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-

Table 1. The Lattice Constants and Crystal Systems of (ALa)(MgMo)O_6 (A = Ca, Sr and Ba)

A	a(Å)	b(Å)	c(Å)	(degree)	crystal system
Ca[a]	5.551(1)	5.622(1)	7.875(1)		Orthorhombic
	7.901(1)	7.901(1)	7.875(1)	89°16′	Monoclinic
Sr	7.932(1)				Cubic
Ba	8.019(3)				Cubic

[a]For (CaLa)(MgMo)O_6, all the diffraction lines in their powder patterns are indexed by a body-centered orthorhombic unit cell ($a'<b'<c'$) containing four monoclinic perovskite units ($a=b>c$, $\beta=90°$). The monoclinic unit cell parameters are represented to emphasize the distortion from the ideal perovskite cell.

Table 2. The Powder X-ray Diffraction Data for (CaLa)(MgMo)O_6

	h	k	l	H	K	L	d_o	d_c	I_o	I_c(I)	I_c(II)	I_c(III)	I_c(IV)
*	0	1	1	1	**1**	1	4.5750	4.5756	13	20.1	11.5	31.6	0
*	1	0	1	1	$\bar{1}$	1	4.5372	4.5371	6	19.7	11.2	31.0	0
	1	1	0	2	0	0	3.9500	3.9500	3	0.7	0.7	0.7	0.7
	0	0	2	0	0	2	3.9369	3.9375		0.3	0.3	0.3	0.3
	0	2	0	2	2	0	2.8100	2.8110	23	25.5	25.5	25.5	25.5
	1	1	2	2	0	2	2.7884	2.7887	100	100	100	100	100
	2	0	0	2	$\bar{2}$	0	2.7757	2.7755	21	2.47	24.7	24.7	24.7
*	1	2	1	3	1	1	2.3893	2.3896	5	7.9	4.6	12.5	0
*	0	1	3	1	**1**	3	2.3781	2.3785		3.9	2.3	6.2	0
*	2	1	1	3	$\bar{\mathbf{1}}$	1	2.3731	2.3731	11	7.8	4.5	12.3	0
*	1	0	3	1	$\bar{1}$	3	2.3727	2.3730		3.9	2.3	6.1	0
	0	2	2	2	2	2	2.2875	2.2878	7	9.6	9.6	9.6	9.6
	2	0	2	2	$\bar{2}$	2	2.2686	2.2686	7	9.3	9.3	9.3	9.3
	2	2	0	4	0	0	1.9750	1.9750	49	40.2	40.2	40.2	40.2
	0	0	4	0	0	4	1.9684	1.9688		19.9	19.9	19.9	19.9
	1	3	2	4	2	2	1.6184	1.6186	27	20.2	20.2	20.2	20.2
	0	2	4	2	2	4	1.6123	1.6126		10.0	10.0	10.0	10.0
	2	0	4	2	$\bar{2}$	4	1.6057	1.6058	30	9.8	9.8	9.8	9.8
	3	1	2	2	$\bar{4}$	2	1.6050	1.6050		19.6	19.6	19.6	19.6
	0	4	0	4	4	0	1.4053	1.4055	4	5.9	5.9	5.9	5.9
	2	2	4	4	0	4	1.3942	1.3943	18	23.0	23.0	23.0	23.0
	4	0	0	4	$\bar{4}$	0	1.3879	1.3878	1	5.7	5.7	5.7	5.7
	2	4	0	6	2	0	1.2538	1.2539	4	4.3	4.4	4.4	4.4
	3	3	2	6	0	2	1.2487	1.2487	13	8.6	8.6	8.6	8.6
	1	1	6	2	0	2	1.2454	1.2455		8.5	8.5	8.5	8.5
	4	2	0	6	$\bar{2}$	0	1.2444	1.2444	5	4.3	4.3	4.3	4.3
Reliability factor (%)										11.2	9.8	16.4	25.4

(*h k l*)'s and (*H K L*)'s are indexed by orthorhombic and monoclinic unit cell, respectively. (see the footnote in Table 1). d_o, d_c; Observed and calculated lattice spacings, respectively. I_o; Relative intensity observed. I_c; Calculated intensities based on the following four assumptions. I_c(I): Only the A-site ions (Ca^{2+} and La^{3+}) are ordered. I_c(II): Only the B-site ions (Mg^{2+} and Mo^{5+}) are ordered. I_c(III): Both site ions are ordered. I_c(IV): All the ions are randomly distributed in each site. Reliability factors are calculated by the equation, $R(\%) = [\Sigma|\sqrt{I_o} - \sqrt{I_c}|]/[\Sigma\sqrt{I_o}] \times 100$.

ponding sites, he concluded that the superlattice reflections observed in (SrLa)($B^{2+}B^{5+}$)O_6 are due only to the ordered arrangement of B^{2+} and B^{5+} ions. Because a possible ordering between A and A′ ions would result in superlattice reflections with the same *d*-values, a careful conclusion should be drawn to determine the ordering type.

