parable to the analogous distances found in a Cu(II) hexahydroporphyrin[12a] whereas Cu–N3 and Cu–N4 are typical of Cu–N distances reported in several Cu porphyrins.[13]

The macrocycle itself is nearly planar (see Figure 1) with the largest displacements from the plane of the four nitrogens of 0.12 Å at C3, C13, and C17, of 0.13 Å at C15, and of 0.24 Å at O1. The oxygens lie 0.08 and 0.07 Å out of the planes of rings I and II, respectively. The molecule is slightly buckled: angles between the planes of the rings are 5.6° (I and II), 5.7° (I and III), 1.9° (II and III), 7.4° (I and IV), 2.3° (II and IV), and 1.9° (III and IV). Overall, these deviations from planarity are small compared to those of some free base[14] and nickel iBC's.[12a,15] The "planarity" is consonant with that of some other Cu porphyrins[13] and with the additional rigidity imposed by the exocyclic double bonds to the oxygens. Some of the deviations from planarity may also be due to the packing: the molecules of **2** form dimers in which rings III of neighbors overlap with a mean plane separation of 3.77 Å and a Cu–Cu distance of 6.12 Å. (An illustration of the overlap is included in the supplementary material.)

The redox chemistry of oxochlorins and dioxo iBC's and BC's has been examined by cyclic voltammetry. The results are listed in Table I. Surprisingly, the oxo compounds exhibit ring oxidation potentials very similar to those of the parent porphyrin, in sharp contrast to those of C's, iBC's, and BC's, which are significantly easier to oxidize than the porphyrin (by as much as 0.6 V[16,17]). An immediate consequence of this invariance is that the Fe^{II}CO complex of **1** oxidizes to Fe(III) with concomitant loss of CO as opposed to Fe^{II}(CO)iBC, which yields a stable Fe^{II}(CO)iBC^{+} π cation on oxidation.[16] Again, in contrast to the behavior of iBC derivatives, which are harder to reduce than P's by $\sim$0.3 V,[16,17] the dioxo iBC's are *easier* to reduce by $\sim$0.2 V for a net change of $\sim$0.5 V in reduction potential upon introduction of the dioxo functions onto the iBC skeleton. Note that the Fe(II)/Fe(III) couples also shift so that metal-centered reductions become easier.

Extended Hückel MO calculations help rationalize the observed redox trends and indicate that the HOMOs in P's, oxo C's, and dioxo iBC's and BC's fall within a narrow energy range, unlike those in C's, BC's, and iBC's. For example, the calculated energies for the HOMOs of model Zn complexes are as follows: ZnP, −11.159; Zn oxo C, −11.189; Zn dioxo iBC, −10.953; Zn dioxo BC, −10.935; ZnC,[16] −10.823; ZniBC,[16] −10.338; ZnBC,[16] −10.279 eV. The more negative orbital energies correspond to harder to oxidize molecules. For reduction potentials, the more negative LUMOs will translate into easier to reduce molecules. LUMO energies are as follows: ZnP, −9.195; Zn oxo C, −9.394; Zn dioxo iBC, −9.276; Zn dioxo BC, −9.547; ZniBC,[16] −8.752 eV. The calculated net charges on the metal also increase with addition of oxo groups, which should therefore result in the metal being harder to oxidize, as observed. The experimental redox trends are thus reasonably well predicted by the MO calculations.

The consequences of these properties in the chemistry of oxo compounds with substrates such as nitrites and nitrosyls, and their possible biological roles in dissimilatory nitrite reductases, are under investigation.

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Supplementary Material Available: Positional and thermal parameters for the non-hydrogen atoms of **2** and an illustration of the overlap of neighboring molecules (3 pages). Ordering information is given on any current masthead page.

