differential bulk susceptibility effect invoked by Herz, *et al.*,[43] or the contact contribution suggested by Tjan and Visser.[64] There are two possible explanations for the opposite sign of the "normal" shifts induced by **1** and **19**: the 1:1 adducts of **1** presumably have a threefold axis of symmetry with the Eu–substrate bond along the magnetic axis so that either (a) in adducts of **19**, the substrate is perpendicular to the principal axis, ϕ is greater than 54.7° and the anisotropy of the Eu^{3+} ion has the same sign as **1** or (b) the anisotropy has a different sign and the substrate lies along the principal magnetic axis. The evidence on this point is ambiguous as the adducts of **19** are of unknown stoichiometry and symmetry. An asymmetric adduct without a principal axis actually has a more complex PC shift expression than eq 30, requiring extra angular terms, but the great similarity of behavior of the nitrone with **1** and **19** implies that the simple equation is, to a reasonable approximation at least, adequate.

The sign reversals of lanthanide-induced shifts indicate that the r^{-3} "distance only" criterion, which frequently gives a good fit to the data, must be used with caution. Shift reagents will associate with substrates so as to minimize steric interactions (consistent with association occurring) and inspection of models reveals that frequently such configurations are ones in which ϕ variations are minimized. Large ϕ variations are expected only where the substrate is forced to envelop the metal ion, as is the case with all reported examples.

Experimental Section

Nmr spectra were measured at normal probe temperatures on Varian Associates HA 100 or XL 100-15 instruments operated at 100 MHz for proton work and 40.5 MHz for ^{31}P work. CCl$_4$ and CDCl$_3$ were dried over preheated 4A molecular sieves. Proton chemical shifts in organic solution are in δ units (parts per million) from internal TMS, while in D$_2$O solutions tetramethylammonium iodide (NMe$_4^+$, δ 3.19) was used as an internal standard as DSS appeared to interact with the lanthanide nitrates.

Ln(NO$_3$)$_3$·6H$_2$O were prepared by dissolving the oxides (99.9%, Koch-Light) in the stoichiometric amount of standardized AR nitric acid and evaporating the solutions. Deuterated samples were obtained by repeatedly dissolving the hydrated salts in D$_2$O and evaporating to constant weight over P$_2$O$_5$ *in vacuo*. Ln(DPM)$_3$ samples were prepared by standard procedures,[65] but without precautions to exclude air. A more rapidly soluble form of the complex is obtained if the pure sublimed material is dissolved in dry AR benzene and stripped down on a rotary evaporator. Eu(PTA)$_3$ was prepared by the method of Shigematsu, *et al.*[16] All shift reagents were stored *in vacuo* over P$_2$O$_5$ until just before use.

Substrates were prepared by standard procedures or donated by colleagues in this laboratory. We are particularly grateful to Dr. D. R. Crump for the synthesis of the ethylene thioketal **22** and several other steroids.

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Carbon-13 Chemical Shifts in Monoalkyl Benzenes and Some Deuterio Analogs[1]

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Abstract: Carbon-13 chemical shifts are reported for all carbons in toluene, ethylbenzene, cumene, and *tert*-butylbenzene, and for six deuterium-substituted analogs. Monotonic trends are observed for the ^{13}C shieldings of all carbon positions, except for two small shifts in the *tert*-butylbenzene case. The ranges of the shifts are in the order C(β) > C(1) > C(α) > C(2) > C(4) > C(3). All of the regular trends are toward decreased shielding with increased methyl substitution at the α carbon, except for the C(2) trend, which has the opposite sense.

