substituents in polysilanes, linear high MW polymers with $\bar{M}w$ of $\sim 10^6$ were obtained with yield up to 27%. However the yields of linear high MW polymers were influenced by the steric bulkiness. Those polysilanes shows the characteristic electronic transitions and may used to various applications. Also TGA results of crosslinked polysilanes showed the possiblity for a ceramic precursor. Preparation of polysilanes by sonochemical methods and measurements of other properties such as photochemical reactivity, nonlinear optical property are in progress.

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Synthesis and Molecular Structure of Calix[4]arene Butanoate 1,2-Alternate Conformer

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Three conformational isomers of calix[4]arene butanoate were isolated from the reaction of calix[4]arene and butanoyl chloride in the presence of NaH and their structures were determined by NMR spectra as 1,2-alternate **2a**, partial cone **2b** and 1,3-alternate conformer **2c**, respectively. The crystal structure of **2a** has been determined by X-ray diffraction method. The crystals are monoclinic, space group C2/c, a=18.435 (4), b=13.774 (2), c=16.941 (3) Å, β=116.23 (1)°, Z=4, V=3858.8 (12) $Å^3$, D_c=1.21 g cm^{-3}, D_m=1.21 g cm^{-3}. The molecule is in the 1,2-alternate conformation. It has two-fold symmetry axis along the line connecting between C (7AA') and C (7BB') parallel to the *b* axis of crystal lattice.

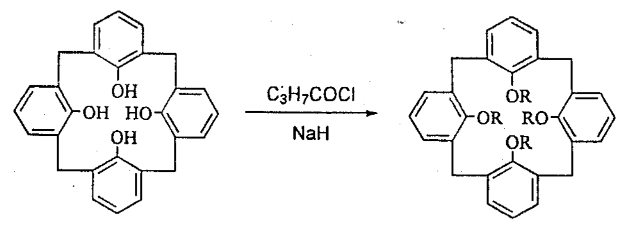
Introduction

Calixarenes, a class of synthetic macrocycles having phenolic residues in a cyclic array linked by methylene groups at the position "ortho" to the hydroxy groups, have cavities of sufficient size to form host-guest complexes and thus are particularly attractive compounds for attempting to construct systems that mimic the catalytic activity of the enzyme and have received a great deal of attention in recent years.[1~3] The calixarene is conformationally mobile[4] and exists as four possible conformational isomers; cone, partial cone, 1,2-alternate and 1,3-alternate. However, upon replacement of the phenolic hydrogens with larger groups than ethyl, calix[4]arenes become conformationally inflexible, which exist as in the cone, the partial cone, the 1,3-alternate conformation, or mixture of these, depending on the substituent and on the reaction conditions.[5,6] The 1,2-alternate conformer seems to be excluded as a product in case of tetra-substitution except few cases. An 1,2-alternate conformation has been reported by Atwood[7] for the adduct of *p-tert*-butylcalix[4]arene methyl ether with two molecules of $AlMe_3$ in the solid state, but in this case the conformation is determined by the steric demands of the binding of $AlMe_3$ moieties. Gutsche and coworkers[8,9] reported the first example of 1,2-alternate conformer of tetra-substituted calix[4]arene in which the tetrakis-(dimethylthiocarbamate) of *p-tert*-butylcalix[4]arene was identified as an 1,2-alternate conformer by X-ray crystallography. However, the existence of 1,2-alternate conformer in a solution of conformationally flexible calix[4]arene tetra ether was reported by Shinkai and Reinhoudt independently.[10~14] Shinkai and coworkers[10,11] reported that the *p-tert*-butylcalix[4]arene ethyl ether is flexible, and claimed that the partial cone, when dissolved in 1,1,2,2-tetrachloroethane and heated to above 100 ℃, isomerized to a 1,2-alternate conformation until equilibrium was reached. And the same authors[12] isolated 1,2-alternate conformer in 6% yield from the product mixture obtained by the treatment of calix[4]arene with PrBr in DMF in the presence of Cs_2CO_3. They[13] also synthesized 1,2-alternate conformer of tetrakis{(ethoxycarbonyl)methoxy}-*p-tert*-butyl-calix[4]arene by protection-deprotection method using a benzyl group as protecting group. Reinhoudt[14] reported that in solution tetra substituted calix[4]arenes adopt all four possible conformation, including 1,2-alternate, when these are in the thermodynamic equilibrium, and sometimes the 1,2-alternate is even in the thermodynamically most stable conformation depending on the substituent and they synthesized the 1,2-alternate conformer of *p-tert*-butylcalix[4]arene ethyl ether using the protection and deprotection route similar method to Shinkai and determined the structure by X-ray crystallography. We also isolated a 1,2-alternate conformer from the product mixture of calix[4]arene and butanoyl chloride and this paper deals with the synthesis and molecular structure determination of this molecule.

