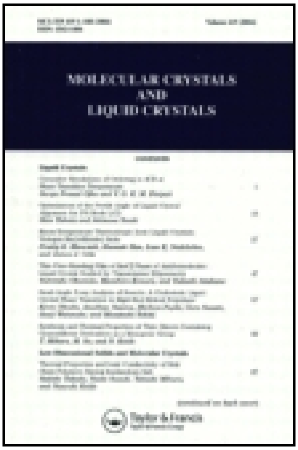

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Interpreting Substituent Effects on the Crystal Packing of Long-Chain Diacyl Peroxides. The Crystal Structures of D1 (11 Bromoundecanoyl) Peroxide and Di (Undecanoyl) Peroxide

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INTERPRETING SUBSTITUENT EFFECTS ON THE CRYSTAL PACKING OF LONG-CHAIN DIACYL PEROXIDES. THE CRYSTAL STRUCTURES OF DI(11-BROMOUNDECANOYL) PEROXIDE AND DI(UNDECANOYL) PEROXIDE

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ABSTRACT Although crystals of di(11-bromoundecanoyl) peroxide and di(undecanoyl) peroxide have different space groups ($P4_32_12$ and $C222_1$), the molecules pack in almost identical layers. They differ only in the nature of stacking across interfaces involving the terminal groups. Because the 90° twist about the O-O bond locks neighboring molecules together within the layer, each peroxide shows a single solid phase from 5K to the melting point. Analysis of the stacking pattern in terms of the six possible orientational relationships suggests special stability for an L-shaped motif of C-Br···Br-C. Other substituents create different stackings of the same layer structure to give three crystal classes and five space groups among 14 compounds. Unsymmetrical peroxides are useful both for forcing a variety of substituted chains (particularly odd-even homologues) to pack with identical layer structures, and for controlling the stacking pattern. Because structural differences are localized in the vicinity of the substituents, this series of "substitutional polytypes" will allow systematic investigation of substituent effects on the physical and chemical properties of solids.

Over the past half century substituent effects have contributed a great deal to understanding properties of individual molecules, such as reactivity, thermodynamic stability, conformation, and spectroscopy.[1] They have also allowed systematic adjustment of such properties to suit practical needs. The ability to predict substituent effects on collective chemical and physical properties of molecular solids might have even greater utility. Since understanding these effects would provide insight on intermolecular interactions, it would also be valuable in solution, gas-phase, and surface studies and in such related fields as natural and artificial host-guest chemistry. Efforts toward crystal engineering, that is toward systematic design of crystal properties, have achieved some qualitative successes and have demonstrated the role of such secondary bonding interactions as C-H···O hydrogen bonding and chlorine-chlorine contact.[2] On the whole, however, substituent effects have not been nearly as useful for understanding and controlling molecular solids as they have been for fluids.

The reason for this lack of success is clear. Even in fluids, when a substituent influences a particular property by more than one or two mechanisms, a linear-free-energy treatment of the Hammett type quickly degenerates into numerological parameter fitting, which, whatever its empirical utility, cannot yield fundamental understanding. The problem is more acute in solids. The regularity and rigidity of crystalline solids mean that intermolecular influences are less averaged than in fluids, and are often stronger. Thus a molecular substituent may exert strong influence not only directly within a substituted molecule, but also indirectly by influencing the mutual arrangement of neighboring molecules. A modest change in molecular substitution usually causes a profound change in crystal packing. The resulting changes in crystal properties are ultimately due to the substituent, but it is generally hopeless to try interpreting the effect by untangling the long chains of causality. Because a molecule has many contacts with its neighbors, all of which can change with a single substitution, substituent effects are multiple as well as indirect.

Beginning to understand substituent effects on molecular crystals should be much easier when structural change is localized within the vicinity of the substituent, because the investigator can focus attention on a limited number of mechanisms for substituent influence.

The long-chain diacyl peroxides, whose reactions we have been studying for some time,[3] are well suited for analyzing the influence of substituents on the terminal carbon. In this paper we report, analyze, and compare the crystal structures of di(undecanoyl) peroxide (UP) and of its brominated analogue di(11–bromoundecanoyl) peroxide (BrUP). Particular attention is paid to six alternative possibilities for interlamellar packing. The bias in favor of one of these motifs in BrUP is interpreted as evidence for some secondary bonding interaction between C-Br groups. This bias is then used to engineer the packing of unsymmetrical peroxides that also contain other groups, so that their substituent effects can be interpreted.

In the following discussion various acyl chains are denoted by their number of carbon atoms and terminal substituent. Thus $C_{11}Br$ stands for 11–bromoundecanoyl, and C_{11} for undecanoyl.

EXPERIMENTAL

Materials. Unsubstituted alkanoic acids, 11-bromoundecanoic acid, and 12–bromododecanoic acid were used as obtained from Aldrich Chemical Co. (typically 99+% purity). 11-Chloro-, 11-iodo, and 11-cyanoundecanoic acids were prepared from the 11-bromo acid by treating with LiCl/DMF, NaI/acetone, and KCN/Methanol/H_2O, respectively. 11-Hydroxyundecanoic acid was prepared by treating the 11-bromo acid with NaOH/H_2O and converted to the methyl ester with methanol/H_2SO_4. The distilled ester was treated with diethylaminosulfur trifluoride, and the distilled fluoroester was hydrolyzed with NaOH/H_2O/EtOH to give 11-fluoroundecanoic acid. Acyl chorides were prepared by treating the acids with $SOCl_2$ at room temperature and were purified by distillation under vacuum.

Symmetrical peroxides were prepared by dropwise addition of 3 eq. pyridine in diethyl ether to a mixture of 1 eq. acyl chloride and 2 eq. 30% H_2O_2 in diethyl ether at 0°, stirring at room temperature for 1 hr. After aqueous workup, peroxides were recrystallized from 2:1 pentane:diethyl ether, containing CH_2Cl_2 if necessary for dissolution.

11-Bromoperoxyundecanoic acid was prepared in an open beaker at 23° by dropwise addition of 2 eq. of 90% H_2O_2 to a slurry of 1 eq. 11–bromoundecanoic acid with 3 eq. of methanesulfonic acid and enough diethyl ether to allow stirring. After aqueous workup it was recrystallized from 2:1 pentane:diethyl ether.