Table 3. The Powder X-ray Diffraction Data for (SrLa)(MgMo)O_6

	h	k	l	d_o	d_c	I_o	I_c(I)	I_c(II)	I_c(III)	I_c(IV)
*	1	1	1	4.578	4.580	11	4.7	11.0	15.7	0
	2	0	0	3.967	3.966	4	5.3	5.3	5.3	5.3
	2	2	0	2.801	2.804	100	100	100	100	100
*	3	1	1	2.392	2.392	6	2.7	6.6	9.4	0
	2	2	2	2.289	2.290	10	15.7	15.7	15.7	15.7
	4	0	0	1.984	1.983	29	36.6	36.6	36.6	36.6
*	3	3	1	1.820	1.820	3	1.2	3.0	4.2	0
	4	2	0	1.776	1.774	2	2.7	2.7	2.7	2.7
	4	2	2	1.619	1.619	39	40.1	40.1	40.1	40.1
*	3	3	3	1.528	1.527	2	0.23	0.56	0.79	0
*	5	1	1	1.528	1.527		0.69	1.69	2.37	0
	4	4	0	1.402	1.402	13	21.6	21.6	21.6	21.6
	6	2	0	1.254	1.254	12	17.5	17.5	17.5	17.5
Reliability factor (%)							14.9	8.0	10.0	28.0

All the definitions are the same as in Table 2 except that Sr^{2+} is substituted for Ca^{2+}.

In the present study, an attention was made to determine the cation ordering in the complex perovskite (ALa)(MgMo)O_6 by comparing the observed intensities with calculated ones in powder X-ray diffraction pattern, where A is a bivalent alkali earth metal cation (Ca^{2+}, Sr^{2+} and Ba^{2+}) and (MgMo) has a pair of (2^+, 5^+). The investigation of the valency pair (MgMo) is especially interesting, because it contains an unpaired *d*-electron. The valency pair ($Mg^{2+}Mo^{5+}$) in (ALa)(MgMo)O_6 was previously determined with magnetic susceptibility, electron spin resonance spectroscopy and thermogravimetric analysis.[10-12]

The (ALa)(MgMo)O_6 (A = Ca, Sr and Ba) has been prepared from $CaCO_3$, $Sr(NO_3)_2$, $Ba(NO_3)_2$, La_2O_3 or $La(NO_3)_3 \cdot 6H_2O$, $Mg(CH_3COO)_2 \cdot 4H_2O$ or $Mg(NO_3)_2 \cdot 6H_2O$ and MoO_3 with an appropriate molar ratio at 1350 °C under nitrogen flowing atmosphere. The detailed preparation methods are described in the previous papers.[10-12] Identification of the resultant phases, determination of lattice constants and observed intensities have been carried out by a Rigaku X-ray diffractometer with nickel-filtered Cu-Kα radiation (wavelength = 1.5418 Å). The theoretical intensities have been calculated by the computer program made in our laboratory, which is based on the equation $I = |F|^2 p\{(1+\cos^2 2\theta)/(\sin^2\theta\cos\theta)\}e^{-2M}$. The lattice constants and crystal systems of each compound are shown in Table 1. In Table 2-4 the observed lattice spacings and diffraction intensities are compared with those calculated. The intensity calculations have been performed according to the previous four assumptions (three ordered and one disordered structures). For (CaLa)(MgMo)O_6 as shown in Table 2, the reflection lines (*h,k,l* = 011, 101, 121, 013, 211 and 103) indicated by asterisk (*) correspond to superlattice lines, which do not appear in simple perovskite ABO_3. Because all the calculated intensities are the same between the columns except those from superlattice ones, they are the most important clues to determine the ordering and the disordering of cations in the lattice. Clearly, the observed intensities are consistent with I_c(II), which is based

