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XXII. THE INFRARED, ULTRAVIOLET, AND NUCLEAR MAGNETIC RESONANCE SPECTRA OF SOME SUBSTITUTED 2-INDANONES AND REFERENCE COMPOUNDS<sup>1,2</sup>

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#### ABSTRACT

Infrared, ultraviolet, and nuclear magnetic resonance spectra of the following compounds are reported: 2-indanone (I), *trans*- and *cis*-hexahydro-2-indanone (V and XI), 1-chloro-2-indanone-1,3,3- $d_3$  (III), 1-bromo-2-indanone-1,3,3- $d_3$  (IV), 1-chloro-*trans*-hexahydro-2-indanone (VII), 1-bromo-*trans*-hexahydro-2-indanone (VIII), some deuterated forms of these compounds, 2-chlorocyclohexanone-2,6,6- $d_3$ , and 2-bromocyclohexanone-2,6,6- $d_3$ .

2-Indanone and trans-hexahydro-2-indanone each display two peaks in the carbonyl infrared region with intensity ratios of approximately 40:1. The origin of these doublets is discussed. Nuclear magnetic resonance spectra were determined to indicate the presence or absence of ring mobility, and spin-spin coupling data were used to support some of the conclusions deduced from the infrared data for some of the compounds.

### INTRODUCTION

It has previously been reported (see ref. 1 and references cited there) that film, solution, and KBr pellet infrared spectra of the 2-indanone ring system consistently gave a carbonyl doublet, whereas only one carbonyl frequency is reported for the 1-halo-2-indanones (2). To determine the origin of this doublet, we have re-investigated these spectra and prepared some appropriate  $\alpha$ -substituted indanones. In addition, the ultraviolet and nuclear magnetic resonance (n.m.r.) spectra of these compounds are reported.

#### EXPERIMENTAL

Most of the infrared spectra were determined in replicate on a Perkin-Elmer model 21 spectrophotometer calibrated against atmospheric water vapor peaks at 1784.95, 1772.6, 1768.17, and 1756.82 cm<sup>-1</sup> (25°), with a calcium fluoride prism at a computed spectral slit width (S') of 1.75 cm<sup>-1</sup> in the carbonyl band region (3). The precision of the carbonyl band positions is estimated to range between 0.5 and 0.1 cm<sup>-1</sup> depending on the symmetry of the peaks that are measured. The frequency accuracy of the  $\nu^{I}$  values is believed to be better than  $\pm 1 \text{ cm}^{-1}$ , but the lower frequency  $\nu^{\text{II}}$  peaks may be accurate to only  $\pm 2 \text{ cm}^{-1}$ 

<sup>1</sup>For part XXI in this series see A. Balasubramanian et al., Can. J. Chem., 43, 2603 (1965). Earlier papers in this series appeared under the general title "Light Absorption Studies". <sup>2</sup>Contribution No. 739 from the Department of Chemistry, Fordham University.

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because of overlapping with the stronger, higher frequency peaks. The integrated absorption intensities  $(mole^{-1} l cm^{-2} \times 10^{-4})$  were calculated from the equation (4)

$$A = \frac{2.303}{2cl} \pi \log_{10} (T_0/T)_{\max} \times \Delta \nu_{\frac{1}{2}}^{a}.$$

The accuracy of the A values is estimated to be  $\pm 5\%$ . Solute concentrations were about  $0.015 \pm 0.002$  mole/l. Base lines were determined by Wright's method (5). The cell thickness (0.548 mm) was determined from interference fringes. A Perkin-Elmer heated cell assembly (sodium chloride windows; Bodenseewerk, Germany) was used to obtain spectra of liquids at elevated temperatures.

Ultraviolet absorption spectra were determined by standard methods in 1 cm cells with a Cary model 15 spectrophotometer. The accuracy of the  $\lambda_{max}$  values is estimated to be  $\pm 1 \text{ m}\mu$ , and the precision of the molar absorptivities  $\pm 5\%$  or better. Most molar absorptivity values were reproducible to within  $\pm 2\%$ .

Nuclear magnetic resonance spectra were obtained in carbon tetrachloride solutions on a Varian A 60 model with tetramethylsilane as an internal standard. A microcell (Varian) was used for compounds which were available only in small amounts.