Synthesis

Three conformational isomers of calix[4]arene butanoate were prepared as shown in Figure 1.

A mixture of calix[4]arene and NaH in THF was treated with butanoyl chloride to afford the crude product as a mixture of three conformational isomers, which was triturated with acetone to give the 1,2-alternate conformer **2a** in 14% yield as acetone insoluble material. Flash chromatographic separation of the residue obtained by evaporation of solvent from acetone soluble portions afforded the partial cone **2b**



1 2

R : C_3H_7CO

Figure 1. Synthesis of calix[4]arene butanoate.

and 1,3-alternate conformer **2c** in 28 and 50% yield, respectively. When the same reaction was carried out at room temperature the yield of three isomers **2a-c** were 3, 42 and 34%, respectively. If the mixture of calix[4]arene and NaH was heated to reflux and then butanoyl chloride was added, the yield of **2a** was decreased to 2%. Structure of three conformational isomers were determined by ^1H and ^{13}C NMR spectroscopy. In the ^1H NMR spectrum of **2a**, the protons of bridge methylene shows one singlet and a pair of doublet in the ratio of 2 : 1 : 1. ^{13}C NMR shows one peak from carbonyl carbons, six peaks from aromatic carbons, and two peaks from bridge methylene carbons at 38.02 and 29.33 ppm. These spectral data support the 1,2-alternate conformation of **2a**. ^1H NMR spectrum of **2b** shows two singlets and a pair of doublets for the $ArCH_2Ar$ protons, three sets of triplet in the ratio of 1 : 1 : 2 for the methyl protons of propyl groups. ^{13}C NMR spectrum shows three peaks for the carbonyl carbons, fourteen peaks for aromatic carbons and two peaks at 37.09 and 30.41 ppm for the bridge methylene carbons. Therefore **2b** is a partial cone conformer. Compound **2c** shows singlet each from protons of aromatics and bridge methylene groups in ^1H NMR spectrum. ^{13}C NMR spectrum is also commensurated with the 1,3-alternate conformation.

X-ray Structure Analysis. Colorless crystals of **2a** were recrystallized from a mixture of dichloromethane and acetone. The crystal system is monoclinic with space group C2/c. X-ray intensity data were measured on an Enraf-Nonius CAD-4 diffractometer using graphite monochromatized Cu-Kα (λ=1.5418 Å) radiation by using $\omega/2\theta$ mode with a ω-scan width of $0.08°+0.14°\tan\theta$. Three standard reflections were monitored for intensity and the crystal orientation. There was no significant intensity variation during the data collection. Among the 3158 independent reflections measured in the range of $2°\leq\theta\leq65°$, the 2605 reflections with the $|F_o|>4\sigma|F_o|$ were used in the structure determination and refinements. Accurate cell constants were obtained by least-squares analysis of 25 reflections, with θ in the range of 14-22°.

Data were corrected for Lorentz and polarization effects, but absorption was ignored. All of the crystal data are summarized in Table 1.

The Structure was solved by direct method of the program Shelxs-8615 using 424 reflections whose $|E|$ values were greater than 1.6. All the nonhydrogen atoms were located in the E-map. The structure was refined by the full-matrix least-squares using the program Shelxl-93.[15] Some of the hy-

