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NONEXPONENTIAL PROTON-SPIN-LATTICE-RELAXATION AND INTERNAL MOTION IN BIPHENYLTRICARBONYLCHROMIUM COMPOUNDS

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Summary

Nonexponential relaxation of methyl signals in some chromium carbonyl complexes of diphenic acid derivatives has been analysed by direct observation of the two coincident compounds of a methyl signal after a 180° pulse. From these observations correlation times for internal rotation of the methyl group and local reorientation were determined. This method should be generally applicable to the study of internal motion, association behaviour, and solute solvent interactions in medium or large molecules bearing methyl groups.

Introduction

Complexation of various diphenic acid derivatives with hexacarbonyl chromium leads to biphenylmono- and bis-tricarbonylchromium compounds [1]. Photochemical removal of the $Cr(CO)_3$ moiety is possible and has been used to prepare various optically active compounds [2,3] via their diastereomeric tricarbonyl chromium complexes. Recently configuration [1], conformation [4] and chiroptical properties of some $Cr(CO)_3$ complexes of diphenic acid derivatives have been investigated. NMR spectra have made valuable contributions during this work. In some cases, e.g. diphenic acid dimethylestermonotricarbonylchromium (Fig. 1), the assignment of the ester methyl groups based on chemical shift arguments could not be made unambiguously. On the other hand, methyl relaxation measurements have been shown to provide solution to difficult assignment problems and moreover give valuable information about the dynamic behaviour of the molecules in solution [5—11]. We have investigated the relaxation behaviour of the ester methyl groups in compounds 1—4. In addition to the assignment of the ester methyl signals in compound 2 we were able to get the correlation times for internal rotation of the methyl groups and for the overall motion of the ester fragments.

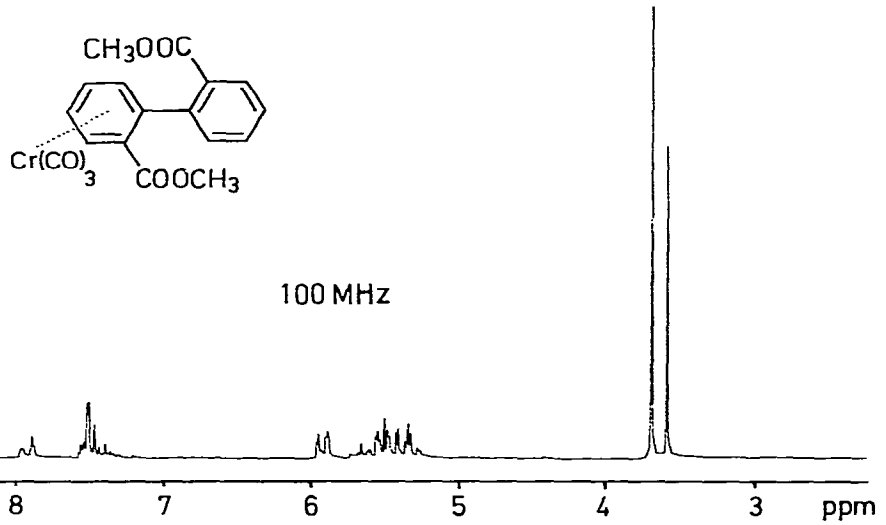


Fig. 1. ^{1}H NMR spectrum of compound **2** in $CDCl_3$.

