

Figure 2. Net spin density of the distorted tetrahedral (4) CoCl_4^{2-} ion in Cs_2CoCl_6 constructed from a multipole population analysis of magnetic structure factors measured by Figgis et al.² The section is the (mirror) plane containing two chlorines and the cobalt center. The contours are in the same intervals as in Figure 1.

which is calculable from the multipoles derived from least-squares analysis. Such an evaluation is not, provided obvious tests are carried out on the completeness of the multipole expansion, subject to the termination effects of a Fourier series based on simple inversion of magnetic structure factors.

The multipole refinement of the Wedgwood data for CrF_6^{3-} has been described fully:⁴ the multipole-based spin density synthesis is shown in Figure 1a. The transformation of the multipole populations into "local orbital" populations⁴ demonstrated a $t_{2g}^{2.67(1)}$ configuration, a spin density of 0.31 (10) in a metal 4s orbital, and a spin transfer to the fluorines which effectively includes a redistribution of 0.02e from the σ - to the π -bond framework with a negative $p_z[p(\sigma)]$ orbital population of 0.05e (+0.03e in the $2p\pi(x,y)$ orbitals). All of this is clearly indicated in Figure 1a.

Two spin polarized calculations^{5,6} give spin transfer coefficients for Cr(III) in CrF_6^{3-} , viz. $-0.022e$ and $+0.026e$ for $f\sigma^*$ and $f\pi$ from a semi-empirical model and $0.048e$ and $+0.010e$ from an X- α calculation. Broadly, it appears that the calculations do not adequately reflect the magnitude of exchange correlation effects. We have therefore calculated a molecular spin density within the formalisms of both restricted and unrestricted Hartree-Fock theory and by using a double zeta basis. Full details will be published elsewhere but the two theoretical densities are shown in Figure 1b and 1c. We note the close agreement between the unrestricted Hartree-Fock solution (Figure 1c) and the experimental result (Figure 1a), indicating the sensitivity of the polarized neutron experiment to spin correlation effects, which appear as negative p_z orbital densities. Clearly in this case only unrestricted Hartree-Fock calculations provide sufficiently accurate eigenfunctions to match experiment.

The spin density in the CoCl_4^{2-} ion is shown in Figure 2. The correlation negative spin density separating the spin densities around the cobalt and chlorine atoms is striking. Orbital populations are $t_{2g}^{2.62(7)}$ (cobalt) (the e population is not statistically significant) with chlorine p_x being -0.01 (2) and the (σ) p_y and p_z populations being 0.03 (2) and 0.06 (1), respectively.

We have carried out a similar analysis of the molecular ferromagnet, aquabis(bipyridyl)di- μ -hydroxo-(sulfato)dycopper(II) and have shown⁷ how the experimental spin density reflects indirect exchange between the magnetically coupled copper atoms.

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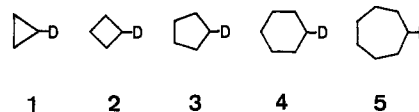
Secondary $^2\text{H}/^1\text{H}$ Isotope Effects on Carbon-13 Chemical Shifts in Cycloalkanes. Downfield Shifts Over Three and Four Bonds

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Isotope effects on chemical shifts are well-known¹ but so far have found only limited chemical applications. Mainly two reasons are responsible for this situation: (1) the theoretical interpretation of these parameters in polyatomic molecules is still incomplete; (2) systematic studies on large systems are rare. Through the introduction of the new generation of superconducting magnets with B_0 fields of up to 10 T, isotope effects transmitted through several bonds can now be measured in a straightforward manner, and new experimental information becomes available. In particular, deuterium isotope effects on carbon chemical shifts are of potential use for spectral assignments, structure determinations, and related investigations.² Additional experimental results bearing on these parameters are, therefore, of interest. In this communication we report secondary $^2\text{H}/^1\text{H}$ isotope effects on ^{13}C chemical shifts for cycloalkanes as measured from the monodeuterated systems 1-5. At the same time the $^{13}\text{C},^2\text{H}$ coupling constants of 1-5 were determined.