All solvents that were used were commercially available, spectroanalyzed solvents, redistilled when necessary. Chloroform was freed from its preservative by shaking it with concentrated sulfuric acid. After separation and filtration through soda lime and anhydrous sodium sulfate, the chloroform was distilled; a center fraction was used.

Some of the compounds were prepared and purified by standard methods, as described in the literature, or were commercially available. The remaining compounds were prepared as follows (melting and boiling points are corrected; elemental analyses by Schwarzkopf Microanalytical Laboratory, 56-19 37th Avenue, Woodside 77, New York; deuterium analyses by Mr. J. Nemeth, Department of Chemistry, University of Illinois, Urbana, Illinois).

2-Indanone-1,1,3,3- $d_4$  (II) was prepared by refluxing 2-indanone (I; 6.6 g) eight times for 4 h with 10 ml portions of D<sub>2</sub>O (99.5%, Isomet Corp.). No basic catalyst was used since its presence was found to accelerate self-condensation. The product was purified by steam distillation (with D<sub>2</sub>O), chromatographed from a 10 cm column of silica (Mallinckrodt, 100 mesh) with redistilled pentane (Eastman) containing 5% reagent grade anhydrous ether (Fisher), and finally crystallized from pentane to yield 2-indanone-1,1,3,3- $d_4$  (II; 2.2 g), m.p. 57.0-57.5 °C.

Anal. Calcd. for  $C_9D_4H_4O$ : D, 50.00 atom % excess D. Found: D, 49.05 atom %.

trans-Hexahydro-2-indanone-1,1,3,3- $d_4$  (VI) was prepared by refluxing trans-hexahydro-2-indanone (V; prepared by Hückel's method (6)) four times for 4 h with 10 ml portions of D<sub>2</sub>O, each containing 15 mg of sodium carbonate. After extraction with peroxide-free anhydrous ether, the product was dried (Na<sub>2</sub>SO<sub>4</sub>), evaporated in vacuum to 2 ml, and chromatographed on a 19 mm (inside diameter) column of specially prepared silicic acid. (Mallinckrodt 100 mesh silicic acid (300 g) was washed five times with distilled water (3 l), the water being decanted after ca. 5 min settling. After filtration, this silicic acid was further washed with 95% ethanol and absolute ethanol and then heated for 2 days at 120 °C. To this was then added 3% D<sub>2</sub>O, and the mixture was shaken for 24 h.) Elution with pentane containing 3% anhydrous ether and solvent removal gave trans-hexahydro-2-indanome-1,1,3,3- $d_1$ ,  $n_D^{26}$  1.4741. The infrared spectrum showed complete  $\alpha$ -deuteration in a freshly prepared sample (see Discussion).

1-Chloro-*trans*-hexahydro-2-indanone (VII) was prepared by direct chlorination at 0 °C of *trans*-hexahydro-2-indanone (V; 500 mg) in the presence of a small amount of water (3 ml) until a slight excess of the theoretical amount of chlorine that was necessary (257 mg) had been added. After extraction with peroxide-free ether, the products were dried (Na<sub>2</sub>SO<sub>4</sub>), reduced in volume, and chromatographed as previously described, but protected from light and heat as much as possible. Re-chromatography gave 1-chloro-trans-hexahydro-2-indanone (VII; 25 mg),  $n_{\rm D}^{26}$  1.4998.

Anal. Calcd. for C<sub>9</sub>H<sub>13</sub>OCl: C, 62.6; H, 7.6; Cl, 20.5. Found: C, 62.6; H, 7.45; Cl, 20.7.

1-Bromo-trans-hexahydro-2-indanone (VIII) was prepared by direct bromination (bromine; 578 mg dissolved in methylene chloride; 10 ml) of trans-hexahydro-2-indanone (V; 500 mg) dissolved in methylene chloride (15 ml). Sunlight was usually necessary to initiate and to accelerate the reaction, and sometimes more concentrated solutions had to be used. After solvent removal under vacuum, the products were worked up as described for the chloro compound, but in addition all processes were carried out in an atmosphere of nitrogen. 1-Bromo-trans-hexahydro-2-indanone (VIII) thus obtained had  $n_D^{25.2}$  1.5289.