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Magnetic Alignment Effects in the 500-MHz ^{1}H NMR Spectrum of *o*-Dichlorobenzene in Acetone-d_6

Frank A. L. Anet

Department of Chemistry and Biochemistry
University of California
Los Angeles, California 90024

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High magnetic fields (e.g., 10 T) can induce an observable partial alignment of diamagnetic molecules in ordinary isotropic solutions.[1] Because this effect is extremely small, detection by ^{1}H NMR has only been realized in polycyclic molecules that have large anisotropic magnetic susceptibilities.[2] The NMR spectra of such molecules have a field dependence which allows direct coupling constants (D's) to be obtained.[3] In deuterated molecules, ^{2}H NMR at a single magnetic field can provide information on the alignment of even simple aromatic molecules,[2] but this method has some limitations.[4]

Strongly resolution enhanced ^{1}H NMR spectra at a single high magnetic field of *symmetrical* systems are now shown to give information on extremely small direct coupling constants (down to a few millihertz), provided that frequencies can be measured to a fraction of 1 mHz.[5] The presence of residual second-order J splittings is essential for observing very small D's in these cases. The simplest example of a second-order splitting occurs in the three-spin A_2X–A_2B system, which in the first-order limit (i.e., a large chemical shift difference) shows a 1:1 doublet (separation = J_{AX}) for the A_2 nuclei. When the A–X chemical shift difference is no longer very large, the system becomes strictly of the A_2B type, and both A_2 lines split into narrowly spaced doublets. These second-order splittings are modified when D_{AA} is nonzero: one splitting increases whereas the other decreases.[6] The values and the relative signs of D_{AA} and J_{AB} can be determined, even if D_{AA} is less than the line width. Similar effects are predicted for other *symmetrical* spin systems, such as A_3B, A_3B_2, and AA′BB′. In all cases, only D's between *isochronous nuclei* are easily measured at a single high magnetic field.

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[1] For a recent review on molecular alignment in *normal* liquids, see: van Zijl, P. C. M.; Ruessink, B. H.; Bulthuis, J.; MacLean, C. *Acc. Chem. Res.* **1984**, *17*, 172–180.

[2] Gayathri, C.; Bothner-By, A. A.; van Zijl, P. C. M.; MacLean, C. *Chem. Phys. Lett.* **1982**, *87*, 192–196. The molecules studied were coronene and a porphyrin derivative. A referee has pointed out that some simpler molecules, namely, berberine and adenine, have also been successfully studied: Gayathri, C. Ph. D. Thesis, Carnegie-Mellon University, Pittsburgh, PA.

[3] The definition of D in this paper is the same as that used by MacLean and co-workers.[1,2] These D's must be divided by two when used with computer programs such as MIMER (Manschen, O. H.; Jacobson, J. P.; Schaumberg, K. QCPE, University of Indiana, Bloomington, IN, Program 394). The value of D_{HH} depends on the square of the magnetic field, the inverse cube of the H–H distance, and the averaged orientation of the H–H vector with respect to the magnetic field.

[4] (a) Alignment effects on ^{2}H spectra are larger than those on ^{1}H spectra because the quadrupole coupling constant in a C–D bond is up to an order of magnitude larger than the dipole–dipole interaction for a typical proton pair.[1,2] However, relaxation effects, which lead to line broadening, are proportional to the square of the (unaveraged) interactions, and consequently ^{1}H spectra are inherently more sensitive to alignment effects than are ^{2}H spectra.

[5] For other examples of ultrahigh resolution and/or ultrahigh accuracy in NMR spectra, see: Allerhand, A.; Addleman, R. E.; Osman, D. *J. Am. Chem. Soc.* **1985**, *107*, 5809–5810. Ellison, S. L. R.; Fellows, M. S.; Robinson, M. J. T.; Widgery, M. J. *J. Chem. Soc., Chem. Commun.* **1984**, 1069.

[6] Diehl, P.; Khetrapal, C. L. In "NMR, Basic Principles and Progress"; Diehl, P., Fluck, E., Kosfeld, R., Eds.; Springer: Berlin, 1969; Vol. 1, pp 1–95. An expansion of the expressions for the transition frequencies in the near A_2X limit with the D's being small gives the second-order splittings as $|J_{AB}^{2}/2\Delta\nu_{AB} \pm (3/2)D_{AA}|$.