1-5 were synthesized from the corresponding Grignard compounds by hydrolysis, except for 1, where cyclopropyl lithium was the intermediate. In order to allow for an accurate determination of the isotope effect, 4:1 mixtures of the monodeuterated and the isotope-free system were investigated, prepared either by hydrolysis with $\text{D}_2\text{O}/\text{H}_2\text{O}$ (4:1) or by mixing. In the case of 1 methanolysis with $\text{CH}_3\text{OD}/\text{CH}_3\text{OH}$ (5:1) was employed. ^{13}C NMR spectra were measured at 9.4 T (100.61 MHz) by using the Fourier transform technique. In all cases the chemical shift equivalence of the ring carbons was removed. The assignment of the carbon resonances was based on the triplet splittings due to $^{13}\text{C},^2\text{H}$ spin-spin coupling and the order $^1J \gg ^3J > ^2J > ^4J$ valid for these parameters as indicated by the corresponding $^{13}\text{C},^1\text{H}$ coupling constants. The results are collected in Table I. In a few cases the $^{13}\text{C},^2\text{H}$ splittings measured were corrected for quadrupolar relaxation effects according to the theoretical treatment given by Pople.³ For this purpose the spin-lattice relaxation times T_1^Q for 2-5 were determined by using the inversion recovery technique.

Regarding the isotope effects, the most important new findings are the *downfield shifts* measured for C-3 in 3 and C-4 in 5. This unusual behavior is most clearly illustrated by a comparison of the spectra of 3 and 4 (Figure 1). So far, the majority of the isotope effects reported were *highfield* shifts, except for a few observations made for carbonyl compounds or deuterated hydroxy groups,^{1b,4} where hydrogen bonding is involved. No simple explanation for the exceptional result in the case of cyclopentane

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Table I. Deuterium Isotope Effects on Carbon Chemical Shifts $^n\Delta$, a ^{13}C - ^1H Coupling Constants (Hz), and Spin-Lattice Relaxation Times T_1^{Q} (s) for 1-5^b

compd	$^1\Delta$	$^2\Delta$	$^3\Delta$	$^4\Delta$	1J	2J	3J	T_1^{Qg}
1 ^c	0.3087	0.0641			24.61			
2 ^c	0.3630	0.1466	0.0272		20.51	(-) 0.54 ^e	0.88	3.70 ± 0.35
3 ^d	0.3737	0.1031	-0.0121		19.72	(-) 0.46 ^e	0.61	3.21 ± 0.13
4 ^d	0.4180	0.1037	0.0249		19.20	(-) 0.56 ^{e,f}	0.79	2.07 ± 0.04
5 ^d	0.4125	0.1098	0.0267	-0.0140	18.98	(-) 0.57 ^{e,f}	0.92	1.77 ± 0.04

^a Positive values are shifts to higher field. ^b Solvent $\text{CS}_2/\text{CD}_2\text{Cl}_2$ (4:1), concentration 1 M (3, 4, 5), 2.5 M (2), 5 M (1). ^c Experimental error ±0.0014 ppm and ±0.14 Hz, respectively. ^d Experimental error ±0.0009 ppm and ±0.09 Hz, respectively. ^e Negative sign assumed. ^f Corrected for quadrupolar relaxation effects. ^g Measured at 72.3 MHz.

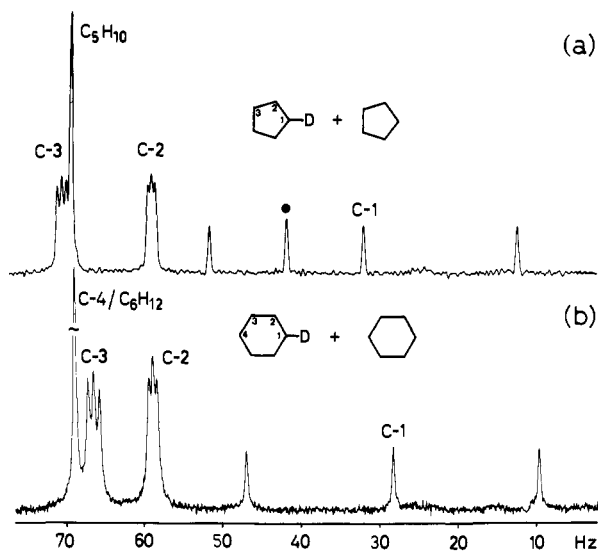


Figure 1. 100.61-MHz ^{13}C NMR spectra of (a) cyclopentane/cyclopentane- d_1 and (b) cyclohexane/cyclohexane- d_1 with ^1H broadband decoupling; signal marked with ● is due to unknown impurity.

