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Highly Twisted *t*-Butoxycarbonyl Groups in Hexa-*t*-butyl Benzenehexacarboxylate. The Structural Origin of Steric Hindrance-Induced Dual Fluorescence

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Comparative X-ray crystallographic analyses of tetra-*t*-butyl 1,2,4,5-benzenetetracarboxylate (**1**) and highly congested hexa-*t*-butyl benzenehexacarboxylate (**2**) have shown that *t*-butoxycarbonyl groups in **2** are much more twisted with respect to the benzene ring and bond-elongated in the peripheral positions than those in **1** or hexamethyl benzenehexacarboxylate. Such deformations and the staggered carbonyl orientation, all arising from the steric hindrance, may be responsible for the unusual dual-fluorescence behavior of the sterically congested hexaester **2**.

We have demonstrated that some bulky hexaalkyl benzenehexacarboxylates constitute an unusual dual-fluorescing molecular system[1] involving a novel mechanism distinctly different from the well-documented protonation/deprotonation,[2] excimer formation,[3] and twisted intermolecular charge transfer mechanisms.[4] Thus, more or less bulky isopropyl, *t*-butyl, menthyl, bornyl, and adamantyl benzenehexacarboxylates give apparently bulkiness-dependent dual fluorescence peaks with small and large Stokes shifts at the ambient and/or lower temperatures, but the corresponding methyl ester never shows such unusual fluorescence behavior even at low temperatures.[1] This dual fluorescence phenomenon has been attributed to the decelerated conformational relaxation from the initially produced near-Franck–Condon singlet to the fully relaxed singlet state, for which the steric hindrance between neighboring bulky alkoxycarbonyl groups appears to be responsible. Since a Franck–Condon singlet is believed in general to conserve the structure in the ground electronic state,[5] it is interesting and useful in elucidating the structural orgin of this unusual fluorescence to compare the ground-state structure of dual-fluorescing, highly congested bulky alkyl benzenehexacarboxylate with that of less-congested 1,2,4,5-benzenetetracarboxylate.

In this study, we did comparative X-ray crystallographic analyses of tetra-*t*-butyl 1,2,4,5-benzenetetracarboxylate (**1**) and hexa-*t*-butyl benzenehexacarboxylate (**2**) as representative single- and dual-fluorophores, and discuss their conformations in comparison with the structure of the least-hindered hexamethyl benzenehexacarboxylate (**3**) reported recently[6] (Chart 1).

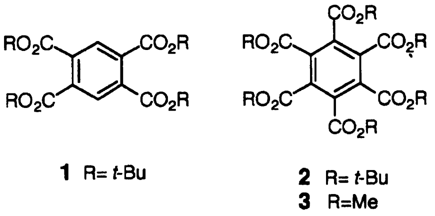

Chart 1.

Experimental

Materials. The samples (**1** and **2**) for the crystallographic analyses were prepared in the reaction of the corresponding acid chloride and potassium *t*-butoxide in the presence of 18-crown-6,[1] and the subsequent recrystallization from methanol.

Single-Crystal X-Ray Analysis. Crystal structural analyses were done on an Enraf Nonius automated four-circle X-ray diffractometer (CAD-4), using graphite-monochromated Mo $K\alpha$ radiation (λ=0.71073 Å). The crystallographic data are shown in Table 1.

All of the calculations were done on a DEC PDP 11/34 system using an SDP-Plus program. The structures were solved by the direct method (MULTAN 82) and refined by the full matrix least-squares method. In the last cycle of the refinement with anisotropic temperature factor for non-hydrogen atoms, all of the parameter shifts were less than one-third of the corresponding standard deviations. After the refinement, hydrogen atoms were located at positions calculated for a C–H bond length of 0.950 Å. Table 2 lists the final atomic parameters of **1** and **2**; for the numbering of non-hydrogen atoms, see Chart 2. Tables of the observed and calculated structure factors, anisotropic temperature factors, and bond distances and angles have been deposited as Document No. 67007 at the Office of the Editor of Bull. Chem. Soc. Jpn.

