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[4+4] Cyclodimer of *tert*-Butyl 9-Anthroate and Furan and [4+4] Cyclodimers of Alkyl 9-Anthroate

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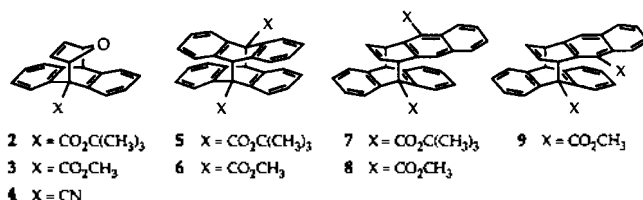*Department of Chemistry Education, Seoul National University, Seoul 151-742, Korea*
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Irradiation of *tert*-butyl 9-anthroate and furan through a Uranium glass filter gave the [4+4] cyclodimer (21.8%) of *tert*-butyl 9-anthroate and furan and the 1,4-10',9' cyclodimer (4.2%) of *tert*-butyl 9-anthroate as well as the 9,10-10',9' cyclodimer (65.7%) of *tert*-butyl 9-anthroate. The [4+4] cyclodimer of *tert*-butyl 9-anthroate and furan was found to be thermally dissociated into their unit components with the activation enthalpy of 35.6 kcal/mole and the activation entropy of 7.6 eu, and photochemically dissociated to produce excited *tert*-butyl 9-anthroate. Quantum yields for the photodissociation to *tert*-butyl 9-anthroate and the formation of excited *tert*-butyl 9-anthroate in cyclohexane at room temperature were determined to be 0.56 and 0.19, respectively. The 1,4-10',9' cyclodimer of *tert*-butyl 9-anthroate in DMF was thermally dissociated into *tert*-butyl 9-anthroate with the activation enthalpy of 34.8 kcal/mole and the activation entropy of 16.4 eu. Upon irradiation, the [4+4] cyclodimers of *tert*-butyl 9-anthroate and the [4+4] cyclodimers of methyl 9-anthroate were quantitatively dissociated. However, no adiabatic photoreversion was observed from any of the cyclodimers. Quantum yields for the photodissociation in cyclohexane at room temperature were measured and compared.

Introduction

Since the first dimer of an aromatic compound, the 9,10-10',9' anthracene cyclodimer, was discovered over a hundred years ago, many arene-arene dimers have been synthesized.[1] Recently, synthesis of energy-rich cyclodimers and investigation of their properties have been carried out for studying unusual chemical behaviors such as adiabatic photodissociation and chemiluminescence.[2] Adiabatic photodissociation has been reported in some anthracene-benzene dimers,[3,4] naphthalene-benzene dimers,[5-7] anthracene-naphthalene dimers,[8] and dibenzenes.[9] The photoreversion of [4+4] anthracene-benzene cyclodimer was found to be one of the most efficient adiabatic processes. However, the synthesis of the cyclodimers has been accomplished by multistep strategies,[2-4] because benzene itself does not add photochemically to the anthracene ring. Therefore, the extension of its chemistry to the derivatives is rather limited. Recently, we studied the photolysis and the thermolysis of [4+4] anthracene-furan cyclodimers,[10] which can be prepared from direct irradiation of anthracenes and furan. Although the efficiency of adiabaticity is relatively low, the

photoreversion of [4+4] anthracene-furan cyclodimers was found to produce excited anthracenes. In addition, we found the first example of intermolecular photodimerization of *meso*-substituted anthracene involving the 1, 4, 9', and 10' positions of the anthracene rings in the irradiation of methyl 9-anthroate.[11] In this paper, we report the photoreaction of *tert*-butyl 9-anthroate (1) and furan, and the properties of [4+4] cyclodimer (2) of 1 and furan and [4+4] cyclodimers (5-9) of alkyl 9-anthroate.

2 X = CO₂C(CH₃)₃   5 X = CO₂C(CH₃)₃   7 X = CO₂C(CH₃)₃   9 X = CO₂CH₃
3 X = CO₂CH₃   6 X = CO₂CH₃   8 X = CO₂CH₃
4 X = CN

Results and Discussion

The irradiation of 1 in the presence of excess furan with a medium-pressure mercury lamp through a Uranium glass filter gave three products, one of which was the desired [4+
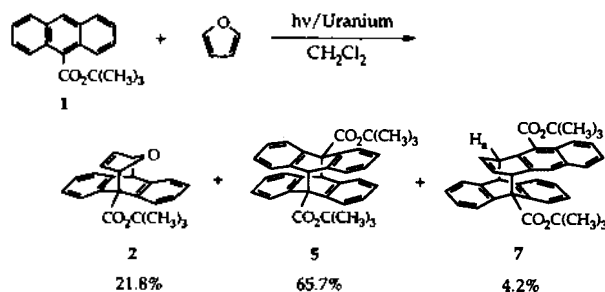
Scheme 1.

