H), 0.57 (t, $J = 7.0$ Hz, CH_3, 12 H), 0.80–1.08 (m, CH_2 and CH_3, 28 H), 1.10–1.33 (m, CH_2, 8 H), 1.35–1.62 (m, CH_2, 16 H), 6.06 (s, Ar_3CH, 4 H), 6.41 (s, ArH ortho to silyloxy, 4 H), 6.80 (s, ArH meta to silyloxy, 4 H), 6.94 (d, $J = 7.0$ Hz, ArH meta to **I**, 8 H), 7.54 (d, $J = 7.0$ Hz, ArH ortho to I, 8 H); MS (FAB, NOBA) *m/e* 1857 ($M^+ + 1$, 100). Anal. Sample dried 12 h at 10^{-1} Torr, 65 °C. Calcd for $C_{84}H_{100}I_4Si_4O_8$: C, 54.31; H, 5.43. Found: C, 54.48; H, 5.50.

5,5,9,9,13,13,17,17-Octabutyl-1,21,23,25-tetrakis[4-[(trimethylsilyl)ethynyl]phenyl]-2,20:3,19-dimetheno-1*H*,21*H*,23*H*,25*H*-bis[1,3,2]dioxasilocino[5,4-*i*:5′,4′-*i*′]benzo[1,2-*d*:5,4-*d*′]bis[1,3,2]benzodioxasilocin (Stereoisomer, 30). To a suspension of 0.743 g (0.400 mmol) of tetraiodide **29** in 50 mL of triethylamine were added 0.48 mL (3.42 mmol) of (trimethylsilyl)acetylene, 0.041 g (0.214 mmol) of copper(I) iodide, and 0.125 g (0.175 mmol) of bis(triphenylphosphine)palladium(II) dichloride. The mixture slowly turned green and then black. After 18 h the mixture was diluted with 50 mL of CH_2Cl_2 (to dissolve the product) and filtered, and the solvent was removed in vacuo. The residue was partitioned between CH_2Cl_2 and distilled water. The organic phase was dried ($MgSO_4$) and filtered. The solvent was removed in vacuo. The residue was chromatographed on 15 g of silica gel with 7:3 C_6H_{12}/CH_2Cl_2. Fractions corresponding to product were combined, and the solvent was removed in vacuo. The residue was dissolved in 80 mL of $(CH_3)_2NCHO$. The solution was allowed to cool very slowly to −10 °C. The precipitate was collected by filtration to give 0.367 g (53%) of compound **30** as a white powder: mp 349–350 °C; R_f 0.80 (silica gel, 3:2 C_6H_{12}/CH_2Cl_2); ^1H NMR ($CDCl_3$), δ 0.25 (s, Me_3Si, 36 H), 0.33 (br t, J indet, $SiCH_2R$ (in), 8 H), 0.57 (t, $J = 7.0$ Hz, CH_3, 12 H), 0.90–1.05 (m, CH_2, 16 H), 0.92 (t, $J = 7.0$ Hz, CH_3, 12 H), 1.08–1.30 (m, CH_2, 8 H), 1.32–1.61 (m, CH_2, 16 H), 6.09 (s, Ar_3CH, 4 H), 6.41 (s, ArH ortho to silyloxy, 4 H), 6.74 (s, ArH meta to silyloxy, 4 H), 7.13 (d, $J = 8.0$ Hz, ArH meta to ethynyl, 8 H), 7.34 (d, $J = 8.0$ Hz, ArH ortho to ethynyl, 8 H); MS (FAB, NOBA) *m/e* 1736 (M^+, 100). Anal. Sample dried 12 h at 10^{-1} Torr, 110 °C. Calcd for $C_{104}H_{136}O_8Si_8$: C, 71.83; H, 7.88. Found: C, 71.74; H, 7.90.