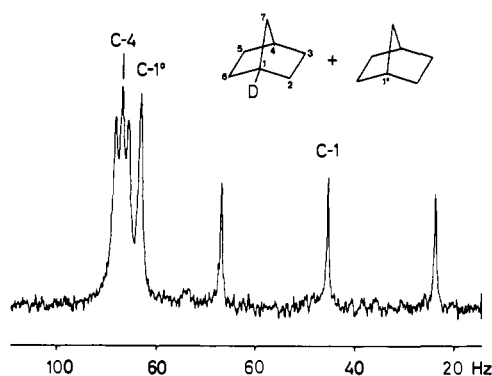


Figure 2. Partial 100.61-MHz ^{13}C NMR spectrum of norbornane and norbornane- $1-d$ (^1H broadband decoupled, concentration 1 M in CDCl_3).

and cycloheptane is at present available. On the other hand, the existing possibility that the downfield shifts are the consequence of an isotopic perturbation of degenerate conformational processes⁵ seems unlikely, since we were able to demonstrate that downfield isotope shifts also exist in rigid systems. Figure 2 shows the

(4) See for example, G. E. Maciel, P. D. Ellis, and D. C. Hofer, *J. Phys. Chem.*, **71**, 2160 (1967); F. W. Wehrli, D. Jeremić, M. L. Mihailović, and S. Milosavljević, *J. Chem. Soc. Chem. Commun.*, 302 (1978); D. H. O'Brien and R. D. Stipanović, *J. Org. Chem.*, **43**, 1105 (1978); as pointed out already by Anet [F. A. L. Anet and A. H. Dekmezian, *J. Am. Chem. Soc.*, **101**, 5449 (1979)], the observed shifts in these cases are presumably not "intrinsic" isotope effects but rather "equilibrium" chemical shift isotope effects.⁵ For downfield ^{13}C shifts upon deuterium substitution in paramagnetic molecules see F. H. Köhler and W. Prössdorf, *J. Am. Chem. Soc.*, **100**, 5970 (1978).

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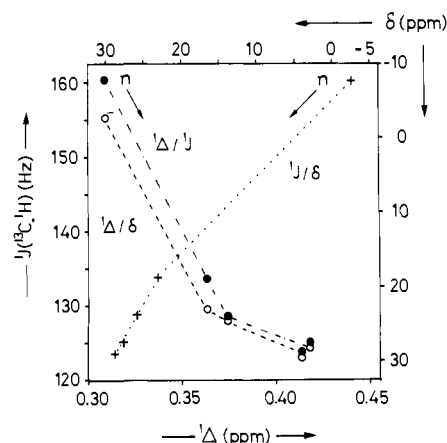


Figure 3. Correlations between $^1J(^{13}\text{C},^1\text{H})$ and $^1\Delta$ (●---●), $\delta(^{13}\text{C})$ and $^1\Delta$ (○—○), and $\delta(^{13}\text{C})$ and $^1J(^{13}\text{C},^1\text{H})$ (+...+) for cycloalkanes up to cycloheptane; ring size n . The $^1J(^{13}\text{C},^1\text{H})$ data are those of Table II. The nearly linear correlation between $^1J(^{13}\text{C},^1\text{H})$ and $\delta(^{13}\text{C})$ has already been noted.¹⁸

Table II. ^{13}C - ^1H Coupling Constants (Hz) in 1-5^a

compd	1J	2J	3J
1 ^b	160.32	(-) 2.55 ^e	
2 ^b	133.61	(-) 3.52	5.73 (2.87 ^d)
3 ^c	128.46	(-) 3.00	3.97
4 ^c	125.08	(-) 3.65	5.15
5 ^c	123.64	(-) 3.71	5.99

^a As calculated from the data of Table I, according to eq 1.

^b Experimental error ±0.91 Hz. ^c Experimental error ±0.59 Hz.

^d Value for one coupling path (cf. text). ^e Reference 14.

expanded region of the tertiary ^{13}C resonances of a mixture of norbornane and norbornane- $1-d$ where the downfield shift for C-4 is clearly visible ($\Delta_{\text{exp}} -0.0370 \pm 0.0006$).⁶ Formally, norbornane contains five- and six-membered rings, and the observed effect on C-4 is the sum of $^3\Delta$ for the five-membered and $^4\Delta$ for the six-membered partial structure. Since the latter effect is zero within experimental error for cyclohexane (cf. Table I), the relatively large downfield shift is not surprising. In the 3 position, on the other hand, $^3\Delta$ for the five- and six-membered rings coincide, and partial cancellation is expected. The small upfield shift observed here ($\Delta_{\text{exp}} +0.0079 \pm 0.0006$) is in perfect agreement with the data of Table I. These results clearly show that intrinsic $^2\text{H}/^1\text{H}$ isotope effects on ^{13}C chemical shifts can be

