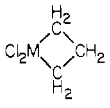
Ti bonded to an appropriate orbital on the ligand (1s for H or an sp^3 hybrid orbital for C). On the other hand, the two Ti–Cl bonds are quite ionic and can be rather accurately visualized as two chloride (Cl^-) ligands. Thus the electronic states of the Ti can be most accurately described as Ti(II) with both d electrons of the d^2 configuration involved in covalent bonds to the C (or H) ligands. Often such a system would be described formally as Ti(IV), with the C (or H) ligands considered as anions. We recommend strongly against such formal assignments of the oxidation state since it provides a distorted picture of where the electrons are actually located.

An interesting question here is what bond angle is expected for a d^2 system making two covalent bonds. An s^2 atom leads to bond angles of 180° (e.g., BeH_2) and p orbitals lead to bond angles of 90–92° [e.g., SiH_2, PH_2, and SH_2. See, e.g., W. A. Goddard III and L. B. Harding, *Annu. Rev. Phys. Chem.*, **29**, 363 (1978)]. For two $d\sigma$ orbitals to be orthogonal, they must be at 54.7° (or 125.3°), as in Figure 1a. However, intraatomic electron repulsion destabilizes this optimum $d\sigma\, d\sigma'$ configuration[18] and favors a $d\sigma\, d\delta$ configuration that would lead to a 90° bond angle. The observed optimum angle of ~75° is a compromise between these two effects.

The highly covalent character of the Ti–C (or Ti–H) bonds is critically dependent upon the highly ionic character in the Ti–Cl bonds. Similar results should obtain if the two Cl are replaced by other electronegative ligands such as cyclopentadienyl (Cp), F, or alkoxy.

The same considerations should apply to Zr and Hf and with similar energetic factors so that similar bond angles are expected.

For systems such as



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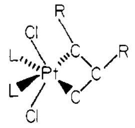
where M = Ni, Pd, or Pt, the above results suggest ionic M–Cl bonds and fairly covalent M–C bonds so that these systems are best described as d^8 with two singly occupied d orbitals involved in M–C bonds and the remaining three d orbitals doubly occupied. [Often **6** would be denoted as involving the M(IV) oxidation state.] The arguments for d^2 systems of Ti, Zr, and Hf apply equally to these d^8 systems of Ni, Pd, Pt, Rh, and Ir, and hence we expect similar geometries, θ(CMC) = 75°. Indeed, structural studies[5] on



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lead to θ = 74–76°.

In summary, we find that tetracoordinate compounds of the Ti and Ni columns having two bonds to electronegative species (e.g., Cl, Cp, OR) and two bonds to alkyl groups (or hydrogens) have covalent metal–alkyl (or metal–H) bonds involving nearly pure d orbitals on the metal. Because of bonding and electron repulsion considerations for these d^2 and d^8 systems, the optimum CMC angle is ~75° for a system without large strain or steric effects.

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Registry No. 2, 79953-32-5; **3**, 79899-81-3; **4**, 79953-33-6.

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(18) For example, a p^2 configuration leads to one triplet state (^3P), while a d^2 configuration leads to two triplet states (^3F and ^3P), separated by ~20 kcal/mol. It should be pointed out that previous theoretical work on preferred bond angles [e.g., J. W. Lauher and R. Hoffman, *J. Am. Chem. Soc.*, **96**, 1729 (1976)] has ignored this intraatomic electron repulsion effect.

Deuterium Isotope Effects on Carbon-13 Chemical Shifts in Cyclophanes. Deshielding Intrinsic Through-Space and Through-Bond Effects

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Deuterium isotope effects on ^{13}C NMR chemical shifts are often used for spectral assignments,[1] and studies on their correlation with molecular structure are therefore desirable. Most deuterium isotope effects on ^{13}C shifts reported so far are *shielding*,[2] and only relatively few examples of *deshielding* effects have been observed.[3] Some of these unusual deshielding effects[3f] are rationalized[4,5] in terms of isotopic perturbations of degenerate conformational equilibria;[6] others[3d,3e] could be a consequence of the slightly different hydrogen-bonding abilities of OH relative to OD groups. The deshielding by deuterium of the positively charged carbon in classical static β-deuteriocarbocations (C^+–C–D) results from less efficient hyperconjugative electron release by C–D compared to C–H bonds.[3h]

We now report the first examples of *intrinsic through-space* deuterium isotope effects on ^{13}C chemical shifts as well as a number of long-range *through-bond* effects in cyclophanes carrying deuterated methyl groups.[7] Importantly, the majority of both types of isotope shifts are *deshielding*. Table I contains the data,[8,9]

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(1) Wehrli, F. W.; Wirthlin, T. "Interpretation of Carbon-13 NMR Spectra"; Heyden: London, 1978; pp 107–110.