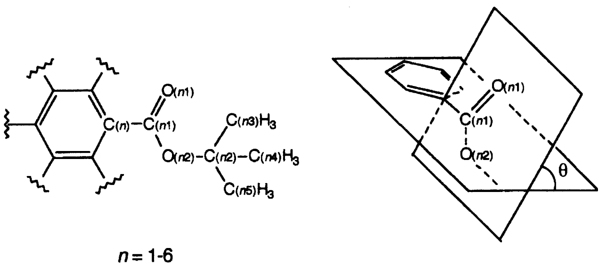

Chart 2. Numbering of non-hydrogen atoms in *t*-butyl benzenetetracarboxylate or benzenehexacarboxylate and definition of torsion angle (θ) of alkoxycarbonyl group against benzene ring.

Table 1. Crystallographic Data and Summary of Data Collection and Structure-Refinement Parameters

	1	2
Formula	$C_{26}H_{38}O_8$	$C_{36}H_{54}O_{12}$
Formula weight	478.58	678.82
Crystal system	Monoclinic	Monoclinic
Space group	$P2(1)$	Cc
Z	2	4
a/Å	11.696(3)	16.332(0)
b/Å	10.450(5)	14.074(5)
c/Å	11.176(5)	16.872(4)
β/deg	95.14(3)	92.98(1)
V/Å^3	1360.5	3944.2
D_x/g cm^{-3}	1.168	1.143
D_m/g cm^{-3}	1.166	1.130
μ(Mo $K\alpha$)/cm^{-1}	0.80	0.80
F(000)	516	1464
T/K	298	298
Crystal shape and dimension (mm)	Rod-shaped 0.5×0.5×0.8	Rod-shaped 0.8×0.4×0.3
Number of reflection used in cell dimensions	25 reflections with $36<2\theta<64°$	
Range of measurement	$-16<h<16$ $-14<k<14$ $0<l<15$	$-15<h<15$ $-13<k<13$ $0<l<16$
Number of reflection measured	7922	3741
Number of relection observed	2434	486
$R(wR)$	0.068 (0.066)	0.081 (0.087)
S	0.816	3.915
$(\Delta\sigma)_{\max}$	0.00	0.00
Final residual electron density (eÅ^{-3}) for max peaks	+0.47	0.49

Resutls and Discussion

Deformed Benzene Ring. ORTEP drawings of the refined structures of tetraester **1** and hexaester **2** are shown in Fig. 1, and selected bond lengths and angles in **1** and **2** are listed in Table 3, where the numbering of non-hydrogen atoms is as in Chart 2.

First of all, it is noted that the steric hindrance caused by six bulky *t*-butoxycarbonyl groups introduced at the adjacent positions in **2** does not appear to spoil significantly the planarity of the benzene ring, but is rather released mostly by twisting the bulky ester moieties as discussed below. Thus the standared deviations of the departure of aromatic carbons (C*n*) from the least-square benzene plane are calculated as ±0.01 Å for **1** and ±0.03 Å even for **2**, although the benzene ring of the latter is slightly bent at C2 and C5 constituting a very shallow boat form. However, the benzene ring, though almost planar, is appreciably deformed in bond length and angle; see rows C1–C2 to C6–C1 for bond lengths and C2–C1–C6 to C5–C6–C1 for bond angles in Table 3. Differences in the bond lengths/angles in **1** and **2** are impressive. The mean bond length and angle of benzene ring do not significantly differ in **1** and **2**, but the individual bond lengths/angles deviate much more extensively from the mean values in the highly congested hexaester **2**. Thus, the bond length and angle in **2** vary fairly widely from 1.28 to 1.49 Å and from 110 to 129°, respectively, to give much larger standard deviations; i.e. bond length=1.39±0.02 Å for **1** and 1.40±0.09 Å for **2**; bond angle=120.0±1.3° for **1** and 119.9±7.9° for **2**. Quite similar tendencies are seen in the butoxycarbonyl group except for its periphery; the corresponding bond lengths/angles around the core of **1** and **2** are almost the same on the average, but appreciably differ in their deviations.

