The application of resolution enhancement techniques to the study of factors affecting group frequencies—I. Coupling of symmetric methyl deformation frequencies in o-xylene

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(Received 20 August 1984)

Abstract—Deconvolution of methyl symmetric deformation frequencies of o-, m- and p-xylene yields a fully resolved doublet with 10 cm^{-1} spacing in o-xylene, but singlets in m- and p-xylene. Resolution enhancement of the methyl bending mode of 1-methyl-2-[methyl- d_3]-benzene yields a single band near 1380 cm⁻¹. The relative intensity of the heavy to light band systems is ~ 0.4 . The data indicate that spatial coupling exists between the symmetric methyl deformation modes of o-xylene.

INTRODUCTION

The characteristic doubling of the symmetric methyl deformation frequency in isopropyl, gem-dimethyl and t-butyl systems has been recognized for some time [1]. The effect is often implied [1, 2, 3] to involve valence bond coupling to give rise to in-phase and out-ofphase modes. SHEPPARD et al. [4] established, however, that this splitting increases to a maximum in the case of dimethyl gold(III) derivatives (square planar complex). The massive gold atom insulates the terminal methyl groups from any type of coupling through the valence bond system. An alternative mechanism involving a steric interaction term has been proposed for these compounds by TOBIAS et al. [5] and also for the apparent coupling in the carbon analogs [6, 7, 8]. The observation [6, 7] that the magnitude of Δv is inversely proportional to the C-C-C bond angle adds further support to the latter argument. The band separation in carbon systems is found to be $\sim 20 \text{ cm}^{-1}$ at 109° and near 0 cm^{-1} at 120°. The in-phase mode would be expected to be polarized in the Raman effect and to occur at higher frequencies than the out-of-phase mode in the sterically crowded systems. As the central angle opens up, the spatial interaction decreases and, as at wide angles the opportunity for valence bond coupling would become maximized, the two modes might be expected to reverse position under these conditions. This latter possibility appears to be observed in the case of acetone [9] (argon matrix, $\Delta v \ 8 \ \text{cm}^{-1}$).

Further support for the idea that steric interaction is

responsible for the splitting of symmetric methyl deformations in crowded aliphatic systems can be found in aromatic molecules possessing methyl substituents rigidly held so that spatial interactions approximate to the tetrahedral *gem*-methyl condition.

The simplest possible example of this type to be found is the series o-, m- and p-xylenes [6, 10]. In this case the *meta*- and *para*-derivatives possess clear sharp singlets whereas the *ortho*-derivative possesses a poorly resolved doublet. Similar band shapes with somewhat more highly resolved splitting can be found in the case of 1,12-dimethylbenzo[c]phananthrene, 1',9-dimethyl-1,2-benzanthracene and 4,5-dimethylphananthrene [6].

While data consistent with a steric interaction term have been observed, no direct evidence of coupling has been obtained in any of these series.

EXPERIMENTAL

Synthesis of 1-methyl-2-[methyl-d₃]-benzene

By employing the coupling reaction described by TAMAO et al. [11, 12], 1-methyl-2-[methyl- d_3]-benzene was synthesized from 2-chlorotoluene in the following manner. Into an ovendried 50-ml three-necked flask fitted for nitrogen purge were placed 1.39 g (0.0572 mole) of magnesium ribbon with the surface oxide removed and 20 ml of anhydrous ether. Following N₂ purge methyl iodide- d_3 , 8.292 g (0.0572 moles), dissolved in 5 ml of anhydrous ether, was added (equalizing addition funnel) over a 20 min period with stirring (magnetic). The reaction mixture was then refluxed for 40 min.

Into an oven-dried 250-ml three-necked flask equipped with magnetic stirring bar were placed 5.06 g (0.04 moles) of 2-chlorotoluene, 65 mg of dichloro-[1,3bis(diphenylphosphino)propane]nickel(II) and 30 ml of anhydrous ether. The methyl- d_3 magnesium iodide previously prepared was then added over a 10 min period to the reaction flask with stirring. The resulting reaction mixture, which developed a green coloration, was first stirred for 2 hr and then refluxed for 18 hr. Over the latter period of time the

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reaction mixture turned a brownish-black. The reaction product was cooled in an ice-bath and hydrolysed with 2 N HCl. The organic layer was washed with distilled water (15 ml), saturated sodium bicarbonate, 10% sodium thiosulphate and distilled water. The ether layer was then dried over anhydrous calcium chloride and filtered. Removal of the solvent yielded 1-methyl-2-[methyl-d₃]-benzene, 3.67 g (84\% yield).

The product possessed a single band on gas chromatographic analysis with a retention time identical to that of *o*-xylene. The i.r. spectrum confirmed that no starting material was detectable in the product.

o-, m- and p-Xylene were obtained from Polyscience as "Quantitative Grade". Methyl- d_3 iodide and o-chlorotoluene were obtained from Aldrich Chemical Co. The dichloro[1,3-bis(diphenylphosphino)propane]nickel(II) was freshly prepared [12].

Spectra were obtained with a Perkin-Elmer model 1500 Fourier transform i.r. spectrophotometer interfaced with a model 3600 data station. Data were collected by storing 128 scans at one point/wavenumber, with trapezoidal apodization and no zero filling to give an effective resolution of

1379 cm⁻¹ respectively) indicated no observable substructure to these bands. The 1380 cm^{-1} band of oxylene, however, is clearly shown to possess a weaker shoulder on the low frequency side which becomes fully resolved following treatment by smoothing and difference routines. The band centers in the fully deconvolved spectra occur at 1385 and 1375 cm⁻¹ (see Fig. 1a). In order to establish that the resolution enhancement manipulation of the data is not responsible for generating sideband artifacts in the spectrum of o-xylene, we have undertaken the synthesis of isotopic derivatives of this system. The preparation of 1-methyl-2-[methyl-d₃]-benzene has been carried out in excellent yield by coupling o-chlorotoluene with methyl- d_3 magnesium iodide in ether employing dichloro-[1,2bis(diphenylphosphino)propane [nickel(II) as the catalyst.



Reflux 18 hr

4.0 cm⁻¹. Resolution enhancement [13] was achieved by employing a 13-point Golay–Savitzky smoothing function and subtracting the smoothed spectra from the unsmoothed data with a difference factor of 0.84916. (Collection in half range mode of 1280 scans storing one point/0.5 cm⁻¹ with trapezoidal apodization and no zero filling to give an effective resolution of 2 cm⁻¹ yielded deconvolved spectra with essentially an equivalent absorption profile to the above routine.)

RESULTS AND DISCUSSION

Deconvolution of the singlet bands occurring in the 1380 cm^{-1} region of *m*- and *p*-xylene (1377 and



These observations strongly support the assignment of the deconvoluted doublet in o-xylene to spatially coupled symmetric methyl deformation modes as deuterium substitution would be expected to result in collapse of the doublet to a singlet possessing a



Fig. 1. (a) Deconvoluted band system of o-xylene. (b) Deconvoluted band system of 1-methyl-2-[methyl- d_3]-benzene.

wavenumber value near 1380 cm^{-1} with approximately one-half the intensity of the doublet. In addition, the observed behavior of the deuterium derivative also supports the interpretation of the deconvolution results with the light system.

The data offer *direct* evidence of methyl deformation coupling in aromatic systems. As suggested above, the most likely mechanism to support this coupling is through a spatial interaction term.

The use of deconvolution techniques in combination with deuterium isotopic substitution would appear to offer a powerful approach to extending the interpretation of factors affecting group frequencies in relatively complex molecular systems.

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