Anal. Calcd. for C<sub>9</sub>H<sub>13</sub>OBr: C, 49.8; H, 6.0. Found: C, 49.0; H, 5.8.

1-Chloro-*trans*-hexahydro-2-indanone-1,3,3- $d_3$  (IX) was prepared by direct chlorination of *trans*-hexahydro-2-indanone-1,1,3,3- $d_4$  (VI; 447.5 mg) as described for the preparation of 1-chloro-*trans*-hexahydro-2-indanone (VII), except that D<sub>2</sub>O was used instead of H<sub>2</sub>O in all instances. *1-Chloro-trans*-hexahydro-2-indanone-1,3,3- $d_3$  (IX; 35 mg) thus obtained had  $n_D^{21.4}$  1.5002.

Anal. Calcd. for C<sub>9</sub>H<sub>10</sub>D<sub>3</sub> $\overline{O}$ Cl: C, 61.5; H (+ D), 7.65; Cl, 20.2; D, 23.1 atom % excess D. Found: C, 61.7; H (+ D), 7.9; Cl, 20.1; D, 18.5 atom %.

1-Bromo-trans-hexahydro-2-indanone-1,3,3- $d_3$  (X) was prepared by bromination of trans-hexahydro-2indanone-1,1,3,3- $d_4$  (VI; 391.8 mg) as described for the preparation of 1-bromo-trans-hexahydro-2-indanone

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(VIII), except that  $D_2O$  was used instead of  $H_2O$  in all instances and that fluorotrichloromethane (Freon 11) was used as the solvent. *1-Bromo-trans-hexahydro-2-indanone-1,3,3-d*<sub>3</sub> (X) was obtained in poor yield (9 mg) and, not consistently so, as a light yellow-brown liquid.

Anal. Calcd. for C<sub>9</sub>H<sub>10</sub>D<sub>3</sub>OBr: C, 49.1; H (+ D), 6.1. Found: C, 47.5; H (+ D), 5.9.

Irradiation with a mercury lamp resulted almost exclusively in the dibromo compound.

1-Chloro-*cis*-hexahydro-2-indanone (XII) was prepared from *cis*-hexahydro-2-indanone (XI; prepared as described in ref. 6) as in the preparation of the corresponding *trans* isomer. It showed  $n_D^{25}$  1.5068, but the elemental analysis indicated that, even after three chromatographs, the product still contained some dichloro impurity.

Anal. Calcd. for C9H13OC1: C, 62.6; H, 7.6; Cl, 20.5. Found: C, 61.5; H, 7.3; Cl, 23.2.

*1-Bromo-cis-hexahydro-2-indanone* (XIII) was prepared in the same way as the *trans* isomer (VIII) and had  $n_D^{24}$  1.5283. The elemental analysis indicated the presence of some dibromo compound as an impurity. Anal. Calcd. for C<sub>9</sub>H<sub>13</sub>OBr: C, 49.8; H, 6.0; Br, 36.8. Found: C, 49.3; H, 5.8; Br, 38.2.

2-Chlorocyclohexane-2,6,6- $d_3$  was prepared from cyclohexanone-2,2,6,6- $d_4$  (489.4 ng) by chlorination (343.5 ng chlorine) as in the preparation of 1-chloro-*trans*-hexahydro-2-indanone-1,3,3- $d_3$  (IX). 2-Chlorocyclohexanone-2,6,6- $d_3$  (123.2 ng) thus obtained had  $n_D^{23.5}$  1,4827.

Anal. Calcd. for  $C_6H_6D_3OCl$ : C, 53.1; H (+ D), 6.9; Cl, 26.1; D, 33.3 atom % excess D. Found: C, 53.3; H (+ D), 7.1; Cl, 26.1; D, 31.5 atom %.

2-Bromocyclohexanone-2,6,6-d<sub>3</sub> was prepared from cyclohexanone-2,2,6,6-d<sub>4</sub> (748 mg) by sunlight-catalyzed bromination (1.17 g bromine) as in the preparation of 1-bromo-*trans*-hexahydro-2-indanone (VIII). Purification and redistillation yielded 2-bromocyclohexanone-2,6,6-d<sub>3</sub> (149.7 mg),  $n_D^{22.5}$  1.5107.