Unsymmetrical peroxides were prepared by adding a solution of 1 eq. of 11-bromoperoxyundecanoic acid in diethyl ether to a solution of 1 eq. of an acyl chloride in the same solvent at 0°, adding dropwise 3 eq. of pyridine in diethyl ether, and stirring for 1 hr. at room temperature. After aqueous workup the peroxide was recrystallized from pentane/diethyl ether.

Single crystals of the various peroxides for x-ray diffraction were grown from a number of solvents (including acetone, CCl_4, CH_3OH, hexanes/ethyl acetate, $CH_3OH/CHCl_3$, and CH_3OH/CH_2Cl_2) by evaporation at room temperature or by slow cooling to 6°C. The peroxides which were prepared and their melting points are included in Table I.

TABLE I. Crystal Properties of Diacyl Peroxides, A-O-O-B.

A*	B*	Sp.Gp. (or.)◊	Δa#	Δb#	c#	γ°	m.p.(°C)
C_{11}	C_{11}	$C222_1$ (**-ab**)	37	-	40.0	92.6	33
C_{13}	C_{13}	"	13	-	46.5	93.5	49-50
$C_{11}F$	$C_{11}F$	"	24	-	40.2	93.4	32
$C_{11}Cl$	$C_{11}Cl$	$P4_32_12$ (**a**)	-36	-	84.3	90	65
$C_{11}Br$	$C_{11}Br$	"	-17	-	85.5	90	71-73
$C_{11}I$	$C_{11}I$	"	50	-	87.4	90	74
$C_{11}CN$	$C_{11}CN$	"	-14	-	84.3	90	65
$C_{11}Br$	$C_{11}Cl$	"	-23	-	85.0	90	65-68
$C_{11}Br$	C_{10}	$P2_12_12_1$ (**a**)	-10	-2	79.4	90	47-49
$C_{11}Br$	C_{12}	"	7	10	85.5	90	53-55
$C_{11}Br$	C_{14}	"	2	3	92.2	90	59-61
$C_{11}Br$	C_{11}	$P4_12_12$ (**-ab**)	-23	-	167.9	90	46-48
$C_{11}Br$	C_{13}	"	-15	-	180.5	90	50-53
$C_{11}Br$	$C_{12}Br$	$P2_1$ (**b**)	-32	4	45.1	90	38-42

* The acyl groups are coded by the number of carbons in the straight chain (including the carbonyl carbon) and the terminal substituent other than hydrogen.

◊ Together with the space group symbol is given the orientation at the Group B interface, which determines the space group. See text and Figures 4 and 5.

\# To emphasize similarities, unit cell parameters refer to the primitive cell, and **c*** is taken normal to the layer plane. The **c** length is given in Å; the **a** length is given as Δ**a** = (**a** - 5.450 Å) x 1000; **b** is given in the same way, when it differs from **a**.

X-ray Diffraction of (11-Bromoundecanoyl) Peroxide, ($C_{22}H_{40}O_4Br_2$, for. wt. 528.36) was carried out using a Rigaku AFC5S diffractometer and analyzed with the TEXSAN software package (version 2.1). The crystal, a doubly truncated rectangular bipyramid 0.18 x 0.22 x 0.18 mm, was mounted with epoxy glue on a quartz fiber and measured at room temperature. The tetragonal system was suggested by the observation that the pyramid axis is an optical axis. To minimize x-ray damage the lattice parameters and space group were determined previously on other crystals: a,b = 5.441(1), c = 85.51(4) Å, sp. gp. $P4_12_12$ (#92) or $P4_32_12$ (#96), Z = 4, ρ_{calc} = 1.39. Although absorption of monochromated CuK_α radiation was high (μ = 46.9 cm^{-1}), the long wavelength was helpful for resolving adjacent reflections differing only in their *l* index. During a total exposure of 1.8 hrs 666 independent reflections ($\sin(\theta)/\lambda < 0.439$) were collected using ω-scan (widths of standards 0.9-1.1° before data collection, 1.0-1.25° after). Intensities were corrected empirically for absorption (by using ψ-scans of three reflections) and for 30% decay of standards. The final set of unique data consisted of 575 3σ reflections.

Successive application of the MITHRIL and DIRDIF routines revealed the non-hydrogen atoms. Positions and anisotropic thermal parameters for the non-hydrogen atoms were refined by full matrix least squares with hydro-

TABLE II. Atomic Parameters of BrUP.*

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O1	216	2071	206	55	92	97	3	18	-34
O2	3120	3458	1829	66	154	106	41	-19	-58
C1	1164	3577	1354	70	67	52	-5	22	-9
C2	-898	5360	1748	64	63	58	-2	-1	-6
C3	-403	6870	3184	65	57	59	11	7	-3
C4	-2574	8467	3635	56	66	65	1	1	-6
C5	-2127	10067	5069	78	67	55	1	4	-13
C6	-4369	11507	5558	65	45	58	3	-4	-9
C7	-3952	13173	6968	58	49	59	-6	-9	-13
C8	-6254	14577	7431	87	51	53	10	7	-16
C9	-5837	16205	8833	66	66	63	19	- 4	-9
C10	-8126	17591	9293	76	52	58	-8	-3	-10
C11	-7760	19124	10700	63	60	74	5	5	-35
Br	-10678	21042	11281.8	69	84	77	10	3	-23

* Fractional coordinates x 10^4 for x and y , x 10^5 for z; thermal parameters x 10^3. Estimated std. dev. of x and y are 0.002, except 0.003 for C1, 0.001 for O1, and 0.0003 for Br. Estimated std. dev. of z are 0.0001, except 0.00001 for Br. Estimated std. dev. of U values are 0.01, except 0.001 for Br.

gens held at calculated positions (127 variables). Conventional residuals were R = 0.044, R_w = 0.047 for space group $P4_32_12$ and R = 0.046, R_w = 0.050 for the enantiomeric $P4_12_12$. When the 220 reflection was omitted, the former space group gave R = 0.039, R_w = 0.041 and the largest peak in the final difference map was 0.31 e/Å^3. Positions and thermal parameters are presented in Table II.

