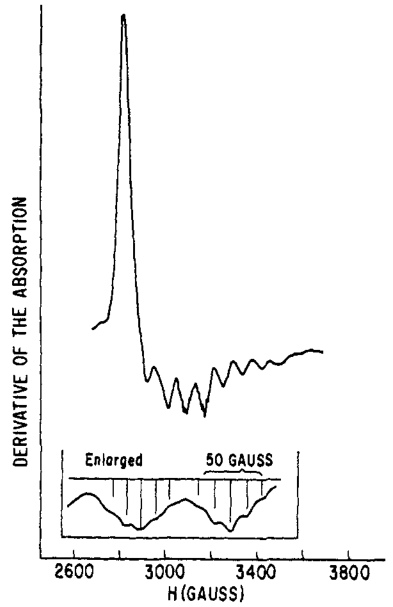

Figure 5. Esr spectrum of cobaloxime(II) in the presence of excess pyridine, at 90°K (frozen solutions in water), with the enlarged portion showing $^{14}$N shf splitting due to the interaction of the cobalt with two molecules of the base.

paramagnetic species in solution.[6] In solid solutions at 90°K the esr spectra of the 1:1 adducts of cobaloximes(II)[7] with acetonitrile or imidazole are almost indistinguishable from those of vitamin $B_{12r}$ (Figure 4, Table I). It is furthermore of interest that a 1:2 adduct is formed with pyridine (Figure 5), in conspicuous analogy to the behavior of Factor $B_r$.

**Acknowledgment.** This work was supported by National Science Foundation Grant GB 6174 and PRF Grant No. 3486-A3 from the Petroleum Research Fund, administered by the American Chemical Society.

(6) G. N. Schrauzer and R. J. Windgassen, *Chem. Ber.*, **99**, 602 (1966).

(7) "Cobaloximes" are bis(dimethylglyoximato)cobalt complexes. Dmg in Table I denotes the dimethylglyoximato monoanion.

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## Proton Couplings in Cyclohexane

*Sir:*

An uncounted number of vicinal and geminal proton couplings are known for substituted cyclohexanes.[1] As these parameters are unknown for cyclohexane, we wish to present our determination of them here.

Specifically deuterated cyclohexene, **1**, of greater than 97% isotopic purity was synthesized through the Diels–Alder dimerization of perdeuteriobutadiene[2] and ethylene. The synthesis of **2** was accomplished by homogeneous catalytic deuteriumation of **1** using tris(triphenylphosphine)rhodium(I) chloride catalyst,[3] nitrogen purged benzene solvent, and 2 atm of deuterium at room temperature.

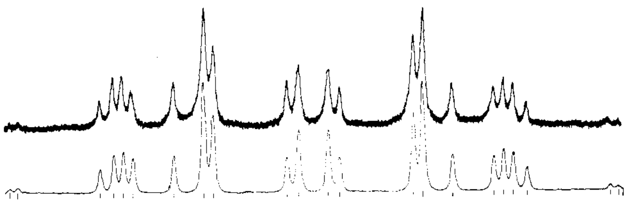
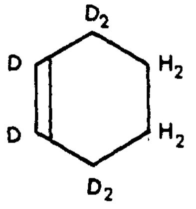
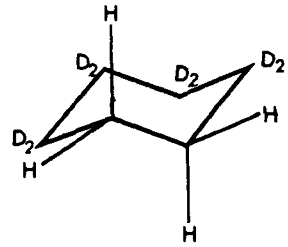


Figure 1. Deuterium-decoupled pmr spectrum of a 5% solution of **2** in $CS_2$ (mole/mole) at −103°. The total width of the spectrum is 63.58 cps. The bottom spectrum is the computed one.[7]

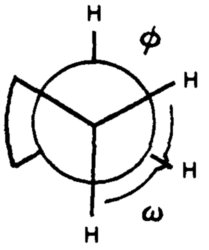
At 38°, the deuterium decoupled pmr spectrum[4] of a 5% (mole/mole) solution of **2** in $CS_2$ consists of a single resonance at $\tau$ 8.6014 ± 0.0003 ppm. Comparison with $\tau$ 8.5805 ± 0.0003 ppm for cyclohexane, determined under the same conditions, gives a deuterium isotope shift (upfield) of −1.25 cps. Lowering the sample temperature to −103° reduced the frequency of chair–chair conformational interconversion[5] to the extent necessary to give the AA′BB′ spectrum shown in Figure 1. Each absorption of the spectrum has a full width at half-height comparable to that for TMS (*i.e.*, between 0.4 and 0.5 cps). Six TMS side-band calibrated spectra were determined at this temperature and the averaged[6] transition frequencies used for a hand analysis based upon repeated spacings.[7] Statistical refinement of the parameters was effected through an iterative least-squares fit of the observed and computed spectra.[8] The resulting solution parameters are collected in Table I.



