COMMUNICATIONS TO THE EDITOR

Structural Determination of Symmetrical Disubstituted Polycyclic Aromatic Hydrocarbons by Carbon-13 Nuclear Magnetic Resonance Spectral Analysis

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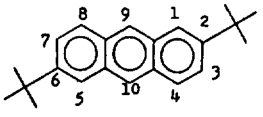
Polycyclic aromatic hydrocarbons (PAHs) are mutagenic and carcinogenic environmental pollutants[1,2]. Study of the mechanisms on how PAHs can induce cancer has long been a major research in the field of chemical carcinogenesis. Studies of PAHs are also important in the fields of physical chemistry, analytical chemistry, and petroleum chemistry[3]. Alkyl substituted PAHs consist of the major fraction of PAHs detected in the environment[4]. Structural elucidation and determinating the geometric isomers of substituted PAHs by analysis of their high resolution proton nuclear magnetic resonance (NMR) has been the most convenient and reliable method. However, we have found that the structures of some symmetrical disubstituted PAHs can not be determined by analysis of their proton NMR spectra[5]. For example, proton NMR spectral analysis can not distinguish 2,6-di-*tert*-butylanthracene(1) from its 2,7-di-*tert*- butylanthracene(2) isomers. It required to chemically convert compound 1 to the 9-bromo derivatives followed by high resolution proton NMR analysis both of these compounds and the 9-brominated derivatives[5]. Furthermore, this derivatization approach cannot determine the symmetrical disubstituted PAHs including compounds **3**-**6**.



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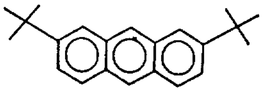

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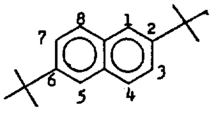

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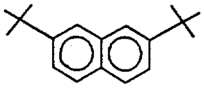

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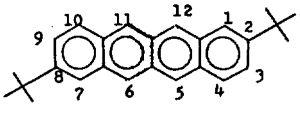

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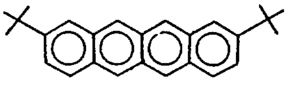

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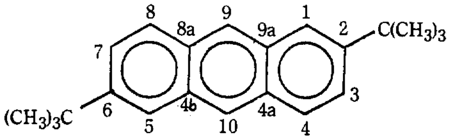
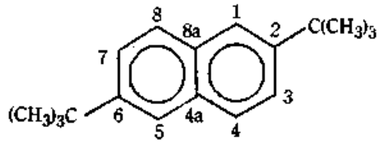
We have found that analysis of the carbon-13 NMR spectra of these compounds represents a simple and convenient method for determinating the structures of compounds of this type from their structural isomers. The reason is that the highly symmetrical disubstituted-PAH isomers, such as compounds **1** and **2**, have different sets of carbons. While the carbon-9 and carbon-10 of compound **1** are magnetically identical, these two carbons are not the same in compound **2**. Thus, there are only 9 different sets of carbon for compound **1**, and there are ten in compound **2**. Similar differences are also found for compounds **3** and **4**, and for compounds **5** and **6**. For this purpose, compounds **1** and **3** were synthesized and their carbon-13 NMR spectra were obtained for analysis. The assignments of these spectra, tabulated in Table 1, were assisted by comparison of these spectra with those of related compounds[6,7], and by analysis of their coupling patterns (*eg.* g, singlet, doublet, and triplet *etc.*). For both compounds, the resonance peaks at 31.0 and 31.1 ppm, respectively, contained six carbons with a quartet pattern clearly indicated that they are the carbons of the methyl groups. The resonance

Carbon-13 NMR measured in $CDCl_3$



35.0 ppm	(singlet, 2C, $C(CH_3)_3$)
31.0	(quartet, 6C, $C(CH_3)_3$)
122.3	(duublet, 2C, C_3 and C_7)
124.8	(doublet, 2C, C_1 and C_5)
125.4	(doublet, 2C, C_4 and C_8)
127.8	(doublet, 2C, C_9 and C_{10})
130.5	(singlet, 2C, C_{4b} and C_{9a})
131.6	(singlet, 2C, C_{4a} and C_{8a})
147.3	(singlet, 2C, C_2 and C_6)