Alkyl benzenes have been the subject of earlier ^{13}C nmr (cmr) studies.[3–8] However, the early cmr equipment and techniques were incapable of providing chemical shifts with the precision of today's standards, or unequivocal assignments of certain ring carbons. As precise cmr data are now routinely attainable, and because alkyl benzenes often serve as models for concepts such as "inductive effects" and "hyperconjugation," precise ^{13}C shieldings of these species are needed. Furthermore, such data will serve as useful and reasonable challenges to emerging theories of ^{13}C shielding. On this point, these data are especially pertinent, in that they provide good cases for gauging the ability of a theory to account for substituent effects (*e.g.*, methyl substitution), without introducing the uncertainties of

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Table I. ^{13}C Chemical Shifts for Monoalkyl Benzenes[a]

Alkyl group	Aromatic carbons[b]				Aliphatic carbons[c]	
	1	2	3	4	α	β
CH_3	137.69	129.26	128.46	125.64	21.35	
	[−0.10][e]	[−0.01]			[−0.86]	
CH_2CH_3	144.09	(127.99)[d]	(128.48)[d]	125.90	29.24	15.82
					[−0.71]	[−0.15]
$CH(CH_3)_2$	148.59	(126.50)[d]	(128.49)[d]	125.99	34.45	24.11
					[−0.44]	[−0.10]
$C(CH_3)_3$	150.55	125.07	128.10	125.42	34.47	31.42

[a] Values given in parts per million with respect to 20% TMS (internal reference). More positive values correspond to lower shielding. Shifts accurate to ±0.03 ppm. [b] The indices 1, 2, 3, and 4 refer to the substituted ortho, meta, and para carbons, respectively. [c] The symbols α and β refer to the positions of aliphatic carbons relative to the substituted carbon of the aromatic ring. [d] Values in parentheses are based on arbitrary assignments of the ortho and meta carbons. [e] Numbers in brackets are the effects on the observed ^{13}C chemical shifts of deuterium substitution of all α hydrogens.

heteroatoms into the theory. Thus, initially the theory may be designed and tested only for handling hydrocarbon frameworks.

As part of a continuing, systematic study of structural and substituent effects on ^{13}C chemical shifts, we have determined the effect of simple alkyl groups and their deuterio analogs on the ^{13}C shieldings of the substituted benzene ring.

Experimental Section

Nmr Measurements. ^{13}C nmr measurements on the undeuterated substances were carried out at 25.1 MHz on a modified HA-100 spectrometer, equipped for multiple-scan, centerband-sweep, ^{19}F-lock operation, as described previously.[9] Natural abundance samples of pure substances in 8-mm sample tubes were employed, with 20 vol % internal tetramethylsilane added as the reference; ambient probe temperature was typically 45°. Both pseudorandom proton noise decoupling and off-resonance proton decoupling were employed for each compound.

^{13}C measurements on the deuterium-labeled compounds were obtained in the pulse/Fourier transform mode at 22.6 MHz on a Bruker HFX-90 spectrometer equipped with a Digilab FT/NMR pulse and data system. The samples were contained in 5-mm tubes, which were held concentrically inside 10-mm tubes with Teflon spacers; the outer annulus of this arrangement was filled with C_6F_6, which provided the ^{19}F lock signal. The Fourier transforms were based upon 8K data points and employed either the power spectrum, or phase-corrected, absorption mode. The data were obtained at an ambient probe temperature of 39°.

Materials. Toluene, ethylbenzene, isopropylbenzene (cumene), and *tert*-butylbenzene were Eastman White Label Materials. Toluene-*α,α,α-d*$_3$ was obtained from Isomet, Inc.

Toluene-*3-d*. The reaction of 3-lithiotoluene (prepared at 0° in anhydrous ether from *m*-bromotoluene and *n*-butyllithium) with deuterioacetic acid gave, according to the procedure of Mowery and Streitwieser,[10] more than a 50% yield of toluene-*3-d* after gc purification.

***tert*-Butylbenzene-2-*d*$_1$.** The reaction of 2-lithio-*tert*-butylbenzene, prepared from *o*-bromo-*tert*-butylbenzene (K and K), with deuterioacetic acid gave, by the same procedure,[10] a nearly quantitative yield of *tert*-butylbenzene-*2-d*$_1$. Mass spectral analysis showed that 87% was monodeuterated.