(2) For a list of pertinent references, see: Hansen, P. E.; Led, J. J. *Org. Magn. Reson.* **1981**, *15*, 288–293.

(3) (a) Maciel, G. E.; Ellis, P. D.; Hofer, D. C. *J. Phys. Chem.* **1967**, *71*, 2160–2164. (b) Morris, D. G.; Murray, A. M. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1579–1584. (c) Hawkes, G. E.; Randall, E. W.; Hull, W. E.; Gattegno, D.; Conti, F. *Biochemistry* **1978**, *17*, 3986–3992. (d) Kurobane, I.; Vining, L. C.; McInnes, A. G. *Tetrahedron Lett.* **1978**, 4633–4636. (e) O'Brien, D. H.; Stipanović, R. D. *J. Org. Chem.* **1978**, *43*, 1105–1111. (f) Wehrli, F. W.; Jeremić, D.; Mihailović, M. L.; Milosavljević, S. *J. Chem. Soc., Chem. Commun.* **1978**, 302–303. (g) Newmark, R. A.; Hill, J. R. *Org. Magn. Reson.* **1980**, *13*, 40–44. (h) Servis, K. L.; Shue, F.-F. *J. Am. Chem. Soc.* **1980**, *102*, 7233–7240. (i) Hansen, P. E.; Led, J. J. *Org. Magn. Reson.* **1981**, *15*, 288–293. (j) Aydin, R.; Günther, H. *J. Am. Chem. Soc.* **1981**, *103*, 1301–1303.

(4) Anet, F. A. L.; Dekmezian, A. H. *J. Am. Chem. Soc.* **1979**, *101*, 5449–5451.

(5) Andrews, G. C.; Chmurny, G. N.; Whipple, E. B. *Org. Magn. Reson.* **1981**, *15*, 324–325.

(6) Anet, F. A. L.; Basus, V. J.; Hewett, A. P. W.; Saunders, M. *J. Am. Chem. Soc.* **1980**, *102*, 3945–3946.

(7) All compounds apart from **1d** were prepared via the aldehydes which were obtained by formylation of [2.2]paracyclophane, 4-methyl[2.2]paracyclophane, and $[2_4]$(1,2,4,5)cyclophane, respectively, with dichloromethyl methyl ether/$TiCl_4$. The aldehydes were reduced with $LiAlH_4$ or $LiAlD_4$ as appropriate, the alcohols treated with PBr_3, and the bromides reduced with $LiAlH_4$ ($LiAlD_4$) to give the methyl derivatives. Compound **3a** had mp 198–199 °C (from petroleum ether); **1d** was obtained via the sequence $RH \rightarrow RCOCH_3 \rightarrow RCO_2H \rightarrow RCD_2OH \rightarrow RCD_2Br \rightarrow RCD_3$ (R = [2.2]-paracyclophan-4-yl).

(8) 100.6-MHz ^{13}C and 400.1-MHz ^1H NMR spectra were recorded. Molar ratios of deuterated and nondeuterated compounds were distinctly different from unity to facilitate distinction between the resonances of the two species. Narrow spectral widths and Lorentzian-to-Gaussian transformation [Ferrige, A. G.; Lindon, J. C. *J. Magn. Reson.* **1978**, *31*, 337–340] were used to resolve small chemical shift differences.

