plete reduction of the naphthalene. When the sodium reduction of the naphthalene is not complete, it is readily sublimed from the solid mixture at room temperature.

All of the above mentioned data indicate that the solid salt of the naphthalene anion radical reacts with water to yield ~40% of the theoretical amount of hydrogen gas expected from eq 3. This production of H_2 compared with the lack of it from

$$2\,\text{[naphthalene anion]} + 2H_2O \longrightarrow 2\,\text{[naphthalene]} + H_2 + 2OH^- \quad (3)$$
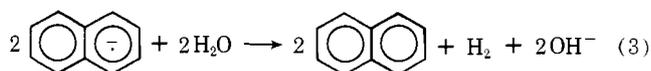
the other polyacene systems is probably associated with its lower electron affinity (larger energy difference between the neutral molecule and the anion radical). It seems reasonable that the reaction proceeds through an intermediate that consists of a hydrogen bond between the water and the charged π cloud of the anion radical.[7] The extra electron could then be pulled out of the antibonding MO and into the hydrogen 1s orbital with simultaneous breaking of the H–O bond in water.

This H_2 evolution via anion radical cleavage of water is in sharp contrast to the fact that only protonation has been observed previously. The possibility of photogeneration of anion radicals to be used for water cleavage and H_2 production with recovery of the neutral substrate should not be overlooked.

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A Self-Consistency Criterion for Two-Structure Theories

Sir:

Two-structure theories have been proposed for systems where the properties are thought to be intermediate between those of the individual structures. Thus water[1] has been described as a mixture of regions of ice-like material and regions of more closely packed molecules (or normal liquid). Aqueous electrolytes have been described[2,3] as mixtures of ionic lattice-like regions with "Debye–Hückel" ("D–H") regions of random structure modified by electrostatic forces. It is not my purpose at this time to discuss the over-all merits of any of these theories, but there is a self-consistency criterion which should be imposed upon any two-structure theory. The relative proportion of material in each structure should be given by the appropriate expression for equilibrium between the two structures. Thus the total Gibbs energy must be at its minimum with respect to distribution of material between the two structures. Also the activity or chemical potential for a component of the system must be the same for one structure as for the other structure.

Many recent theories[4] conform either exactly or approximately to this equilibrium criterion. However, certain two-structure theories for strong electrolytes grossly violate this principle. Both the theory of Singh[2] and the earlier theory of Lietzke, Stoughton, and Fuoss[3] use arbitrary transfer functions to shift the proportion of "D–H" solute to that of "lattice" solute with increasing concentration. For the first example of Singh, namely HCl, and with his equations and parameters, the chemical potential of the "D–H" solute is lower at all substantial concentrations than that of the "lattice" solute. This difference in chemical potential in favor of the "D–H" structure increases with concentration. Thus, at equilibrium there would be no shift to the "lattice" structure and the expected properties of the two-structure model, treated consistently, would be just those of the "D–H" structure.

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Nitroxide Radical as a Nuclear Spin Decoupling Reagent. Application to Carbon-13 Nuclear Magnetic Resonance Studies of Organothallium Compounds[1]

Sir:

We wish to report here a novel use of a stable nitroxide radical as a nuclear spin decoupling reagent in the ^{13}C NMR spectra of organothallium compounds which are very complicated owing to large $^{13}C-Tl$ nuclear spin couplings. We have currently been interested in the use of stable free radicals as NMR spin probes (paramagnetic shift and relaxation reagents) for studying the intermolecular interaction associated with hydrogen bonding,[2] charge transfer interaction,[3] and π-stacking interaction.[4] Here we are concerned with the Lewis acid–base interaction[5] between thallium in organothallium compounds and nitroxide radical which manifests itself as decoupling effect of long range $^{13}C-^{205}Tl$ coupling and simplifies the spectra enough to be assigned very easily.

It is well established that thallium in organothallium compounds serves as a Lewis acid toward electron-donating Lewis bases such as pyridine and triphenylphosphine oxide.[6] This suggests that nitroxide radical may also form a weak complex with organothallium compounds at the central metal atom, resulting in effective relaxation of thallium nuclei. This nitroxide-thallium interaction may lead to Tl–^{13}C nuclear spin decoupling.