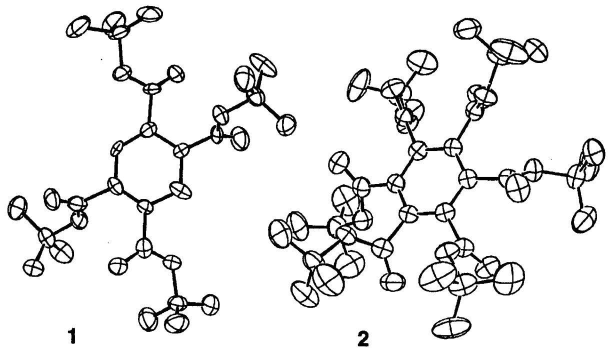

Fig. 1. ORTEP drawings of tetra-*t*-butyl benzenetetracarboxylate (**1**) and hexa-*t*-butyl benzenehexacarboxylate (**2**).

Table 2. Positions and B_{eq} Values[a] for Tetra-*t*-butyl Benzenetetracarboxylate (**1**) and Hexa-*t*-butyl Benzenehexacarboxylate (**2**)

Atom	x	y	z	$B_{\mathrm{eq}}/\mathrm{Å}^2$	Atom	x	y	z	$B_{\mathrm{eq}}/\mathrm{Å}^2$
Tetra-*t*-butyl 1,2,4,5-benzenetetracarboxylate (**1**)					Hexa-*t*-butyl benzenehexacarboxylate (**2**)				
O11	0.6774(2)	0.124	−0.0039(2)	3.8(1)	O11	0.696	0.2889(5)	0.370	5.3(2)
O12	0.7634(2)	0.2633(3)	0.1285(2)	3.6(1)	O12	0.8301(4)	0.2586(4)	0.3751(4)	4.2(2)
O21	0.4815(2)	−0.1126(3)	0.0484(3)	4.1(1)	O21	0.9456(4)	0.2884(5)	0.5558(5)	4.8(2)
O22	0.6560(2)	−0.0972(2)	0.1538(2)	3.2(1)	O22	0.8116(4)	0.2535(5)	0.5553(4)	4.6(2)
O41	0.3228(3)	0.2164(3)	0.5015(2)	3.7(1)	O31	1.0176(4)	0.5082(5)	0.5644(4)	4.7(2)
O42	0.2359(2)	0.0772(3)	0.3693(2)	3.2(1)	O32	0.9294(3)	0.4658(4)	0.6544(4)	3.3(1)
O51	0.5159(2)	0.4474(3)	0.4558(3)	4.3(1)	O41	0.9073(5)	0.6772(5)	0.5920(4)	4.9(2)
O52	0.3455(2)	0.4388(2)	0.3435(2)	3.1(1)	O42	0.9169(4)	0.7102(4)	0.4573(4)	3.8(1)
C1	0.5902(3)	0.1740(3)	0.1772(3)	2.7(1)	O51	0.7408(4)	0.6792(5)	0.3390(4)	4.9(2)
C2	0.5247(3)	0.0653(3)	0.1824(3)	2.7(1)	O52	0.7303(4)	0.7118(5)	0.4647(4)	3.8(2)
C3	0.4365(3)	0.0617(3)	0.2568(3)	2.6(1)	O61	0.6203(4)	0.5062(5)	0.3627(4)	4.4(2)
C4	0.4106(3)	0.1639(3)	0.3257(3)	2.7(1)	O62	0.7118(4)	0.4709(5)	0.2709(4)	4.5(2)
C5	0.4746(3)	0.2769(3)	0.3191(3)	2.6(1)	C1	0.7900(5)	0.3919(6)	0.4320(6)	3.3(2)
C6	0.5663(3)	0.2830(4)	0.2462(3)	3.1(1)	C2	0.8507(6)	0.4030(6)	0.4954(5)	2.9(2)
C11	0.6807(3)	0.1838(3)	0.0880(3)	3.2(1)	C3	0.8852(6)	0.4810(6)	0.5232(5)	3.3(2)
C12	0.8604(3)	0.2938(3)	0.0588(3)	3.1(1)	C4	0.8522(5)	0.5723(6)	0.4914(5)	2.9(2)
C13	0.8177(4)	0.3471(5)	−0.0619(4)	5.1(1)	C5	0.7872(5)	0.5634(6)	0.4343(5)	3.1(2)
C14	0.9339(4)	0.3774(5)	0.1381(5)	5.8(1)	C6	0.7595(5)	0.4855(6)	0.4055(5)	2.8(2)
C15	0.9301(4)	0.1704(5)	0.0429(5)	5.8(1)	C11	0.7673(5)	0.3102(7)	0.3932(6)	3.3(2)