Table 1. Summary of Crystal Data

Formular	$C_{44}H_{48}O_8$
Mw, amu	704.8
Crystal system	monoclinic
Space group	C2/c
a, Å	18.435 (4)
b, Å	13.774 (2)
c, Å	16.941 (3)
β, deg	116.23 (2)
Z	4
V, Å^3	3858.8 (12)
μ (Cu-Kα), cm^{-1}	6.65
Density, gcm^{-3}	1.21 (calc.)
	1.21 (meas. by flotation in CCl_4 and CH_3OH)
Diffractometer	Enraf-Nonius CAD-4
Radiation	Cu-Kα (λ=1.5418 Å)
	graphite monochromator
Crystal size, mm	0.3×0.2×0.4
θ lumits, deg	65
Scan type	ω/2θ
Scan range, deg	0.80+0.14tanθ
no. of observed reflections	2605 $\|F_o\|>4\sigma\|F_o\|$
R	0.078

drogen atoms were found in the difference Fourier map, the remaining ones were taken in their calculated positions. A total of 332 parameters were refined. In the final refinement, the positional parameters of all atoms, anisotropic temperature factors of the carbon and oxygen atoms and isotropic thermal parameters for the hydrogen atoms were refined. Mean (Δ/σ) was 0.73 and maximum and minimum peak height on final difference Fourier map were $\Delta\rho_{max}=0.46$ and $\Delta\rho_{min}=-0.45$ eÅ^{-3} respectively. All the atomic scattering factors are obtained from the International Table of X-ray Crystallography.[16] The final positional and thermal parameters of nonhydrogen atoms are listed in Table 2.

Description of the Structure. The bond distances and angles are listed in Table 3. These are mainly as expected for the type of bonds involved.

The molecule has a two fold symmetry. The symmetry axis is along the line connecting between C(7AA') and C(7BB') atoms. The molecule adopts a 1,2-alternate conformation, in which two phenyl groups (A, B) are down and symmetry related other two phenyls (A', B') are up (see Figure 2). The dihedral angles between the four aromatic rings and the mean plane of the macrocyclic ring CH_2 groups are 48.5° and 81.0° for A and B rings, respectively. The A and A' rings are more flattened than the other two rings B and B'.

The orientation of the functional groups with respect to its benzene ring can be described by the ∠C(4)---C(1)-O(1)-C(8) torsion angles of −167.2 and −6.7° for units A and B, respectively. Therefore two butanoyloxy groups point outwards. Other two groups point inwards the macrocyclic ring, and these partly fill the cavity of the molecule and also could major part in flattened phenyl units.

Table 2. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Thermal Parameters for Non-hydrogen Atoms.* The e.s.d.'s are in parentheses. $U_{eq}=1/3\ \sum_i\sum_j U_{ij}\ a_i^*a_j^*a_{ij}$ (Å^2)

Atom	x	y	z	Ueq
O(1A)	4868 (1)	425 (1)	1580 (1)	.0485 (5)
O(2A)	5248 (2)	−723 (2)	893 (2)	.0679 (6)
C(1A)	4169 (2)	−87 (2)	1461 (2)	.0445 (5)
C(2A)	3437 (2)	348 (2)	924 (2)	.0493 (6)
C(3A)	2730 (2)	−122 (3)	819 (2)	.0619 (7)
C(4A)	2769 (2)	−983 (3)	1257 (3)	.0656 (7)
C(5A)	3502 (2)	−1378 (2)	1801 (2)	.0572 (6)
C(6A)	4227 (2)	−942 (2)	1921 (2)	.0464 (5)
C(7AA)+	5000	−1466 (3)	2500	.0525 (8)
C(8A)	5378 (2)	28 (2)	1285 (2)	.0508 (6)
C(9A)	6107 (2)	666 (3)	1553 (3)	.0641 (7)
C(10A)	6677 (3)	378 (3)	1203 (4)	.0978 (14)
C(11A)	7414 (4)	1003 (5)	1491 (6)	.111 (2)
C(7BB)+	5000	4076 (3)	2500	.0710 (11)
O(1B)	4706 (1)	2706 (2)	1128 (2)	.0591 (5)
O(2B)	4029 (2)	3814 (2)	105 (2)	.1006 (9)
C(1B)	4119 (2)	2778 (2)	1448 (2)	.0537 (6)
C(2B)	4236 (2)	3474 (2)	2093 (2)	.0616 (7)
C(3B)	3632 (3)	3568 (3)	2364 (3)	.0691 (8)
C(4B)	2957 (2)	2974 (3)	2022 (3)	.0701 (8)
C(5B)	2885 (2)	2261 (3)	1431 (2)	.0615 (7)
C(6B)	3473 (2)	2139 (2)	1132 (2)	.0626 (6)
C(7AB)	3397 (2)	1325 (2)	501 (2)	.0557 (6)
C(8B)	4580 (2)	3268 (2)	420 (2)	.0592 (7)
C(9B)	5209 (3)	3094 (4)	112 (3)	.0777 (9)
C(10B)	5092 (4)	3610 (4)	−705 (4)	.112 (2)
C(11B)	5775 (3)	3561 (4)	−945 (4)	.1021 (13)

*Tables for anisotropic thermal parameters of the non-hydrogen atoms, coordinates of hydrogen atoms and structure factors are available from the author (YJP). +occupancy 0.5.