4] anthracene-furan cyclodimer (2) (Scheme 1). The reaction mixture was separated by a silica gel column chromatography. The isolated yield of 2 was 21.5% based on the starting 1 and 21.8% yield based on the consumed 1. The other products were the 9,10-10',9' cyclodimer (5) of 1 and 1,4-10',9' cyclodimer (7) of 1. The yields of 5 and 7 based on the consumed 1 were 65.7% and 4.2%, respectively.

The spectroscopic data of 2 are comparable to those of 3.[11] In the ^{1}H NMR spectrum, three resonance peaks around 4.0-5.2 ppm indicate the existence of three bridgehead protons. Its mass spectrum (FAB) exhibits the molecular ion peak at m/e 347 (MH^+), which reveals that the product is an 1:1 adduct of 1 and furan. The ^{1}H NMR spectrum of 5 reveals the presence of 16 aromatic protons, 2 bridgehead protons (sharp singlet at 5.68 ppm) and 18 protons of the two *tert*-butyl groups, and is consistent with the classical arrangement of the anthracene photocyclodimers (e.g., 6). The structural assignment for 7 was made particularly by the analyses of its ^{1}H NMR and NOESY spectra. Different peaks for the two *tert*-butyl groups, three bridgehead protons, and two olefinic protons in the ^{1}H NMR spectrum clearly indicate the connections between the 1, 4 positions of one ring and the 9', 10' positions of the other ring. Its UV spectrum also exhibits a naphthalene pattern. In the NOESY spectrum (Figure 1), aromatic protons show NOE with the bridgehead proton at position 4 (5.20 ppm) but not with the bridgehead proton at position 1 (4.29 ppm, H_a in Scheme 1) to indicate
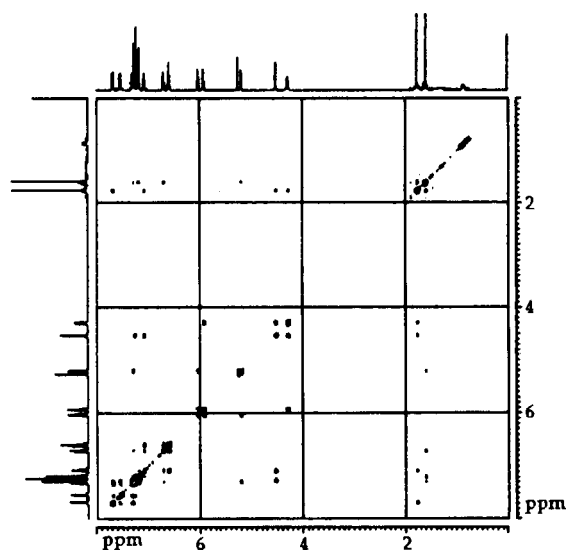
Figure 1. NOESY specrum of 7 in $CDCl_3$.

that the dissymmetrical cyclodimer is in the head-to-tail structure. In the mass spectrum, 7 has no molecular ion peak. Under the conditions, 7 easily dissociates to give the corresponding ion peak at m/e 278.

In contrast to the previous report,[12] a dissymmetrical dimerization product (7) was observed in the irradiation of 1 and furan. The results are similar to those in the irradiation of methyl 9-anthroate and furan. In the latter case, the isolated yields of 3, 6, and 8 based on the consumed methyl 9-anthroate were 35.5%, 56.7%, and 6.54%, respectively.[10] This dissymmetrical mode of dimerization through the vertices 1 and 4 of the anthracene ring may be explained by slower rate of closure between the positions 9, 10 and 10', 9' due to steric effect. This dimerization mode has been reported in the intramolecular photodimerization of some tethered anthracenes[13] and the intermolecular photodimerization of some laterally substituted anthracenes.[14] However, this is the second example in the intermolecular photodimerization of *meso*-substituted anthracene.[11,15] In the photodimerization of 1 in dichloromethane with the aid of a medium-pressure mercury lamp through a Uranium glass filter, the isolated yields of 5 and 7 based on the consumed 1 were 80.5% and 3.6%, respectively. Although the head-to-head dissymmetrical dimer (9) was observed in the irradiation of methyl 9-anthroate,[11] no dissymmetrical dimer in the head-to-head structure was isolated in the case of 1.