31.1 ppm	(quartet, 6C, $C(CH_3)_3$)
35.1	(singlet, 2C, $C(CH_3)_3$)
119.4	(doublet, 2C, C_3 and C_7)
124.0	(doublet, 2C, C_4 and C_8)
125.0	(doublet, 2C, C_1 and C_5)
128.6	(singlet, 2C, C_{4a} and C_{8a})
146.4	(singlet, 2C, C_2 and C_6)

peaks at 35.0 ppm for compound **1** and 35.1 ppm for compound **2** were singlet, indicative of a quarterly carbon. They were easily assigned as the carbons of the *tert*-butyl groups. Similarly, because of their resonance peaks as a singlet, the ring-fused carbons, such as carbon-4a of compound **1** and compound **2**, were easily distinguished from the aromatic carbons bearing a proton. The assignments shown in Table 1 are consistent with the structural assignments of these compounds. There are only nine different groups of carbons in compound **1**. These results confirm that this compound is indeed 2,6-di-*tert*-butylanthracene, and is not 2,7-di-*tert*- butylanthracene. There are only seven sets of carbons in compound **3**, which confirms that it is 2,6-di-*tert*- butylnaphthylene. This can help distinguish this compound from compound **4** which should have eight sets of carbons in its carbon-13 NMR spectrum.

This approach can be conveniently employed to determine other symmetrical di-*tert*-butylated PAHs including compounds **5** and **6**, and should be applicable to determine the symmetrical disubstituted PAHs with different substituents.

Experimental Section

Materials. Naphthalene, anthracene, *tert*-butyl alcohol, and trifluoroacetic acid were purchased from Aldrich Chemical Co., Milwaukeee, U.S.A. Both naphthalene and anthracene were recrystallized from benzene-hexane before use, 2,6-Di-*tert*-butylanthracene **1** was synthesized as previously described[5].

Physical Data. Mass spectra were recorded with a Finnigan model 4000 system. Carbon-13 NMR spectra were obtained with a Bruker WM 270 spectrometer. Deuterium chloroform was employed as the solvent and chemical shifts were referenced to internal tetramethylsilane.

2,6-Di-*tert*-butylnaphthalene (2). A mixture of naphthalene (1.28 g, 10 mmol), *tert*-butyl alcohol (2.22 g, 30 mmol) and trifluoroacetic acid (15 m*l*) was heated at reflux for a period of 28 h. The resulting solution was cooled to room temperature, and water (50 m*l*) was added. The solution was then neutralized with sodium bicarbonate and extracted with ethyl acetate. The organic layer was collected and solvent evaporated under reduced pressure. The residue was chromatographed over silica gel column (2 × 20 mm). Elution with hexane gave crude compound **2** which was crystallized from methanol as colorless solid, mass spectrum (70 eV) *m/z* 240; carbon-13 NMR.

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Structural Studies on New Ordered Perovskites (ALa)(MgMo)O_6, where A = Ca, Sr and Ba

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In perovskite type oxides like $A_2(BB')O_6$, $(AA')B_2O_6$ and $(AA')(BB')O_6$, the larger A and A' and the smaller B and B' cations are coordinated with twelve and six oxygen ligands, respectively. It is well known that in $A_2(BB')O_6$ type perovskite an ordered distribution of the two types of B and B' ions along (111) planes is most probable when a large difference between B and B' cations exists in either their charges or ionic radii.[1] Few compounds such as $(AA')B_2O_6$ type perovskite, however, have been found to have an ordered arrangement of A and A' ions on the twelve coordinated site.[2] For a complex perovskite $(AA')(BB')O_6$, there can be three types of ordered and one disordered structures: 1) A and A' are ordered, but B and B' randomly distributed, 2) B and B' are ordered, but A and A' disordered, 3) both A and B-site ions are ordered, and 4) both A and B-site ions are disordered. The positions of the ordered ions are like those of cations and anions in the rocksalt structure. For all the compounds with the formula of $(CaLa)(BB')O_6$[3-5] where {B(II), B(V)} = (MgTa), (MgRu), (MgIr), (CaTa), (MnMo) and (MnTa), with that of $(SrLa)(BB')O_6$[6] where {B(II), B(V)} = (CoNb), (CoSb), (CoTa), (NiNb), (NiSb), (NiTa), (CuNb), (CuSb) and (CuTa), and with that of $(BaLa)(BB')O_6$[7-9] where {B(II), B(V)} = (MgRu), (CoRu), (NiRu), (ZnRu), (MnMo), (MnTa), (MgTa) and (FeTa), the perovskite superstructure due to ordered arrangement of B and B' ions were reported without presenting any evidence of disordering between A and A' ions except Blasse's report[6]. From the fact that all the cations in $(SrLa)(B^{3+}B^{4+})O_6$ are randomly distributed in their corres-