The crystal structure is illustrated in Figure 3. The molecules are packed together by van der Waals forces.

Experimental

25,26,27,28-Tetra-butanoyloxycalix[4]arene 2. A solution of calix[4]arene **1** (1.00 g, 2.35 mmole) in 50 mL of dry THF was placed in an oil bath, treated with NaH (1.51 g, 4 mole equivalent per OH group, 60% oil dispersion), and stirred for a while and then heated to 40 ℃. A solution of the butanoyl chloride (5.02 g, 5 mole equivalent per OH group) in 10 mL of dry THF was added dropwise, and the reaction mixture was refluxed an additional 2 h. The solvent was removed on a rotary evaporator, and the residue was treated with water. The product was extracted with 20 mL portions of $CHCl_3$ twice, the combined organic layer was washed with water three times, dried, concentrated, and treated with 20 mL of methanol to yield crude product (1.63 g, 98%), which was triturated 15 mL of acetone at room temperature to leave 232 mg (14%) of 2a as acetone insoluble crystalline solid; **2a** (1,2-alternate conformer) mp 309-310 ℃; IR (KBr)

Table 3. Bond Distances (Å) and Angles (°). The e.s.d.'s are in parentheses

	A	B		
O(1)-C(1)	1.403 (4)	1.411 (4)		
O(1)-C(8)	1.359 (4)	1.359 (4)		
O(2)-C(8)	1.196 (4)	1.185 (4)		
C(1)-C(2)	1.388 (4)	1.398 (4)		
C(1)-C(6)	1.391 (4)	1.384 (4)		
C(2)-C(3)	1.394 (5)	1.384 (6)		
C(3)-C(4)	1.383 (6)	1.384 (6)		
C(4)-C(5)	1.367 (5)	1.367 (6)		
C(5)-C(6)	1.396 (5)	1.395 (5)		
C(8)-C(9)	1.498 (5)	1.488 (6)		
C(9)-C(10)	1.470 (7)	1.483 (8)		
C(10)-C(11)	1.496 (8)	1.488 (8)		
C(2A)-C(7AB)	1.511 (4)	C(6A)-C(7AA)	1.509 (4)	
C(7BB)-C(2B)	1.513 (4)	C(6B)-C(7AB)	1.513 (4)	
O(2)-C(8)-O(1)	123.4 (3)	122.5 (3)		
C(2)-C(1)-O(1)	116.3 (2)	118.0 (3)		
C(3)-C(2)-C(1)	117.8 (3)	117.0 (3)		
C(4)-C(3)-C(2)	120.4 (3)	120.8 (4)		
C(5)-C(4)-C(3)	120.3 (3)	120.6 (3)		
C(5)-C(6)-C(1)	116.9 (3)	117.2 (3)		
C(6)-C(1)-O(1)	120.5 (3)	118.8 (3)		
C(6)-C(1)-C(2)	123.0 (3)	123.2 (3)		
C(6)-C(5)-C(4)	121.6 (3)	120.9 (3)		
C(8)-O(1)-C(1)	119.1 (2)	115.9 (2)		
C(9)-C(8)-O(1)	109.1 (2)	111.2 (3)		
C(9)-C(8)-O(2)	127.5 (3)	126.3 (3)		
C(10)-C(9)-C(8)	115.2 (4)	115.8 (4)		
C(11)-C(10)-C(9)	114.8 (5)	116.2 (5)		
C(6A)-C(7AA)-(C6A)*	122.9 (3)			
C(7AA)-C(6A)-C(1A)	125.8 (3)	C(7AA)-C(6A)-C(5A)	117.2 (3)	
C(7AB)-C(2A)-C(1A)	121.6 (3)	C(7AB)-C(2A)-C(3A)	120.5 (3)	
C(6B)-C(7AB)-C(2A)	110.8 (2)			
C(7AB)-C(6B)-C(1B)	122.6 (3)	C(7AB)-C(6B)-C(5B)	120.2 (3)	
C(1B)-C(2B)-C(7BB)	121.5 (3)	C(3B)-C(2B)-C(7BB)	121.4 (3)	
C(2B)-C(7BB)-C(2B)*	113.6 (3)			