The thermolysis of 2 (~10^{-4} M) resulted in quantitative dissociation into 1. Kinetic analyses for the thermolysis of 2 in DMF at the temperature range of 111.6-138.9 °C were performed by UV spectroscopy. The kinetic activation parameters, obtained from the transition state theory, are summarized in Table 1. The activation enthalpy for the thermolysis of 2 was found to be 35.6 kcal/mole, which is 6.6 kcal/mole higher than that of 4. The half-life times of 2 and 4 at 100 °C are estimated to be 363 and 1.5 hours, respectively. Although the *tert*-butoxycarbonyl group seems to be more sterically hindered than the cyano group, 2 was found to be kinetically more stable than 4. Similar effect of cyano group has been also observed in the isomerization of quadricyclane to norbornadiene.[16]

Thermal stability of 2 is sufficient to allow the study of photoreaction at room temperature. The cyclodimer 2 has absorption maxima at 272 and 280 nm and a tail that reaches beyond 290 nm. Irradiation into this band through a Pyrex glass filter caused clean cycloreversion to 1. In order to study the nature of the electronic state of 1 formed in the photolysis, a fluorescence study was performed. Upon the photoexcitation of 2 at 280 nm in cyclohexane, the only emission observed was attributed to the fluorescence of 1

Table 1. Activation parameters for the thermoreversion of [4+4] anthracene-furan cyclodimers and dissymmetrical [4+4] cyclodimers of alkyl 9-anthroate

	2^a	4^b	7^a	8^c
E_a (kcal/mole)	36.1±1.1	29.6±0.5	35.4±1.3	33.4±0.2
$\Delta H^{\ddagger}$ (kcal/mole)	35.6±1.1	29.0±0.5	34.8±1.3	32.9±0.2
$\Delta S^{\ddagger}$ (eu)	7.6±3.7	1.0±1.6	16.4±4.3	9.8±0.6
$\Delta G^{\ddagger}$ (kcal/mole)	33.3±2.2	28.7±0.9	29.9±2.6	29.9±0.3

^{a}In DMF at 298.15 K. ^{b}Taken from ref 10, in DMF. ^{c}Taken from ref 11, in DMF.
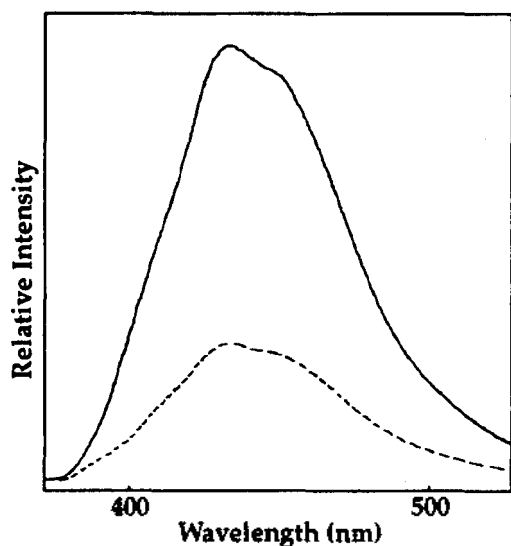
Figure 2. Emission spectra of **1** (solid line) and **2** (dotted line) in cyclohexane. These emission spectra were taken by the irradiation of UV light at 280 nm with the same absorbance at that wavelength.