C21	0.5527(3)	−0.0584(3)	0.1171(3)	2.7(1)	C12	0.8225(7)	0.1757(7)	0.3145(8)	5.4(3)
C22	0.7061(4)	−0.2155(4)	0.1122(4)	3.8(1)	C13	0.7928(8)	0.2125(9)	0.2377(6)	6.3(3)
C23	0.7138(5)	−0.2063(5)	−0.0268(4)	5.5(1)	C14	0.9166(8)	0.147(1)	0.3093(9)	7.8(4)
C24	0.8189(4)	−0.2245(4)	0.1819(4)	4.4(1)	C15	0.7767(7)	0.0958(7)	0.3511(7)	5.3(3)
C25	0.6394(5)	−0.3317(5)	0.1472(5)	5.6(1)	C21	0.8793(6)	0.3028(6)	0.5413(6)	4.0(2)
C41	0.3190(3)	0.1569(3)	0.4094(3)	2.8(1)	C22	0.8140(8)	0.1703(7)	0.6060(6)	5.1(3)
C42	0.1370(3)	0.0538(3)	0.4424(4)	3.8(1)	C23	0.7316(7)	0.1349(8)	0.5983(9)	7.2(3)
C43	0.0691(4)	−0.0487(5)	0.3626(4)	4.7(1)	C24	0.881(1)	0.0994(8)	0.5717(8)	8.0(4)
C44	0.0762(4)	0.1720(5)	0.4598(5)	5.1(1)	C25	0.847(1)	0.202(1)	0.6938(8)	7.9(4)
C45	0.1816(5)	−0.0210(5)	0.5570(4)	5.4(1)	C31	0.9515(5)	0.4861(7)	0.5851(6)	3.2(2)
C51	0.4516(3)	0.3963(4)	0.3849(3)	3.1(1)	C32	0.9832(7)	0.4811(9)	0.7321(7)	6.3(3)
C52	0.2982(3)	0.5610(4)	0.3907(4)	3.2(1)	C33	0.9303(7)	0.448(1)	0.7930(6)	6.0(3)
C53	0.3675(4)	0.6692(4)	0.3578(5)	4.5(1)	C34	1.0490(8)	0.391(1)	0.7242(7)	7.1(4)
C54	0.1765(4)	0.5560(5)	0.3218(5)	5.7(1)	C35	1.0170(9)	0.5769(9)	0.7346(7)	7.1(4)
C55	0.2872(3)	0.5495(4)	0.5196(4)	4.2(1)	C41	0.8971(5)	0.6572(6)	0.5233(6)	3.4(2)
					C42	0.9646(6)	0.8052(9)	0.4725(8)	6.5(3)
					C43	0.9662(8)	0.8353(8)	0.3855(8)	7.5(3)
					C44	1.0489(6)	0.7522(8)	0.5140(9)	6.9(4)
					C45	0.9310(8)	0.8680(7)	0.5323(9)	7.1(4)
					C51	0.7535(5)	0.6643(7)	0.4095(5)	2.9(2)
					C52	0.6687(6)	0.7902(6)	0.4544(6)	3.2(2)
					C53	0.7095(7)	0.8732(8)	0.4068(7)	5.6(3)
					C54	0.6591(8)	0.8250(9)	0.5416(8)	6.7(3)
					C55	0.5877(7)	0.761(1)	0.4241(8)	6.0(3)
					C61	0.6857(6)	0.4871(6)	0.3458(5)	3.4(2)
					C62	0.6526(5)	0.4696(8)	0.2029(5)	3.6(2)
					C63	0.5877(7)	0.4037(9)	0.2098(7)	6.1(3)
					C64	0.6166(8)	0.5786(9)	0.1997(9)	7.3(4)
					C65	0.7122(8)	0.464(1)	0.1306(8)	7.6(4)

a) $B_{\mathrm{eq}}=1/3\sum_i\sum_j B_{ij}a_i^*a_j^*\boldsymbol{a}_i\cdot\boldsymbol{a}_j$.