*two-fold symmetry related atom

Table 4. Selected Torsion Angles(°). The e.s.d.'s are in parentheses

	A	B
C(8)-O(1)-C(1)-C(2)	−116.3 (3)	−90.1 (3)
C(8)-O(1)-C(1)-C(6)	68.5 (3)	92.1 (4)
C(1)-O(1)-C(8)-O(2)	3.3 (3)	2.6 (3)
C(1)-O(1)-C(8)-C(9)	−175.3 (3)	−176.9 (4)
O(1)-C(1)-C(2)-C(3)	−177.5 (4)	176.7 (5)
O(1)-C(1)-C(6)-C(5)	176.6 (4)	−177.1 (4)
O(1)-C(8)-C(9)-C(10)	−174.4 (4)	175.0 (5)
O(2)-C(8)-C(9)-C(10)	7.3 (4)	−4.5 (4)
C(8)-C(9)-C(10)-C(11)	−178.5 (6)	171.1 (7)
C(6A)*-C(7AA')-C(6A)-C(1A)	37.2 (5)	
C(7AA')-C(6A)-C(1A)-C(2A)	178.5 (5)	
C(6A)-C(1A)-C(2A)-C(7AB)	174.2 (5)	
C(1A)-C(2A)-C(7AB)-C(6B)	−83.6 (3)	
C(2A)-C(7AB)-C(6B)-C(1B)	115.5 (4)	
C(7AB)-C(6B)-C(1B)-C(2B)	−173.7 (5)	
C(6B)-C(1B)-C(2B)-C(7BB')	172.5 (5)	
C(1B)-C(2B)-C(7BB')-C(2B)*	−55.9 (4)	

*two-fold symmetry related atom

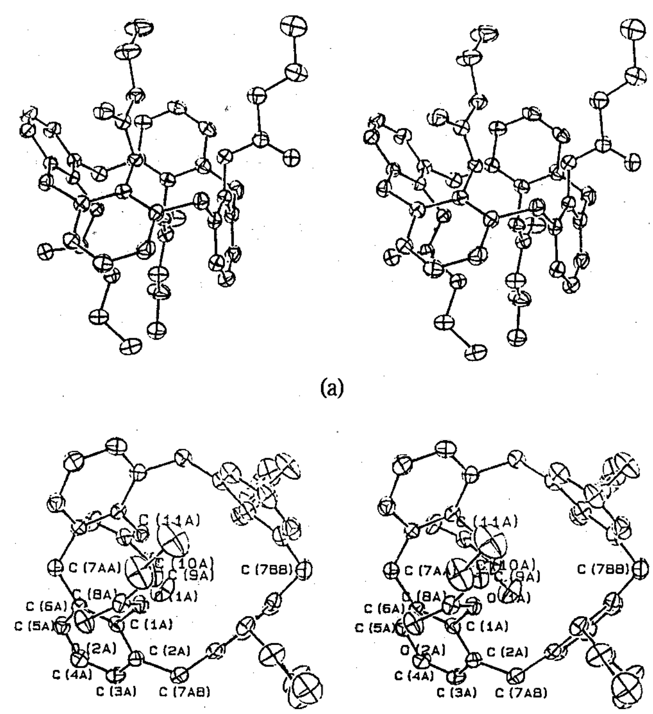


Figure 2. Conformation and atomic numbering.

