

## The Nuclear Magnetic Resonance Spectrum of 1-Chlorobutane

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The NMR spectra of butane,<sup>1,2</sup> 1,4-dibromobutane,<sup>3</sup> and 1,4-dichlorobutane<sup>4</sup> have been studied in previous papers. In this communication we report an analysis of the 60 MHz NMR spectrum of 1-chlorobutane.

Five different staggered rotamers exist for this molecule. The interconversion of the rotational isomers is, however, so rapid at room temperature that only the averaged NMR spectrum is observed. The rotational averaging simplifies the spectrum to one of the  $A_3BB'CC'DD'$  type. The experimental spectrum can, however, be completely reproduced on basis of an  $A_3BB'CC'D_2$  spin system. This implies that the chloromethyl protons are magnetically equivalent within the accuracy of the experiment. The analysis of the spectrum of 1-chlorobutane is, nevertheless, tricky owing to the large number of strongly coupled protons.

The NMR spectrum of the  $A_3BB'CC'D_2$  spin system can be explained in terms of four chemical shifts ( $\nu_A$ ,  $\nu_B$ ,  $\nu_C$ ,  $\nu_D$ ), two geminal coupling constants ( $J_{BB'}$ ,  $J_{CC'}$ ), four vicinal coupling constants ( $J_{AB}$ ,  $J_{BC}$ ,  $J_{BC'}$ ,  $J_{CD}$ ) and three long-range coupling constants ( $J_{AC}$ ,  $J_{AD}$ ,  $J_{BD}$ ). The secular matrices of this spin system can be considerably reduced using the composite particle approach<sup>5</sup> and symmetry. The simplest possible composite spin state, however, comprises an  $ABB'CC'$  spin system and is unamenable to calculation by hand.<sup>6</sup> The spectrum of 1-chlorobutane has, however, been analyzed by means of a computer using the computer programs UEANMR II<sup>7</sup> and UEAITR.<sup>8</sup> The programs make use of magnetic equivalence factoring to reduce the size of the secular

matrices. The UEANMR II program was used only in conjunction with the subroutine KOMBIP<sup>9</sup> to obtain "stick" and line-shape plots. The iterative fitting of experimental and calculated transitions was performed by means of the UEAITR program. The root-mean-square deviation was 0.072 for the 550 matched lines. The calculated probable error for the parameters was 0.01 Hz or less. The spectral parameters are listed in Tables 1 and 2.

Table 1. Chemical shifts (in Hz from TMS) measured at 60 MHz of neat 1-chlorobutane.

$\nu_A$	$\nu_B$	$\nu_C$	$\nu_D$
54.98	84.80	100.95	205.17

The agreement between the experimental and calculated spectra in Figs. 1 and 2 is excellent.

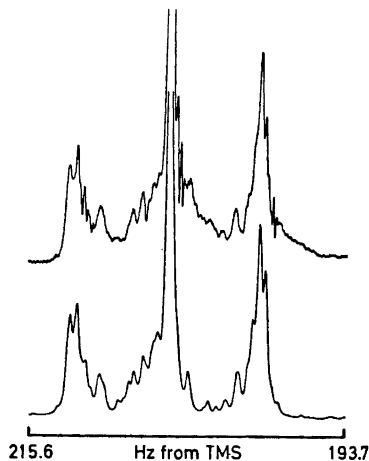


Fig. 1. Experimental (upper part) and calculated (lower part) 60 MHz spectra of the chloromethyl protons in 1-chlorobutane.

Table 2. Spin-spin coupling constants (in Hz) measured at 60 MHz of neat 1-chlorobutane.

$J_{AB}$	$J_{AC}$	$J_{AD}$	$J_{BB'}$	$J_{BC}$	$J_{BC'}$	$J_{BD}$	$J_{CC'}$	$J_{CD}$
7.335	-0.177	0	-12.474	5.813	8.827	-0.217	-12.527	6.711