Crystal Structure Data. Compound **16**·C_6H_6 crystallizes from CH_2Cl_2 as colorless parallelepipeds in the orthorhombic system $P2_12_12$. Unit-cell dimensions are as follows: $a = 11.969$ (4) Å, $b = 16.858$ (5) Å, $c = 11.410$ (4) Å, $V = 2302$ Å^3, $Z = 2$ (four half molecules, related by a two-fold axis). The crystal was examined on a modified Picker FACS-1 diffractometer, with Mo Kα radiation, at 128 K. The structure was determined by direct methods. Refinement of 308 parameters (2020 reflections with $I > 3\sigma(I)$) has an agreement value, R, currently at 0.068.

Compound **16**·CH_2Cl_2·$(CH_3)_2C{=}O$ crystallizes from $CH_2Cl_2/(CH_3)_2C{=}O$ as large colorless, irregular fragments in the triclinic system $P\bar{1}$. Unit-cell dimensions are as follows: $a = 10.836$ (2) Å, $b = 12.356$ (2) Å, $c = 20.057$ (4) Å, $\alpha = 90.597$ (5)°, $\beta = 80.509$ (6)°, $\gamma = 114.290$ (5)°, $V = 2404$ Å^3, $Z = 2$. The crystal was examined on a modified Picker FACS-1 diffractometer, with Mo Kα radiation, at 128 K. The structure was determined by direct methods. Refinement of 103 parameters (5826 reflections with $I > 3\sigma(I)$) has an R currently at 0.09.

Compound **20**·2$C_6H_5CH_3$ crystallizes from $C_6H_5CH_3$ as colorless fragments in the rhombohedral system $R3$. Unit-cell dimensions are as follows: $a = 18.52$ Å, $\gamma = 109.60°$, $V = 4880$ Å^3, $Z = 3$. Hexagonal indices are $a = 30.298$ (3) Å, $c = 18.422$ (2) Å, $V = 14645$ Å^3, $Z = 9$. The crystal was examined on a modified Picker FACS-1 diffractometer, with Mo Kα radiation, at 128 K. The structure was determined by heavy-atom methods. Refinement of 348 parameters (2656 reflections with $I > 3\sigma(I)$) has an R currently at 0.10.

Compound **20**·2C_6H_5Br crystallizes from C_6H_5Br as colorless multifaceted crystals in the rhombohedral system $R3$. Unit cell dimensions are as follows: $a = 18.777$ (2) Å, $\gamma = 109.81$ (2), $V = 5030$ Å^3, $Z = 3$. Hexagonal indices are $a = 30.749$ (3) Å, $c = 18.459$ (2) Å, $V = 15097$ Å^3, $Z = 9$. The crystal was examined on a Huber diffractometer, with Mo Kα radiation, at 298 K. The structure was determined by heavy-atom methods. Refinement of 305 parameters (2790 reflections with $I > 3\sigma(I)$) has an R currently at 0.10.

Compound **23**·3$(CH_3)_2C{=}O$·$CHCl_3$ crystallizes from CH_2Cl_2 as colorless parallelepipeds in the orthorhombic system *Pbnn* (standard setting *Pnna*). Unit-cell dimensions are as follows: $a = 12.772$ (10) Å, $b = 24.284$ (18) Å, $c = 22.276$ (17) Å, $V = 6950$ Å^3, $Z = 4$. The crystal was examined on a modified Picker FACS-1 diffractometer, with Mo Kα radiation, at 128 K. The structure was determined by direct methods. Refinement of 225 parameters (2880 reflections with $I > 3\sigma(I)$) has an R currently at 0.18.

Compound **28** crystallizes from $(C_2H_5)_2O$ as colorless needles in the monoclinic system $C2/c$. Unit-cell dimensions are as follows: $a = 29.561$ (2) Å, $b = 18.486$ (1) Å, $c = 22.594$ (2) Å, $\beta = 119.745$ (2)°, $V = 10725$ Å^3, $Z = 4$ (eight half molecules related by a two-fold axis). The crystal was examined on a modified Picker FACS-1 diffractometer, with Mo Kα radiation, at 298 K. The structure was determined by direct methods. Refinement of 305 parameters (3342 reflections with $I > 3\sigma(I)$ has an R currently at 0.089.