1735 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 7.27-7.26 (m, 4, ArH), 7.12-7.06 (m, 8, ArH) 3.82 (s, 4, CH_2), 3.65 (d, 2, CH_2, J=13.5 Hz), 3.34 (d, 2, CH_2, J=13.5 Hz), 1.86 (t, 2, $COCH_2$, J=7.5 Hz), 1.80 (t, 2, $COCH_2$, J=7.5 Hz), 1.43 (sextet, 8, CH_2, J=7.5 Hz), 1.29 (t, 2, $COCH_2$, J=7.5 Hz), 1.23 (t, 2, $COCH_2$, J=7.5 Hz), 0.87 (t, 12, CH_3, J=7.5 Hz); ^{13}C NMR ($CDCl_3$) δ 171.66 (C=O), 147.38, 133.68, 132.15, 129.74, 129.30, 125.34 (Ar), 38.02 ($ArCH_2Ar$), 34.34 (CH_2), 29.33 ($ArCH_2Ar$), 17.36 (CH_2), 13.33 (CH_3). Acetone filtrate and washing were combined, evaporated solvent to afford the residue which was the mixture of **2a** (trace), **2b** and **2c**. Compound **2b** and **2c** were separated by flash chromatography (eluent was mixture of hexane and acetone) to afford pure **2b** and **2c** in 830 mg (50% yield) and 465 mg (28% yield) respectively; **2b** (partial cone) mp 236-237 ℃; IR (KBr) 1750 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 7.28-7.13 (m, 7, ArH), 6.89-6.66 (m, 5, ArH), 3.61 (s, 2, CH_2), 3.59 (s, 2, CH_2), 3.50 (d, 2, CH_2, J=13.7 Hz), 3.23 (d, 2, CH_2, J=13.7 Hz), 2.57 (t, 2, $COCH_2$, J=7.6 Hz), 2.54 (t, 2, $COCH_2$, J=7.6 Hz), 2.34 (t, 2, $COCH_2$, J=7.6 Hz), 2.32 (t, 2, $COCH_2$, J=7.5 Hz), 1.80 (m, 6, CH_2), 1.67 (sextet, 2, CH_2), 1.13 (t, 3, CH_3, J=7.6 Hz), 1.11 (t, 3, CH_3, J=7.6 Hz), 1.08 (t, 6, CH_3, J=7.6 Hz); ^{13}C NMR ($CDCl_3$) δ 173.26, 171.84, 171.35 (C=O), 149.40, 147.86, 146.17, 135.25, 134.21, 132.79, 131.52, 130.12, 129.56, 129.46, 129.09, 125.97, 125.51,

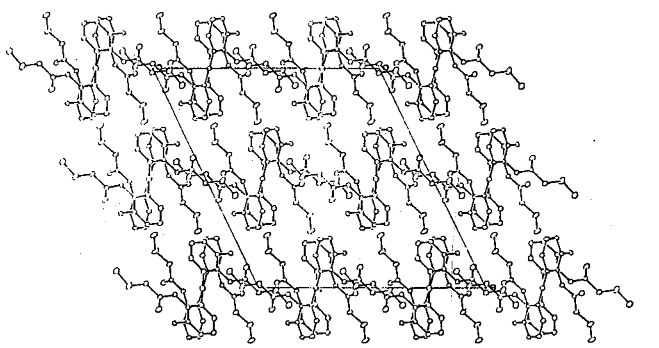


Figure 3. Crystal sturucture viewed down b axis.

124.51 (Ar), 37.09, 30.41 ($ArCH_2Ar$), 35.80, 35.71, 33.44 (CH_2), 18.10, 17.77, 17.33 (CH_2), 13.69, 13.59, 13.44 (CH_3). **2c** (1,3-alternate) mp 224-225 ℃; IR (KBr) 1740 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 7.04 (s, 12, ArH), 3.74 (s, 8, $ArCH_2Ar$), 1.64-1.51 (m, 16, $COCH_2$ and CH_2), 0.92 (t, 12, CH_3, J=6.9 Hz); ^{13}C NMR ($CDCl_3$) δ 170.76 (C=O), 148.63, 133.30, 129.22, 125.14 (Ar), 37.49 ($ArCH_2Ar$), 34.63 ($COCH_2$), 17.08 (CH_2), 13.49 (CH_3).