(6) Prior to these findings, a referee had suggested that the downfield shifts $^3\Delta$ and $^4\Delta$ observed for 3 and 5, respectively, are due to conformational isotope effects (see also footnote 4). While the introduction of deuterium certainly affects the populations of the existing conformers (for a recent example see R. Aydın and H. Günther, *Angew. Chem.*, in press), it is difficult to devise a convincing mechanism for the downfield shifts on this basis. Without further experiments it was, however, equally difficult to exclude this possibility rigorously. We have therefore included our findings for norbornane, which are part of a more complete study on rigid systems presently in progress in our laboratory, in this communication.

negative, and we believe that the same mechanism is responsible for the negative Δ values found for **3** and **5**.⁷

Comparing the Δ values of the cycloalkanes with the $^1J(^{13}\text{C}, ^1\text{H})$ data, we observe an inverse relation similar to the one derived from ^{31}P NMR data¹¹ (Figure 3). A closely related curve is obtained by plotting Δ against $\delta(^{13}\text{C})$ of the cycloalkanes,¹² and this finding parallels observations made for $^{13}\text{C}/^{12}\text{C}$ isotope effects on ^{19}F chemical shifts and $^{13}\text{C}, ^{19}\text{F}$ coupling constants.^{1a} The earlier empirical relations were restricted to systems with similar hybridization, and linearity was found. In our case sp^2 - (cyclopropane) and sp^3 -hybridized C-H bonds (cyclohexane, etc.) are included. Indeed, the nonlinearity in Figure 2 is primarily due to the entries for cyclopropane and, in part, cyclobutane. Since it is known that the s character in the C-H bond hybrids increases with decreasing ring size, both 1J and $\delta(^{13}\text{C})$ follow the s character, whereas Δ is proportional to the p character and thus should increase with C-H bond length.

From the $^{13}\text{C}, ^2\text{H}$ coupling constants the corresponding $^{13}\text{C}, ^1\text{H}$ coupling constants can be calculated by using eq 1.¹³ These

$$^nJ(^{13}\text{C}, ^1\text{H}) = 6.5144^nJ(^{13}\text{C}, ^2\text{H}) \quad (1)$$

results are given in Table II. From the 1J values precise data are available only for **1** and **4** (160.45 and 124.56 Hz, respectively^{14,15}), and no primary isotope effect can be recognized.¹⁶ The 2J and 3J values have not been measured so far. The latter show an interesting linear dependence on ring size if the value for **2** is divided by 2, due to the fact that two equivalent coupling pathways exist. The fact that the data measured are average values for different conformations precludes, however, a detailed discussion of their structural dependence. The same is true for the stereochemical aspects concerned with Δ in **2-5**.

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Note Added in Proof: Most recently, downfield ^{13}C NMR $^2\text{H}/^1\text{H}$ isotope shifts have been found over two bonds in carbocations (K. L. Servis and F.-F. Shue, *J. Am. Chem. Soc.*, **102**, 7233 (1980)) and over three bonds in cyclobutene (P. E. Hansen and J. J. Led, private communication).

(7) The present finding also supports the possibility of a negative (downfield) vicinal isotope effect in tropylium ion,⁸ where we had found $|\Delta| > |\Delta|$ from measurements on $\text{C}_4\text{H}_6\text{D}^+\text{BF}_4^-$ and $\text{C}_7\text{HD}_6^+\text{BF}_4^-$; $\Delta < 0$ was rejected at that time on the basis of the experimental evidence available.⁹ Furthermore, at least part of the downfield vicinal isotope effect reported by Saunders et al.¹⁰ for cyclopentenyl cation might be due to an intrinsic contribution rather than to "isotopic perturbation of resonance".

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(16) There are theoretical indications of a negative isotope effect on $^1J(^{13}\text{C}, ^1\text{H})$ ¹⁷ of less than 1%; a clearcut experimental proof is still lacking, however, since the observed changes were always within experimental error [see, for example, a recent investigation by M. Alei, Jr., and W. E. Wageman, *J. Chem. Phys.*, **68**, 783 (1978)].