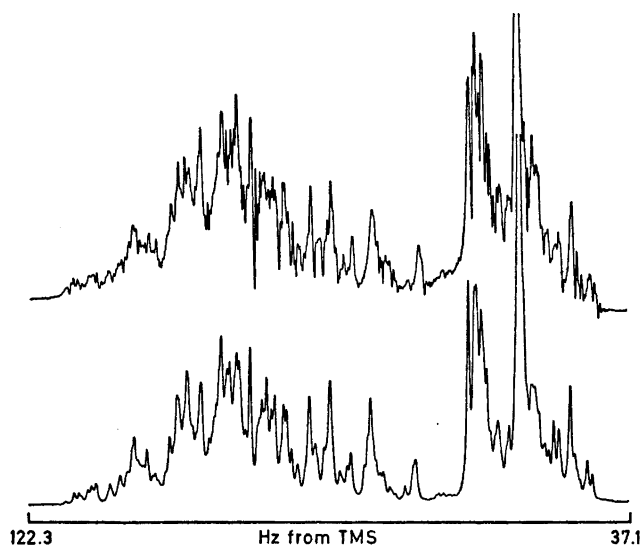


Fig. 2. Experimental (upper part) and calculated (lower part) 60 MHz spectra of the  $\text{CH}_3\text{CH}_2\text{CH}_2$ -protons in 1-chlorobutane.

The terminal  $\text{CH}_2\text{X}$  protons in propyl halides<sup>10,11</sup> 1,4-dibromobutane,<sup>3</sup> and 1,4-dichlorobutane<sup>4</sup> have also been found to be practically magnetically equivalent. This indicates extra stability of rotamers possessing *gauche* halogens. This has indeed been observed in the gas phase of 1-chlorobutane where the rotamers possessing *gauche* chlorine account for nearly 80% of the staggered forms.<sup>12</sup> Moreover, in the liquid phase dipole interactions would tend to stabilize rotamers having the larger dipole moments, that is, *gauche* chlorine forms.

The internal chemical shift differences at 60 MHz of adjacent  $\text{CH}_2-\text{CH}_2$ -protons are 121.2 Hz,<sup>13</sup> 46.53 Hz,<sup>11</sup> 29.82 Hz, and 24.12 Hz<sup>2</sup> for 1-chloroethane, 1-chloropropane, 1-chlorobutane, and butane, respectively. These shifts demonstrate the expected rapid attenuation of the inductive effect of chlorine as the number of intervening carbon atoms increases. The comparable internal shift differences of vicinal  $\text{ClCH}_2-\text{CH}_2-$  protons in 1-chlorobutane, 1,4-dichlorobutane, and 1-chloropropane, however, reflect similar inductive effects of chlorine as expected.

The four coupling constants of the  $\text{CH}_3-\text{CH}_2-\text{CH}_2$ -fragment of 1-chlorobutane have similar values as the corre-

sponding coupling constants observed in butane.<sup>2</sup> Furthermore, the vicinal coupling constants,  $J_{\text{BC}}$  and  $J_{\text{BC}'}$ , are also comparable to the same parameters in 1,4-dibromobutane<sup>3</sup> and 1,4-dichlorobutane.<sup>4</sup> Since these coupling constants are little affected by the chlorine substituent it follows that the relatively small deviations between corresponding parameters can be ascribed to conformational effects. Larger deviations might have been expected on basis of the estimated distribution of *anti* and *gauche* conformations about the central  $\text{C}_2-\text{C}_3$  bond.<sup>1-4,12</sup>

Further NMR studies on substituted butanes are in progress.

*Experimental.* 1-Chlorobutane (*puriss.*) was obtained from Fluka A.G. and used without further purification. Small quantities of benzene and TMS were added to the neat liquid to serve as NMR locking and reference substances, respectively. The NMR sample tube was thoroughly degassed and sealed under vacuum.

The NMR spectra were run at ambient temperature (*ca.* 27°C) on a JEOL-C-60H spectrometer. The spectra used for the analysis were recorded at 54 Hz sweep width and calibrated every 5 Hz using a frequency coun-

ter. Line positions were obtained by averaging the results of four scans.

Computations were performed on the IBM/50H computer at the University of Bergen. The graphical output was obtained on a Calcomp Plotter.