Anal. Calcd. for C<sub>6</sub>H<sub>6</sub>D<sub>3</sub>OBr: C, 40.0; H (+ D), 5.2; Br, 44.4; D, 33.3 atom % excess D. Found: C, 40.2; H (+ D), 5.3; Br, 44.1; D, 29.6 atom %.

1-Chloro-2-indanone-1,3,3- $d_3$  (III) was prepared from 2-indanone-1,1,3,3- $d_4$  (II; 509.9 mg) by chlorination (150 mg chlorine) as in the preparation of 1-chloro-*trans*-hexahydro-2-indanone-1,3,3- $d_3$  (IX). After crystallization from pentane, *1-chloro-2-indanone-1,3,3-d\_3* (III; 174.1 mg) had m.p. 71–71.5° (Brutcher *et al.* (7) report m.p. 71–71.5° for the non-deuterated analogue).

Anal. Calcd. for C<sub>9</sub>H<sub>4</sub>D<sub>3</sub>OCl: C, 63.7; H (+ D), 4.36; Cl, 20.9; D, 42.9 atom % excess D. Found: C, 63.9; H (+ D), 4.5; Cl, 21.1; D, 42.9 atom %.

1-Bromo-2-indanone-1,3,3- $d_3$  (IV) was prepared by direct bromination (bromine; 471.8 mg dissolved in methylene chloride; 10 ml) of 2-indanone-1,1,3,3- $d_4$  (II; 401.9 mg) dissolved in methylene chloride (10 ml). After solvent removal under vacuum, the products were worked up as for compound II. 1-Bromo-2-indanone-1,3,3- $d_3$  (IV; 424.7 mg) was crystallized from 5% ether in pentane and had m.p. 90-91° (Brutcher et al. (7) report m.p. 91° for the non-deuterated analogue).

Anal. Calcd. for  $C_9H_4D_9OBr$ : C, 50.5; H (+ D), 3.45; Br, 37.3; D, 42.9 atom % excess D. Found: C, 50.2; H (+ D), 3.3; Br, 37.2; D, 41.0 atom %.

# DISCUSSION

# Infrared Spectra

The relevant spectral data are listed in Table I. 2-Indanone-1,1,3,3- $d_4$  (II) and 2-indanone (I) are presumably planar or near-planar molecules (see also discussion of n.m.r. spectra). The frequency displacements of the main carbonyl bands in carbon tetrachloride solution observed on halogen substitution for compounds III and IV relative to these bands in compound II (20 and 9.9 cm<sup>-1</sup>; see Table I) are similar to the displacements observed on halogen substitution of the non-deuterated analogues (19 and 13 cm<sup>-1</sup>; see Table II) and in other related molecules (7). The halogen-substituted indanones III and IV may be slightly non-planar (see discussion of n.m.r. spectra), but there is no reason to suppose that the planarity of the indanone system is appreciably disturbed.

A small spectral displacement is observed between the main carbonyl bands of compounds I and II ( $0.5 \text{ cm}^{-1}$ ), if the bands are measured under identical conditions; similar small displacements may occur between compounds III and IV and their respective nondeuterated analogues. Inspection of the actual traces (Fig. 1) also shows that for 2indanone (I) and compound V subsidiary bands occur at 1 728.8 cm<sup>-1</sup> and 1 706.1 cm<sup>-1</sup>, respectively, which are less intense and displaced in the deuterated compounds II and VI.

A number of possible explanations can account for the appearance of two carbonyl bands. Before these are discussed, however, a number of possibilities may be ruled out.

First, the absence of any concentration dependence within the concentration range 0.25

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to 0.025 mole/l for compounds I and V (see Table I) eliminated intermolecular association complexes. The absence of such interactions is also indicated by the absence of a subsidiary band in the *cis* isomer (XI).