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Relatively High-Yield Syntheses of Rotaxanes. Syntheses and Properties of Compounds Consisting of Cyclodextrins Threaded by α, ω -Diaminoalkanes Coordinated to Cobalt(III) Complexes

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Rotaxane is a compound consisting of a ring threaded by a chain having such large end groups that the chain cannot be extruded from the ring. This paper describes the syntheses of rotaxanes in relatively high yield, where the ring is α - or β -cyclodextrin (α - or β -CDX)¹ and the chain is the dimeric cobalt(III) complex, μ -(α, ω -diaminoalkane)bis[chlorobis(ethylenediamine)cobalt(III)] ($[(\text{en})_2\text{ClCo}(\text{N}-\text{N})\text{CoCl}(\text{en})_2]^{4+}$).²

The reaction between $[\text{CoCl}_2(\text{en})_2]\text{Cl}$ and N-N gives *cis*- $[\text{CoCl}(\text{en})_2(\text{N}-\text{N})]^{2+}$ and *cis*- $[(\text{en})_2\text{ClCo}(\text{N}-\text{N})\text{CoCl}(\text{en})_2]^{4+}$.³ Dimethyl sulfoxide (Me_2SO) has been found to be an excellent solvent for this purpose.^{3,4} Moreover, CDX has the notable property of forming inclusion compounds with various substrates.⁵ Therefore, the reaction between $[\text{CoCl}_2(\text{en})_2]\text{Cl}$ and N-N in the presence of CDX is expected to give rotaxane in the sequence shown in Scheme I.⁶ As the internal diameter of the cavity of CDX is 4.5 Å for α -CDX and 7.0 Å for β -CDX,⁵ $[\text{CoCl}(\text{en})_2]^{2+}$ moiety is bulky enough to prevent dethreading.⁷ This expectation was indeed realized.

Synthesis of [2]- $[(\text{en})_2\text{ClCo}(\text{don})\text{CoCl}(\text{en})_2](\text{ClO}_4)_4$]- β -CDX]-rotaxane- $3\text{H}_2\text{O}$.^{2,8} Method I: 2 mmol of don was dissolved in 10 mL of Me_2SO saturated with β -CDX and 2 mmol of *cis*- $[\text{CoCl}_2(\text{en})_2]\text{Cl}$ was added. The solution was kept at 75 °C for 30 min and then acidified with 2 mL of glacial acetic acid. Chromatographic separation by an SP-Sephadex C-25 (SPC) column afforded the rotaxane with a yield of $5 \pm 2\%$ (2 preparations). Method II: β -CDX and *cis*- $[\text{CoCl}(\text{en})_2(\text{donH})]\text{Cl}_3 \cdot 0.5\text{H}_2\text{O}$ ¹⁰ were dissolved in Me_2SO . After the addition of diethylamine, *cis*- $[\text{CoCl}_2(\text{en})_2]\text{Cl}$ was added. The solution was then treated as described in method I; yield was $7 \pm 1\%$ (6 preparations). Figure 1 shows an example of the chromatograms. The species f1, f5, f6, and f7 were characterized as $[\text{CoCl}_2(\text{en})_2]^{2+}$, $[\text{Co}(\text{Me}_2\text{SO})_2(\text{en})_2]^{3+}$, $[\text{CoCl}(\text{en})_2(\text{donH})]^{3+}$, and $[(\text{en})_2\text{ClCo}(\text{don})\text{CoCl}(\text{en})_2]^{4+}$, respectively. The species f2 and f3 are considered to be geometric isomers of $[\text{CoCl}(\text{Me}_2\text{SO})(\text{en})_2]^{2+}$. When the reaction was carried out in the absence of β -CDX, the chromatogram lacked only the band corresponding to f4. The solution containing the f4 species (LiClO_4 medium) was evaporated. The addition of acetone yielded a pink powder. Anal. Calcd for $[(\text{en})_2\text{ClCo}(\text{don})\text{CoCl}(\text{en})_2](\text{ClO}_4)_4 \cdot \beta\text{-CDX} \cdot 3\text{H}_2\text{O}$: C, 33.60; H, 6.19; N, 6.32; Co, 5.32; β -CDX, 51.2. Found: C, 33.76, H, 6.50; N, 5.91; Co, 5.14; β -CDX, 50.5 ± 2.0 .¹¹

All observations which will be given below lead to the conclusion

(1) α -CDX = cyclohexaglucofuranose. β -CDX = cycloheptaglucofuranose.

(2) Abbreviations used here: en, ethylenediamine; den, 1,10-diaminododecane; don, 1,12-diaminododecane; N-N, α, ω -diaminoalkane.

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(6) The absolute configuration of cobalt(III) moieties and the direction of the threaded CDX are not specified. Some ionic charges are omitted.

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(8) After Schill's nomenclature.⁹

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(10) donH⁺ denotes monoprotonated don.