1. Aksnes, D. W. and Albrigtsen, P. *Acta Chem. Scand.* **24** (1970) 3764.
2. Aksnes, D. W. and Albrigtsen, P. *Acta Chem. Scand. In press.*
3. Aksnes, D. W. *Acta Chem. Scand.* **26** (1972) 164.
4. Aksnes, D. W. *Acta Chem. Scand. In press.*
5. Diehl, P., Harris, R. K. and Jones, R. G. *Progr. Nucl. Magn. Resonance Spectrosc.* **3** (1967) 1.
6. Emsley, J. W., Feeney, J. and Sutcliffe, L. H. *High Resolution Nuclear Magnetic Resonance Spectroscopy*, Pergamon, New York 1966, Vol. 1, p. 416.
7. Woodman, C. M. *Personal communication.*
8. Johannesen, R. B., Ferretti, J. A. and Harris, R. K. *J. Magn. Resonance* **3** (1970) 84.
9. Aksnes, D. W. *KOMBIP*, Quantum Chemistry Program Exchange, Indiana University, Chemistry Department, Indiana, U.S.A.
10. Schruppf J. *Magn. Resonance* **6** (1972) 243.
11. Aksnes, D. W. and Støgård, J. *To be published.*
12. Ukaji, T. and Bonham, R. A. *J. Am. Chem. Soc.* **84** (1962) 3631.
13. Brügel, W. *Nuclear Magnetic Resonance Spectra and Chemical Structure*, Academic, New York 1967, Vol. 1.

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### On the Phases $\text{Cr}_2\text{As}$ , $\text{Fe}_2\text{As}$ , $\text{Co}_2\text{As}$ , and $\text{Rh}_2\text{As}$

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Despite numerous studies on the metal rich pnictides and chalcogenides of the transition elements there is a general lack

of detailed information concerning their chemical and physical properties. The present paper concerns the composition, range of homogeneity, and magnetic properties for the phases  $\text{Cr}_2\text{As}$ ,  $\text{Fe}_2\text{As}$ ,  $\text{Co}_2\text{As}$ , and  $\text{Rh}_2\text{As}$  (*cf.* Refs. 1–22).

*Experimental.* Samples were prepared from 99.999+ % As (Johnson, Matthey & Co.), 99.999 % Cr (Koch-Light Lab.), 99.9+ % Fe (Riedel-DeHaën AC.), 99.7 % Co (Baker Chemical Co.), and 99.99+ % Rh (Johnson, Matthey & Co.) by heating weighed quantities of the components in evacuated, sealed silica tubes at temperatures between 400 and 900°C for 4 days. (The iron and cobalt powders were obtained by hydrogen reduction (600°C) of their oxides.) The sintered powders were ground and reannealed at temperatures between 500 and 900°C for 4–15 day periods and, finally, quenched in iced water.

X-Ray powder photographs of all samples were taken in a Guinier type camera of 80 mm diameter with monochromatized  $\text{CuK}\alpha_1$ -radiation using KCl as internal standard. The lattice dimensions were refined by applying the method of least squares to the diffraction data and the indicated error limits correspond to the standard deviations.

Magnetic susceptibilities were measured between 80 and 1000 K by the Faraday method (maximum field  $\sim 8 \text{ kO}$ ) using 10–100 mg samples.

*Results.* The compositions of the  $\text{Cr}_2\text{As}$ ,  $\text{Fe}_2\text{As}$ ,  $\text{Co}_2\text{As}$ , and  $\text{Rh}_2\text{As}$  phases, which have no appreciable ranges of homogeneity, were determined by applying the disappearing phase principle to Guinier photographs of samples with different nominal compositions. The results showed the phases to be stoichiometric according to the general formula  $T_2X$  ( $T_{2.00 \pm 0.05}X$ ). The unit cell dimensions listed in Table 1, are reasonably consistent with those reported in the literature.<sup>2–4,7,11,12,15,17,22</sup>

The magnetic properties of  $\text{Cr}_2\text{As}$  and  $\text{Fe}_2\text{As}$  are well established through earlier magnetic susceptibility, magnetization, and neutron diffraction studies.<sup>5,10,13,14,16–19</sup> The thermomagnetic data for  $\text{Cr}_2\text{As}$  and  $\text{Fe}_2\text{As}$  obtained during the present investigation are consistent with the previous studies, and are accordingly not included here. No magnetic studies have hitherto been reported for  $\text{Co}_2\text{As}$  and  $\text{Rh}_2\text{As}$ .

The temperature dependence of the reciprocal magnetic susceptibility for  $\text{Co}_2\text{As}$  is shown in Fig. 1. The experimental data refer to a single sample, but measurements