Inspection of calculated structure factors showed that the $21l$ reflections are particularly sensitive to the difference between enantiomers for l = 3 and 4 and for l = 21 and 25. In $P4_12_12$ their respective F_{calc} values are 6.73, 7.21, 4.42, 7.58; in $P4_32_12$ they are 6.44, 7.37, 4.66, 7.27; the F_{obs} were 6.34, 7.56, 4.79, 7.22, leaving no doubt that $P4_32_12$ is correct. Because of the long **c** axis, the two reflections within each pair are very close in reciprocal space, so their relative intensities are insensitive to absorption. Careful measurement of these and other sensitive reflections using fragments cut from larger crystals showed that crystals which rotate the plane of polarized light clockwise as it travels toward the viewer along the **c** axis are $P4_32_12$, while levorotatory crystals are $P4_12_12$. Mr. W. B. Hetzel used a Perkin-Elmer 241 Polarimeter to show that the strength of rotation of five single crystals grown from hexane/ethyl acetate/methylene chloride, including both enantiomers, had the same absolute value indicating that each crystal consists of a single enantiomeric domain. The rotation was 3.6(2) °/mm at 589 nm and 9.7(1) °/mm at 365 nm.

X-ray Diffraction of Di(undecanoyl) Peroxide, ($C_{22}H_{42}O_4$, for. wt. 370.58) was carried out using an Enraf-Nonius CAD-4 diffractometer with monochromated MoK_α radiation and analyzed using Enraf-Nonius SDP software (Jan. 1977 and June 1979). The crystal, 0.45 x 0.5 x 0.2 mm, was mounted in a sealed quartz capillary and data were collected at about -40°C. The crystals were orthorhombic, sp. gp. $C222_1$ (#20). Lattice parameters from 20 high-angle reflections were a = 7.421(4), b = 8.036(5), c = 39.99 (2)Å, Z = 4, ρ_{calc} = 1.032. During collection of 770 independent reflections ($\sin(\theta)/\lambda < 0.57$) there was no appreciable decay of intensity standards. Intensities were corrected for Lorentz and polarization effects, but not for absorption (μ = 0.741 cm^{-1}). The structure was solved and refined on the basis of 514 3σ reflections. The final cycle of refining positions and anisotropic thermal parameters of the non-hydrogen atoms with hydrogens in calculated positions gave R = 0.041, R_{wt} = 0.040. The largest peak in the final difference map was 0.136 e/Å^3. Positions and thermal parameters are presented in Table III.

TABLE III. Atomic Parameters of UP.*

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O1	-2128	-9112	49606	50	47	75	13	11	23
O2	94	-9754	46013	94	67	76	31	39	16
C1	-865	-8762	47199	32	54	36	-7	-4	0
C2	-1036	-6929	46376	46	42	41	1	-5	10
C3	60	-6404	43340	47	38	44	-7	-1	9
C4	-301	-4602	42382	41	53	46	-1	0	0
C5	762	-3993	39350	51	45	50	1	4	7
C6	313	-2222	38359	49	55	45	-2	5	-1
C7	1352	-1572	35361	52	50	47	1	-2	4
C8	895	219	34404	56	59	41	-9	3	-2
C9	1886	880	31405	63	48	57	-4	-3	6
C10	1418	2645	30482	77	80	58	-6	7	16
C11	2395	3354	27447	119	95	78	-20	-3	27

* Fractional coordinates x 10^4 for x and y , x 10^5 for z; thermal parameters x 10^3. Estimated std. dev. of x and y are 0.0005 to 0.0009, except 0.004 for O1 and O2. Estimated std. dev. of z are 0.00008 to 0.00013. Estimated std. dev. of U values are 0.002 to 0.004, except 0.005 for C11.

Lattice Parameters and Space Groups of Other Peroxides were established by preliminary diffractometry supplemented by precession photography when crystal quality was not optimal. The space groups and lattice parameters are reported in Table I. In order to emphasize the similarity of packing in the **ab** plane among all of these compounds, the primitive cell is given for the crystals with centered space groups, and the **a** and **b** lengths are given as the deviation (in Å x 10^{-3}) from 5.450 Å. Among these 14 crystals in five different space groups, the largest deviations from 5.45 Å and 90° are 0.05 Å and 3.5°. In two of the unsymmetrical peroxides end-for-end molecular disorder would be sterically feasible. These are the cases where only one terminal bromine of BrUP is replaced by Cl or CH_3. The former case seems to be sufficiently disordered to give approximately the intensity distribution expected for $P4_12_12$, although we have not yet studied carefully the possibility of residual ordering. The CH_3 case seems perfectly ordered in space group $P2_12_12_1$, a subgroup of $P4_12_12$, but a polarizing microscope showed that many of the thin plates had several domains related by 90° rotation about **c**, which would result from a defect, parallel to the **c** axis, across which molecules within every layer are related by end-for-end rotation. The existence of large domains shows that this rotation is far from random and occurs only in a highly cooperative way.

DISCUSSION

Molecular Structure of BrUP and UP

The molecular conformations of BrUP and UP are unexceptional. Like most crystalline diacyl peroxides they have torsional angles near 90° about the central O-O bond (C-O-O-C in $P4_32_12$ BrUP is left-handed, $\tau = -87.3°$, the corresponding angle in UP is -86.3°). Each molecule is bisected by a crystallographic rotation dyad through the peroxide bond, giving the two half-chains identical conformations and local packings. As in most long-chain compounds, each chain is a planar zig-zag with torsional angles near 180°. With two exceptions all torsional angles among chain atoms are within 4° of 180° (within 2° from C5 through C11). The exceptions are τ(O1-C1-C2-C3) and τ(C1-C2-C3-C4), which are 169° and -175°, respectively, in BrUP; and 170° and -174°, respectively, in UP. These torsions bend the long chain slightly toward the obtuse space of the peroxide link. The

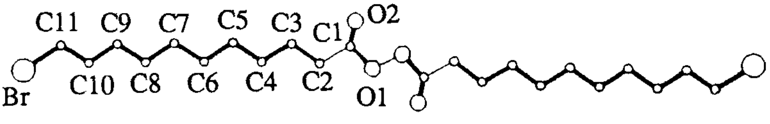

FIGURE 1. BrUP. In the $P4_32_12$ enantiomer the chains are folded away from the viewer about O1-O1', and toward the viewer about C1-C2 and C1'-C2'.

rms difference between corresponding torsional angles along the chains of BrUP and UP is only 1.1°, about the same as their experimental uncertainty. Terminal bromine substitution does not affect the molecular structure.

Intralamellar Structure of BrUP and UP

As in most long-chain compounds, the molecules pack tightly side-by-side to form two-dimensional layers which then stack to complete the crystal. The theme of this paper and of ongoing work in this laboratory is that, by changing substituents, one can alter contacts between layers without significantly affecting the arrangement of atoms within them. Because constancy of intralamellar structure is so important for interpreting substituent effects, we analyze this packing in some detail.