Next, enolization is unlikely as an explanation since no OH absorption could be detected in the infrared spectra, even at elevated temperatures. Figure 2 shows the overtone bands at 2.859  $\mu$  (3 498 cm<sup>-1</sup>) and 2.878  $\mu$  (3 475 cm<sup>-1</sup>) for compounds I and V, respectively, which are identified as such since these bands also occur in the deuterated analogues at 2.863  $\mu$  (3 493 cm<sup>-1</sup>) for compound II and at 2.885  $\mu$  (3 466 cm<sup>-1</sup>) for compound VI (see Fig. 2). Moreover, the n.m.r. spectra of compounds I, V, and XI show no hydroxyl protons (see Figs. 4d, 4i, and 4l).

Conformational isomerism also seems unlikely, since in such an equilibrium, when the



FIG. 1. Carbonyl bands in carbon tetrachloride solutions of 2-indanone (I), 2-indanone-1,1,3,3- $d_4$  (II), trans-hexahydro-2-indanone (V), trans-hexahydro-2-indanone-1,1,3,3- $d_4$  (VI), and cis-hexahydro-2-indanone (XI).

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FIG. 2. Infrared spectra of compounds I, II, V, and VI (carbon tetrachloride solution) in the 2.5-3.5  $\mu$  region.

temperature is raised, the less-favored isomer would be expected to equilibrate with the more stable form. Figure 3 shows no such equilibrium for compounds I and V.

"Hot bands" also probably do not account for the subsidiary bands in compounds I and V, because such an explanation cannot readily account either for the changes observed in the deuterated analogues or for the observed spectral changes when the solvent is altered (see Table I). Moreover, hot transitions would be expected to be temperature dependent, and no such dependence is observed (see Fig. 3).

Finally, the presence of impurities, particularly water vapor, was looked for as a possible explanation of the subsidiary band, but careful repurification did not affect the observed spectra.

On the other hand, weak Fermi coupling is a possible explanation for the subsidiary bands observed in compounds I and V; such weak coupling between overtones and (or) combination bands on the one hand, and the strong carbonyl fundamental band on the other hand, may account partly for the small displacements observed in the main carbonyl bands of compounds II, III, IV, and VI and their non-deuterated analogues. The hypothesis of Fermi coupling similarly may also account, at least partly, for the decreased intensity of the subsidiary band in compound II and in compounds where the  $\alpha$ -hydrogen atoms have been replaced by deuterium (see Fig. 1). If this explanation is correct, Fermi coupling seems to be more effective in compound V than in 2-indanone (I). This can be rationalized on the basis that the cyclopentanone ring in *trans*-hexahydro-2-indanone (V), unlike this ring in 2-indanone (I), is not planar (see discussion of n.m.r. spectra and refs. 7 and 8 and references cited there); possibly the molecule is then in a more favorable conformation for Fermi coupling to occur. No pronounced doublet formation could be detected in the *cis* isomer (see Fig. 1), which, however, may exist in a different conformation.

Moreover, some of the solvent changes (see Table I) are similar to those occurring in cyclopentanone (9) and ethylene carbonate (10), where Fermi resonance has been suggested as an explanation of the observed doublet.

However, there are difficulties with this explanation, based on Fermi coupling. First, the

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F1G. 3. Effect of temperature on the C=O stretching absorption in film and *sym*-tetrachloroethylene solutions of 2-indanone (I) and *trans*-hexahydro-2-indanone (V).

main carbonyl bands in compounds I and V are only weakly sensitive to isotopic substitution; hence, it is unlikely that one of the excitations corresponds to a combination band or overtone involving predominantly  $\alpha$ -hydrogen motions. Also, there are no plausible bands in the infrared spectrum, overtones or combination bands of which could readily account for the Fermi coupling.

Next, it may be noted that the observed weak band could represent a weak fundamental vibration of the complex molecule. Such a vibration may be forbidden in a molecule in which the local symmetry (carbonyl and  $\alpha$ -carbonyl region) is relatively high, as in the *cis* isomer (IX), where no subsidiary band is observed. If this is so, the various changes of position and intensity with substitution may predominantly reflect mass changes.