Table 4. The Powder X-ray Diffraction Data for (BaLa)(MgMo)O_6

	h k l	d_o	d_c	I_o	I_c(I)	I_c(II)	I_c(III)	I_c(IV)
	1 1 1	4.634	4.630	9	0.0	8.4	8.4	0
	2 0 0	4.011	4.010	11	11.4	11.4	11.4	11.4
	2 2 0	2.835	2.835	100	100	100	100	100
*	3 1 1	2.416	2.418	5	0.0	5.1	5.1	0
	2 2 2	2.314	2.315	15	18.0	18.0	18.0	18.0
	4 0 0	2.005	2.005	31	34.3	34.3	34.3	34.3
*	3 3 1	1.839	1.840	4	0.0	2.3	2.3	0
	4 2 0	1.793	1.793	5	5.4	5.4	5.4	5.4
	4 2 2	1.636	1.637	38	40.2	40.2	40.2	40.2
*	3 3 3	1.544	1.543	2	0.0	0.4	0.4	0
*	5 1 1	1.544	1.543		0.0	1.3	1.3	0
	4 4 0	1.416	1.418	16	20.5	20.5	20.5	20.5
*	5 3 1	1.356	1.356	1.3	0.0	1.7	1.7	0
	4 4 2	1.337	1.337	3	2.3	2.3	2.3	2.3
	6 0 0	1.337	1.337		0.6	0.6	0.6	0.6
	6 2 0	1.267	1.268	15	17.5	17.5	17.5	17.5
Reliability factor (%)					23.6	5.0	5.0	23.6

All the definitions as the same as in Table 2 except that Ba^{2+} is substituted for Ca^{2+}.

on the assumption that only B-site ions (Mg^{2+} and Mo^{5+}) are ordered. The reliability factor corresponding to I_c(II), 9.8%, has the smallest value. From these facts, we can conclude that in (CaLa)(MgMo)O_6 only the Mg^{2+} and Mo^{5+} ions have a rock-salt arrangement (1:1 ordering) in the B-sites of the perovskite lattice, while Ca^{2+} and La^{3+} ions are randomly distributed in the oxygen-cuboctahedral A-sites. In case of (SrLa)(MgMo)O_6 (Table 3), Only B-site cations are ordered as (CaLa)(MgMo)O_6, comparing the observed intensities with calculated ones. In (BaLa)(MgMo)O_6, however, whether both A and B-sites ions are ordered or only B-site ions are ordered cannot be distinguished from the intensity calculation (see the column I_c(II) and I_c(III) in Table 4), because the atomic scattering factors of Ba^{2+} and La^{3+} ions are almost the same. However, judging from the result of (CaLa)(MgMo)O_6 and (SrLa)(MgMo)O_6, it would be most probable that Ba^{2+} and La^{3+} ions are also distributed randomly in the oxygen-cuboctahedral A-sites.

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Substituent Effect in the Pyridinolysis of Substituted Phenyl Acetates

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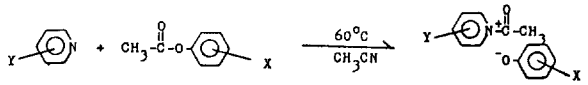
We have previously reported our studies[1] of the pyridinolysis of substituted phenyl acetates in acetonitrile by using ρ_X and ρ_Y. In a through analysis of the mechanism, it reveals that the important thing is to evaluate contribution of the three moieties (substrate, nucleophile, and leaving group) to overall stabilization of the transition state. Knowing the theoretical analysis of the interaction terms, $\rho_{XY}\sigma_X\sigma_Y$, by the Taylor[2] expansion, we first attempted to analyze by experiments.[3-6] In this paper, prior to the study above three moieties, we report the contribution of the two moieties of leaving group and nucleophile.

ρ_X values grow progressibly greater from σ_Y of electron-withdrawing group (EWG) to electron-donating one (EDG) of



nucleophiles, which indicates that the ρ_X is a function of ρ_Y, but the values are very little and not so large dependence of substituents of nucleophile (Table 2(b)). On the other hand, ρ_Y values are negatively large by change of ρ_X value from EWG to EDG of leaving groups (Table 2(a)). These results suggest that the greater (weaker) necleophilicity of nucleophiles, the more(less) bond-breaking of the C···O bond proceeds at the transition state and important fact is that the $|\rho_Y|$ value is larger than the ρ_X value.