**1**



**2**



**3**

(1) See A. A. Bothner-By, *Advan. Magnetic Resonance*, **1**, 149 (1965), for a survey of some of the more reliable proton couplings.

(2) D. Craig and R. B. Fowler, *J. Org. Chem.*, **26**, 713 (1961).

(3) J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc.*, *A*, 1711 (1966).

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(4) The nmr spectra were determined on a Varian A-60 spectrometer with an NMR Specialties HD60A heteronuclear decoupler.

(5) For earlier variable temperature measurements on cyclohexane see F. R. Jensen, D. S. Noyce, C. H. Sederholm, and A. J. Berlin, *J. Amer. Chem. Soc.*, **84**, 386 (1962); F. A. L. Anet, M. Ahmad, and L. D. Hall, *Proc. Chem. Soc.*, 145 (1964); F. A. Bovey, F. P. Hood III, E. W. Anderson, and R. L. Kornegary, *J. Chem. Phys.*, **41**, 2041 (1964).

(6) Standard deviations of all transition frequencies were less than 0.08 cps, with the majority being less than 0.06 cps.

(7) E. W. Garbisch, Jr., *J. Chem. Educ.*, **45**, 480 (1968).

(8) Computations were performed on a CDC 6600 using the LAOCOON III program provided by A. A. Bothner-By. The plotting program was provided by S. Castellano and modified for our use by B. Hawkins.

**Table I.** Proton Chemical Shifts and Coupling Constants for Cyclohexane, **2**[a]

| Spectrum | Proton chemical shifts[b] |  | Proton coupling constants |  |  |  |  |
|---|---|---|---|---|---|---|---|
|  |  |  |  | *trans* |  | *cis* |  |
|  | Equatorial (E) | Axial (A) | Geminal | a,a | e,e | a,e | $^{13}$C–H |
| AA′BB′ (−103°)[c] | 96.96 | 68.20 | −13.05 | 13.12 | 2.96 | 3.65 |  |
| $^{13}$C–H satellite (38°)[d] | 83.92[e] |  | *f* | 8.07[g] |  | 3.73 | 125.00[h] |

[a] In cycles per second. The tabulated parameters are considered accurate to 0.05 cps. The probable errors for the parameters, that arise from the least squares analysis, fall between 0.01 and 0.02 cps. [b] Cycles per second downfield from TMS at 60 Mcps. [c] 5% of **2** in $CS_2$ (mole/mole). [d] Neat **2**. [e] $^1/_2(\nu_a + \nu_e)$. [f] Not accurately determined from the analysis. [g] $^1/_2(J_{a,a} + J_{e,e})$. [h] Neither the least-squares frequency fit nor the relative transition intensities are affected significantly by varying $J_{^{13}C-C-H}$ between 10 and −10 cps.

Analysis of the deuterium decoupled $^{13}$C–H (natural abundance) satellite spectrum of neat **2** at 38° (see Figure 2) verified the AA′BB′ spectral analysis. The low-field $^{13}$C–H satellites were shifted from the $C_6D_8H_4$ band 0.28 cps less than were the corresponding high-field ones. This shift gives an isotope shift of −0.14 ± 0.05 cps for the proton bonded to $^{13}$C. A comparable result has been reported for the $^{13}$C–H satellites of benzene.[9] Ten $C_6D_8H_4$ side-band calibrated spectra were determined and the averaged[6] transition frequencies used for an approximate AA′XX′ ($^{13}CH_AH_{A'}$-$CH_XH_{X'}$) analysis.[7] The solution parameters obtained therefrom were refined by analyzing[8] the spectrum as arising from an AA′A″A‴X system (X = $^{13}$C nucleus). The resulting parameters are given in Table I.