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Compound	Solvent	$(\mathrm{cm}^{\nu_{\mathrm{max}}\mathrm{I}})$	$\frac{\Delta \nu^{\mathrm{I}}}{(\mathrm{cm}^{-1})}$	A	$\nu_{\max}^{II}$ (cm <sup>-1</sup>
I*	$CCl_4 \ CHCl_3 \ CH_2Cl_2 \ CH_3CN$	$\begin{array}{c}1\ 756.8\\1\ 751.8\\1\ 752.6\\1\ 753.2\end{array}$		$     \begin{array}{r}       1.98 \\       2.69 \\       2.59 \\       2.53 \\     \end{array} $	$     \begin{array}{r}       1 728.8 \\       1 731.6 \\       1 729.9 \\       1 731.4 \\     \end{array} $
II	$CCl_4$	1.756.3	8.2	2.58	1713.4
III	$CCl_4$	1776.3			
IV	$CCl_4$	1.766.2			
V*	CCl4 CHCl3 CH2Cl2 CH3CN	1747.1 1736.6 1738.9 1740.4	$10.3 \\ 16.1 \\ 13.4 \\ 12.7$	$2.52 \\ 3.49 \\ 2.45 \\ 3.43$	1 706.1 1 706.0 1 701.1 1 704.0
VI VII VIII IX X XI	CCl <sub>4</sub> CCl <sub>4</sub> CCl <sub>4</sub> CCl <sub>4</sub> CCl <sub>4</sub> CCl <sub>4</sub>	$1\ 744.8\\ 1\ 760.5\\ 1\ 763.0\\ 1\ 759.1\\ 1\ 753.6\\ 1\ 744.2$	10.8 8.7	2.58 2.44	
Cyclopentanone (9)	CCl4 CHCl3 CH2Cl2 CH3CN	$egin{array}{c} 1 \; 747 \ 1 \; 743 \ 1 \; 744 \ 1 \; 745 \end{array}$			$egin{array}{c} 1 & 731 \\ 1 & 728 \\ 1 & 729 \\ 1 & 732 \end{array}$
Ethylene carbonate (10)	CCl4 CHCl3 CH2Cl2 CH3CN	$     1 819 \\     1 811 \\     1 812 \\     1 808   $			1 773 1 780 1 778 1 778 1 778

TABLE I						
Main infrared	carbonyl bands o	of some indanones				

\*These bands were found to be concentration independent (by using different path lengths) within the concentration range 0.25 to 0.025 mole/l.

Also, it is possible that the weak transition corresponds to a combination band which for symmetry reasons, or because of the absence of anharmonic mixing with the carbonyl fundamental vibration, is behaving independently with respect to substitution. That is, no Fermi coupling need be involved for at least some of the molecules studied.

Further, it is possible that in the aromatic systems the symmetry tends to inhibit Fermi coupling but that in some of the *trans*-hexahydro molecules it allows more Fermi coupling. Then, if the local symmetry (carbonyl and  $\alpha$ -carbonyl region) is greater in the *cis* molecule, as seems likely, this could account for the absence of the subsidiary band in the *cis* molecules. In any case, Fermi coupling applies only to the interaction between a fundamental vibration and an overtone or combination tone, and carbonyl stretching modes not only involve stretching of the C==O bond but also motions of the adjacent C---C and C---H bonds and bond angles. Hence, it is probable that changing the adjacent masses changes significantly the form of the mode and thus its frequency. Any Fermi coupling may therefore only be a secondary interaction superimposed on this more fundamental effect. For example, the displacement in the carbonyl band for compound VIII on deuteration (-9.4 cm<sup>-1</sup>; see Table I) may be caused by the non-equivalence of the  $\alpha$ -positions on bromo substitution. Whatever their precise origin, these perturbations are unfortunate, since therefore the displacements observed on 1-chloro or 1-bromo substitution, *in the* 

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absence of the above-mentioned effects, cannot readily be determined. It is these displacements which are used to provide information concerning the conformation of the halogensubstituted compound. The uncorrected displacements obtained for these and some reference compounds on chloro and bromo substitution are listed in Table II.