The dominant feature of packing within the lamellae is arrangement of the long, planar zig-zag segments in a pattern very similar to the triclinic motif found in many hydrocarbons. Figure 2 compares the chain packing of BrUP and UP with that of octadecane, OD, a typical triclinic hydrocarbon .[4] In the right frames, the portions of four neighboring peroxide chains from C4 through C10, with hydrogens, are projected along the C10-C4 vector, and half of four OD chains are projected along the C1-C9 vector. The similarity in arrangement of chain axes is obvious. The largest difference in interaxis spacing is 0.17 Å (between O-B distances of BrUP and OD), and the largest difference between BrUP and UP is only 0.07 Å.

There are larger differences in the relative displacement of neighboring chains in the direction of their long axes. The left frames of Figure 2 are rotated by 90° about the vertical axis from the right frames. They show half of each molecule. The strongest intermolecular interaction is between face-to-face neighbors (O and B), which overlap in this projection and mesh their methylene groups by virtue of longitudinal offset by an odd number of carbons. In OD the offset is one methylene unit; in the peroxides it is three. The deviations from integral offset are 0.19, 0.17, and -0.09 Å, respectively, for BrUP, UP, and OD. Again the difference between the peroxides is very small.

The offset by three carbon atoms is necessary to accommodate the peroxide torsional angle. Figure 3 shows a pair of BrUP molecules related by 5.441 Å translation along the **a** axis. At one end adjacent molecules make face-to-face contact between the zig-zag planes, while at the other they make edge-to-edge contact. Wrapping the near molecule of Figure 3 about the far

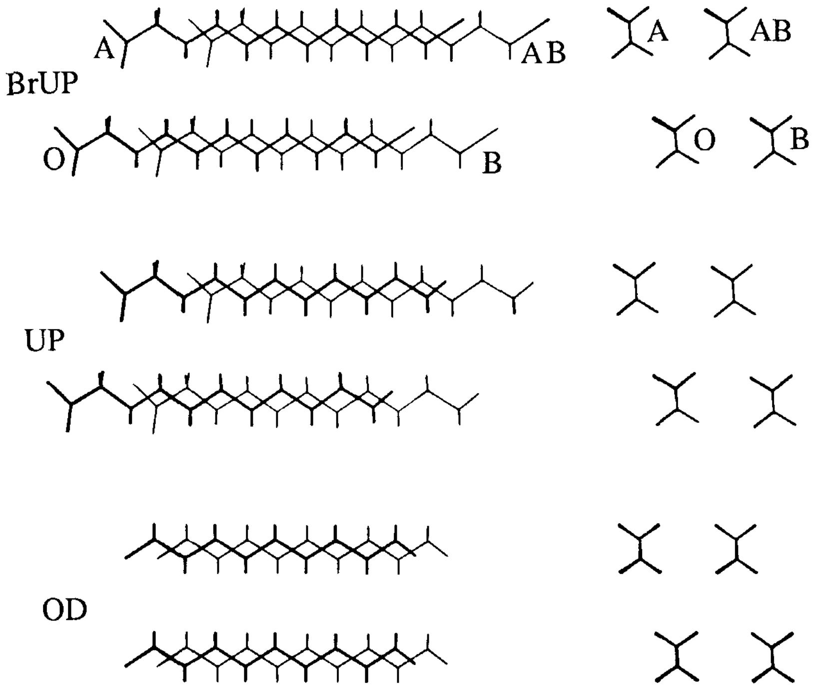

FIGURE 2. Packing of half chains of BrUP (top), UP (middle), and octadecane (OD, bottom). For each compound an origin chain (O) and three of the six nearest neighbors are shown both from the side (left) and from the end (right). Chain labelling is shown for BrUP. In the left frame molecules nearer the viewer are darkened and the center of each molecule is at the far left.

one requires offsetting the face-to-face chains by three carbons, as discussed above. The resulting offset in the edge-to-edge chains (O and A in the left frame of Figure 2) is by two carbons. For OD the edge-to-edge offset is by zero carbons. These even-carbon offsets allow the touching hydrogens to interleave. Deviations from integral offset are 0.33, 0.18, and -0.04 Å, respectively.

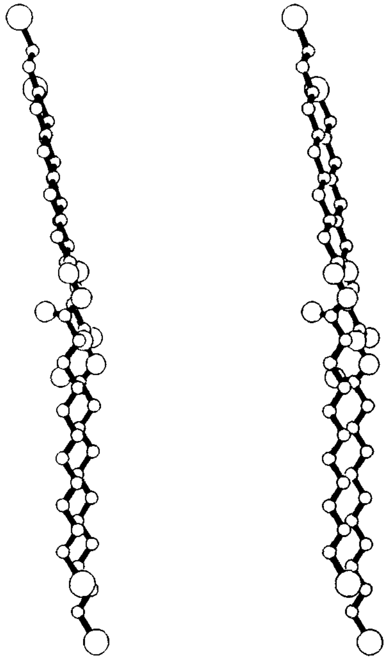

FIGURE 3. *Stereo pair view of adjacent molecules within layer of BrUP.*

Chains O and AB are displaced lengthwise by the sum of the displacements O-A and O-B. That is, the peroxides differ from five-carbon offset by 0.52 and 0.35 Å, and OD differs from one-carbon offset by -0.13 Å. The half chain labelled O in Figure 2 is surrounded by six parallel chains, of which three are shown. Since all these chains are related by the **a** and **b** translations, the three that are not show are related to O in the same way that O is related to the three that are shown. Thus the forces on O, for example those which result from nonintegral longitudinal offset, cancel between opposite neighbors, although torques survive. Torques are transmitted through the chain and cancelled by compensating torques in the other half of the molecule.

What is most important for our present purposes is that structure within the lamellae is virtually unchanged when the terminal hydrogen of UP is replaced by bromine. Not only is the packing motif the same in BrUP as in UP, but structural details in the first coordination shell differ by less than

0.2 Å. Since most contacts between the long, thin molecules are made within the layer and far from the chain ends, it is natural that the lamellar structure should be insensitive to terminal substitution.