Ethylbenzene-*α,α-d*$_2$. To the Grignard reagent prepared from 1.76 g (0.0137 mol) of *α*-chlorotoluene-*α,α-d*$_2$,[11] 1.10 g (0.0452 g-atom) of Mg, and 20 ml of ether was added, with stirring under a nitrogen atmosphere, 3.46 g (0.0274 mol) of freshly distilled dimethyl sulfate. The Grignard reagent was prepared by a procedure analogous to that previously described for *α*-chloro-*m*-fluorotoluene-*α,α-d*$_2$.[11] After being stirred an additional 3.5 hr, the mixture was decomposed by the dropwise addition of a saturated NH_4Cl solution. The organic phase was separated and the aqueous phase was extracted twice with 20-ml portions of ether. After concentrating the combined organic phases to *ca.* 5 ml, 0.986 g (67%) of the desired product was collected from a 0.25 in. × 4 ft gas chromatography column (20% Carbowax 20M on 80–100 mesh Chromosorb P) operated at 75°. A pmr spectrum indicated that *ca.* 96% of the *α* hydrogens were substituted.

Cumene-*α-d*. The material was prepared by a slight modification of the procedure given by Hart and Crocker.[12] To a rapidly stirred, refluxing mixture of 1.6 g (0.041 g-atom) of potassium and 30 ml of hexane under a nitrogen atmosphere was added 2.86 g (0.0190 mol) of 2-methoxy-2-phenylpropane. After refluxing an additional 6 hr, 3.5 ml of D_2O was added; the stirring and refluxing were continued for an additional 15 min. The hexane phase was separated after cooling and washed three times with 50-ml portions of water. Distillation at reduced pressure afforded 1.37 g (59%) of product, bp 58.5–59.5° (27 mm). A pmr spectrum indicated that *ca.* 94% of the *α* hydrogens were substituted.

Results and Discussion

Table I contains the ^{13}C chemical shifts obtained in this work. It includes the shifts of all the ring and alkyl group carbons of toluene, ethylbenzene, cumene (isopropylbenzene), *tert*-butylbenzene, and some deuterio analogs.

Assignments and Methods. Assignments of the substituted carbons (1) of the ring were based upon off-resonance proton decoupling, and are consistent with earlier, less precise measurements.[3–8] Assignments of the para carbons were based upon relative peak intensities and comparison with the earlier assignments for toluene by Spiesecke and Schneider, based upon deuterium substitution.[4] The resonances of the ortho (2) and meta (3) carbons are unassignable on the basis of intensity or off-resonance-decoupling considerations. For toluene and *tert*-butylbenzene the distinctions between these two resonances were based upon the spectra of meta and ortho deuterio-substituted species, respectively. In both cases, the presence of deuterium was detected by the expected 1:1:1 triplet of the ^{13}C resonance of the carbon to which the deuterium atom was attached. For ethylbenzene and cumene, the assignments of the ortho and meta carbons were based upon the assignments for toluene and *tert*-butylbenzene, and the assumption of a monotonic trend in shifts for each carbon position in the homologous series of the four alkyl benzenes. These assignments must be considered only tentative, and are given in parentheses in Table I.

The *α* and *β* carbon assignments of the alkyl groups were based upon both off-resonance experiments and the effect of deuterium substitution on the spectra.

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The values given for the effects of deuterium substitution on ^{13}C shifts were based on both the comparison of spectra on separate samples of isotopically related substances and on the spectra of binary mixtures of the isotopically related species.

Alkyl Group Influence. As shown in Table I, the effects of alkyl group substitution on the ^{13}C chemical shifts of the aromatic carbons are substantial, especially for the substituted carbon atoms, where a range of about 13 ppm is encountered. On the basis of the unequivocal assignments for toluene and *tert*-butylbenzene and the tentative assignments of the ortho and meta carbon resonances of ethylbenzene and cumene given in Table I, the chemical shifts corresponding to each carbon position vary monotonically throughout the series, with two minor exceptions, the C(3) and C(4) resonances of *tert*-butylbenzene. The smallest observed range, about 0.4 ppm, was found for the meta carbons; the relative sensitivities of the various aromatic carbon positions to alkyl group variation are $(1) > (2) > (4) > (3)$. For the last two, which include the two exceptions mentioned, the shift increments between homologous pairs are small; while most of these are well beyond the experimental error of measurement of each sample (± 0.03 ppm), the significance of these small increments in terms of intrinsic, intramolecular effects is rendered uncertain by medium effects, which have been shown to be quite substantial for ^{13}C resonances.[13-15] One might expect solvent shifts of both the aromatic hydrocarbon signals and the TMS resonance. Hence, neither the regular trends for carbons 3 and 4 in toluene, ethylbenzene, and cumene are especially significant, nor are the exceptions to these trends in *tert*-butylbenzene. For all aromatic and aliphatic carbon positions except the ortho carbons, the regular trend is to decreased shielding with increasing methyl substitution at the α position. In the case of the C(1), C(α), and C(β) positions, this is consistent with previously reported patterns of methyl group effects at the position of substitution and at the adjacent position.[16,17] The ortho position exhibits the opposite trend, *i.e.*, increasing shielding with increasing methyl substitution at the α carbon. This pattern is consistent with the "γ effect" that has been discussed in detail by Grant and Paul[17] and by Roberts and coworkers.[18]