# TABLE II

Displacements (in CCl<sub>4</sub> solution) observed on substituting a chlorine or bromine atom in the position adjoining the carbonyl group

	$(\mathrm{cm}^{\nu_{\mathrm{max}}})$	$\nu_{\max}$ (cm <sup>-1</sup> )		Displacement (in cm <sup>-1</sup> ) observed on substitution with:	
Reference compound		1-Chloro derivative	1-Bromo derivative	Cl	Br
2-Indanone <sup>*</sup> (I) 2-Indanone-1,1,3,3-d <sub>4</sub> (II) Cyclohexanone <sup>†</sup> Cyclohexanone-2,2,4,4-d <sub>4</sub> trans-Hexahydro-2-indanone (V) trans-Hexahydro-2-indanone-1,1,3,3-d <sub>4</sub> (VI) cis-Hexahydro-2-indanone (XI)	$\begin{array}{c} 1 \ 753 \\ 1 \ 756 \ .3 \\ 1 \ 712 \\ 1 \ 715 \ .6 \\ 1 \ 747 \ .1 \\ 1 \ 744 \ .8 \\ 1 \ 744 \ .2 \end{array}$	1 772 1 776.3 1 740 1 726.3 1 760.5 1 759.1 1 760.3	17661766.217301718.517631753.61753.3	19     20     28     10.7     13.4     14.3     16.1	13 9.9 18 2.9 15.9 8.8 9.1

\*Data from ref. 2. †Data from ref. 11.

# Ultraviolet Spectra

The data (Table III) show that, in some of the compounds investigated, slight spectral variations are observed in the  $n \rightarrow \pi^*$  carbonyl band transitions on deuteration of the neighboring carbon atom. This is not inconsistent with the infrared data, which have indicated that the carbonyl stretching mode in the ground state is affected by  $\alpha$ -substitution; hence the excited-state carbonyl stretching mode may also be affected by such substitution. However, the ultraviolet data must be interpreted cautiously since most of the compounds studied exhibit, like cyclopentanone, a number of peaks in the region studied; hence the location of the maximal absorption cannot readily be determined. Only the main maxima are recorded in Table III. For compounds I to IV, the low-intensity  $n \rightarrow \pi^*$  electronic transition could not be measured, because of the large benzenoid absorption.

## TABLE III

Main ultraviolet maxima  $(n \rightarrow \pi^* \text{ transitions})$  of *trans*-hexahydro-2indanone and of appropriate reference compounds in cyclohexane solution

Compound		€max
trans-Hexahydro-2-indanone (V) trans-Hexahydro-2-indanone-1,1,3,3-d4 (VI) 1-Chloro-trans-hexahydro-2-indanone (VII) 1-Chloro-trans-hexahydro-2-indanone-1,3,3-d3 (IX) 1-Bromo-trans-hexahydro-2-indanone (VIII) 1-Bromo-trans-hexahydro-2-indanone (VIII) 1-Bromo-trans-hexahydro-2-indanone (VIII) 2-Chloro-trans-hexahydro-2-indanone (VIII) 2-Chlorocyclohexanone 2-Chlorocyclohexanone-2,6,6-d3 2-Bromocyclohexanone 2-Bromocyclohexanone	$\begin{array}{c} 301\\ 301\\ 322\\ 317\\ 321\\ 318\\ 293\\ 291\\ 304\\ 303\\ 312\\ 312 \end{array}$	$\begin{array}{r} 30\\ 30\\ 50\\ 50\\ 70\\ 115*\\ 15\\ 35\\ 35\\ 100\\ 100 \end{array}$

\*Shoulder superimposed on another peak.

# Nuclear Magnetic Resonance Spectra

The n.m.r. spectrum of cyclohexanone exhibits two peaks, one caused by four  $\alpha$ carbonyl hydrogens and the other by the six remaining hydrogens (12). Cyclohexanone-2,2,6,6- $d_4$ , on the other hand, exhibits only one peak with no spin-spin splitting (see

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TMS

тмз

TMS

TMS

0

□. →~ □ (a) (h) >= 0 7A ń TMS X = CI or Br 1.80 (Ⅲ)(Ⅳ) 175 1.51 (i) (b) 190 2.01 0 1.37 2.13 1.87 1.26 TMS 2.14 N (Y) TMS 2.30 (c) () 0 2.21 1.95 (亚) тмз 4.07 3.38 (d) (k)  $(1)^{\circ}$ 7.16 )= o 54 (I) (亚丁) <u>ہ</u> 4.06 2.60 TMS ł (e) <sup>7.21</sup> 2.08 D (1)тмз )= 0 (꼬) (Π) 1.99 1.93 2.29 ∑=0 ң н (f) (m) тмз ∕ci° (<u>XII</u>) 3-87 ≁н н 2.33 3.99 7.43 2.59 5·26 3.61 4.03 K (g) (n) ,Br , ↓ ₽ TMS ¢⊨ 7.50 (工工) 3-58 <u>≬</u>5.10 22 3-92 ' | }0 0 8.0 7.0 6.0 40 30 2.0 4.0 1 30 2.0 7.0 60 50 50 ю