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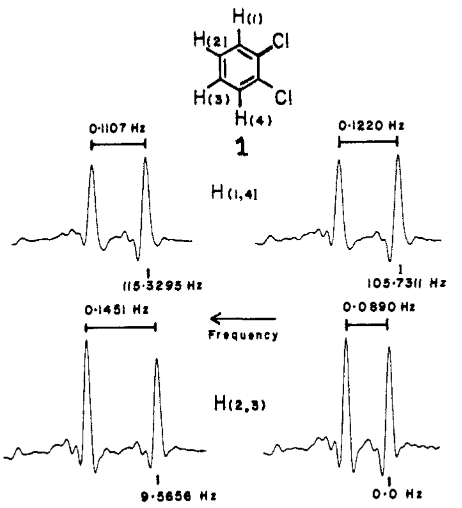

Figure 1. Four doublets arising from second-order J splitting, perturbed by D_{14} (top) or D_{23} (bottom), in the AA′BB′ ^{1}H NMR spectrum of **1** at 500 MHz.

Table I. NMR Parameters for **1**

parameter[a]	value, Hz	error,[b] Hz	parameter[a]	value, Hz	error,[b] Hz
$\nu_1 - \nu_2$	105.4249	±0.0004	J_{14}	0.3283	±0.0004
$J_{12} + D_{12}$	8.0667	±0.0005	D_{23}	−0.0175	±0.0005
$J_{13} + D_{13}$	1.5241	±0.0005	D_{14}	−0.0023	±0.0005
J_{23}	7.4879	±0.0005	σ[c]	0.0004	

[a] From MIMER,[3] with $D_{12} = -0.0170$ and $D_{13} = -0.0034$ Hz. [b] 95% confidence limits. [c] Standard deviation of fit of eight variables to 24 corrected line frequencies.[8]

As a practical example, the ^{1}H NMR spectrum of *o*-dichlorobenzene (**1**) in acetone-d_6 at 500 MHz has been measured.[7] This AA′BB′ spectrum should be symmetrical about its center if all D's are zero. In fact, the small second-order J splittings (ca. 0.1 Hz) do not occur in a symmetrical fashion, as can readily be seen from Figure 1.

The spectrum of **1**,[8] was fitted by means of the iterative program MIMER.[3] The sums, $J_{12} + D_{12}$ and $J_{13} + D_{13}$, are listed in Table I because the individual parameters cannot be determined to a meaningful accuracy at a single magnetic field. The largest deviation between the experimental and calculated line frequencies with the parameters given in Table I is 0.0006 Hz (0.6 mHz), i.e., 6–8% of the apparent line widths in Figure 1.

In **1**, the vectors formed by the H_{14} pair and the H_{23} pair are parallel, with $r_{14} = 2r_{23}$, so that D_{14} should be equal to $D_{23}/8$, i.e., 2.2 mHz, in agreement with the data in Table I. If the reasonable approximation is made that the chlorine atoms have only a small influence on the alignment of **1**, then a single ordering parameter suffices,[6,9] and calculations show that $S_{zz} = {}^1/_2 \langle 3 \cos^2 \theta - 1 \rangle = -2.3 \times 10^{-6}$, which is similar to the value ($\pm 2.5 \times 10^{-6}$, presumed to be negative) found for benzene-d_1 in acetone-d_6.[10] In order to obtain D_{12} and D_{13}, accurate measurements on **1** at lower fields are being undertaken, and the method described in this paper is being applied to other molecules.[11]

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[7] Spectra of a 10% solution of **1** in acetone-d_6 were measured on a Bruker AM 500 spectrometer at 23 °C. The spectrum width (SW) was 212 Hz and the acquisition time was 58 s. After applying a Lorentzian–Gaussian resolution enhancement (LB = ca. −0.07 Hz), the FID was zero-filled to 512 K points and Fourier-transformed. The final digital resolution was 0.8 mHz and the apparent line widths were 10–15 mHz (^{1}H T_1's in **1** are greater than 30 s). When no resolution enhancement was applied, the full line width at half-height was 0.07 Hz. The peak frequencies were measured to 0.1 mHz by increasing the SW parameter by a factor of 10 before calling the (interpolating) peak listing routine.

[8] Very small, but systematic, errors were found when fitting the experimental spectrum. The small splittings were made larger by the negative lobes introduced by the resolution enhancement (cf.: Sibisi, S. P. *J. Magn. Reson.* **1982**, *48*, 447–456). The lines of such doublets (separation <150 mHz) in **1** were therefore moved toward the doublet centers by (0.17 − Δν)/70 Hz, where Δν is the experimental splitting. These corrections ranged from 0.3 to 1.1 mHz, and for the second-order splittings that control the value of D_{14} (see Figure 1), the *difference* in the corrections to the observed splittings was only 0.2 mHz. The final peak positions were the average obtained from three slightly different resolution enhancements of the same FID data. Other data, with smaller acquisition times, gave peak positions in excellent agreement with the above, except for the very closely spaced doublets. Because of the resolution enhancement, the noise in Figure 1 is not random. Other treatments of the data, e.g., maximum entropy (Laue, E. D.; Skilling, J.; Staunton, J. *J. Magn. Reson.* **1985**, *63*, 418–424 and references therein), may have advantages and are being explored.