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Appendix

Table Anisotropic Temperature Factors (Å^2×10^3) for the Non-hydrogen Atoms. The temperature factor expression used is exp $[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}b^{*2}+\cdots+2U_{12}hka^*b^*)]$. The e.s.d.'s are in parentheses

Atom	U11	U22	U33	U23	U13	U12
O(1A)	44 (1)	44 (1)	58 (1)	−2 (1)	23 (1)	−3 (1)
O(2A)	75 (2)	61 (1)	80 (2)	−20 (1)	45 (1)	−12 (1)
C(1A)	42 (1)	44 (1)	47 (2)	−6 (2)	19 (1)	−4 (1)
C(2A)	47 (2)	51 (2)	46 (2)	0 (1)	17 (1)	2 (1)
C(3A)	43 (2)	68 (2)	64 (2)	3 (2)	15 (1)	4 (1)
C(4A)	47 (2)	66 (2)	81 (2)	3 (2)	26 (2)	−9 (1)
C(5A)	54 (2)	52 (2)	67 (2)	0 (1)	28 (2)	−6 (1)
C(6A)	46 (2)	43 (1)	47 (2)	−4 (1)	19 (1)	−3 (1)
C(7AA)	51 (2)	42 (2)	59 (2)	0 (0)	19 (2)	0 (0)
C(8A)	51 (2)	49 (2)	55 (2)	2 (1)	26 (1)	2 (1)
C(9A)	57 (2)	56 (2)	89 (3)	−7 (2)	42 (2)	−5 (1)
C(10A)	83 (3)	96 (3)	147 (7)	−38 (3)	81 (3)	−22 (2)
C(11A)	87 (4)	124 (5)	157 (6)	−32 (4)	84 (4)	−31 (3)
C(7BB)	95 (4)	45 (2)	76 (3)	0 (0)	41 (3)	0 (0)
O(1B)	61 (1)	58 (1)	63 (1)	11 (1)	33 (1)	13 (1)
O(2B)	90 (2)	115 (2)	116 (2)	63 (2)	63 (2)	45 (1)
C(1B)	59 (2)	49 (2)	57 (2)	10 (1)	30 (2)	13 (1)
C(2B)	74 (2)	47 (2)	67 (2)	8 (1)	34 (2)	12 (1)
C(3B)	87 (3)	60 (2)	69 (2)	6 (2)	43 (2)	22 (2)
C(4B)	75 (2)	70 (2)	78 (2)	14 (2)	46 (2)	22 (2)
C(5B)	60 (2)	65 (2)	64 (2)	15 (2)	31 (2)	15 (2)
C(6B)	55 (2)	50 (2)	52 (2)	12 (1)	22 (1)	13 (1)
C(7AB)	56 (2)	59 (2)	50 (2)	7 (1)	20 (2)	8 (1)
C(8B)	56 (2)	57 (2)	64 (2)	8 (2)	25 (2)	2 (1)
C(9B)	69 (2)	94 (3)	78 (3)	15 (2)	40 (2)	9 (2)
C(10B)	135 (5)	114 (4)	131 (4)	28 (3)	101 (4)	21 (3)
C(11B)	108 (4)	110 (4)	112 (4)	−14 (3)	70 (3)	−16 (3)

Table Fractional Atomic Coordinates for the Hydrogen Atoms

Atom	x	y	z	Ueq
H3A	0.2220(19)	0.0191(23)	0.0476(20)	0.084(9)
H4A	0.2262(20)	−0.1332(24)	0.1141(22)	0.087(9)
H5A	0.3495(19)	−0.2007(24)	0.2106(21)	0.072(9)
H7A1	0.4846(18)	−0.1895(22)	0.2893(19)	0.072(8)
H9A1	0.5930(20)	0.1300(27)	0.1498(23)	0.080(10)
H9A2	0.5951(40)	0.0972(52)	0.0933(48)	0.220(25)
H103	0.6381(31)	0.0344(39)	0.0500(36)	0.222(19)
H104	0.6824(25)	−0.0287(34)	0.1289(28)	.140(13)
H114	0.7825(28)	0.0695(32)	0.1274(30)	0.127(14)
H115	0.7220(36)	0.1630(50)	0.1232(42)	0.168(24)
H116	0.7713(33)	0.1053(38)	0.2097(37)	0.158(20)
H7B'	0.5061(23)	0.4502(26)	0.2099(25)	0.096(11)
H3B	0.3751(19)	0.4109(25)	0.2808(22)	0.078(9)
H4B	0.2514(24)	0.3031(27)	0.2167(26)	0.090(12)
H5B	0.2404(21)	0.1806(25)	0.1166(22)	0.081(10)
H7B1	0.3834(16)	0.1333(17)	0.0325(17)	0.050(6)
H7B2	0.2873(18)	0.1400(20)	−0.0010(20)	0.067(8)
H9B1	0.5539(30)	0.2737(40)	0.0419(33)	0.135(19)
H9B2	0.5644(54)	0.3625(64)	0.0301(62)	0.207(36)
H101	0.5009(26)	0.4236(35)	−0616(29)	0.150(14)
H102	0.4324(32)	0.3611(40)	−0.1300(36)	0.220(20)
H111	0.5661(30)	0.3887(35)	−0.1592(35)	0.216(17)
H112	0.5973(25)	0.2795(33)	−0.0903(27)	0.134(13)
H113	0.6375(30)	0.3886(34)	−0.0392(32)	0.207(16)