(9) Assignment of the ^{13}C NMR spectra was made by selective $^{13}C\{^1H\}$ double resonance, by SFORD, by comparison of the spectra with those of a number of dimethyl[2.2]paracyclophanes and of $[2_4]$(1,2,4,5)cyclophane, respectively, and from two- and three-bond C,D coupling constants. The ^1H NMR spectra were assigned by homonuclear decoupling and extensive NOE difference experiments. ^{13}C chemical shifts (relative to $CDCl_3$, δ 77.05): **1a**, 139.49, 139.37, 139.35 (C-6,11,14), 138.20 (C-3), 136.97 (C-4), 135.32 (C-5), 134.13 (C-8), 133.26, 133.20 (C-12,13), 132.03 (C-16), 129.94 (C-7), 127.62 (C-15), 35.42 (C-10), 35.04 (C-9), 33.89 (C-1), 33.43 (C-2), 20.16 (CH_3); **2a**, 139.29 (C-11,14), 137.82 (C-3,6), 136.30 (C-5,8), 134.28 (C-4,7), 132.37 (C-13,16), 128.46 (C-12,15), 33.59 (C-1,10), 33.06 (C-2,9), 19.64 (CH_3); **3a**, 141.76, 141.71, 141.26 (C-6,8,11,15,12,14), 140.35 (C-3,5), 139.85 (C-16), 139.00 (C-4), 137.24 (C-7), 132.94 (C-13), 34.33, 33.26 (C-9,18,10,17), 32.23 (C-1,20), 29.06 (C-2,19), 18.80 (CH_3).

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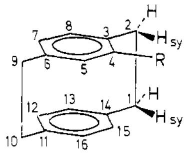
Table I. Deuterium Isotope Effects on ^{13}C Chemical Shifts in Deuterated Methylcyclophanes[a-c]

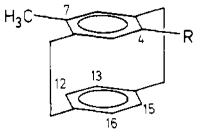
carbon	1b	1c	1d	2c	3c
C-1	n.m.[d]	+10	+13	n.m.	+10
C-2	n.m.	−6	−10	n.m.	-6
C-3	+12	+17	+26	+16	+13
C-4	−26	−52	−80	−52	−43
C-5				+6	+13
C-6		br[e]	−7	−3	
C-7			+10	+5	+12
C-8		−11	−15	−9	
C-9	n.m.	br	+4	n.m.	
C-13				[f]	+30
C-15	+11	+23	+35	+22	

[a] Values given in ppb (1 ppb = 0.001 ppm); positive sign denotes deshielding in the deuterated compound. [b] Measured at 100.6 MHz, solvent $CDCl_3$, relative to the chemical shifts of **1a**, **2a**, and **3a**, respectively. [c] Digital resolution 1.2 ppb. A conservative error estimate for the isotope shifts is ±3 ppb. [d] Not measured. [e] Only line broadening observed; chemical shift difference not resolved. [f] $|\delta_{13} - \delta_{16}| = 4$ ppb. The resonances for C-13 and C-16 in **2c** could not be assigned individually.

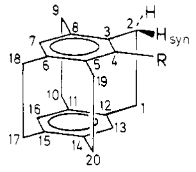
which were obtained from mixtures of the deuterium and protium analogues.



1a-d



2a,c



3a,c

[R= CH_3(a); CH_2D(b); CHD_2(c); CD_3(d)]

The isotope shifts over two and four bonds at the carbons ipso and meta to the methyl substituents are found to be shielding.[10] Ortho and para carbons, however, are deshielded,[11] and we interpret this by decreased electron donation of the benzylic C–D relative to the C–H bonds, i.e., we are dealing with the same "hyperconjugative" effect (though smaller by two orders of magnitude) as advanced by Servis[3h] to explain the shifts in his static classical β-deuteriocarbocations. Indeed, we suggest the same mechanism also to be responsible for a number of previously reported deshielding deuterium isotope effects, viz., on the carbonyl carbon in acetone-d_6[3a] and in 3,3-dideuteriocamphor derivatives,[3b] on C-β in *N*-deuterioenamines,[3c] on C-4 in *O*-deuteriophenols,[3g] and on C-1 in 3-deuteriocyclobutene.[3i] In all these cases, the X–D bond (X = C, N, O) is either adjacent to an electron-deficient carbon atom or to an unsaturated C=C fragment.