Unlike many crystals of long-chain molecules, these structures are stable over a wide temperature range, facilitating study of the same crystal by many different techniques. Single-crystal diffraction at 130K and above, electron spin resonance spectroscopy and x-ray powder diffraction to 5K,[5] and differential scanning calorimetry above 240K show the absence of phase transitions up to the melting point for both UP and BrUP. The other peroxides of Table I showed similar phase stability.[6] Phase transitions in long alkanes involve slippage of chains past one another.[7] We suggest that the 90° twist about the O-O bond, which keeps neighboring chains aligned, is crucial to phase stability.

Interlamellar Packing of BrUP

Despite their similarity in lamellar structure, BrUP and UP belong to completely different space groups ($P4_32_12$ and $C222_1$, respectively). This is hardly surprising, since interlamellar contact is made between different terminal groups. For understanding the difference it is helpful to enumerate the possible modes of lamellar stacking. There is no general requirement for symmetry between facing surfaces in lamellar crystals, but the present discussion focusses on the common case where symmetry does exist, and where all terminal groups within one surface are related by translation.

A symmetry transformation consists of orientational and translational components. For example, a symmetry element between two surfaces must obviously reverse the orientation of atoms along the surface normal, which is the **c** axis in BrUP. The translational component of the z transformation is given by the value along the **c** axis about which z is inverted. This position has a particular fractional value (0.125, 0.25, etc.) according to the space group, but more fundamentally its cartesian value is determined by the optimal distance between facing surfaces. As terminal groups are changed the cartesian position for z inversion floats up and down along **c**.

In considering symmetry transformation of the x and y coordinates, it is convenient to treat orientation and translation separately. First we will discuss the mutual orientation of facing surfaces, then how they mesh by sliding across one another. The cross section of a BrUP molecule at z = 0.125 (the height of the symmetry element between lamellae) will serve to illustrate the discussion. It consists of a large circle for bromine and smaller ones for C11 and one of its hydrogens. The radius of each circle is determined both by the van der Waals radius of the atom (Br, 1.90; C, 1.75; H 1.17 Å) and by the distance of the atom from the section.

The six possible orientational relationships between patterns in facing layers are shown in Figure 4. The number is limited by the requirements that each pattern have the same orientation in the two-dimensional lattice of its own layer and that the facing two dimensional lattices be coherent. The parallelogram in the center of Figure 4, whose sides are the lattice translations, must be unchanged by the xy reorientation. The simplest relationship, with unchanged signs of x and y, could represent either a mirror or a glide, depending on translation. Since glides are more common than mirrors, we label this orientation **g**. The parent pattern is not shown explicitly in Figure 4, but it has the same orientation as **g**.

A second possibility is to change the signs of both x and y. Since z must also be reversed, this orientation creates an inversion center between the surfaces and is labelled **i**.

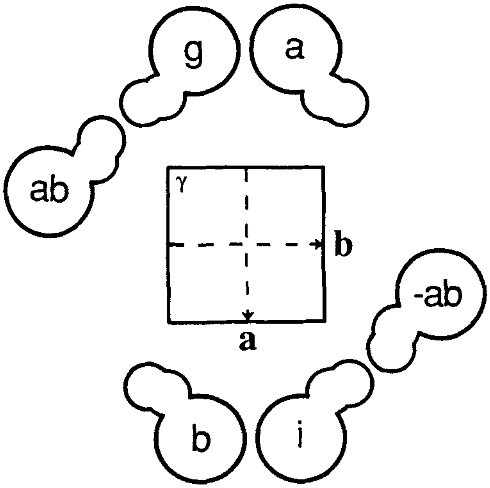

FIGURE 4. Possible orientations of a terminal group cross section in one surface when those in the facing surface have the same orientation as **g**. The pattern in the center shows the two-dimensional surface cell and its **a** and **b** directions. In BrUP the intramolecular dyad through O-O bisects the angle γ.

The other four possible orientations involve two-fold rotation (or screw) axes. These elements impose conditions on the two-dimensional surface lattice, if facing layers are to be coherent. For example, rotation about the **a** axis (inverting the sign of y) superimposes the angle γ of one surface on 180°-γ of the opposite surface and requires that each be 90° to maintain registry. This orientation is labelled **a**, and the analogous rotation about **b** (inverting the sign of x) is labelled **b**.

Finally it is possible to create meshing lattices by rotation about one of the diagonal axes. This superimposes **a** of one surface on **b** of the other and thus requires that **a** = **b**. These orientations are labelled **ab** and **-ab**. In both BrUP and UP the dyad through the peroxide bond in the center of each layer is in the diagonal direction, so both have **a** = **b** without regard to the surface interaction.

One can test each of these six orientational possibilities for steric allowedness by sliding it over the corresponding pattern of four adjacent molecules in the facing layer to a position of minimum overlap. If the surfaces are to remain equivalent, there are constraints on the sliding. For a mirror there is no xy freedom; for a glide there is only the choice of one of three directions for the glide by half a lattice spacing (**a**, **b**, or **ab**). For a rotation or screw axis there is lateral freedom in locating the axis, and thus there is translational freedom normal to the axis. Only **i** has freedom to slide along both the **a** and **b** directions. Figure 5 shows the translation of minimum overlap for each orientation. Translation generates two other local minima for **g**, one for **i**, and one for **-ab**, but these alternatives have greater steric overlap than those shown in Figure 5. The figure shows that orientations **g**, **ab**, and **-ab** are sterically excluded, that **i** would give a very tight fit, and that both **a** and **b** would fit well.

The orientation actually observed in BrUP is **a**; between lamellae there is a two-fold screw axis parallel to **a**. This axis requires right angles in the surface lattice. The rotation dyad through the peroxide bond in the center of the layer bisects the **ab** angle and gives the lattice equal sides. Together the two axes 45° apart create a tetragonal lattice. They also effect a 90° rotation from layer to layer, which results in the four-fold screw axis of $P4_32_12$.