[9] The symmetry point group of **1** is C_{2v}, and the z axis is taken to be perpendicular to the ring plane.

[10] Bothner-By, A. A.; Gayathri, C.; van Zijl, P. C. M.; MacLean, C. *J. Magn. Reson.* **1984**, *56*, 456–462.

[11] Anet, F. A. L.; Kopelevich, M., work in progress. Previously obtained lower field NMR parameters of **1** have insufficient accuracy for the present purpose.

Deuterium Isotope Effects on the Ring Inversion Equilibrium in Cyclohexane: The *A* Value of Deuterium and Its Origin

Frank A. L. Anet* and Max Kopelevich

Department of Chemistry and Biochemistry
University of California
Los Angeles, California 90024

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It has been reported recently that the deuterium in cyclohexane-d_1 prefers the equatorial over the axial position by "about 200 J/mol" (i.e., ca. 50 cal/mol), as shown by three different kinds of NMR measurements.[1] Such an isotope effect is unexpectedly large,[1–5] and this has led us to reinvestigate the problem using Saunder's isotopic perturbation method.[6] We have thereby established that the free energy difference (the *A* value for deuterium[7]) is 6.3 ± 1.5 cal/mol, with deuterium more stable equatorial than axial. Our value is supported by molecular mechanics calculations based in part on experimental vibrational frequencies.

The selectively deuterated cyclohexane-d_{10} *cis*-I and *trans*-I (Figure 1) were chosen for NMR study, since a 1:1 mixture of these isotopomers can be easily prepared and they are very suitable for the application of Saunders' method.[8] The 200-MHz ^{1}H{D} NMR spectrum of this mixture in CS_2 at 25 °C shows two lines

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[3] Bovey, F. A.; Hood, F. P., III; Anderson, E. W.; Kornegay, R. L. *J. Chem. Phys.* **1964**, *41*, 2041–2044.

[4] Chertkov, V. A.; Sergeyev, N. M. *J. Am. Chem. Soc.* **1977**, *99*, 6750–6752.

[5] Data on cyclohexane-d_{11} at about −100 °C show that the intensities of the two ^{1}H NMR peaks are the same within experimental error (ca. 2%).[2–4] An energy difference of 50 cal/mol would give an easily observed intensity difference of about 15%. The results obtained by Ayden and Günther[1] are based on differences between large numbers in the integration of deuteron NMR peaks at low temperatures or on the assumption of extremely good additivity of isotope and temperature effects on chemical shifts. Thus, despite the great experimental care that was taken, the conclusions reached by these authors are not really convincing.

[6] (a) Saunders, M.; Jaffe, M. H.; Vogel, P. *J. Am. Chem. Soc.* **1971**, *93*, 2558–2559 (b) Anet, F. A. L.; Basus, V. J.; Hewitt, A. P. W.; Saunders, M. *J. Am. Chem. Soc.* **1980**, *102*, 3945–3946 and references therein.

[7] The definition of the *A* value as the conformational free energy difference in a *monosubstituted cyclohexane* (Winstein, S.; Holness, N. J. *J. Am. Chem. Soc.* **1955**, *77*, 5562–5578) is precise and also very useful, since cyclohexane is the prototype for all other saturated six-membered rings.

[8] Birch reduction of benzene-d_6 was carried out with a mixture of lithium, triethylamine, ethylenediamine, and methanol, and the cyclohexadiene-d_6 was isolated by VPC. The addition of deuterium was done in the presence of Wilkinson's catalyst [Rh(PPh$_3$)$_3$Cl] (cf.: Garbisch, E. W., Jr.; Griffith, M. G. *J. Am. Chem. Soc.* **1968**, *90*, 6543–6544). The isotopic purity of I from GC/MS was 95%.

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