Further crystallographic details will be published elsewhere.

Quantitative Binding of CD_3CN by 26. These studies were conducted by utilizing chemical shift changes in the 200-MHz ^1H NMR spectra of 0.0016–0.0035 M **26** in CCl_4 (containing 0.3% by volume of $(CH_3)_4Si$) induced by incremental guest additions at three different temperatures. An internal coaxial tube containing C_6D_6 or $(CD_3)_2CO$ was employed to provide a deuterium lock signal. A small quantity (2–10 μL) of a 1–100% v/v solution of the guest in CCl_4 was then added via a syringe and the ^1H NMR spectrum of the solution was redetermined. If the experiment was conducted at a temperature other than 298 K, the sample was equilibrated in the spectrometer probe 10 min before determination of the spectrum. This process was repeated until a minimum of five points were obtained which appeared to be reasonably well spaced with regard to the chemical shift changes occurring in the host. Table IV of the supplemental material tabulates the resulting chemical shift changes.

Supplementary Material Available: Table of chemical shifts (Table IV), plots of chemical shift vs concentration of CH_3CN (Figures 6–10), van't Hoff plots (Figures 11 and 12) (4 pages). Ordering information is given on any current masthead page.

Bilayer-Type Crystal Structure of 4-(2-Anthryl)-1-butanoic Acid

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Abstract: 4-(2-Anthryl)-1-butanoic acid crystallizes in the centrosymmetric, monoclinic space group $C2/c$; $a = 51.337$ (9) Å, $b = 6.022$ (2) Å, $c = 8.969$ (2) Å, $\beta = 92.68$ (2)°, $Z = 8$. This crystal has a bilayer structure with two bilayers per unit cell. The packing of the anthracene moieties is quite similar to that of unsubstituted anthracene. Neighboring anthracene bilayers are separated by hydrogen-bonded butanoic acid chains.

Truly crystalline molecular two-dimensional systems of molecular chromophores are of considerable interest since unusual properties are expected for coherent electronic excited states[1,2] and for incoherent exciton and charge-carrier transport.[3,4] A

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possible choice for the realization of such a system is the Langmuir–Blodgett (LB) technique. The latter has become very popular in the last years for the construction of organic mono- and multilayers.[5-7] An advantage of the LB technique is its great versatility: a large number of spectroscopically interesting molecules can be incorporated into LB films, and the films can be transferred to various solid substrates.[5,8-11] LB multilayers are laminar and often show very good periodicity perpendicular to the film plane.[11,12] However, it turned out that in-plane order was poor in most of the LB films. In-plane order was found in LB multilayers of pure C_{18}–C_{22} fatty acids[13-15] and of two recently described fatty acid substituted anthracene compounds.[11,16,17] It can be ascribed to the formation of small crystalline islands with preferential macroscopic orientation.[16] This is not sufficient for carrying out interesting spectroscopic and transport experiments in a two-dimensional molecular system. Crystalline islands of macroscopic dimensions have been found before in LB films after polymerization of certain compounds[18] and after aggregation of certain chromophores.[19] It does not appear easy to investigate spectroscopic properties and in particular transport of excitons and of charge carriers in an individual domain or island of such a system. Therefore we have looked for a different experimental system that could make the latter type of measurements easier, providing a truly macroscopic two-dimensional lattice of molecular chromophores.

It is well-known that pure fatty acids[20,21] and also certain phospholipids[22] form macroscopic, layered single crystals. There are also interesting layered single crystals of inorganic–organic compounds.[23,24] Inspired by the above layered crystals, we have grown from the vapor phase molecular single crystals composed of butanoic acid substituted anthracene. We describe here the structure of these crystals.[25] They contain the anthracene chromophores in bilayers which are separated from the neighboring anthracene bilayers by hydrogen-bonded butanoic acid chains. In the bilayers the anthracene moieties pack in a similar way as in the *ab* planes of the single crystal of unsubstituted anthracene.[26]