Theory

The relaxation behaviour of a triad of three identical spin 1/2 nuclei, e.g. a methyl group, can be understood by recalling that the total magnetization can be described as a composite of two submagnetizations. A methyl group can be represented by a doublet and a quartet state with total groups angular momentum of 1/2 and 3/2 respectively [12]. In the simplest approximation each submagnetization is characterized by an intrinsic relaxation rate. These relaxations are coupled by cross relaxation and mixed into two components M_A and M_B

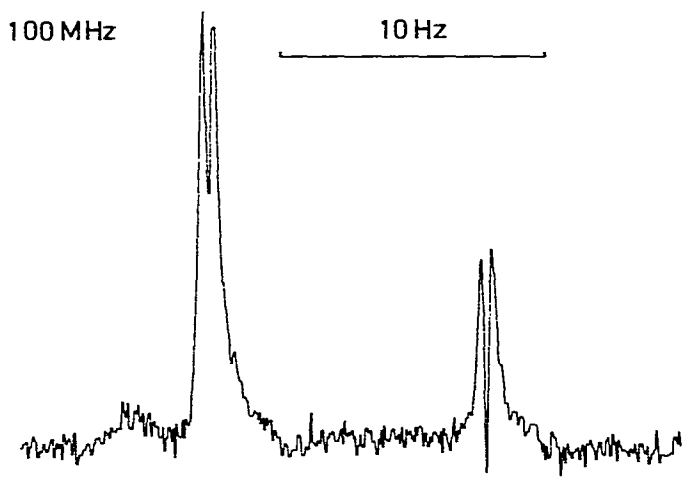


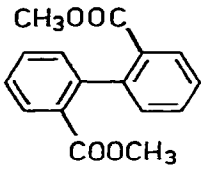
Fig. 2. Partially relaxed ^{1}H NMR spectrum of the methyl groups of compound **2**, 1.7 s after the 180° pulse.

which are coincident [9] but have different relaxation times T_{1A} and T_{1B} [6], thus leading to nonexponential relaxation of the methyl signal. After a 180° pulse the A and B components relax independently, so that near the null point the faster-relaxing component may be positive, while the other component is still negative. As long as the extreme narrowing approximation is valid, both components have different T_2 values and the spectrum after a 90° pulse shows a broad positive line with a superimposed sharper negative line. (Fig. 2). From a series of several spectra taken at different times after the 180° pulse one can get the individual null points for both components A and B. By comparing theoretical and observed line shapes we obtained the relative intensities of the A and B components α.

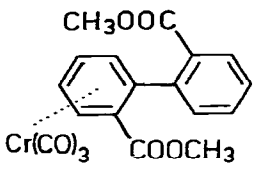
Assuming that the methyl group is rotating relative to an isotropically reorienting frame work one can define two different correlation times for the motion about the methyl axis τ_M and the motion of the axis τ_C. It has recently been shown [6] that analysis based on the theoretical considerations of Bain and Lynden-Bell [13], can give the correlation times τ_M and τ_C.

Results and discussion

We have analysed the nonexponential methyl relaxation of the compounds 1—4 by fitting the theoretical to the experimental line shapes by a computer program, thus giving "best values" for T_{1A}, T_{1B} and α. From these the programme gave τ_C and τ_M, on the assumptions that dipolar relaxation is dominant and the random field is uncorrelated (Table 1).



(1)



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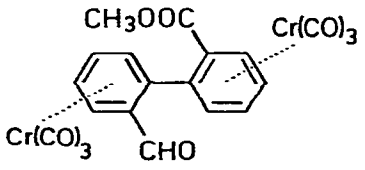
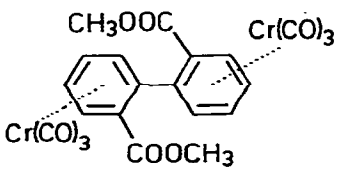


(3)
"racemic" [1]



(4)
"racemic" [1]

Comparing the τ_C values of compound 1 one can see that the correlation time for the overall motion is somewhat longer in the more concentrated solution, whereas the internal rotation τ_M is essentially the same. The slower overall motion in the more concentrated solution may be caused by increased viscosity or enhanced stacking. Thus these measurements provide a method for the study of the stacking behaviour of big molecules in solution [10].