The bias in favor of the **a** orientation over **b** and **i** is strong. Occurrence of a few **b** (or **i**) interfaces within the x-ray coherence length would result in a disordered superposition of roughly equally populated domains of molecules rotated by 180° (or of enantiomeric molecules). The same interlamel-

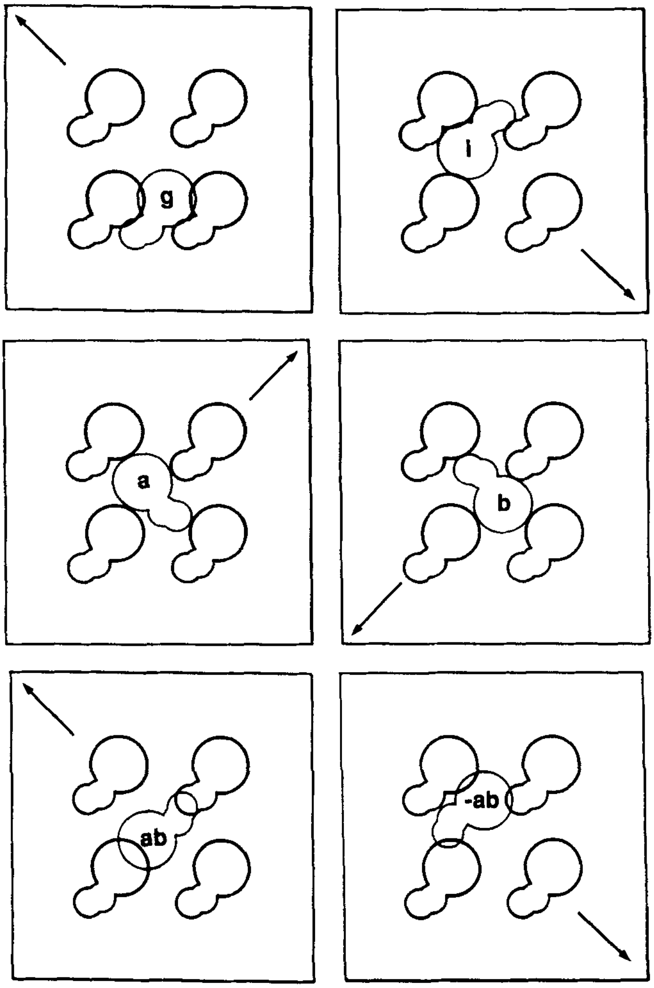

FIGURE 5. Minimum overlap translation for each relative orientation of facing BrUP surfaces. Arrows show the direction of the intramolecular dyad through O-O in the layer with one molecule.

lar packing motif is favored by 11-bromoundecanoic acid,[8] 1,12-dibromododecane,[9] and 1,10-dibromodecane.[10]

The strong preference for **a** does not result from simple van der Waals forces, because **a** and **b** have the same number and type of contacts (two Br-Br, two H-Br), and nearly identical distances; and the contacts in **i** are almost the same (two Br-Br, one H-Br, and one C-Br). The preference must be due to the different relative orientations of the terminal groups.

Figure 6 shows the pattern of terminal group contacts for **a**, **b**, and **i**. Each has a chain of touching bromines, but **a** is closest to an ideal L-shaped motif for C-Br···Br-C, where one C-Br···Br angle is near 90° and the other is near 180°. Ramasubbu, Parthasarathy, and Murray-Rust have identified

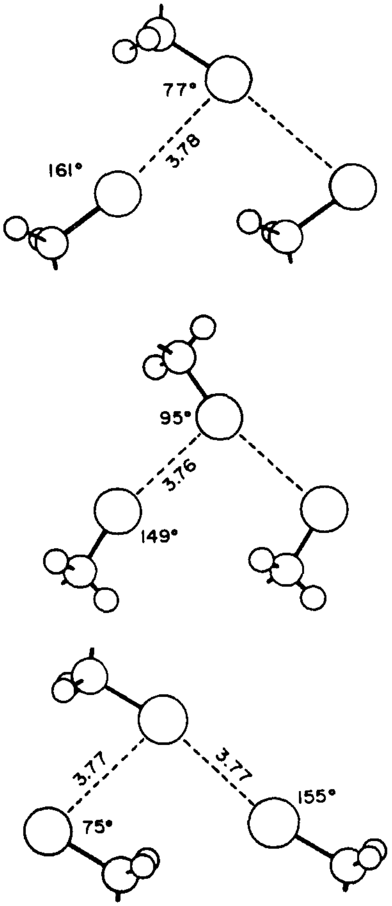

FIGURE 6. Interlamellar contacts between CH_2Br groups for three packings of BrUP. Top, observed packing, **a** orientation; middle, hypothetical packing, **b** orientation; bottom, hypothetical packing, **i** orientation, with layers separated by an additional 0.513 Å to give reasonable Br···Br distance.

this motif in a number of crystals containing chlorine, bromine, or iodine, and suggested that it may be due to secondary bonding between an unshared electron pair on one bromine and the σ* orbital of the other C-Br group.[11] Note that along the infinite screw-related chain these coordinate bonds reinforce one another, each bromine serving as both donor and acceptor

In the hypothetical **b** packing for BrUP, the C-Br···Br angle at the bromine acting as donor is 95°, close to the ideal 90° for lone pair participation, but the angle at the bromine acting as acceptor is 149°, far from the ideal 180°. Overlap should be approximately proportional to the magnitude of the cosine of this angle, which is 9% smaller than that of the 161° angle in motif **a**.[12]

In the **i** packing there is no possibility for donor-acceptor complimentarity, since the two C-Br···Br angles related by a center of inversion must be equal. In the hypothetical **i** packing of BrUP, one interaction would have two 74° angles (lone-pair to lone-pair) while the other would have two 164° angles (σ* to σ*).

Melting point data tend to support the idea of a significant difference in packing energy between the **a** and **i** motifs. Both α,ω-dibromoalkanes and ω-bromoalkanoyl peroxides show strong melting point alternation between odd and even carbon chains. BrUP, with the favorable **a** packing, is unusually high melting, while 1,15-dibromopentadecane, with the unfavorable **i** packing, is unusually low melting.[13] BrUP melts at 72°C, 40° higher than the average of its neighboring homologues with two $C_{10}Br$ or $C_{12}Br$ chains (23° and 42°, respectively). 1,15-Dibromopentadecane melts at 27°C, 25° lower than the average of the C_{14} and C_{16} homologues (48° and 56.5°).[14] We will discuss the influence of packing on melting points more fully in a subsequent paper.