Figure 1 shows the representative ^{13}C NMR spectra[7] of benzonorbornadiene–thallium(III) acetate cis-exo adduct (**1**)[8] in the absence (bottom) and presence (top) of di-*tert*-butyl nitroxide radical (DTBN) in CDCl$_3$ solution. The spectrum recorded without addition of DTBN looks quite complicated owing to direct and long range ^{13}C–Tl spin couplings. In this proton decoupled ^{13}C spectrum, identification of the doublet pair due to ^{13}C–^{205}Tl coupling is essential to assign the ^{13}C signal. This is not readily accessible by inspection of the spectrum. The ^{13}C signal of C$_2$ bonded with Tl(OAc)$_2$ appears as two pairs of doublet at +186.1 and −38.3 ppm and +185.1 and −37.3 ppm for the outer and inner pairs, respectively. The outer pair arises from ^{13}C–^{205}Tl coupling (5645 Hz) and the inner one from $J_{^{13}C-^{203}Tl}$ (5593 Hz), with relative intensity of 7:3, equal to the natural abundance ratio of ^{205}Tl and ^{203}Tl. This is also confirmed by noting that $J_{^{13}C-^{205}Tl}/J_{^{13}C-^{203}Tl}$ = 1.0093 is quite close to $\gamma_{^{205}Tl}/\gamma_{^{203}Tl}$ = 1.0099. Although the methyl and carbonyl ^{13}C resonances of Tl(OAc)$_2$ group are assigned without any difficulty, it appears difficult to assign the remaining resonances. Spectral measurements at different frequencies and in different solvents did not help us identify each coupling pair. Addition of small amount of DTBN[9] simplifies the spectrum as shown in Figure 1 (top spectrum). Some of the signals are broadened out beyond detection and some of the doublet peaks are converted to singlet peaks without any significant shift. The most prominent DTBN effect is manifested in the ^{13}C resonances of benzene carbons located at 120–130 ppm. The spectrum in this region consisting of eight peaks is simplified into four peaks by the addition of DTBN, two of them (w and x in Figure 1) being superimposed. This is also due to DTBN-induced decoupling of long range couplings between thallium and the benzene protonated carbons. One of the nonprotonated benzene carbons resonates as a doublet signal at 142.9 ppm which also exhibits DTBN-induced decoupling. In the aliphatic carbon region, the doublet signals at 50.0 ppm and 47.5 ppm are also decoupled to singlet peaks. The methyl carbon of the 3-acetoxyl group is also decoupled as is visualized in the figure. The ^{13}C doublet pair with spacing of >150 Hz is not decoupled and rather broadened out by the addition of DTBN. The carbons which exhibit such substantial ^{13}C–^{205}Tl couplings are usually situated close to thallium atom and thus susceptible to DTBN-induced signal broadening. This broadening effect is also helpful to assign the ^{13}C signal arising from the thallium-linked carbon or the carbon two bonds from thallium. Together with proton-coupling experiments, the ^{13}C spectrum of **1** is finally assigned as designated in Figure 1. To further substantiate these ^{13}C signal assignments for **1** we have measured the ^{13}C NMR spectrum of corresponding mercury analogue of **1** (**1** (Hg)) which consists of noncoupled and satellite signals arising from ^{201}Hg (I = 0) and ^{199}Hg (I = $^1/_2$) containing species, respectively. In this case, signal assignments are not difficult because the coupling pair of the satellite signal is readily identified and ^{13}C–^{199}Hg coupling constants are usually much smaller than ^{13}C–^{205}Tl ones. The ^{13}C chemical shifts of **1** (Hg) are very close to those of **1** (see Table I). The present technique of ^{13}C–^{205}Tl decoupling by the use of DTBN enabled us to analyze the ^{13}C spectra of the related organothallium compounds, **2** and **3**. In the ^{13}C spectra of these compounds, identification of ^{13}C–^{205}Tl coupling pairs was made by DTBN-induced decoupling and broadening effects. We have also examined the applicability of this technique in different solvents such as Me$_2$SO and pyridine. It was found that it also works in these solvents, although these solvent molecules serve as a Lewis base toward the thallium atom and make DTBN-induced decoupling less effective compared with the experiment in CDCl$_3$ solution.