Table I. Crystallographic Data

formula	$C_{18}H_{16}O_2$
M_r	264.3
radiation	λ(Cu Kα) = 1.541 78 Å
$F(000)$	1120
space group	$C2/c$
lattice constants	
a	51.337 (9) Å
b	6.022 (2)
c	8.969 (2)
β	92.68 (2)°
V	2769.5 (12) Å^3
Z	8
D_{calcd}	1.268 (1) g cm^{-3}
μ	5.66 cm^{-1}
N	1727 $I > 2.5\sigma(I)$
NP	264
R	4.7%
S	1.05
R_{INT}	0.016 (for $C2/c$)

Table II. Interatomic Distances (in Å) (ESD's in Parentheses)[a]

C1–C2	1.360 (3)	C12–C11	1.429 (3)
C2–C12	1.428 (3)	C13–C14	1.432 (3)
C12–C9	1.391 (3)	C1–C101	1.508 (3)
C9–C13	1.394 (3)	C101–C102	1.519 (3)
C13–C3	1.422 (3)	C102–C103	1.520 (3)
C3–C4	1.360 (3)	C103–C104	1.500 (3)
C4–C5	1.413 (4)	C104–O1	1.204 (8)
C5–C6	1.355 (3)	C104–O1A	1.240 (7)
C6–C14	1.426 (3)	C104–O2	1.195 (7)
C14–C10	1.393 (3)	C104–O2B	1.186 (9)
C10–C11	1.392 (3)	O1–O2*	2.75 (1)
C11–C7	1.423 (3)	O1–O2B*	2.63 (1)
C7–C8	1.356 (3)	O1A–O2*	2.66 (1)
C8–C1	1.423 (3)	O1A–O2B*	2.75 (1)

[a] * = symmetry-related atoms.

Table III. Bond Angles (in deg) (ESD's in Parentheses)[a]

C8–C1–C2	118.9 (2)	C7–C11–C12	118.4 (2)
C8–C1–C101	119.0 (2)	C11–C7–C8	121.1 (2)
C2–C1–C101	122.1 (2)	C7–C8–C1	121.3 (2)
C1–C2–C12	121.9 (2)	C1–C101–C102	112.0 (2)
C2–C12–C9	122.6 (2)	C101–C102–C103	112.1 (2)
C2–C12–C11	118.4 (2)	C102–C103–C104	111.7 (2)
C9–C12–C11	119.0 (2)	C103–C104–O1	120.0 (5)
C12–C9–C13	121.7 (2)	C103–C104–O1A	116.9 (4)
C9–C13–C3	122.5 (2)	C103–C104–O2	122.3 (4)
C9–C13–C14	119.2 (2)	C103–C104–O2B	119.8 (6)
C3–C13–C14	118.3 (2)	O1–C104–O2	104.0 (7)
C13–C3–C4	121.2 (2)	O1–C104–O2B	120.0 (7)
C3–C4C5	120.2 (2)	O1A–C104–O2	120.8 (5)
C4–C5–C6	120.8 (2)	O1A–C104–O2B	110.3 (6)
C5–C6–C14	120.7 (2)	O1–C104–O1A	41.7 (6)
C6–C14–C10	122.1 (2)	O2–C104–O2B	34.7 (7)
C6–C14–C13	118.8 (2)	C104–O2–O1*	111.6 (4)
C10–C14–C13	119.1 (2)	C104–O2–O1A*	120.9 (4)
C14–C10C–11	121.5 (2)	C104–O2B–O1*	117.7 (7)
C10–C11C7	122.1 (2)	C104–O2B–O1A*	112.5 (7)
C10–C11–C12	119.5 (2)		

[a] * = symmetry-related atoms.