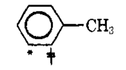
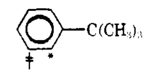
It should be noted that all of the C(3) chemical shifts fall close to the value (128.50 ppm) obtained in this study for benzene under the same experimental conditions. Indeed, the C(3) values for benzene, toluene, ethylbenzene, and cumene are all within experimental error of each other.

Although there is not currently available a reliable theory of ^{13}C shieldings that is capable of predicting or accounting for substituents, even with the input of gross approximations, it was of interest to explore the relationships between ^{13}C shieldings and calculated electron density patterns. Such relationships are often assumed, *a priori*, in nmr applications, and there have been some approximate theoretical treatments that bear upon such relationships. Accordingly, CNDO/2[19] calculations were carried out for the four alkyl benzenes of this study, and the density matrices were examined for possible correlations with the experimental data. The CNDO/2 method is an approximate, semiempirical SCF-MO method which has experienced considerable popularity and apparent success in a wide variety of applications in recent years. No single correlation was found, either within a particular compound or for a given carbon position within the series of four species, between the experimental shifts and either the calculated total electron density of each carbon or the π-electron density of each carbon.

It is of interest to compare the ethyl substituent effects on the ring-carbon resonances relative to the influences of a methyl group with the corresponding effects on ^{19}F chemical shifts. Thus, for the meta position, Table I shows only a slightly lower shielding for ethylbenzene than for toluene, assuming the assignments are correct for ethylbenzene. Data on *m*-fluorotoluene and *m*-fluoroethylbenzene show a corresponding difference between the ^{19}F chemical shifts of about 0.3 ppm.[20] The para carbon in ethylbenzene is about 0.3 ppm less shielded than the para carbon in toluene; data on *p*-fluorotoluene and *p*-fluoroethylbenzene show that the ^{19}F shielding in the latter is about 0.4 ppm lower than in the former.[21]

Deuterium Isotope Effects. Substantial deuterium isotope effects on ^{13}C shifts are shown in Table I. Some additional values, obtained on ring-deuterated compounds that were prepared for peak assignments, are given in Table II. In all cases for which measurable effects were detected, the shieldings at the attached carbon and at the adjacent carbon(s) are *increased* by deuterium substitution. A measurable isotope effect at an aromatic carbon due to deuterium substitution at

Table II. Miscellaneous ^{13}C Data on Deuterium-Substituted Monoalkyl Benzenes[a]

Compound	$^*\delta_D{}^* -$ $^*\delta^*{}_H$[b]	$^*\delta^{\ddagger}{}_D -$ $^*\delta^{\ddagger}{}_H$[c]	$J^*{}_{CD}$[d]
	−0.29	−0.12	24.1
	−0.31	−0.12	23.6

[a] Chemical shift differences in parts per million, accuracy ±0.02 ppm; negative values correspond to higher shielding of the deuterium substituted carbon. [b] Chemical shift difference, for the carbon indicated by *, between the species with deuterium attached to that carbon and the corresponding species with no deuterium. [c] Chemical shift difference, for the carbon indicated by ‡, between the species with deuterium attached to the carbon indicated by * and the corresponding species with no deuterium. [d] Absolute value of the directly bonded C–D coupling constant of the carbon indicated by asterisk.