The results of ^{13}C spectral assignments for **1**, **2**, and **3** are summarized in Table I. Now that the detailed ^{13}C NMR data

Table 1. ^{13}C Chemical Shifts[a] and ^{13}C–^{203,205}Tl and ^{13}C–^{199}Hg Coupling Constants[b] of **1**, **2**, **3**, and **1**(Hg)

		Carbon								2-*CH$_3$COO	3-*CH$_3$COO	2-CO	3-CO	w[c]	x[c]	y[c]	z[c]
Compd	Solvent	1	2	3	4	5	6	7									
1	CDCl$_3$	47.3 (244)	73.9 (5645) [5593]	76.3 (569)	50.0 (45)	142.9 (11)	147.2 (1149)	47.5 (7)	22.8	21.4 (68)	179.1	169.7 (51)	127.3 (18)	127.0 (77)	123.2 (65)	121.3 (86)
1	Py-d_5	47.7 (215)	68.9 (6321) [6262]	77.1 (554)	50.8 (59)	144.1 (15)	148.9 (1101)	47.8 (5)	23.0	21.4 (56)	177.5	169.9 (46)	127.4 (17)	126.7 (71)	123.2 (59)	121.4 (78)
1 (Hg)	CDCl$_3$	47.3 (43)	54.2 (1730)	78.1 (119)	50.1	142.5	149.0	48.2	23.4	21.6	177.2	170.1	126.8	126.3	122.9	120.5
2	CDCl$_3$	45.7 (244)	72.9 (5471) [n.o.][d]	75.2 (420)	48.2 (<3)	135.5 (120)	140.3 (1057)	47.4 (17)	22.8	21.2 (49)	179.4	n.o.[d]				
3	CDCl$_3$	40.5 (320)	76.4 (5750) [5696]	78.7 (681)	42.8 (27)	23.9 (64)	29.4 (1301)	35.7 (32)	22.6	20.8 (59)	179.1	169.2 (66)				

[a] Given in parts per million downfield from internal Me$_4$Si. [b] $J_{^{13}C-^{205}Tl}$ and $J_{^{13}C-^{203}Tl}$ are shown in parenthesis (hertz); $J_{^{13}C-^{203}Tl}$ is shown in brackets (hertz). [c] w, x, y, and z are referred to as ^{13}C signals of benzene peripheral carbons (8, 9, 10, 11). [d] Not observed.
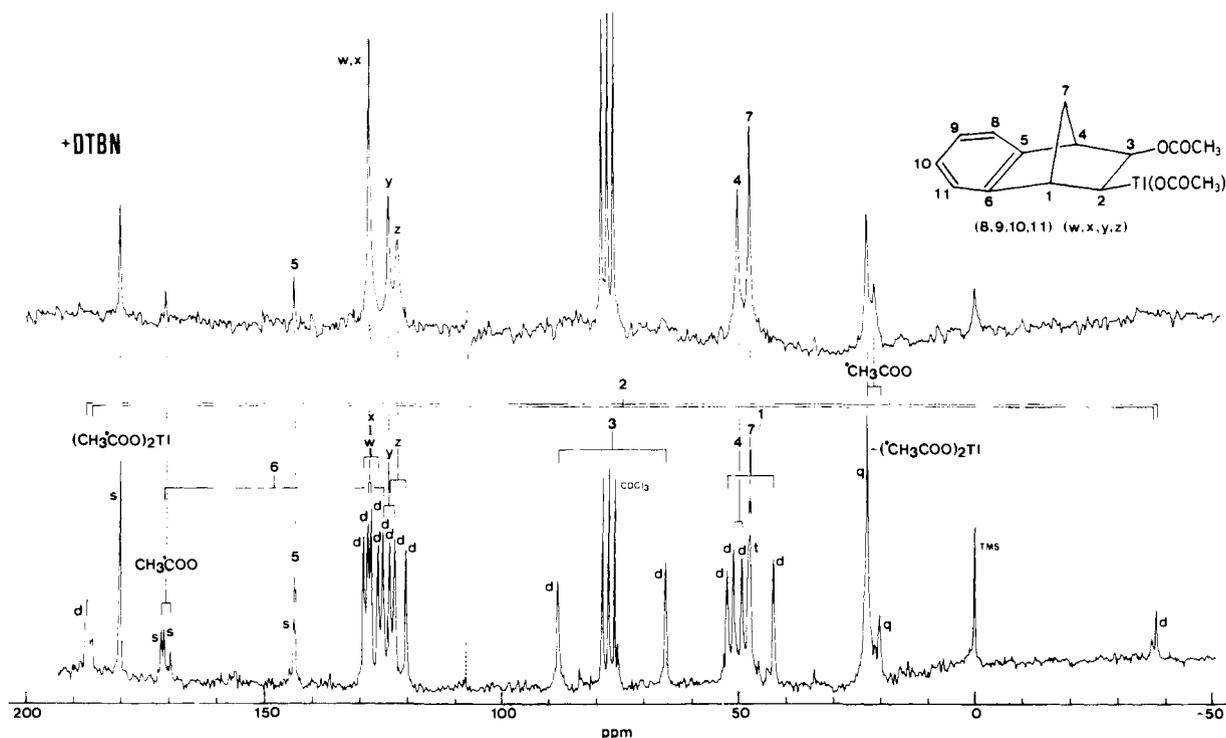
Figure 1. ^{13}C NMR spectra of 1 dissolved in CDCl$_3$ (150 mg/1 mL) in the absence (bottom) and presence (top) of DTBN (2 μL/1 mL). The signs of s, d, t, and q in the botton spectrum designate singlet, doublet, triplet, and quartet patterns in the proton nondecoupled spectrum, respectively.