The most remarkable finding in the cyclophane systems are the deshielding isotope effects upon the carbons pseudogeminal to the deuterated methyl groups, formally seven bonds apart. Clearly, these are through-space effects, due to the close proximity of the interacting nuclei. This is the first occurrence of isotope effects on ^{13}C chemical shifts which are not transmitted through chemical bonds[12] and which are not of conformational origin. Conformational factors can be excluded for two reasons. Firstly, the effects are of similar magnitude both in the relatively flexible molecules **1c** and **2c** and in the very rigid framework of **3c**. Secondly, as pointed out by Andrews et al.,[5] lifting of conformational degeneracy by isotopic substitution must leave unchanged the average shift of nuclei which can be interchanged by symmetry operations on the average structure. Thus, if the assumption were correct that the deshielding of C-15 in **2c** is caused by a change of the average distance between C-4 and C-15, then increased shielding of the same magnitude would be expected for C-12, which is not observed. Further, yet much smaller, through-space isotope effects are found on C-1 and C-2 of the ethano bridges. The effect on C-2 is shielding which may indicate that the relative orientation of the carbon affected and the deuterium-containing group governs both sign and magnitude of the through-space isotope effect.

We also observed deuterium isotope effects on the chemical shifts of some protons close in space to the deuterium nuclei. In **1d**, H-2_{syn} and H-15 are shielded relative to **1a** by 4.0 ± 0.1 and 6.0 ± 0.2 ppb, respectively. The signals for H-1_{syn} are only broadened so that an effect of ca. 1 ppb can be estimated. In **3c**, isotope effects are discernible on the chemical shifts of H-2_{syn} (−4.7 ± 0.1 ppb) and H-13 (−5.8 ± 0.3 ppb). Further studies of the dependence of deuterium isotope effects on ^{13}C and ^{1}H chemical shifts are required to define their dependence on geometrical factors.

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Registry No. 1a, 24262-07-5; **1b**, 80028-60-0; **1c**, 80028-61-1; **1d**, 80028-62-2; **2a**, 35117-18-1; **2c**, 80028-63-3; **3a**, 80028-64-4; **3c**, 80028-65-5.

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(10) For convenience, this effect of the deuterons has occasionally been termed "inductive"[3h] because hydrogen and deuterium *act* as if their electronegativities were different. One referee disagrees with the use of this term and, to avoid confusion, stresses that all isotope effects arise because the different isotope masses cause differences in the amplitudes of zero-point motions on the potential-energy surface of the isotopomers.

(11) Similarly, successive replacement by deuterium of the benzylic protons in toluene causes decreased shielding of the para carbon (+13 ppb for $PhCD_3$); unpublished results from our laboratory.

(12) Anet[4] reported steric deuterium isotope effects on ^{1}H chemical shifts in two systems in which the distances between the interacting protons and deuterons were estimated to be 1.6 and 2.0 Å, respectively. No influence of deuterium on the ^{13}C shifts could be observed in these cases. Molecular models indicate that the corresponding internuclear distances in our systems are larger than in Anet's.

Crystal Structure of Tetrakis(trimethylsilyl)ethylene at −70 °C[1]

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The molecular structures of overcrowded olefins are of interest in order to determine how the molecules relieve their inherent repulsive nonbonded interactions. Widening bond angles, nonplanar distortions of the double bond, and/or carbon atom pyramidalization can be factors determining the most stable conformations of the molecules.[2]

We have recently reported the preparation and some interesting properties of tetrakis(trimethylsilyl)ethylene (**1**).[3,4] Preliminary investigations indicate that the olefin should be twisted from planarity. We now wish to report the molecular structure of **1** which shows several unusual features.

Tetrakis(trimethylsilyl)ethylene was prepared as described before,[3,5] and crystals appropriate for the X-ray diffraction study were grown from hexane. Since **1** sublimes quickly at room temperature under X-ray irradiation, diffraction data were collected at −70 °C by using a specimen coated with thin layers of

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(1) Chemistry of Organosilicon Compounds. 151.

(2) For reviews, see: (a) Liebman, J. F.; Greenberg, A. *Chem. Rev.* **1976**, *76*, 311. (b) Tidwell, T. T. *Tetrahedron* **1978**, *34*, 1855.

(3) Sakurai, H.; Nakadaira, Y.; Kira, M.; Tobita, H. *Tetrahedron Lett.* **1980**, *21*, 3077.

(4) Sakurai, H.; Tobita, H.; Kira, M.; Nakadaira, Y. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 620.

(5) Low temperature (0 °C) reaction improved the yield of **1** up to 74%.