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the α carbon was detected unequivocally only for the substituted carbon of toluene-α,α,α-d_3, with a small shift apparently occurring for the ortho carbon of the same compound. As might be expected on intuitive grounds, there is a monotonic decrease in the magnitude of the effects on the resonances of carbons at the α or β positions due to complete deuterium substitution at the α carbon in the order, toluene > ethylbenzene > cumene. The same kind of relationship between observed isotope shifts and the number of deuterium-for-protium replacements is also observed within the series, toluene, toluene-α,α-d_2 and toluene-α,α,α-d_3. Information on this relationship was obtained in the spectrum of the deuterated substance, which contained small amounts of the partially deuterated material. The effect on the α carbon of the first two deuterium substitutions at that position is 0.54 ppm, and the effect of adding the third is an additional 0.32 ppm. From Table II it is seen that the substitution of deuterium at an aromatic carbon increases its shielding by about 0.3 ppm, and that of the adjacent carbon by about 0.1 ppm.

There are few closely related data in the literature with which these deuterium isotope effects can be compared.[22] Nevertheless, some points of interest can be raised within the framework of so-called "substituent isotope effects."[23] Halevi and coworkers[24,25] have presented justification for considering the essentially vibronic phenomena of isotope effects in terms of popular substituent characteristics such as *inductive* and *hyperconjugative* effects. Along these lines, interpretations of chemical isotope effects have been advanced on the basis of an apparently greater inductive electron-donating tendency of D or C–D compared with H or C–H and a reduced hyperconjugative ability of C–D compared with C–H. It could be argued that primarily an inductive isotope effect might be expected at the β carbon(s) due to deuterium substitution at the α position, whereas both inductive and hyperconjugative isotope effects might be anticipated at the ring carbons. Since a tendency toward cancellation would be expected for the inductive and hyperconjugative effects in the latter case, this might account for the fact that significant isotope effects were observed at the β carbons in ethylbenzene-α,α-d_2 and cumene-α-d, while no isotope effects were observed for C(1). This would imply that the "hyperconjugative isotope effect" leads to a decrease in shielding at the ring-carbon positions. These results can be compared with the isotope effect of 0.28 ppm (lower shielding in deuterium-substituted compound) reported for the carbonyl ^{13}C resonance of acetone-d_6.[26] It should, of course, be kept in mind that these qualitative ideas are not meant to supplant the more fundamental vibronic point of view (with which they are consistent), and should not be employed without caution.

It can be noted that no deuterium-isotope effect was detected in the ^{19}F resonance of *m*-fluorotoluene-α,α,α-d_3, and an effect of only 0.01 ppm was detected in *p*-fluorotoluene-α,α,α-d_3.[11] Hence, the ^{13}C spectra reflect the essentially insensitive response of the ^{19}F shifts to deuterium substitution at the α position.

Carbon–Hydrogen Coupling Constants. In addition to the data reported in Tables I and II, some carbon–hydrogen coupling constants were obtained without proton decoupling. The directly bonded C–H coupling constants of the α and β carbons of ethylbenzene and cumene were all measured to be 125.5 Hz, within experimental error (±0.4 Hz). The J_{CH} value for the α carbon of toluene was found to be 124.9 Hz and that of the β carbon of *tert*-butylbenzene to be 123.9 Hz. The geminal C–H coupling constants of the alkyl groups of ethylbenzene, cumene, and *tert*-butylbenzene were all found to have magnitudes of 4.8 Hz, within experimental error.

Conclusions

The data presented here demonstrate that monoalkyl benzenes provide regular trends in ^{13}C shielding of sufficient magnitude to constitute good tests for theories of substituent effects on ^{13}C chemical shifts. They also provide a further demonstration of the high sensitivity of ^{13}C shieldings to substituent effects of a relatively subtle nature, even at rather long range, *i.e.*, a span of nearly 0.6 ppm at C (4) due to altering the identity of an alkyl substituent at C(1). This sensitivity appears to be of the same order of magnitude as that of ^{19}F shieldings of the corresponding fluorine-substituted compounds.

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