590. *The Infrared Spectra of Deuterium Compounds. Part I. The* C–H *Stretching Bands of* OMe *and* NMe *Groups.*

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The assignment of specific bands in the CH stretching region of the infrared spectrum to OMe and NMe groups [1,2] has been confirmed by examining compounds containing trideuteromethyl groups.

Previously [1,2] it was shown that attachment of a methyl group to oxygen or nitrogen causes displacement of the CH stretching bands from the positions normally found with hydrocarbons. This led to a spectrographic method for detecting methoxyl and various types of methyl- and dimethyl-amino-groups: the validity of the correlations proposed has now been confirmed by examining trideuteromethyl compounds.

Trideuteromethyl bromide [3] was prepared *via* diacetyltartaric anhydride, carbon suboxide, tetradeuteromalonic acid, and tetradeuteroacetic acid. Although each step is known,[4] the procedures (see Experimental section) developed for the reaction of carbon suboxide with heavy water (dioxan as solvent) and for the decarboxylation of the deuteromalonic acid are simpler and more effective than previous ones. Reaction of the bromide with the sodium salts of cyclohexanol, phenol, and acetanilide (and subsequent acid hydrolysis in the last case) gave the trideutero-compounds whose infrared spectra are shown in the Figure. Comparison of methoxy- and [$^2H_3$]methoxy-cyclohexane (curves 1 and 2) supports the assignment [1] of the 2975 and 2817 cm.$^{-1}$ bands to the methoxy-group, since these bands are absent from the spectrum of the deuterated compound. Similarly, the peaks at 2835 cm.$^{-1}$ in anisole (curve 3) and at 2814 cm.$^{-1}$ in *N*-methylaniline (curve 5) are shown to be the most useful ones for detecting these methyl groups. (The frequencies and intensities of the bands mentioned differ slightly from those previously reported: [1,2] the present results were obtained under higher dispersion and are therefore to be preferred.)

The bands at 2933 and 2854 cm.$^{-1}$ in methoxycyclohexane are primarily associated with the antisymmetric and symmetric CH stretching vibrations of the methylene groups. However, in the deuterated analogue these bands (particularly the higher-frequency component) are weaker, and it is unlikely that removal of the neighbouring methyl absorption is the sole cause of this effect. [The decrease ($\Delta\varepsilon = 70$) in the 2933 cm.$^{-1}$ peak is greater than the intensity ($\varepsilon = 55$) of the adjacent methyl band.] This suggests that the methoxy-group in ethers, as in methyl esters,[5] gives more than two bands in the CH stretching region: the presence of at least three bands in the CD stretching region of [$^2H_3$]methoxy-cyclohexane (see Fig.) supports this conclusion.

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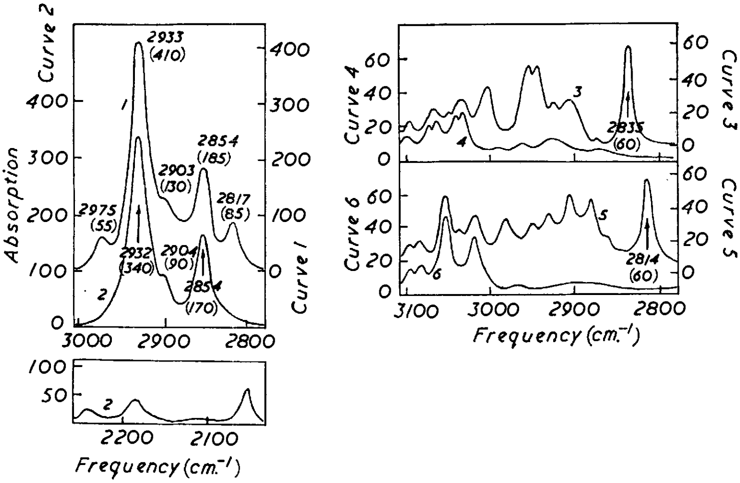
[1] Henbest, Meakins, Nicholls, and Wagland, *J.*, 1957, 1462.
[2] Hill and Meakins, *J.*, 1958, 760.
[3] Leitch and Nolin, *Canad. J. Chem.*, 1953, **31**, 153; Leitch and Renaud, *ibid.*, 1956, **34**, 179.
[4] For references see Murray and Williams, "Organic Syntheses with Isotopes," Interscience Publishers Inc., New York, 1958, pp. 1262—1264.
[5] Nolin and Jones, *Canad. J. Chem.*, 1956, **34**, 1382.

Absorption spectra of (1) *methoxy- and* (2) [$^2H_3$]*methoxy-cyclohexane;* (3) *methoxy- and* (4) [$^2H_3$]*methoxy-benzene;* (5) N-*methyl- and* (6) N-[$^2H_3$]*methyl-aniline.*



(The absorption scales are in mole^{-1} l. cm.$^{-1}$ units: for some bands the molecular extinction coefficients are given in parentheses under the peak frequency values.)