(Figure 2). This was confirmed by the excitation spectrum of **2** which exhibits the peaks similar to those exhibited in the UV spectra of **1** and **2** (Figure 3). The relative intensities indicated that the emission was mainly from the photoreversion of **2**, but the sample contained a small amount of **1**. Quantum yield for this photoreversion in degassed solution at room temperature was determined by comparing with the quantitative photodissociation of *anti*-dibenzene.[9] Quantum yield for the formation of excited **1** upon direct irradiation at room temperature was determined by comparing with the fluorescence of **1** (see Experimental). The results are shown in Table 2. The quantum yield for the photodissociation and the quantum yield of adiabaticity are lower than those of [4+4] anthracene-benzene cyclodimers,[3] but higher than those of [4+4] anthracene-cyclohexa-1,3-diene
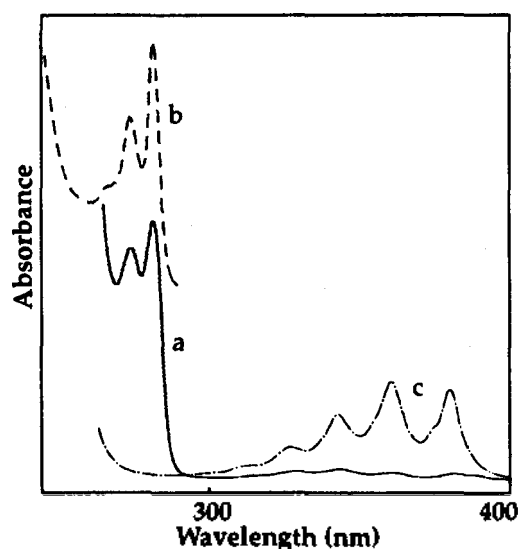
Figure 3. Excitation spectrum (a, λ_{em}=440 nm) and UV spectrum (b) of **2**, and UV spectrum (c) of **1** in cyclohexane.

Table 2. Quantum yields in the photoreversion of [4+4] anthracene-furan cyclodimers

	2^a	3^b	4^b
Φ_{An}	0.56±0.01	0.33±0.05	0.45±0.02
Φ_{An^*}	0.19±0.02	0.12±0.02	0.15±0.00

[a] The average of two separate determinations in cyclohexane.
[b] Taken from ref 10, in cyclohexane.

cyclodimers.[17] These results may be explained by the energy gain in the dissociations which can be relatively estimated by the resonance energies of benzene (36 kcal/mole), furan (17 kcal/mole), and cyclohexa-1,3-diene (1.8 kcal/mole).[18] The higher exothermicity in the photoreversion tilts the excited-state surface more and thus allows greater production of the excited-state arene.[19]

Although several dissymmetrical photodimers of anthracenes have been synthesized, there have been few studies on the thermal reaction. The thermolytic behavior of **7** in degassed DMF solution was studied. The thermolysis of **7** quantitatively yielded **1**. Kinetic analyses for the thermolysis of **7** at the temperature range of 92.2-109.5 °C were performed by UV spectroscopy. The activation parameters, obtained from the transition state theory, are shown in Table 1. The activation enthalpy for the thermolysis of **7** was found to be 34.8 kcal/mole, which is higher than that of **8** by 1.9 kcal/mole. The half-life times at 100 °C in the thermoreversion reactions of **7** and **8** are estimated to be 1.5 and 3.2 hours, respectively. This kinetic instability of **7** may be explained by the steric repulsion of the bulky *tert*-butyl group. The large positive activation entropy indicates the biradical mechanism for the thermoreversion.[3]

The irradiations of **5, 6, 7, 8,** and **9** ($\sim$10^{-4} M) through a Vycor glass filter quantitatively yielded **1**. However, no emission from **5-9** was observed on direct irradiation. Quantum yields for the photodissociation of **5-9** in degassed cyclohexane solution at room temperature were determined, and the results are summarized in Table 3. It was found that the cyclodimers (**5** and **7**) with the *tert*-butoxycarbonyl group were photochemically less stable than those (**6** and **8**) with the methoxycarbonyl group. The head-to-head dissymmetrical cyclodimer (**9**) was also found to be less stable than the head-to-tail dissymmetrical cyclodimer (**8**). These results may be also explained by the steric effect of substituents.

Experimental

Materials and instruments. All chemicals were reagent grade and used as received. Solvents for spectroscopic measurements were spectroscopic grade and used as received. Solvent for photoreaction was purified by reflux-

Table 3. Quantum yields for the photodissociation of cyclodimers of alkyl 9-anthroate[a]

	5	6	7	8	9
Φ_{An}	1.05±0.04	0.50±0.02	0.64±0.03	0.52±0.02	0.60±0.02

[a] The average of at least two separate determinations in cyclohexane.

ing over phosphorus pentoxide followed by distillation. Melting points were taken on a MEL-TEMP II melting point apparatus. Mass spectra (MS) were obtained on a Hewlett-Packard 5890-JMS AX505WA double focusing magnetic sector mass spectrometer. ^{1}H NMR spectra were routinely obtained at 200 MHz on a Varian VXR 200S spectrometer and/or 500 MHz on a AMX Bruker spectrometer. Chemical shifts (δ) are reported as ppm downfield from TMS. Infrared spectra were recorded on a JASCO IR-810 spectrometer. Ultraviolet and visible spectra were recorded on a Shimadzu UV/VIS-2600 spectrophotometer. Fluorescence spectra were recorded on a JASCO FP-777 spectrophotometer.