Interlamellar Packing in Undecanoyl Peroxide

Because the lamellar surface of UP has hydrogen in place of bromine, it differs from that of BrUP both sterically and electronically. The interlamellar contacts are more difficult to analyze graphically, because they do not all occur at the same height along the **c** axis. The slight interpenetration of the UP surfaces results from orientation of the final C-C bond almost perpendicular to the interface plane. This gives a surface of widely spaced methyl groups as shown in Figure 7. In BrUP the final C-Br bond is almost parallel to the interface, giving a tighter, flatter surface of CH_2Br groups.[15]

For our present purposes we will simply note that the favored orientational relationship between facing layers in UP is **-ab** of Figure 4. This diagonal axis, like the **ab** rotation through the center of the molecules, requires only that the nearest neighbor translations be equal, not that they be orthogonal. By crystallographic convention a primitive cell with equal sides and an obtuse angle is doubled to give a centered cell with unequal sides and right angles. Thus UP, with nearly the same intralayer structure as BrUP, has space group $C222_1$. Since the intra- and interlamellar rotations of UP are 90° from one another (instead of 45°), adjacent lamellae turn 180°; that is they are related by a two-fold (instead of a four-fold) screw axis normal to the layer. This difference between UP and BrUP is illustrated at the top of Figure 8. The unconstrained angle in the primitive cell of UP is 92.5°, close enough to 90° that the lattice may distort to higher symmetry in BrUP in order to give the preferred interlamellar orientation for bromine.

Interlamellar Packing in Other Symmetrical Peroxides

The analogues of BrUP with chloro, iodo, or cyano end groups also pack in $P4_32_12$ (or $P4_12_12$) and have very similar lattice parameters, as shown in Table I. We have not yet collected intensity data on these crystals, but we expect them to show the same packing motif as BrUP. The cyano case suggests that cyano can be regarded as a pseudohalogen for inter- as well as intramolecular purposes. Using typical bond distances and van der Waals radii, one predicts an overall distance for linear $C\text{-}C{\equiv}N\cdots C$(nitrile) nearly the same as for $C\text{-}Br\cdots Br$ (5.7 vs. 5.8 Å), although the the nitrile carbon at the bend of the L is an electron pair acceptor rather than a donor and the nitrogen in the long arm of the L is a donor rather than an acceptor.

Unlike the other halogens, the fluoro analogue of BrUP packs in space group $C222_1$, as does the hydrogen analogue, UP. Again we lack intensity data, but the steric similarity of fluorine and hydrogen is probably important. It is not surprising that the tightly bound lone pairs of fluorine are unable to coordinate with σ^* as strongly as those of the other halogens do.

Tridecanoyl peroxide with C_{13} chains packs in $C222_1$, as does UP with C_{11} chains. Double homologation in a zig-zag chain leaves the surface structure unchanged, so the same packing would be expected for peroxides from other odd-carbon acids.

Because they have the same intralamellar structure, these symmetrical peroxides allow systematic investigation of how substituents influence many

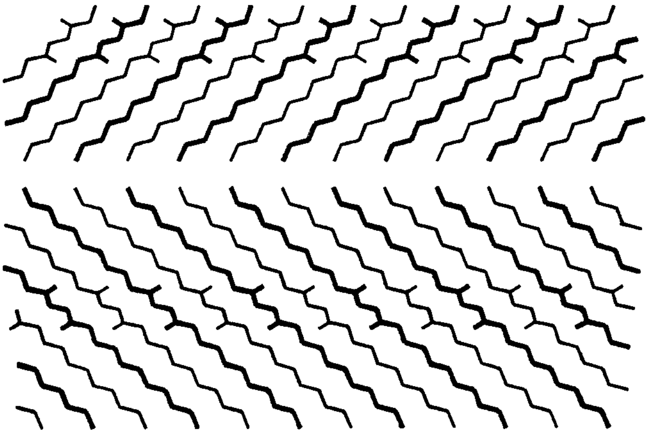

FIGURE 7. Lamellar stacking in UP viewed along the crystallographic a axis. Note that the terminal C-C bond is nearly perpendicular to the interface.

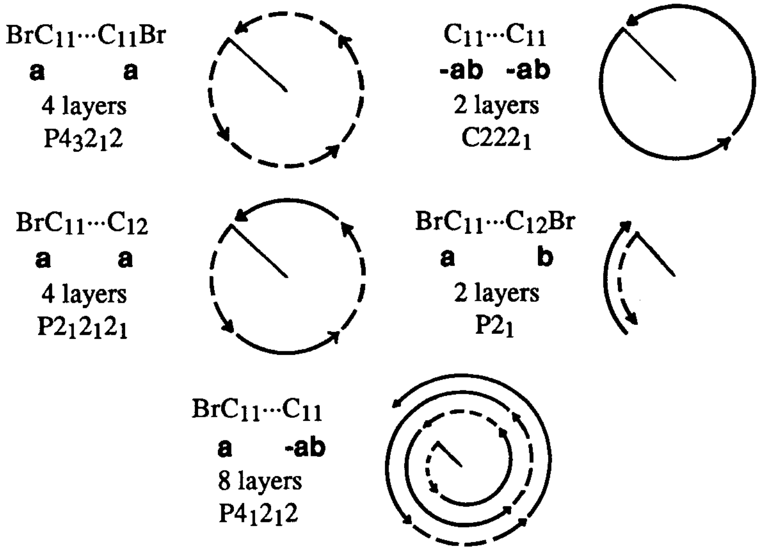

FIGURE 8. Layer-to-layer reorientation through one unit cell, number of layers per cell, and space group for various diacyl peroxides. Dashed arrows show type **a** reorientation across $C_{11}Br$ interface. Radius shows intramolecular dyad direction in bottom layer

solid-state properties, including melting point, compressibility, thermal expansion, crystal growth, and reactivity.[15] It is particularly challenging to find substituents that will favor each of the six orientations for interlamellar packing, and thus allow more flexibility in crystal design of these and other long-chain compounds.

The list of substituents that may be studied is limited in two ways. First, substituents must not be so large as to exclude packing in a cell with a cross section of some 30 $Å^2$. Second, they must not for any other reason force the compound to adopt a different intralamellar packing motif.

The limitation on cross section is coupled to an advantage for studying bulk properties. Dense packing of substituents at the interlamellar surface helps make their influence easy to observe experimentally. Limitation to a single intralamellar motif is more annoying, because it appears to prohibit study of some important effects. For example, we would like to study the molecular basis for alternation in melting point and many other properties between odd and even chain lengths, but almost invariably the packing motif changes so drastically with the chain-length parity that identifying the source of the alternation is impossible. This difficulty applies to symmetrical homologues of both UP and BrUP.

Interlamellar Packing in Unsymmetrical Peroxides

Diacyl peroxides with different terminal substituents on the two chains offer several advantages over their symmetrical analogues. First, they provide a way of forcing a particular substituent into an otherwise uncongenial intralamellar packing motif. Second, they provide versatility in designing new space groups for a particular class of molecules. Third, they allow checking additivity of substituent effects at different interfaces in determining bulk properties. In this discussion we concentrate on the first two advantages.