EXPERIMENTAL

[$^2H_4$]*Acetic Acid.*—A mixture of 99·5% deuterium oxide (5 c.c.) and pure dioxan (30 c.c.) was distilled (by using a vacuum manifold) into a reaction vessel cooled in liquid air. (The reaction vessel consisted of a round-bottomed 100 ml. flask sealed on to a condenser. The lower end of the condenser was tapered down and continued for a short distance inside the flask, finally being bent into a semicircle. This device prevented "spluttering" of the deuterated malonic acid during stages described below. A B14 cone was fitted to the upper end of the condenser, and the tubing from this cone continued upwards for a further 5 cm.) Carbon suboxide (6 g.; prepared by pyrolysing [6] diacetyltartaric anhydride and purified by several distillations at 0·05 mm. through tubes packed with dry calcium oxide) was distilled into the cooled reaction vessel, which was then sealed off *in vacuo* above the B14 cone. After removal of the cooling bath, the vessel was allowed to warm to room temperature. The exothermic reaction which occurred was moderated by periodically cooling the vessel in acetone–solid carbon dioxide. When no more heat was evolved the vessel was kept at 20° for 24 hr., then cooled in liquid air, opened, and immediately connected to the manifold through the B14 cone. Volatile material was removed at 20°/0·05 mm., and the solid residue ([$^2H_4$]malonic acid) was kept at 60°/0·05 mm. for 4 hr. Dry air was admitted to the apparatus, and water was run through the condenser. The vessel was heated to 170° for 3 hr. to decarboxylate the [$^2H_4$]-malonic acid. Two distillations of the product at 0·05 mm. using receivers cooled in liquid air gave [$^2H_4$]acetic acid (4·8 g.).

Following Leitch's procedure,[3] the acid was converted into [$^2H_3$]methyl bromide (80% yield), shown by mass analysis to contain 98 atoms % of deuterium.

[$^2H_3$]*Methoxycyclohexane.*—A vigorously stirred mixture of powdered sodium (5 g.), cyclohexanol (50 c.c.), and dry ether (500 c.c.) was refluxed for 48 hr. under nitrogen. The resulting sodium salt was collected under nitrogen and washed with ether. Lumpy material was discarded, and the remaining powder was kept at 100°/0·05 mm. for 24 hr. to remove adsorbed cyclohexanol. A vessel containing the salt (2·44 g.) and ether (30 c.c.) was attached to the vacuum manifold and cooled in liquid air. [$^2H_3$]Methyl bromide (1·1 c.c.) was distilled (0·05 mm.) from a graduated flask into the suspension, and the vessel was then sealed off. After 2 weeks at 20° with periodic shaking, the mixture was filtered and the insoluble material washed with ether. The solution so obtained was treated with phosphorus pentoxide (5 g.) for 1 hr., filtered, and evaporated at 60° through a fractionating column. The residue was

[6] Hurd and Pilgrim, *J. Amer. Chem. Soc.*, 1933, **55**, 757.

distilled twice from sodium to give [$^2H_3$]methoxycyclohexane (0·82 g.), b. p. 132—133°, shown by mass analysis to contain $-OC[^2H_3]$, 90; $-OC[^2H_2]H$, 6; $-OC[^2H]H_2$ and $-OCH_3$, 4%. No impurities were detected by gas-phase chromatography.

[$^2H_3$]*Methoxybenzene.*—Phenol (1·94 g.) was added to sodium ethoxide (from 0·46 g. of sodium) in ethanol (10 c.c.), and the sodium salt so obtained was dissolved in purified dioxan (60 c.c.). [$^2H_3$]Methyl bromide (2·2 g.) was distilled into the solution as described above. The containing vessel was sealed and kept at 80° for 2 hr. Addition of water (200 c.c.) containing sodium chloride (10 g.) and sodium hydroxide (2 g.), followed by extraction with ether (5 × 20 c.c.), gave material which was dissolved in pentane and filtered through alumina (50 g., Grade H). Evaporation of the solution, followed by two distillations of the product, gave [$^2H_3$]anisole (0·79 g.), b. p. 152—153°, n_D^{22} 1·5140; no impurities were detected by gas-phase chromatography.

N-[$^2H_3$]*Methylaniline.*—A solution of the sodium salt of acetanilide [from acetanilide (4·6 g.) and sodium (0·78 g.) in refluxing toluene (80 c.c.)] and [$^2H_3$]methyl bromide (3·55 g.) in dioxan (60 c.c.) was kept at 60° for 3 hr. Insoluble material was collected and washed with ether. Evaporation of the combined filtrates and crystallisation of the residue gave *N*-[$^2H_3$]methylacetanilide (2·9 g.), m. p. 99—100°, which was refluxed with 10N-hydrochloric acid for 5 hr. Basification with 4N-sodium hydroxide solution, extraction with ether, and two distillations of the product gave *N*-[$^2H_3$]methylaniline (1·9 g.), b. p. 193—194°, n_D^{22} 1·5700; no impurities were detected by gas-phase chromatography.

Spectroscopy.—Approximately 0·1% solutions of the compounds in carbon tetrachloride were examined in 1-mm. cells, on a Unicam S.P. 100 spectrometer fitted with a prism-grating monochromator. Under the conditions used, the spectral slit width was probably about 5 cm.$^{-1}$.

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