Twisted Ester Groups. More significant and essential conformational changes caused by steric hindrance are found in the torsion angles (θ) of the carbonyl plane against the benzene ring. In this study, the torsion angle θ is defiend as an absolute value of the dihedral angle O(n1)–C(n1)–C(n)–C(n+1) or, if obtuse, its supplementary angle, as shown in Chart 2. In Table 4 are listed the dihedral angles and the torsion angles θ (in the parentheses) for **1** and **2**, along with the corresponding angles reported for the two independent molecules of hexamethyl benzenehexacarboxylate (**3**) packed in a unit cell.[6]

As can be seen from Table 4, all carbonyl groups in **1**—**3** are more or less twisted with respect to the ben-

Table 3. Selected Bond Length (Å) and Angles (°) in Tetra-*t*-butyl Benzenetetracarboxylate (**1**) and Hexa-*t*-butyl Benzenehexacarboxylate (**2**)

Bond length	**1**	**2**	Bond angle	**1**	**2**
C1–C2	1.374(11)	1.44(1)	C2–C1–C6	120.2(7)	110.2(7)
C2–C3	1.382(11)	1.31(1)	C1–C2–C3	119.8(8)	129.2(8)
C3–C4	1.366(11)	1.49(1)	C2–C3–C4	122.2(7)	116.6(8)
C4–C5	1.403(11)	1.42(1)	C3–C4–C5	118.8(8)	115.0(7)
C5–C6	1.406(11)	1.28(1)	C4–C5–C6	120.4(8)	125.7(8)
C6–C1	1.417(10)	1.47(1)	C5–C6–C1	118.5(8)	122.8(8)
C1–C11	1.521(10)	1.37(1)	C2–C1–C11	120.5(8)	127.8(8)
O11–C11	1.200(11)	1.262(9)	O11–C11–C1	123.6(8)	125.5(8)
O12–C11	1.343(11)	1.32(1)	O12–C11–C1	110.1(8)	111.8(8)
O12–C12	1.461(10)	1.55(1)	O11–C11–O12	126.2(8)	122.4(8)
C12–C13	1.504(15)	1.46(2)	C11–O12–C12	121.1(7)	121.8(7)
C12–C14	1.467(15)	1.62(2)	C3–C2–C21	117.8(7)	115.6(8)
C12–C15	1.544(14)	1.51(2)	O21–C21–C2	121.9(9)	120.1(8)
C2–C21	1.533(11)	1.67(1)	C21–O22–C22	123.4(8)	121.3(8)
O21–C21	1.219(11)	1.14(1)	O22–C21–C2	110.1(8)	107.1(8)
O22–C21	1.306(11)	1.35(1)	O21–C21–O22	127.8(8)	132.7(9)
O22–C22	1.461(10)	1.45(1)	C4–C3–C31		117.4(8)
C22–C23	1.57(2)	1.46(2)	O31–C31–C3		117.5(9)
C22–C24	1.47(2)	1.62(2)	O32–C31–C3		113.4(7)
C22–C25	1.580(15)	1.61(2)	O31–C31–O32		129.2(8)
C3–C31		1.48(1)	C31–O32–C32		123.9(7)
O31–C31		1.21(1)	C5–C4–C41	119.5(7)	131.7(8)
O32–C31		1.27(1)	O41–C41–C4	122.7(8)	125.5(9)
O32–C32		1.56(1)	O42–C41–C4	111.5(7)	105.9(8)
C32–C33		1.46(2)	O41–C41–O42	125.8(8)	128.4(8)
C32–C34		1.68(2)	C41–O42–C42	119.8(8)	117.6(8)
C32–C35		1.46(2)	C6–C5–C51	115.5(7)	123.9(8)
C4–C41	1.487(11)	1.49(1)	O51–C51–C5	125.8(9)	117.1(8)
O41–C41	1.200(11)	1.20(1)	O52–C51–C5	107.8(8)	114.3(7)
O42–C41	1.327(10)	1.40(1)	O51–C51–O52	126.3(9)	127.2(9)
O42–C42	1.495(11)	1.57(1)	C51–O52–C52	120.7(7)	123.3(7)
C42–C43	1.56(2)	1.53(2)	C1–C6–C61		117.4(7)
C42–C44	1.448(14)	1.71(2)	O61–C61–C6		124.1(8)
C42–C45	1.55(2)	1.47(2)	O62–C61–C6		108.5(8)
C5–C51	1.484(12)	1.58(1)	O61–C61–O62		127.1(8)
O51–C51	1.171(12)	1.22(1)	C61–O62–C62		119.1(7)
O52–C51	1.361(11)	1.23(1)			
O52–C52	1.506(10)	1.51(1)			
C52–C53	1.458(14)	1.59(2)			
C52–C54	1.557(15)	1.57(2)			
C52–C55	1.46(2)	1.47(2)			
C6–C61		1.55(1)			
O61–C61		1.17(1)			
O62–C61		1.38(1)			
O62–C62		1.47(1)			
C62–C63		1.43(2)			
C62–C64		1.65(2)			
C62–C65		1.61(2)			