FIG. 4. Nuclear magnetic resonance spectra in carbon tetrachloride solution of (a) cyclohexanone-2,2,6,6- $d_4$ , (b) 2-chlorocyclohexanone-2,6,6- $d_3$ , (c) 2-bromocyclohexanone-2,6,6- $d_3$ , (d) I, (e) II, (f) 1-bromo-2-indanone, (g) 1-chloro-2-indanone, (h) III and IV, (i) V, (j) VII, (k) VIII, (l) XI, (m) XII, and (n) XIII (TMS = tetramethylsilane).

8.0

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Fig. 4a). This shows that the ring is mobile. Likewise, the n.m.r. spectrum of 2-chlorocyclohexanone (12) gives no indication of ring rigidity. The n.m.r. spectra of the chlorinated and brominated trideuterio analogues (see Figs. 4b and 4c) show two distinct peaks, one caused by the two hydrogens vicinal to the halogen and the other by the remaining four hydrogens on the ring. All these data confirm the mobility of the cyclohexanone ring.

The n.m.r. spectrum of compound I does not show any splitting (Fig. 4d), and that of its deuterated analogue (II; see Fig. 4e) shows only one sharp peak. 1-Bromo-2-indanone (see Fig. 4f) and 1-chloro-2-indanone (see Fig. 4g) yield three peaks in the ratio 4:2:1. Both spectra show a small amount of fine structure in the peak caused by the aromatic hydrogen atom; similar effects are observed in the deuterated analogues (III and IV; see Fig. 4h). This splitting is ascribed to the inductive effect of the halogen atom. The spectrum of 1-bromo-2-indanone shows a doublet for the geminal hydrogens (see Fig. 4f), thus suggesting that these hydrogens are not identical, one being slightly axial and the other slightly equatorial, presumably because of the steric effect of the larger bromine atom and its more axial character.

The spectra of *trans*-hexahydro-2-indanone (V) and its halogenated analogues (VII and VIII) suggest a rigid system with considerable spin coupling (see Figs. 4i, 4j, and 4k). The spectrum of the corresponding hydrocarbon also indicates a rigid system (13). Moreover, 1-chloro-trans-hexahydro-2-indanone (VII) gives a single peak (see Fig. 4i) at 4.07 p.p.m. with a band width of about 8 c.p.s. This relatively large band width suggests a limited amount of splitting between the angular hydrogen and the hydrogen geminal to the chlorine atom. Such a splitting is consistent if the angle between the two hydrogen atoms is about 85° (see Karplus' corrected equation (14)), but splitting probably also occurs across the carbonyl group with the methylene protons. 1-Bromo-trans-hexahydro-2-indanone (VIII) shows a similar peak with a band width of about 16 c.p.s. (Fig. 4k); this splitting is consistent with an angle, as defined above, of about 40°. The chloro and bromo derivatives (IX and X) of the appropriate deuterated compound (VI), as anticipated, give n.m.r. spectra identical with that of the parent compound (VI). The spectrum of cis-hexahydro-2indanone (XI; see Fig. 4l) indicates a mobile molecule, as do the spectra of the corresponding halogen derivatives (XII and XIII; see Figs. 4m and 4n). cis-Hydrindane has been shown to have a low energy barrier to rotation (13).

1-Chloro-*cis*-hexahydro-2-indanone (XII) exhibits four peaks for the hydrogen geminal to chlorine (see Fig. 4m), which can be explained by assuming two non-equivalent  $\alpha$ -positions, located in a molecule which itself can assume two conformational isomers. 1-Bromo-*cis*-hexahydro-2-indanone shows two peaks, with a possibility of further unresolved spin-spin splitting for the hydrogen geminal to bromine. This can be explained by assuming that, for this compound in both isomers, the conformation containing the bromine atom in the axial position is preferred.

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