T* = 27 °C, *t_c* = 1 ms; *T* = 27 °C, *t_c* = 64 ms; *T* = -30 °C, *t_c* = 1 ms.

polarization process is taking place, due to the conformational freezing of the molecule.

The freezing of the molecular motion of quaterthiophene is also obtained by replacing the terminal hydrogens with methyl groups. This is illustrated in Figure 1, which shows the spectrum of the dimethyl-substituted quaterthiophene **6**. In contrast to unsubstituted quaterthiophene, for this dimethyl derivative a contact time of 1.3 ms and 300 scans are sufficient to give a good quality spectrum. The behavior of **3** as a function of the temperature and of the contact time is indicative of a great degree of conformational mobility at room temperature.^[8]

The high conformational mobility of unsubstituted quaterthiophene is probably one of the reasons why crystals suitable for X-ray structure determinations have not yet been obtained for this compounds while, on the contrary, several X-ray diffraction studies of single crystals of α and β methyl-substituted quaterthiophenes have been reported.^[4] The analysis of the nature of the conformational motions of quaterthiophene by the CPMAS technique would require detailed studies of the relaxation times of individual carbon atoms which are beyond the aim of this study.

Results of quantum-mechanical and force-field calculations would suggest that *anti* \rightleftharpoons *anti* conformational equilibria are more probable than *syn* \rightleftharpoons *anti* ones, owing to lower energy barriers.^[10,11] However, this is only speculative since, owing to lattice constraints, conformational processes have generally much higher activation energies in the solid state than in solution or in gas phase and, moreover, in solids, other interactions could be present which do not exist in solution or in the gas phase.

Quinque- and sexithiophene **4** and **5** appear to be much more rigid structures than quaterthiophene, more in line with what is generally observed for organic solids. Indeed, not only good ^{13}C -CPMAS spectra could be obtained with short contact times (1 ms) and a low number of scans even at the probe temperature (27 °C) for both compounds, but variable temperature experiments carried out in the range $-60 \leq T \leq +90$ °C showed relatively little modifications of cross-polarization in response to temperature changes. In sexithiophene, only at 90 °C and for long contact times (64 ms) some signals (those pertaining to C3, C4' and C4'') decrease in intensity more rapidly than the others, indicating a certain degree of conformational mobility of the molecule.

In conclusion, we have shown that ^{13}C -CPMAS NMR is capable of detecting changes in symmetry properties of unsubstituted oligothiophenes and of discriminating between odd- and even-numbered oligothiophenes, the former being characterized by the splitting of the terminal quaternary carbon. One point which is still to clarify is whether and to what extent this splitting can be related to the packing properties of the substrates. ^{13}C -CPMAS NMR also allowed us to establish that quaterthiophene is very peculiar as it shows a much higher degree of conformational mobility in the solid state than all the other oligothiophenes. In particular, quaterthiophene is conformationally much more mobile than sexithiophene which should be regarded, in contrast, as being characterized by a rather 'rigid' aromatic skeleton.

Experimental

Materials: Samples were prepared according to literature methods [9,12] and purified by sublimation. Bithiophene was a commercial (Aldrich) sample used without further purification.

CPMAS experiments: ^{13}C -NMR solid-state spectra were obtained using a Bruker CXP-300 spectrometer operating at 75.45 MHz. The samples were packed into a 7 mm rotor that was spun at the magic angle with a spinning rate of the order of 3–4 KHz. The 90° ^1H pulse duration was 5 ms which was also the value for the ^{13}C as set by the Hartmann–Hahn conditions [8d]. For the cross-polarization the contact times ranged between 1 and 64 ms, while the recycle delay for CP experiments was 8 s and the number of transients required to achieve a good signal to noise ratios varied with the circumstances. The spectrometer was equipped with a BVT-1000 variable temperature device. The low temperatures were obtained by a flow of dry nitrogen precooled in a heat exchanger immersed in liquid nitrogen and were calibrated using the shifts of samarium acetate resonances. High temperatures were obtained by direct heating of the air flow used for spinning the sample. The chemical shifts (with an approximation of 0.5 ppm) were measured with respect to the lower frequency signal of adamantane and scaled to TMS using a $\delta_{\text{TMS}}(\text{adamantane}) = 29.4$ ppm.

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Spontaneous Magnetization in a 2:3 Complex Formed by 3,4',5'-Tris(*N*-oxy-*tert*-butylamino)biphenyl and Manganese(II)-bis(hexafluoroacetylacetonate)*

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The search for molecular materials with strong magnetic properties remains of great interest.^[1] Together with assemblies of entirely 3d spins of metal complexes and those of 2p spins of purely organic radicals, the heterospin systems consisting of transition metal ions and organic free radicals as ligands constitute one of the mainstreams of such studies.^[2,3] The ligands employed are often organic mono-radicals that have two ligating sites, e.g., semiquinones^[3]

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