zene plane, but the torsion angles and their deviation range differ substantially, depending on the number and bulkiness of the substituents introduced. The mean torsion angle (θ) and its standard deviation are 44±19° in tetra-*t*-butyl ester **1**, while the angle θ increases up to 55±16° in hexa-*t*-butyl ester **2** and to 55±6° and 55±8° in the two independent molecules of **3** in a unit cell. It is noted that, as compared with the tetraester **1**, the mean torsion angle is comparably increased by 11° in hexaesters **2** and **3**, regardless of the difference in bulkiness of the alkyl group, but the deviation is much larger in **2** than in **3**; thus, the torsion angle θ varies widely from 38 up to 76° in **2**, but only from 50 to 65° or from 46 to 61° in **3**.

The steric hindrance also causes small bond-elongations particularly in the peripheral *t*-butoxyl groups in **2** more than in **1**. All of the *t*-butyoxyl O(n2)–C(n2) and C(n2)–C(n3), C(n2)–C(n4), and C(n2)–C(n5)

Table 4. Dihedral Angles and Torsion Angles (θ)[a] of Carbonyls Against the Benzene Ring in Tetra-*t*-butyl Benzenetetracarboxylate (**1**), Hexa-*t*-butyl Benzenehexacarboxylate (**2**), and Hexamethyl Benzenehexacarboxylate (**3**)

Dihedral angle	**1**	**2**	**3**[b]	
O11–C11–C1–C2	24.7 (24.7)	142.5 (37.5)	129.9 (50.1)	61.2 (61.2)
O21–C21–C2–C3	59.3 (59.3)	−45.5 (45.5)	−57.4 (57.4)	46.0 (46.0)
O31–C31–C3–C4		−74.1 (74.1)	−53.2 (53.2)	−113.5 (66.5)
O41–C41–C4–C5	−29.7 (29.7)	126.2 (53.8)	127.5 (52.5)	−130.1 (49.9)
O51–C51–C5–C6	−60.8 (60.8)	−45.2 (45.2)	129.0 (51.0)	−119.8 (60.2)
O61–C61–C6–C1		104.5 (75.5)	115.1 (64.9)	49.4 (49.4)

a) Dihedral angles (°) are defined by C(n)–C(nl)–O(nl)–O(n2) (n=1—6), while torsion angles in the parentheses as absolute dihedral angles or, if obtuse, their supplementary angles; for numbering, see Chart 2. b) Two sets of data correspond to two independent molecules in a unit cell (Ref. 6).