Within a layer of UP, or of BrUP, nearest neighbor chains are related by translation, but in the homologues with even-carbon chains there is a glide relationship and a completely different layer structure.[16] This makes it impossible to interpret odd-even effects on crystal properties of these symmetrical compounds. In an unsymmetrical compound where the substituent on one end of the peroxide favors translation among nearest neighbors within the layer and the substituent on the other end favors a glide, either one substituent will dominate in determining the layer structure, or the layer must adopt a completely new motif.

We have prepared a number of unsymmetrical peroxides where one chain is $C_{11}Br$ with a strong preference for packing as in BrUP. When it is paired with a C_{12} or $C_{12}Br$ chain, both of which prefer other intralamellar motifs, the $C_{11}Br$ chain prevails and forces the type of lamellar structure discussed above. In all cases but the disordered $C_{11}Br/C_{11}Cl$ peroxide, the molecules within a single layer are all oriented in the same sense, giving smooth, chemically homogeneous surfaces.

When the C_{12} chain is connected by the peroxide bridge to a $C_{11}Br$ chain and forced to pack as in BrUP, there is a possibility for end-for-end disorder, because C_{12} is sterically very similar to $C_{11}Br$ (van der Waals radii of methyl and bromine are 2.0 and1.9 Å, respectively). Because of the energetic advantage of bromine-bromine contacts, the crystal retains perfect order. One face of each layer contains only bromines, the other only methyl groups. Every other layer is turned upside down to give strict alternation between bromine-bromine and methyl-methyl interfaces. The orientational relationship across the bromine-bromine interface is of course of type **a**, as in BrUP. The relationship across the methyl-methyl interfaces is also of type **a**, rather than of type **-ab** as in the hydrocarbon interface of UP. The distinction between C_{11} and C_{12} chains is that the terminal C-C bond of the latter is parallel to the interface, giving a surface that exposes sides of ethyl groups rather than tips of methyl groups. Although it is reasonable that the sides of ethyl groups pack more like the sides of bromomethyl groups than like the tips of methyl groups, it is not obvious why they do not adopt the **b** or **i** motifs which appear to be sterically allowed for BrUP. Perhaps there is a factor beyond the secondary bonding of bromines which favors **a**.[10]

Since both interfaces of the $C_{11}Br$ /C_{12} peroxide have the same orientational relationship as in BrUP, the packing of this unsymmetrical peroxide is identical to that of BrUP, except that the bromines at alternate interfaces are replaced by methyls. This substitution lowers the symmetry from $P4_32_12$ to $P2_12_12_1$. Figure 8 shows how rotating the peroxide orientation by 90° across each of four layer interfaces completes a unit cell. As expected, the homologous peroxides with C_{10} or C_{14} groups in place of C_{12} also pack in $P2_12_12_1$.

We have no intensity data on the unsymmetrical crystal with $C_{11}Br$ at one end and $C_{12}Br$ at the other, but the lattice parameters and space group show that again $C_{11}Br$ establishes the intralamellar structure of BrUP. Presumably the terminal C12-Br bond is roughly perpendicular to the layer surface, which would then be composed of widely spaced bromine atoms.

Apparently the favored orientation between two of these surfaces is of type **b**, which gives a 90° rotation in peroxide orientation from layer to layer in the opposite sense from the 90° rotation due to the **a** relationship at the $C_{11}Br$ interface. Thus as shown in Figure 8, only two molecular layers are necessary to construct a unit cell in space group $P2_1$. Although the crystal class is only monoclinic, the **ab** lattice is nearly square with a difference of only 0.009 Å between **a** and **b**. The unique monoclinic angle is 89.5°, so the lattice parameters are very close to "tetragonal".

Since BrUP and UP have the same layer structure, it is natural that the hybrid unsymmetrical peroxide with $C_{11}Br$ and C_{11} chains should have this structure as well. Again alternate layers turn over to segregate bromine-bromine and methyl-methyl interfaces. The former has the **a** relationship, and the latter the **-ab** relationship, as expected from the corresponding symmetrical peroxides. Together these two relationships give 90° + 180° = 270° rotation of the skeletal orientation across two layers. This is the same as a -90° rotation, so four *pairs* of layers, or eight molecules, are required to complete a unit cell. The **c** axis of this peroxide is 167.9 Å long, and that of the $C_{11}Br/C_{13}$ homologue is 180.5 Å. Because of the -90° rotation, both of these crystals have space group $P4_32_12$, when individual layers and the relationship across the bromine-bromine interface have the same chirality as in $P4_12_12$ BrUP. The stacking is of course quite different from that of BrUP.

It is notable that BrUP and the $C_{11}Br/C_{12}$ peroxide have different space groups but identical packing patterns, while BrUP and the $C_{11}Br/C_{11}$ peroxide have the same space group but different packing patterns. Obviously it is the packing pattern, not the space group, which should determine most properties of the crystals.

CONCLUSIONS

By altering substituents on one end, or both ends, of a long, narrow molecule, we have been able to generate a series of crystals with important structural differences only in the immediate vicinity of the substituents. These materials provide a basis for beginning systematic investigation of substituent effects on chemical and physical properties of organic solids. Studies on well defined interfaces within such crystals should be useful for understanding more complex interfaces between different phases.

Our success in predicting and designing crystal packings in a number of space groups underlines the truism that it is a favorable packing pattern that determines crystal symmetry, not a favorable symmetry that determines crystal packing.

The variation in layer-to-layer orientation among lamellar peroxides is reminiscent of polytypism, a phenomenon involving the existence of several distinct phases with identical lamellae but different stacking.[17] Many inorganic and organic substances occur as polytypes. A familiar example is the stacking of layers of close packed spheres to give both cubic close packed and hexagonal close packed structures, or structures with a regular or random sequence of ccp and hcp domains. The peroxides we have studied thus far have not shown true polytypism, since the interfacial orientation for a given substituent is invariant and so predictable that one can even confidently design a space group. One might refer to crystals in Table I with different space groups as "substitutional polytypes."

In ongoing work we hope to characterize the magnitude and source of the orientational preferences more quantitatively. We also hope to find substituents that will provide still greater flexibility in designing crystal packings and studying substituent effects on crystal properties.

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