have been presented, it becomes possible to interpret the long-range ^{13}C–^{205}Tl couplings presented here for the first time[12] in terms of molecular conformation. Although the data for three bond ^{13}C–^{205}Tl coupling constants are limited in the molecular system examined here, a Karplus-type of dihedral angle (θ) dependence of $^3J_{13C-205Tl}$ appears to be experienced for C$_4$ (θ = 120°, J = <59 Hz), C$_6$ (θ = 170°, J = 1301 Hz), and C$_7$ (θ = 85°, J = 5–32 Hz) in the compounds 1–3. The slight conformational change in the norbornane and norbornene carbon skeletons of 1–3 appears to be sensitively manifested in the substantially different values of $J_{13C-205Tl}$ for C$_3$, C$_4$, C$_5$, and C$_7$ carbons in these molecules. It is interesting to see that ^{13}C–^{205}Tl long-range coupling constants in 1–3 are in good parallel with the corresponding ^{13}C–^{199}Hg coupling constants with the ratio of $J_{13C-205Tl}/J_{13C-199Hg} \simeq$ 3–6 which is close to γ_{Tl}/γ_{Hg} = 3.2.

The presence of sizable ^{13}C–^{205}Tl coupling constants for 3-acetoxyl carbonyl and methyl carbons separated by four and five bonds respectively is quite unexpected, and may allow us to attribute them to through-space (or spin-dipolar and/or spin-orbital) coupling. The absence of coupling between ^{205}Tl and 2-acetoxyl carbonyl and methyl carbons may be due to the ionic character of the Tl–OAc bond, unfavorable for Fermi contact coupling. It is also of interest to note the large $J_{13C-205Tl}$ values for benzene peripheral carbons in 1. The large coupling observed for C$_6$, separated by zigzag bonds from thallium, is likely extended onto these four peripheral carbons by the π mechanism.

This decoupling technique is expected to be applicable to ^{1}H NMR spectral analysis of organothallium compounds, as confirmed by our preliminary studies, and to other organometallic compounds of which NMR spectra are too complicated owing to metal–carbon or metal–proton coupling.

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(7) ^{13}C NMR spectra were recorded in a pulse Fourier transform mode on Jeol PFT-100 spectrometer operating at 25.15 MHz. All of the samples were made in 10-mm NMR tube in appropriate solvents. Between 10 000 and 20 000 transients were collected using spectral width of 10 KHz and 8 K data points. The pulse repetition time of 1.0 s with 11-μs pulse width (45°) was employed over the experiments. Chemical shifts are reported in parts per million downfield from internal Me$_4$Si.
(8) The adducts 1,[10] 2,[10] and 3[11] were prepared by the reported methods respectively. All compounds were known to be cis-exo. 1(Hg) was prepared from the reaction of mercury(II) acetate with benzonorbornadiene in CHCl$_3$ at room temperature for 1 h: mp 175–177 °C.
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