bonds of **2** are elongated by 0.04 Å on the average with increased deviations: O(n2)–C(n2)=1.48±0.02 Å in **1** and 1.52±0.05 Å in **2**; C(n2)–C(nm) (averaged for m= 3—5)=1.51±0.05 Å in **1** and 1.55±0.09 Å in **2**. Interestingly, close examinations of three *t*-butyl C–C bonds found that only one of them is specifically elongated more than 0.1 Å in **2**: C(n2)–C(n3), C(n2)–C(n4), and C(n2)–C(n5)=1.49±0.05, 1.52±0.05, and 1.53±0.05 Å in **1**, while 1.49±0.06, 1.52±0.07, and 1.64±0.05 Å in **2**. Probably, the steric hindrance around the peripheral *t*-butoxyl groups in **2** is reduced not only by increasing the torsion angle θ but also by stretching the C–C bond. It may be concluded therefore that the highly congested hexa-*t*-butyl ester **2** manages the steric hindrance, arising from the six adjacent *t*-butoxycarbonyls, by further increasing and fine-tuning the torsion angle θ at the expense of π conjugation and also by elongating the peripheral C–C bonds for minimal steric repulsion.

Another intriguing aspect of these benzenepolycarboxylates is the orientation of neighboring carbonyl, or alkoxyl, groups. The direction of carbonyl oxygen is assigned either upward (*u* or +) for positive dihedral angles or downward (*d* or −) for negative ones (Table 4). In this definition, **1** is assigned as *uu·dd·* (or ++·−−·), **2** as *uddudu* (+−−+−+), and **3** as *udduuu* (+−−+++) and *uudddu* (++−−−+). In less-hindered tetraester **1**, two neighboring carbonyl oxygens point upward, while the other two on the opposite side downward, probably minimizing the dipole moment and stacking barrier. A similar tendency is also observed in **3**, where the adjacent methoxycarbonyl groups do not align in an apparently less-hindered alternative orientation *ududud* (+−+−+−) but line up in the same direction up to three or four continuing groups like *udduuu* (+−−+++) and *uudddu* (++−−−+). This may indicate that two or more neighboring alkoxycarbonyls oriented in the same direction are the preferred conformation even in the presence of small to moderate steric repulsion between bulky substituents on a benzene ring, although the intramolecular interaction in the crystal lattice would affect the conformation to some degree. In this context, the orientation of butoxycarbonyls in **2** is somewhat unexpected, since the direction is inverted frequently around the ring: *uddudu* (+−−+−+). This orientation, altered greatly from that in less-hindered **3**, may originate from the necessity for minimizing the steric repulsion between neighboring *t*-butoxyl groups, and therefore the final conformation fo hexasters must be deformed significantly by the bulkines of the alkoxyl groups introduced, inevitably affecting the electronic properties.

Implication in Dual Fluorescence Behavior. In our previous paper,[1] some bulky hexaalkyl benzenehexacarboxylates display unusual dual fluorescence behavior in solution, but less-congested tetraester **1** and hexamethyl ester **3** show only the usual single fluorescence peak. Of these dual-fluorescing hexaesters, hexa-*t*-butyl ester **2** gives typical well-separated dual fluorescence peaks at 325 and 380 nm of similar intensities in a pentane solution at room temperature. On the basis of the wavelengths of the fluorescence peaks, the two emitting species involved have been assigned as Franck–Condon-like (FC′) and fully relaxed (RX) singlet states.[1] A temperature-dependence study of the relative peak intensities (FC′/RX) further showed that the relaxation from FC′ to RX state requires some activation energy (0—2.5 kcal mol^{-1}) that depends on the bulkiness of the alkoxyl groups.[1]

In spite of possible differences in the environment where the molecules are situated in the solution-phase spectroscopy and in the solid-state X-ray crystallography, these results in the solid state appear to be compatible with the above-mentioned mechanism involving two emitting species of different conformations. The evident differences found in the solid state between highly congested **2** and less-congested **1** or **3** would be deteriorated but still maintained essentially in the solution phase. Thus, the greater torsion angles (θ), elongated peripheral bond lengths, and staggered carbonyl orientations observed for **2** in the solid state well explain at least qualitatively the dual fluorescence behavior of highly congested benzenehexacarboxylates like **2**, since the dual fluorescence involves the decelerated conformational relaxation due to the steric hindrance caused by the peripheral bulkiness.

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