Experimental Results

4-(2-Anthryl)-3-oxobutanoic acid was synthesized in 6% yield[27] and was reduced with hydrazine hydrate in triethylene glycol[28]

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Table IV. Selected Torsion Angles (in deg) (ESD's in Parentheses)

C101–C1–C8C7	178.2 (2)
C101–C1–C2–C12	−177.3 (2)
C8–C1–C101–C102	−80.1 (2)
C2–C1–C101–C102	98.6 (2)
C1–C101–C102–C103	−177.6 (2)
C101–C102–C103–C104	172.7 (3)
C102–C103–C104–O1	41.0 (8)
C102–C103–C104–O1A	88.6 (6)
C102–C103–C104–O2	−93.1 (6)
C102–C103–C104–O2B	−133.8 (7)

Table V. The Angles (in deg) between the Anthracene Molecular Axes (See Figure 1) and the Unit-Cell Axes[a]

	a′	(*c′*)	*b*		*c*	(*a*)
L	29.6	(30.7)	90.6	(97.3)	119.6	(119.6)
M	103.8	(108.4)	152.0	(153.4)	113.8	(108.5)
N	63.7	(66.3)	117.9	(115.4)	40.1	(36.0)

[a] Values for unsubstituted anthracene at 290 K appear in parentheses and are shown for comparison.[17] The *a′* and *c′* axes are perpendicular to the *bc* and *ab* planes of the respective unit cells.

to 4-(2-anthryl)-1-butanoic acid (I). Recrystallization from either acetic acid or toluene resulted in colorless platelets (mp = 197–8 °C, lit. mp = 194–6 °C). Crystals suitable for X-ray diffraction were grown under a 10^{-4} Torr vacuum in a sublimation chamber similar to that described by Karl[29] (crystal size: 0.35 × 0.35 × 0.16 mm).

Cell parameters and intensity data were measured on a Stoe diffractometer by using the $\omega - 2\theta$ scan technique. The orientation matrix was determined from 68 carefully centered reflections with $\theta_{\max} = 25°$, Cu Kα radiation, and the range of *h*, *k*, and *l* at $-56 \rightarrow 56$, $0 \rightarrow 6$, and $-10 \rightarrow 0$, respectively. A total of 2140 unique reflections were measured to $(\sin\theta/\lambda)_{\max} = 0.56$ Å^{-1}. The data were not corrected for absorption (controls = 0,2,0, 24,0,0; max change = 1.6%, 3.0%, respectively).

Analysis of systematic absences showed two possible space groups: *Cc* and *C*2/*c*. The structure was solved by direct methods in *Cc* space group with the program SHELX86.[30] The positions of all non-hydrogen atoms were determined from an *E* map. The refinement was carried out by full-matrix least-squares method on *F* magnitudes with SHELX76[31] and 234 parameters in each block (one molecule in a block). The H atoms connected with carbon atoms were located on a ΔF map; the hydroxy H atom was not found. The refinement converged with $R = 6.0\%$, $S = 1.33$. The max, min height in the final ΔF map was 0.38, −0.20 e Å^{-3}.

There are two molecules in the symmetry-independent unit (with respect to the *Cc* space group). These molecules, except for oxygen atoms, are related by a center of inversion at the point 0.5669 (2), 0.5003 (14), 0.4330 (17). The *b* coordinate of that inversion center is indicative of a genuine inversion rather than a pseudoinversion. Therefore one molecule was rejected from the calculations and the remaining one shifted along *a* and *c* axes by −0.0699 and 0.0670, respectively. Then the ΔF map was calculated for the molecule in the *C*2/*c* space group (the oxygen atoms were not included into the input data file). The ΔF map revealed two positions for each of the oxygen atoms.

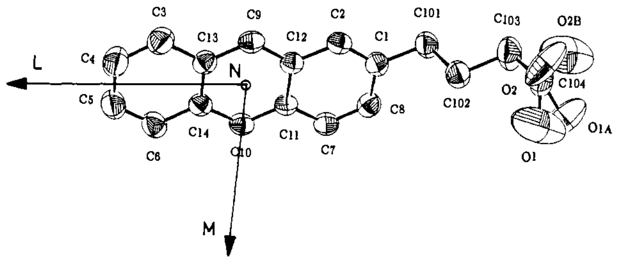

Figure 1. The numbering scheme of the molecule. The anthracene molecular axes where *L* and *M* lie in the anthracene plane and *N* is perpendicular to the plane.