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Lattice Deformation and Electronic Structure of the C_{60}^+ Cation

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The effects caused by the ionization on the electronic structure and geometry on C_{60} are studied by the modified Su-Schriffer-Heeger (SSH) model Hamiltonian. After the ionization of C_{60}, the bond structure of the singly charged C_{60} cation is deformed from I_h symmetry of the neutral C_{60} to D_{5d}, C_1, and C_2, which is dependent upon the change of the electron-phonon coupling strength. The electronic structure of the C_{60}^+ cation ground state undergoes Jahn-Teller distortion in the weak electron-phonon coupling region, while self-localized states occur in the intermediate electron-phonon region, but delocalized electronic states appear again in the strong electron-phonon region. In the realistic strength of the electron-phonon coupling in C_{60}, the bond structure of C_{60}^+ shows the layer structure of the bond distortion and a polaron-like state is formed.

Introduction

Since the recent synthesis[1] of the macroscopic quantity of the fullerene, there has been a great deal of interest in the science of fullerenes from the viewpoint of solid state[2] and molecular[3] science. Spectroscopic[4] and diffraction[5] studies have confirmed the predicted truncated icosahedral structure[6] of the C_{60} molecule. Electrochemical studies[7] have shown that C_{60} is easily reduced but is very difficult to oxidize. It should be pointed out that gas-phase reactions attributed to C_{60}^+, C_{60}^{2+}, and C_{60}^{3+} have been reported by numerous authors.[8] Kato *et al.* have isolated and studied the electronic absorption spectra of C_{60} anion and cation radicals.[9] Kukolich and Huffman have reported the EPR spectra of C_{60} anion and cation radicals.[10] There has long been the Jahn-Teller theorem, on the other hand, that molecules with high symmetry may induce structural deformations and symmetry reductions, when the highest occupied degenerate molecular orbitals (HOMOs) level is partially occupied, which provides a mechanism partly lifting this electronic degeneracy.[11] An interesting question has arisen: where will the holes of C_{60}^+ cation stay? Will they spread over the whole ball or will they be localized in some small area? If the bonds are rigid, the holes will go directly to the HOMOs, in which wave functions are extended. Otherwise, if the bonds are soft enough, the lattice can be distorted by the transferred hole to form a kind of localized state. The soliton model of Su-Schriffer-Heeger (SSH), a tight-binding model with electron-phonon (e-ph) coupling, demonstrates the novel phenomena with the midgap state in polyacetylene.[12] Several groups have studied the electronic and bond structures for the electron doped C_{60}^{n-} ($n=1$, 2, and/or 3) ground state[13~16] with the SSH model Hamiltonian. As for the C_{60}^+ cation, Harigaya[13] showed only the energy level correlation by using the SSH model Hamiltonian based on the parameters of graphite. Bendale *et al.*[17] show that a significant Jahn-Teller distortion takes place in C_{60}^+ as compared to C_{60} by using ZINDO calculations. The calculated CC bond lengths of C_{60}^+ are divided into seven classes. The CC bonds forming the pentagons and hexagons of the C_{60} structure at the top and bottom of the cage are of the same order of magnitude as in neutral C_{60}, but the twenty "equatorial" carbon atoms form CC bonds of having nearly identical bond lengths variation ($\simeq 0.01$), irrespective of whether they are part of a pentagon or a hexagon ring.

As far as we are aware, the general effect of e-ph coupling in charged C_{60}^{n-} ($n=1$, 2, 3) anions ground states is known,[14] but it is not known to the charged C_{60}^+ cation ground state. In this paper, we present the results from self-consistent numerical calculations which allow for a complete relaxation of all π electrons and individual atoms in the ground states of the C_{60}^+ cation. The different electron hopping constants