Irradiation of 1 and furan. A dichloromethane solution of 1 (1.3334 g, 4.80 mmol) containing a large excess of furan (50 mL) under a nitrogen atmosphere was irradiated with a 450 watt Hanovia medium-pressure mercury lamp through a Uranium cylindrical glass filter at ambient temperature for 6 hours. After 5 was filtered, the reaction mixture was separated by a silica gel (70-230 mesh) column chromatography, eluting with *n*-hexane/dichloromethane mixtures of increasing polarity to give three products along with the unreacted 1 (22.5 mg, 0.081 mmol). On the basis of the consumed 1, the isolated yields of 2, 5, and 7 are 21.8% (355.0 mg, 1.03 mmol), 65.7% (859.4 mg, 1.55 mmol), and 4.2% (55.9 mg, 0.10 mmol), respectively. 2: mp 156-157 °C (dichloromethane/*n*-hexane); ^{1}H NMR (CDCl$_3$, 200 MHz) δ 7.50-7.46 (1H, m), 7.25-7.16 (3H, m), 7.05-7.01 (4H, m), 5.88 (1H, dd, J=5.9, 1.7 Hz), 5.81 (1H, dd, J=5.9, 1.7 Hz), 5.10 (1H, d, J=1.7 Hz), 4.60 (1H, dd, J=6.6, 1.7 Hz), 4.04 (1H, d, J=6.6 Hz), 1.66 (9H, s); IR (CHCl$_3$) 3070, 3020, 2980, 1715, 1470, 1460, 1370, 1260, 1160 cm^{-1}; UV (DMF) λ_{nm} (ϵ) 280 (1840), 272 (1340); MS (FAB) m/e 347, 278, 245, 222 (100), 205, 179, 154, 136, 57. 5: ^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.00-6.97 (4H, m), 6.83-6.77 (12H, m), 5.68 (2H, s), 1.59 (18H, s); IR (CHCl$_3$) 3075, 3020, 2980, 2930, 1715, 1480, 1455, 1370, 1250, 1150 cm^{-1}; UV (CHCl$_3$) λ_{nm} (ϵ) 240 (4710). 7: mp 150-151 °C (dichloromethane/*n*-hexane); ^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.68 (1H, d, J=8.0 Hz), 7.55 (1H, d, J=8.0 Hz), 7.33-7.25 (4H, m), 7.21-7.17 (3H, m), 7.08 (1H, dd, J=7.0, 1.8 Hz), 6.71-6.69 (1H, m), 6.62-6.57 (2H, m), 6.03 (1H, t, J=7.8 Hz), 5.92 (1H, t, J=7.7 Hz), 5.20 (1H, d, J=7.0 Hz), 4.52 (1H, d, J=10.7 Hz), 4.29 (1H, dd, J=7.2, 10.7 Hz), 1.76 (9H, s), 1.59 (9H, s); IR (CHCl$_3$) 3030, 3010, 2980, 2930, 1710, 1475, 1460, 1390, 1370, 1250, 1160 cm^{-1}; UV (DMF) λ_{nm} (ϵ) 330 (960), 315 (1080), 266 (9700); MS (FAB) m/e 419, 278, 222 (100), 205, 179, 149, 57.

Kinetic study on the thermolysis. A 3.85×10^{-4} M solution of 2 in DMF was prepared and divided into six degassing tubes with 3 mL volume each. The solutions were degassed with nitrogen and a dry ice-isopropanol bath using a Firestone valve (six freeze-pump-thaw cycles at 0.05 mmHg). Kinetic experiments were performed in thermostatted bath at desired temperatures (e.g., refluxing *n*-butanol at 117.6 °C). The temperature range of the bath was 111.6-138.9 °C, and the overall fluctuation during each thermolysis was ±0.3 °C. To minimize error, at least five kinetic measurements were performed. The increase of 1 was monitored by the UV spectrophotometer. These data were analyzed by the first order reaction rate law. The activation

energy of the reaction was obtained using the Arrhenius equation. By the least square method, the data for the thermolysis of 2 were fitted to the following equation:

$$\ln k = 34.30 - 18190/T \qquad R^2 = 0.997$$

In the thermolysis of 7, a 6.69×10^{-5} M solution in DMF was used. The temperature range of the bath was 92.2-109.5 °C. The data for the thermolysis of 7 were fitted to the following equation:

$$\ln k = 38.70 - 17790/T \qquad R^2 = 0.996$$

Determination of quantum yields for the photodissociation of cyclodimers. Quantum yield for the photodissociation of 2 was determined[20] with reference to the photodissociation of *anti*-dibenzene.[9] Before irradiation, the solutions of 2 and *anti*-dibenzene in cyclohexane were bubbled with nitrogen. In each run, the UV absorption spectrum of the solution was recorded before irradiation, and the optical density was adjusted to 0.049-0.051 at 280 nm. Irradiation of each sample at 280 nm through a 4 nm slit lasted for 10 minutes. After the irradiation, the optical densities for the irradiated solutions of 2 and *anti*-dibenzene were measured at 381 and 280 nm, respectively. The average quantum yield was estimated to be 0.56±0.01. Quantum yields for the photodissociation of cyclodimers 5-9 were determined similarly, and the results are summarized in Table 3.

Determination of quantum yield for the formation of excited 1 upon direct irradiation of 2. Quantum yield for the formation of excited 1 upon direct irradiation of 2 was determined by comparing the emission spectra of 1 and 2 with similar optical density at the same excitation wavelength.[20] The measurements were performed on a JASCO spectrofluorometer at room temperature. The lamp of the spectrofluorometer was warmed up for at least one hour before all measurements. To take the emission spectrum of 2, the excitation wavelength was set at 280 nm to ensure that the light absorbed by decomposed anthracenes was minimized. Both the excitation monochromator slit and emission slit were set at 5.0 nm for all measurements. The optical density of 2 in cyclohexane was 0.042, while the sample of 1 was adjusted to similar optical density. These samples were placed into a degassing apparatus consisting of a sample holder, a quartz fluorescence cell, and a degassing connector. The samples were degassed at 0.05 mmHg using six freeze-pump-thaw cycles. In order to minimize the photodissociation during each run, the emission wavelength was set at 433 nm for quantitative determinations. Quantum yields for the formation of excited 1 on the photolysis of 2 in the two experiments were 0.21 and 0.17.

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¹H NMR Study of Aziridine Derivatives Coordinated to the Paramagnetic Undecatungstocobalto(II)silicate and -nickelo(II)silicate Anions

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¹H NMR spectra of D$_2$O solutions containing 2,2-dimethylaziridine (1) or 2-methylaziridine (2) and [SiW$_{11}$Co^{II}O$_{39}$]$^{6-}$ (SiW$_{11}$Co) or [SiW$_{11}$Ni^{II}O$_{39}$]$^{6-}$ (SiW$_{11}$Ni) exhibit separate signals for the free ligand and the complex, indicating that the ligand exchange is slow on the NMR time scale. Identified are two linkage isomers with the methyl group of 2 at *trans* or *cis* position with respect to the metal. The isotropic shifts of 1 and 2 coordinated to SiW$_{11}$Ni originate mainly from the contact shifts, and they agree reasonably with the relative values reported for similar ligands coordinated to bis(2,4-pentanedionato)nickel(II). The isotropic shifts for the SiW$_{11}$Co complexes were separated into contact and pseudocontact contributions. The pseudocontact shifts show that $(\chi_\parallel - \chi_\perp)$ is positive, while that for the SiW$_{11}$Co complexes of pyridine derivatives is negative. This result indicates that the ordering of d$_{xy}$ and d$_{xz}$, d$_{yz}$ orbitals in SiW$_{11}$Co complexes can be reversed by ligands.

Introduction

Several years ago we discovered that the exchange rates of some ligands coordinated to a Co^{2+} ion could be varied by incorporating it in various polyoxometalates.[1,2] It has been shown that pyridine- and imidazole-type ligands coordinated to [SiW$_{11}$CoO$_{39}$]^6 (SiW$_{11}$Co) or [SiW$_{11}$NiO$_{39}$]$^{6-}$ (SiW$_{11}$-

Ni) undergo slow exchange on the NMR time scale, exhibiting separate signals for the complexes and the free ligands in their ¹H and ¹³C NMR spectra.[1,2] Well-resolved NMR spectra of various ligands coordinated to paramagnetic polyoxometalates can provide useful information on both the ligands and polyoxometalates.[3,4]

The isotropic NMR shifts (δ_{iso}) in a paramagnetic system