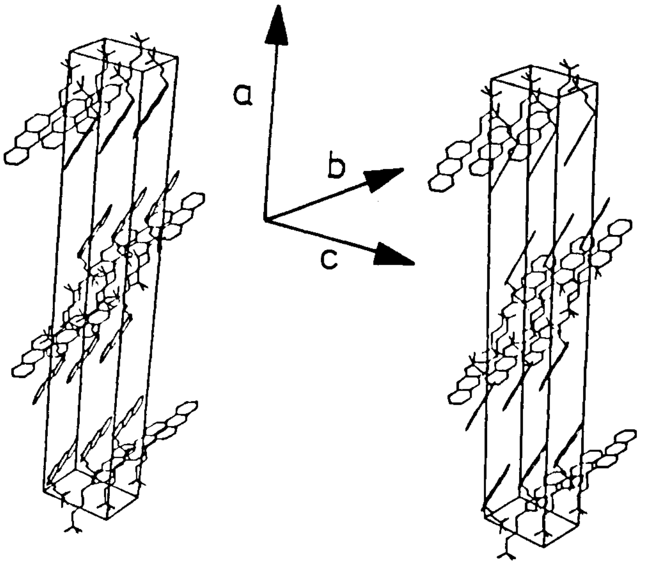

Figure 2. Stereo view of the molecular packing.

The final results show that the structure is almost centrosymmetric and that the oxygen atoms exist in two possible positions with occupancy factors of 0.510 (4) and 0.490 (4), respectively. Hence the refinement of the structure was performed in the *C*2/*c* space group with final values of $R = 4.7\%$ and $S = 1.05$. The largest peak on the final ΔF map was 0.24, −0.16 e Å^{-3}. Scattering factors were taken from SHELX76. For crystallographic data, see Tables I–V. Fractional coordinates, thermal parameters, bond distances and angles with hydrogen atoms, and final structural refinement are included in the supplementary material.

Discussion

4-(2-Anthryl)-1-butanoic acid (I) crystallizes in the centrosymmetric, monoclinic space group *C*2/*c*. The asymmetric unit consists of one molecule located at a general position. Figure 1[32] shows the axes for the anthracene moiety. There are eight molecules in the unit cell. Figure 2[32] shows the molecular packing in the bilayers that are bridged by hydrogen-bonded carboxylic acid groups. The bilayer planes are defined by the unit cell *bc* face. The edge-to-edge distance separating anthracene layers across the butanoic acid chains, calculated from the C8 carbon atoms, is 10.12 (4) Å.

The interatomic distances in the anthracene moieties are similar to those found for crystals of unsubstituted anthracene.[33] As seen in Figure 2, the anthracene moieties pack in a "herringbone" array. Table V lists the angles between the anthracene *L*, *M*, and *N* axes and the *a′*, *b*, and *c* unit-cell axes, where *a′* is perpendicular to the *bc* plane. Linear polycyclic aromatic molecules in the series naphthalene, anthracene, tetracene, and pentacene all crystallize in either monoclinic or triclinic space groups in a "herringbone" arrangement,[34-36] that is, with their long molecular axes (*L*) more or less parallel to one another and to the *c* axis and with their short axes (*M*) staggered relative to the four nearest neighbors in the *ab* plane (compare captions to Table V). That I also packs in this manner is clearly seen in Figure 2. As can be seen in Table

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V, the orientation of the anthracene moiety of I is quite similar to that of unsubstituted anthracene[26] despite the presence of the butanoic acid substituent.

The axis of the butanoic acid chain, calculated from atoms C1, C104–C101, intersects the anthracene least-squares plane at 37.2°, while glide-plane-related chains cross at an angle of 69.9°. Butanoic acid groups in neighboring bilayers form hydrogen-bonded dimers. The disorder in the oxygen atoms is borne out by two positions for each atom with almost equal weight as represented in Figures 1 and 2. Therefore hydrogen bonding cannot be quantified by only one distance (compare Tables II and III). An examination of the anisotropic temperature factors for the carboxylic acid oxygen atoms reveals a fair amount of thermal motion more or less perpendicular to the plane described by the hydrogen-bonded carboxylic acid dimer unit.