TABLE 1

RELAXATION TIMES AND CORRELATION TIMES FOR THE OVERALL MOTION τ_C AND THE INTERNAL ROTATION τ_M

Compound	T_{1A} (s)	T_{1B} (s)	α (%B)	τ_C (ps)	τ_M (ps)	Concentration (mol l^{-1})
1	3.0 ± 0.1	4.8 ± 0.6	18 ± 2	12.2 ± 1.4	3.4 ± 0.8	0.19
1	2.61 ± 0.03	4.9 ± 0.4	17 ± 5	15.6 ± 1.3	3.2 ± 1.3	0.60
2 [a]	1.76 ± 0.05	3.9 ± 0.2	24 ± 2	26.0 ± 1	2.3 ± 0.3	0.12
2 [b]	2.06 ± 0.1	3.8 ± 0.3	24 ± 2	20.1 ± 0.8	3.1 ± 0.8	0.12
3	2.01 ± 0.03	3.2 ± 0.4	18 ± 3	18.3 ± 1.9	5.0 ± 1.6	0.05
4	1.77 ± 0.1	3.7 ± 0.5	17 ± 4	24.4 ± 2.4	3.9 ± 1.6	0.05

[a] Low field methyl signal. [b] High field methyl signal.

The overall correlation times of compound 2 are about twice as long, showing that the chromium tricarbonyl group is slowing down the overall motion of the molecule. One of the methyl signals shows a significantly shorter τ_C value than the other. As the correlation times τ_C do not apply to the whole molecule, but to the local ester framework about which the methyl group is rotating, it is clear, that the phenyl ring, which is bearing the $Cr(CO)_3$ group, has a somewhat decreased internal mobility and that the methyl group connected to this phenyl group must have a longer τ_C value. We can therefore assign the low field methyl signal to this ester methyl group. Compounds 3 and 4 (both of which are *meso*-forms) were measured in more diluted solutions, but have nevertheless high τ_C values showing the influence of both $Cr(CO)_3$ groups on the overall motion. In all cases τ_M, the correlation time for the internal methyl rotation is about the same.

Conclusion

Molecular motion and internal mobility of medium or large molecules can be studied by analysis of the nonexponential relaxation of methyl groups. This method has been used previously for the study of internal motion, association behaviour and signal assignment in large molecules [6,10] and is generally applicable provided that the anisotropy of motion is within a certain range [6]. As the method depends on observing two coincident signals with different values of both T_1 and T_2, there is another condition, namely that the observed line width is mainly determined by T_2. Unresolved long range couplings may obscure the differential width. In this case or under conditions of poorer resolution the methyl signal appears as a single line in a T_1 experiment, which does not decay exponentially. This has been observed in several molecules and analysed into the sum of two exponentials [11,14,15] giving the same information, but this procedure is less easy to perform accurately.

Experimental section

The preparation of the substances 1, 2 and 4 has been previously described [1]. The preparation of compound 3 will be described elsewhere. All inversion

recovery experiments were performed on a Varian XL-100-15 spectrometer. The system computer (Varian 620L-100, 16k core) allowed acquisition of 8k data points. The transformed spectrum was thus represented by 4k (4096) data points. (0.06 Hz per data point at 250 Hz spectral width). The shape of the resonance line was thus represented by 20—40 data points, they were stored using a 2k transient recorder (Biomation Model 805), transferred to a tape and via a Silent 700 ASR Texas Instruments Data terminal to a CDC Cyber 73 Computer. With the two measured quantities t_A and t_B (the null points of the component A resp. B) and a reasonable estimate for α, theoretical line shapes were computed and fitted to the experimental line shapes [15], thus giving corrected values for T_{1A}, T_{1B} and yielding τ_M and τ_C. All measurements were made in sample tubes of 5 mm diameter. The solvent ($CDCl_3$) was filtered through Al_2O_3 and Ar was bubbled through the solutions for several minutes. The temperature in the probe was 34°C and the field homogenity was kept as high as possible. The deuterium resonance of the solvent served as field frequency lock. The 90° pulse was 24 μs.

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