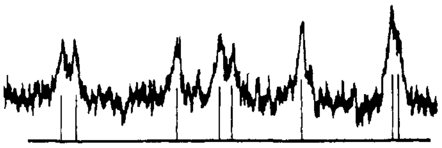

Figure 2. Low-field half of the deuterium-decoupled $^{13}$C–H satellite spectrum of neat **2** at 38°. The total width of the spectrum is 12.1 cps. The bottom stick spectrum is the computed one.

The theoretical relationship between dihedral angles ($\phi$) and vicinal proton couplings in saturated systems is given[10] by

$$J = A(\cos^2 \phi + n \cos \phi)$$

If $\phi$ is taken as the angle shown in **3**, the following set of three equations in four unknowns can be written. Solution of these equations using the values obtained

$$J_{a,a} = A[\cos^2 (\omega + \phi) + n \cos (\omega + \phi)]$$

$$J_{e,e} = A[\cos^2 (\omega - \phi) + n \cos (\omega - \phi)]$$

$$J_{a,e} = A(\cos^2 \phi + n \cos \phi)$$

for the vicinal proton couplings in **2** at −103° gives for $\omega = 120°$: $A = 13.13$, $n = 0.00$, and $\phi = 58.2°$; and for $\omega = 118°$: $A = 12.95$, $n = -0.02$, and $\phi = 57.2°$. The latter solution probably is the most reliable, as the H–C–H bond angles in cyclohexane are smaller than the tetrahedral value.[11] The value of $\phi$ of about 57° should be compared with that of about 55° as estimated[12] from electron diffraction data[11] on cyclohexane.

**Acknowledgment.** We appreciate support of this work by the National Science Foundation (Grant GP-8315).

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(9) J. M. Read, Jr., R. E. Mayo, and J. H. Goldstein, *J. Mol. Spectrosc.*, 22, 419 (1967).

(10) M. Barfield and D. M. Grant, *Advan. Magnetic Resonance*, 1, 149 (1965).

(11) M. Davis and O. Hassel, *Acta Chem. Scand.*, 17, 1181 (1963); E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, New York, N. Y., 1965, p 455.

(12) R. A. Wohl, *Chimia*, **18**, 219 (1964).

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## Intramolecular 1,3-Proton Transfers during Isofluorene–Fluorene Isomerization

*Sir:*

The substantial intramolecular components of 1,3- and 1,5-proton transfers in conjugated unsaturated systems catalyzed by strong bases in weakly acid solvents have been well documented by Cram, Schriesheim, and others.[1] Cram's approach is exemplified by the allylic rearrangement of 3-phenyl-1-butene to the more stable isomeric 2-phenyl-2-butenes, catalyzed by potassium *t*-butoxide in *t*-butyl alcohol. With a deuterium label in either the substrate (at $C_3$) or solvent (*t*-$C_4H_9$-OD) deuterium loss or incorporation into product was followed in order to measure intermolecularity.[1] Formation and rapid collapse of hydrogen-bonded delocalized carbanions, during which exchange of the bonding alcohol molecule with surrounding solvent does not occur, has been invoked to account for the frequently noted high degree of intramolecularity.[1] We now wish to report the overwhelming intramolecular nature of a 1,3-proton transfer carried out in strongly acidic trifluoroacetic acid (TFA), wherein trifluoroacetate is the strongest base available.[2] The systems

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(1) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, Chapter 5.

(2) A concerted uncatalyzed 1,3-electrocyclic hydrogen shift would have to be antarafacial, according to the Woodward–Hoffmann rules (R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968)) which is obviously impossible in our systems. On the other hand, our rearrangements could also come about by a series of 1,5-suprafacial hydrogen shifts. We cannot rigorously disprove this possibility, but it is not consistent with the variation in $k_{intra}/k_{inter}$ for cyclization of VI when deuterium is in the substrate as compared with solvent (less intermolecular protonation), nor with the apparent catalytic effect of added sodium trifluoroacetate.[3a]

(3) (a) Qualitative evidence for base catalysis was obtained with VI, which gave essentially no 9-phenyl-1,2-benzfluorene (VII) in refluxing trifluoroacetic anhydride during 6 hr, whereas addition of 2 equiv of sodium trifluoroacetate in an otherwise comparable experiment produced 65% of VII. In highly ionized TFA itself, the greatest yield of VII (~100%) resulted. The increased yields in these reactions roughly parallel the higher concentrations of trifluoroacetate in the medium. Ad-