The crisscrossing of the butanoic acid chains represents a departure from the usual crystal packing of most fatty acids, where the chains are parallel to each other in an orthorhombic subcell.[20,21] This configuration is realized, however, by certain potassium salts of short chain fatty acids.[37] In monoclinic potassium caproate, for instance, the alkyl chains within a given *ac* layer are parallel, but chains in neighboring layers are inclined at 57.5° to one another.[37,38] In I this crossing of the butanoic acid chains apparently permits the crystalline packing of both alkyl and aromatic groups despite their different space-filling requirements.

Bilayer-type single crystals with aromatic moieties are interesting systems for the study of various structural and spectroscopic phenomena. Temperature-dependent studies, such as have been carried out with other layered systems,[23] might show interesting phase changes and additional low-temperature structures. Varying the length of the fatty acid chain could indicate the relative contribution of the aromatic, alkyl, and carboxylic acid groups to the energetics of crystal packing.

Electronic excitations involving the anthracene moiety of I might prove interesting.[1,2] Transport of excitons and charge carriers in two dimensions[3,4] can also be profitably studied in such bilayer-type crystals.

Bilayer-type single crystals have several obvious advantages over conventional multilayer assembly techniques. Long-range crystallinity, for instance, is not possible in LB assemblies. Materials such as I can also be zone-refined and crystals can be grown by sublimation under inert atmosphere, thus affording extremely high purity. Bilayer-type single crystals can serve as well-ordered reference systems when interpreting local order and island formation in LB films containing related molecules.

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Supplementary Material Available: Tables of fractional coordinates, thermal parameters, bond distances and angles, and the final structural refinement (6 pages); tables of structure factors (56 pages). Ordering information is given on any current masthead page.

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Tetra(pentafluorophenyl)porpholactone

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Abstract: Tetra(pentafluorophenyl)porphyrin [H_2(TFPP)] in refluxing acetic acid with $AgNO_3$ converts to tetra(pentafluorophenyl)porpholactone, I; i.e. one exo C_2H_2 unit becomes CO_2. This change is proven by mass spectrometry and supported by ^{1}H NMR, ^{19}F NMR, and FTIR. I has a porphyrinic absorption spectrum and a strong fluorescence, with a quantum yield of 0.2. Addition of oxalic acid allows reproducible conversion of H_2(TFPP) → I, and a 15% yield has been obtained. Iterative extended Hückel (IEH) calculations confirm a porphyrinic electronic structure with the π orbitals on both the oxa and oxo oxygen present in three of the porphyrin "four orbitals" responsible for the optical spectra. Under similar conditions another metal-free porphyrinic substance has been made, which is tentatively identified as a porphodilactone. Also Ag, Ni, and Cu derivatives have been made that are presumed to be porpholactones or porphodilactones. IEH calculations predict that in the free bases the central protons are trans, avoiding the azlactone ring in the porpholactone and the opposite porphodilactone; in the adjacent porphodilactone, they are also predicted to be trans rather than cis.

Three years ago a species with an unusual porphyrin spectrum was made serendipitously in our laboratory, as described herein. We propose that this species is tetra(pentafluorophenyl)porpholactone, I; i.e. one of the pyrrole rings has been converted to the azlactone ring[1] as shown in Figure 1. Furthermore, as described below, the same synthetic procedure has yielded a second metal-free porphyrinic substance as well as metal derivatives. Analogy suggests that the metal-free species may be a porphodilactone (IIA–IIE in Figure 1) and that the metal species are either porpholactones or porphodilactones. As shown in Figure 1, porphodilactone has five isomers.

Our serendipitous synthesis occurred when one of the authors (G.E.K.) was attempting to synthesize silver tetra(pentafluorophenyl)porphyrin [Ag(TFPP)]. $AgNO_3$ (0.5 g) and the free base,

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